

## Review

# Long-Term Performance of Zero-Valent Iron Permeable Reactive Barriers: A Critical Review

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### ABSTRACT

Permeable reactive barriers (PRBs) have shown great promise as an alternative to pump and treat for the remediation of groundwater containing a wide array of contaminants including organics, metals, and radionuclides. Analyses to date have focused on individual case studies, rather than considering broad performance issues. In response to this need, this study analyzed data from field installations of *in situ* zero-valent iron (ZVI) PRBs to determine what parameters contribute to PRB failure. Although emphasis has been placed on losses of reactivity and permeability, imperfect hydraulic characterization was the most common cause of the few PRB failures reported in the literature. Graphical and statistical analyses suggested that internal  $E_H$ , influent pH, and influent concentrations of alkalinity,  $\text{NO}_3^-$  and  $\text{Cl}^-$  are likely to be the strongest predictors of PRBs that could be at risk for diminished performance. Parameters often cited in the literature such as saturation indices, dissolved oxygen, and total dissolved solids did not seem to have much predictive capability. Because of the relationship between the predictive parameters and corrosion inhibition, it appears that reactivity of the ZVI, rather than the reduction in permeability, is more likely the factor that limits PRB longevity in the field. Due to the sparseness of field monitoring of parameters such as  $E_H$ , the data available for these analyses were limited. Consequently, these results need to be corroborated as additional measurements become available.

**Key words:** permeable reactive barrier; groundwater remediation; performance; reactivity; precipitates; failure

### INTRODUCTION

**T**RADITIONAL GROUNDWATER REMEDIATION METHODS such as pump and treat are of questionable utility: a 1994 study found that 69 of 77 treatment sites using pump and treat had not met cleanup goals (National Research

Council, 1994). Permeable reactive barriers (PRBs) are a promising remediation option involving the emplacement of a hydraulically permeable reactive medium downgradient of a plume of contaminated groundwater. As the water flows through it under the natural hydraulic gradient, the reactive medium degrades or traps the con-

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taminants. Because PRBs offer the possibility of (1) *in situ* plume capture and treatment, obviating the need to manage large volumes of water containing low concentrations of contaminants and the waste generated from the treatment of such water (Blowes *et al.*, 1999); (2) the simultaneous treatment of multiple types of contaminants such as metals, organics, and radionuclides; and (3) low operation and maintenance costs (Powell *et al.*, 1998), they are an alternative remediation technology that has received considerable attention as of late (EPA, 2002; Tratnyek, 2002).

PRBs are a relatively new technology; the oldest full-scale PRB has been in operation for just over a decade. Original work using reduced metals for the treatment of chlorinated organics built on studies of the corrosive effects of chemicals on metals (e.g., Rhodes and Carty, 1925). More recent work began in the 1970s (Sweeny and Fischer, 1972, 1973; Sweeny, 1981a, 1981b) and continued through the 1980s (Senzaki and Kumagai, 1988, 1989; Senzaki, 1991), culminating in a pilot-scale PRB installed in 1991 at the Borden, Ontario site (Reynolds *et al.*, 1990; Gillham and O'Hannesin, 1992; O'Hannesin, 1993; Gavaskar *et al.*, 1997; Morrison *et al.*, 2002d), and a full-scale PRB installed in 1995 at the Intersil Site in Sunnyvale, CA (Warner *et al.*, 2005). Although the Borden PRB did not achieve its removal targets, it was felt that increasing the reactive media to sand ratio (installed as 20:80) would have resulted in complete removal of contaminants (O'Hannesin and Gillham, 1998). The Intersil PRB, on the other hand, used pure ZVI in the reactive zone and was still meeting its cleanup goals as of 2004 (Sorel *et al.*, 2003; Warner *et al.*, 2005).

With the initial success of PRBs, their use has become more widespread. PRBs have been installed to treat organics, heavy metals, radionuclides, and nutrients (RTDF, 2001), with nearly 50% treating organic contam-

inants and nearly 20% treating metals as of 2002 (EPA, 2002). The reactive medium may consist of ZVI, cast iron, steel wool, amorphous ferric oxide, phosphate, zeolite, activated carbon, or limestone, among others (see Scherer *et al.*, 2000); however, of the over 200 PRBs worldwide as of 2004, 120 are iron based (90 in the United States) (ITRC, 2005).

Despite the numerous installations, PRBs are still considered an experimental technology (Warner and Sorel, 2003), perhaps because their long-term performance is not well understood. As Wilkin and Puls (2003) point out, "[f]ew case studies are available that evaluate the long-term performance of these in-situ systems, especially with respect to the long-term efficiency of contaminant removal, the buildup of mineral precipitates, and the buildup of microbial biomass." With the lack of comprehensive retrospective studies, there is disagreement about what factors control PRB longevity, defined as the length of time that a PRB continues to treat groundwater to design levels. Some have argued that PRB longevity is controlled by loss of reactivity (e.g., Roberts *et al.*, 2002; Vikesland *et al.*, 2003), whereas others assert that reduction in permeability is more important (e.g., Phillips *et al.*, 2000; Liang *et al.*, 2003) (Table 1). Depending on assumptions about controlling factors, estimates of PRB longevity can vary by an order of magnitude (e.g., 10 to 117 years for Monticello, UT), as shown in Table 2.

Another impediment to accurate longevity estimation is the difficulty of comparing laboratory column studies with field installations. Laboratory columns are generally aerobic, confined systems, whereas field PRBs are anoxic and unconfined. Studies utilizing high contaminant concentrations may not adequately represent long-term, low contaminant fluxes (Melitas *et al.*, 2002). Short-term column studies with high flow rates—intended to speed the aging of the reactive media and mimic long time scales—

**Table 1.** Factors postulated to control PRB longevity.

<i>Factor</i>	<i>Reference</i>
Loss of media reactivity caused by high TDS and high flow rates.	ESTCP, 2003
Loss of porosity—concentrated at influent interface.	Liang <i>et al.</i> , 2003
Competition for reactive sites, loss of reactive sites (due to corrosion or fouling), or precipitation and loss of permeability resulting from high carbonate, high nitrate, high DOC, and high TDS.	Wilkin and Puls, 2003
Loss of reactivity due to iron corrosion resulting from high influent concentrations of inorganic species such as bicarbonate, sulfate, or nitrate.	Gu <i>et al.</i> , 1999, 2002
Loss of media reactivity and decreases in hydraulic residence time.	Roberts <i>et al.</i> , 2002
Clogging due to precipitation resulting from high DO, carbonates, or sulfates.	Korte, 2001
Clogging due to precipitation resulting from high DO.	Gavaskar, 1999; Mackenzie <i>et al.</i> , 1999

DO, dissolved oxygen; DOC, dissolved organic carbon; TDS, total dissolved solids.

**Table 2.** Select longevity estimates for *in situ* PRBs.

Site	Estimate	Basis of estimate	Contaminant	Ref.
Elizabeth City, NC	20 years	Oxidation of ZVI by all species in groundwater, based on laboratory studies.	Cr; TCE	Blowes <i>et al.</i> , 2000
	750 years	Oxidation of all ZVI by Cr(VI) only (theoretical).		
Monticello, UT	10 years	Precipitation of calcite and resultant pore blockage, based on Ca <sup>2+</sup> mass balance.	U; Mn; Mo; NO <sub>3</sub> <sup>-</sup> ; As; Se; V	Morrison <i>et al.</i> , 2002a
	36 years	Passivation of iron surfaces (estimated by 35% loss of "reactivity efficiency" measured in PRB during first 7 months of operation).		
	117 years	Dissolution of ZVI, based on effluent Fe <sup>2+</sup> measured in column tests.		
Y-12 Plant (Pathway 2), Oak Ridge, TN	>15 years	Visual inspection of corrosion of ZVI.	U; NO <sub>3</sub> <sup>-</sup>	Phillips <i>et al.</i> , 2000

may not be representative of true media aging (Gu *et al.*, 1999; Farrell *et al.*, 2000; Sarr, 2001; Roberts *et al.*, 2002; Kamolpornwijit *et al.*, 2003). Many laboratory studies have used feed water that is not representative of natural systems (Liang *et al.*, 2000; Roberts *et al.*, 2002) and the use of different buffering agents is problematic, as some agents have been shown to alter iron corrosion rates (Uhlig and Revie, 1985; O'Hannesin and Gillham, 1998). Thus, assessments of PRB longevity based on laboratory studies (e.g., Liang *et al.*, 1997; Mackenzie *et al.*, 1999; Simon *et al.*, 2001; Morrison *et al.*, 2002b; Kamolpornwijit *et al.*, 2003; Johnson *et al.*, 2005) may not be applicable to *in situ* PRBs.

Because of these uncertainties, there have been frequent calls in the literature for more comprehensive reporting and analysis of field data (e.g., Scherer *et al.*, 2000; Liang *et al.*, 2001; Yabusaki *et al.*, 2001; Morrison *et al.*, 2002c; Powell and Powell, 2002; Roberts *et al.*, 2002; Phillips *et al.*, 2003; Devlin and Allin, 2005). The collections of PRB performance data that do exist, such as the Remediation Technologies Development Forum (RTDF) Web site (RTDF, 2001), do not necessarily collect uniform data, nor do they look broadly at trends. On the other hand, there are efforts to develop predictive models for declines in PRB performance (Liang *et al.*, 2001; Li and Benson, 2005), and to determine the geochemical parameters that adversely affect PRB performance (Wilkin and Puls, 2003); yet these studies have not been substantiated by an analysis of field data. In order to establish PRBs as an accepted technology, it is necessary to review PRB performance to date, with a focus on elucidating the factors that contribute to longevity in the field.

## BACKGROUND

### *PRB configuration*

PRBs have traditionally been emplaced via excavation and backfilling with reactive media (Gavaskar, 1999), with typical dimensions being 2 to 50 m long (transverse to flow), <1 to 5 m wide (parallel to flow), and <1 to 10 m deep (RTDF, 2001). The backfilled reactive media may be mixed with nonreactive media, such as sand. Some researchers report that this mixing does not affect removal of contaminants (e.g., Kjeldsen and Loch, 2000), others assert that it does affect removal (e.g., Liang *et al.*, 2000; D'Andrea *et al.*, 2005), whereas still others state that mixing is useful since using larger grained media can decrease the hydraulic impact of precipitates (Furukawa *et al.*, 2002).

PRBs may also make use of a pretreatment zone (PTZ), which is placed immediately upgradient of the main body of a PRB and contains a mixture of reactive media and gravel or sand. The high porosity of a PTZ allows for precipitate formation without undue permeability reduction, and can reduce potential clogging at the upgradient face of the main body of a PRB (Dwyer, 2000; Sarr, 2001). While a true PTZ should contain reactive media, some upgradient zones consist of pure sand or gravel. With a higher hydraulic conductivity—especially in the vertical direction—than the native aquifer material, these zones are intended for improved hydraulic distribution of the contaminated groundwater over the face of the PRB. However, these zones have sometimes been observed to degrade contaminants (e.g., at the Denver Federal Center, CO, and Intersil, CA, PRBs), possibly due to the inadvertent mixing

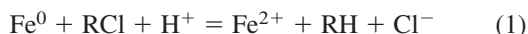
of reactive media into the upgradient nonreactive zone during installation (Blowes *et al.*, 1999; RTDF, 2001).

PRBs may also be constructed *ex situ*, such as at the Portsmouth Groundwater Treatment Facility (Piketon, OR) (Korte *et al.*, 1997b) or the Uranium Mill Tailings Remedial Action (UMTRA) Site (Durango, CO) (Morrison *et al.*, 2002c). At these sites, groundwater is passively collected in gravel-filled trenches and then directed through containers filled with reactive media located below the hydraulic grade line. With the absence of pumping and the frequent use of ZVI, these *ex situ* systems are conceptually similar to *in situ* PRBs, though their performance may differ significantly.

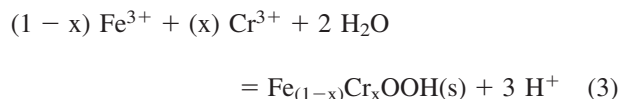
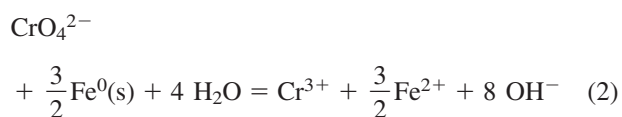
### PRB geochemistry

ZVI, the reactive medium selected predominantly for PRBs, treats contaminated groundwater through a combination of redox processes (some of which may be biologically mediated, such as the reduction of sulfate), precipitation reactions, and sorption. The specific reactions depend on the contaminant(s) and the constituents in the native groundwater, but in the case of both chlorinated organics and heavy metals, the chemical reaction is surface-mediated and requires contact between a reactive surface site and the contaminant (Weber, 1996).

Chlorinated organics are removed via the coupling of the oxidation of ZVI with the reductive dechlorination of the organic, RCl (Powell *et al.*, 1998):



Possible removal mechanisms for metals are surface adsorption via electrostatic attraction, surface complexation (Scherer *et al.*, 2000), or (co)precipitation, which may be coupled to redox reactions for redox-active species (Lien and Wilkin, 2005, and references therein). Equations (2) and (3) show the reduction of chromium to a more insoluble form and the precipitation of a mixed Fe/Cr solid (Powell *et al.*, 1998):

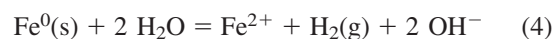


Field data indicate that chromium removed in PRBs is indeed in the trivalent state, although the solids into which it is incorporated are not limited to iron (oxy)hydroxides, as shown above (Wilkin *et al.*, 2005).

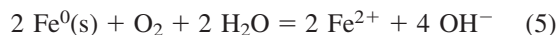
In addition to the contaminants, water itself and the constituents in the native groundwater interact with the

reactive media. Indeed, the contaminant of interest is usually not the controlling oxidizer of the reactive media (Gillham and O'Hannesin, 1994), as other species are present in greater stoichiometric abundance. For example, the reduction of sulfate was estimated to consume 50 times more ZVI than the reduction of Cr(VI) in the USCG PRB (Elizabeth City, NC) (Mayer, 1999).

ZVI may be oxidized by water, increasing pH, and producing hydrogen gas:



If dissolved oxygen is present, ZVI may be oxidized to ferrous or ferric iron, with a concomitant rise in pH:



The anaerobic oxidation of ZVI may also proceed abiotically through the reduction of nitrate to ammonia or nitrogen (Kielemeos *et al.*, 2000), or via the biologically mediated reduction of sulfate to sulfide (Al-Agha *et al.*, 1995).

With the emplacement of ZVI in an aquifer, an excess of electrons is introduced into the system; as the oxidation of ZVI proceeds, these electrons become available. Indeed, a dramatic reduction in the reduction-oxidation potential, or  $E_H$ , is known to accompany the oxidation of iron and has been observed in most PRBs (Powell *et al.*, 1998). Wilkin and Puls (2003) showed that for iron redox couples [e.g.,  $\text{Fe}^{2+}$  with  $\text{Fe}(\text{OH})_3(\text{s})$ ], an increase in pH is accompanied by a decrease in  $E_H$ . In this reducing, alkaline environment, precipitation of solids from native groundwater constituents is favored, leading to the loss of permeability and the possible passivation of the reactive media.

### PRB precipitate mineralogy

A variety of precipitation products have been identified in field PRBs: iron (hydr)oxides, iron and calcium carbonates, iron sulfides, and green rusts (e.g., Liang *et al.*, 2003; Jambor *et al.*, 2005). These precipitates dominate any solids formed with the contaminant. For example, at the UMTRA site (Durango, CO), uranium made up only 0.2% (by weight) of the precipitates (Matheson *et al.*, 2002) and solid-phase uranium was below the detection limit at the Y-12 site (Oak Ridge, TN), although it was being removed in the barrier (Phillips *et al.*, 2000). The exact composition of the solids is difficult to pinpoint, since the metastable nature of the iron species compromises the analysis. For ZVI under field conditions,  $\text{Fe}(\text{OH})_2$  is usually one of the first precipitates formed (Farrell *et al.*, 2000); this precipitate may be oxidized to the electrically conductive species magnetite, or to reactive, yet metastable, green rusts (Melitas *et al.*, 2002; Rit-

ter *et al.*, 2002; Phillips *et al.*, 2003; Su and Puls, 2004). Continued oxidation may produce poorly crystalline ferrous oxyhydroxides such as ferrihydrite, which may age to more crystalline forms, such as goethite ( $\alpha$ -FeOOH) and lepidocrocite ( $\gamma$ -FeOOH) (Abdelmoula *et al.*, 1996).

Each of these mineral species will have different interactions with contaminants, and may enhance, reduce, or alter the reaction mechanism (e.g., ferrihydrite may sorb rather than degrade some organics) (Furukawa *et al.*, 2002). Of particular concern are the carbonate and iron (hydr)oxide solids that may form. First, these solids have been observed to dominate precipitates in many PRBs (Gillham, 1999). Second, carbonate solids (Köber *et al.*, 2002; Roberts *et al.*, 2002; Klausen *et al.*, 2003; Devlin and Allin, 2005) and iron (hydr)oxides (Ritter *et al.*, 2002) have been shown to passivate iron surfaces.

Even electrically conductive layers, such as magnetite, may passivate the reactive media if they inhibit the movement of  $\text{Fe}^{2+}$  to solution (Farrell *et al.*, 2000). Reactivity of surface layers is a function of morphology, distribution, and type of precipitates. For example, the "incoherent and porous" surface of (hydr)oxide solids often allows for continued reaction (Tratnyek, 1996), though (hydr)oxide surfaces tend to inhibit corrosion (Johnson *et al.*, 1998). The distribution of precipitates also controls reactivity, as precipitates may occur on non-reactive sites with little passivating effect (Deng *et al.*, 2003).

### *Corrosion and media aging*

Corrosion directly or indirectly drives contaminant treatment. Equations (1) and (2) are examples of the direct coupling of contaminants to the corrosion process, while the sorption of metals to (oxy)hydroxides relies on corrosion to produce these solids. Because metals may be immobilized through surface complexation reactions without redox changes, changes in corrosion rates due to, for example, the buildup of passivating layers, will affect removal of metals and organics differently (Devlin and Allin, 2005).

In general, higher concentrations of anions tend to increase corrosion (Liang *et al.*, 2003; Devlin and Allin, 2005) and thus iron reactivity, but this is not always the case. Chloride and sulfate have been found to increase iron corrosion and destabilize passivating films (Johnson *et al.*, 1998; Devlin and Allin, 2005). Nitrate has been shown to inhibit corrosion (Farrell *et al.*, 2000; Schlicker *et al.*, 2000; D'Andrea *et al.*, 2005; Devlin and Allin, 2005), as well as nullify the corrosion-promoting effects of chloride (Klausen *et al.*, 2001). Sulfate, along with phosphate, molybdate, chromate, and silicate have been shown to inhibit arsenic removal by ZVI (Lackovic *et al.*,

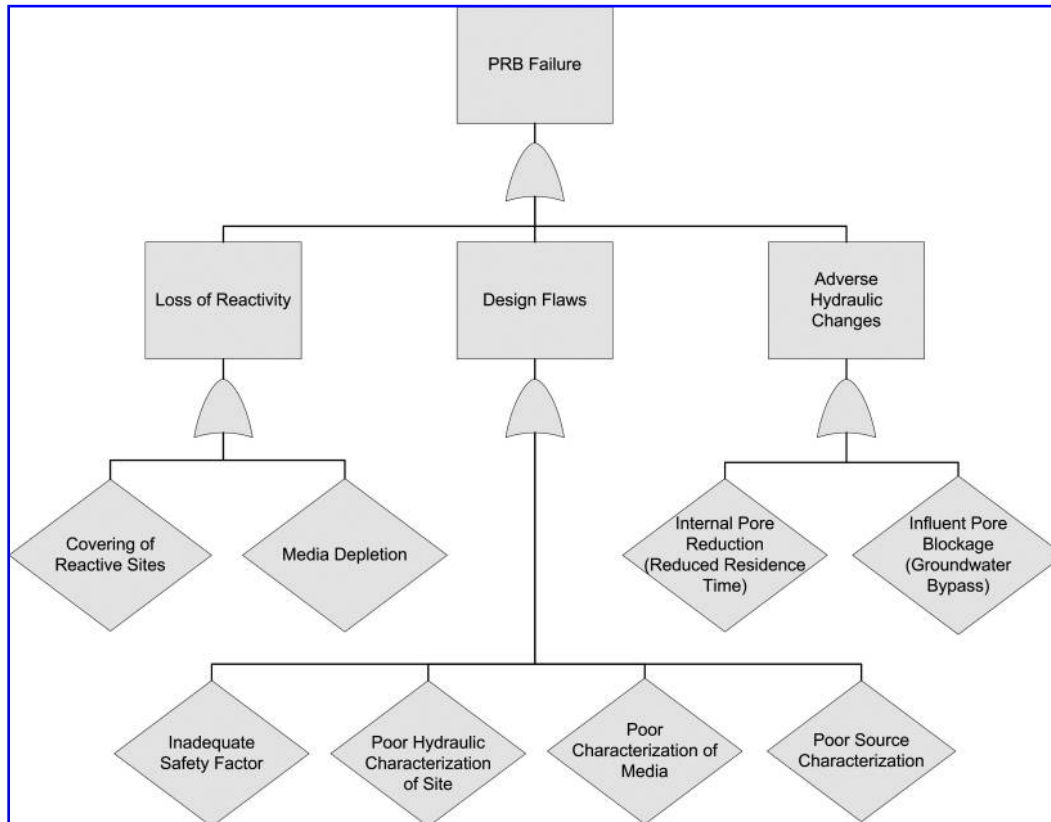
2000; Su and Puls, 2001; Melitas *et al.*, 2002), and silicate has also been shown to inhibit the degradation of TCE (Klausen *et al.*, 2001; D'Andrea *et al.*, 2005). Carbonate can temporarily increase the corrosion of ZVI, although carbonate solids passivate the reactive surface (Wieckowski *et al.*, 1983; Gu *et al.*, 1999; Köber *et al.*, 2002; Klausen *et al.*, 2003; Devlin and Allin, 2005).

Since contaminant removal depends on corrosion and the degree of corrosion is time-dependent, time-varying reaction rates for organic contaminants are commonly noted in batch and column studies, (e.g., Gillham and O'Hannesin, 1994; Agrawal and Tratnyek, 1996; Devlin *et al.*, 1998; Klausen *et al.*, 2003). In column studies, Farrell *et al.* (2000) reported that, in chloride and sulfate solutions, the half-life for trichloroethylene increased from 6.7 to 42 h after 667 days, whereas, in a nitrate solution, the half-life increased from 25 to 58 h over the same time frame. The removal of metals, however, tends to be fast and not as strongly dependent on time. For example, Köber and coworkers noted a temporal decline in reactivity towards 1,2-dichloroethylene, but no change in reactivity towards arsenic (Köber *et al.*, 2005). Although recent work in the laboratory has begun to elucidate reaction mechanisms and kinetics, largely for organic contaminants, the kinetics of reactions in field conditions are not well characterized, due to the complexity of the system and the cost of monitoring. Therefore, it is difficult to accurately judge the degree of impact of media aging on treatment efficiency in the field.

### *PRB failure modes*

To determine what factors influence PRB longevity in the field, performance data for PRBs were compiled and analyzed. Although there are over 200 PRBs operating, there was sufficient specific public information on field operating conditions and performance issues for only about 40. Utilizing this limited data base, three classes of possible failure modes of PRBs were delineated: loss of reactivity, adverse hydraulic changes, and design flaws. Each class may be subdivided, as presented graphically in Fig. 1. Although the emphasis in the literature has been placed on loss of reactivity and adverse hydraulic changes, it is design flaws that has been the most common cause of PRB failure (Warner and Sorel, 2003) and continues to be one of the main challenges to successful PRB implementation (ESTCP, 2003). Failure of *in situ* PRBs due to other modes appears to be rare. The only *in situ* PRBs that have reported operational failures that are not solely due to design flaws (e.g., inadequate hydraulic characterization) are at Monticello (UT) the Copenhagen Freight Yard (Denmark), and Haardkrom





**Figure 1.** Fault tree showing events that contribute to PRB failure. Primary events (shown in diamonds) are combined with logical gates to create fault events (shown in rectangles) (McCormick, 1981).

(Denmark). The Monticello site experienced a hydraulic conductivity loss of three orders of magnitude (Mushovic *et al.*, 2006). The Copenhagen Freight Yard reported loss of permeability due to precipitation of hydroxides and carbonates but also suffered from incomplete plume capture due to poor hydraulic characterization (Kiilerich *et al.*, 2000; RTDF, 2001). The Haardkrom site's problems, however, are attributed to "exhaustion of iron-chromate removal capacity" with little more specific detail given (Kjeldsen and Fulgsang, 2000). *Ex situ* PRBs, on the other hand, tend to clog and fail with regularity: every site where *ex situ* reaction cells were installed has experienced clogging and failure of at least one of those cells [Hill AFB (UT), Portsmouth (Piketon, OR), UMTRA (Durango, CO), and Y-12 Pathway 1 [(Oak Ridge, TN)] (Shoemaker *et al.*, 1995; Liang *et al.*, 1997; Ott, 2000; Morrison *et al.*, 2002b), with the exception of the *ex situ* PRB at Rocky Flats (Golden, CO) at which the crust forming on the reactive media was periodically broken up (Korte, 2001; RTDF, 2001).

Precipitation may also cause PRB failure by decreasing hydraulic residence times, leading to less effective treatment (Sass *et al.*, 1998). In some cases, hydraulic

short circuiting may occur, as preferential flow paths have developed in some column studies, (Kamolpornwijiit *et al.*, 2003; Su and Puls, 2003), and some evidence exists for their occurrence in the field (Liang *et al.*, 2003). However, no performance changes have yet been attributed to reduced residence time. Some sites did not reach treatment goals (e.g., Borden, Ontario), and sometimes incomplete degradation occurred (e.g., CSM, Australia), but these problems were design flaws (i.e., present at installation) and were not due to porosity reduction.

Adverse hydraulic changes may also be caused by gas formation or biomass accumulation. According to Equation (4), hydrogen gas may be produced and the production of other gases is possible; for example, methane was reported at the *in situ* PRB at Copenhagen Freight Yard (Denmark) (Kiilerich *et al.*, 2000) and at the *ex situ* cell C at the UMTRA site (Durango, CO) (Morrison *et al.*, 2002c), presumably from the activity of methanogenic bacteria. *Ex situ* PRBs and laboratory studies, which are confined systems, frequently report plugging due to gas production [e.g., Portsmouth (OR) and UMTRA (Durango, CO)] (Korte *et al.*, 1997a; Mackenzie *et al.*, 1999; Morrison *et al.*, 2002b). However, none of the *in situ*

PRBs report porosity reduction due to gas production, suggesting that any gas that is formed is able to migrate out of the barrier. Similarly, biomass-related hydraulic changes have been observed in some laboratory studies (e.g., Taylor *et al.*, 1990; Vandevivere and Baveye, 1992) but do not seem to be an issue in the field. Microbial growth was minimal at Intersil (Sunnyvale, CA), Moffett Field (Mountain View, CA), Industrial Site (NY), Lowry AFB (CO), and Somersworth (NH) (Gu *et al.*, 1999), and although observed at locations like USCG (Elizabeth City, NC) and Denver Federal Center (CO), it did not impact performance, perhaps because biofouling is unlikely at the high pH and low  $E_H$  values often observed in ZVI PRBs (Liang *et al.*, 2000).

## OBJECTIVES

Since few *in situ* PRBs have failed due to other than design flaws, it is difficult to determine factors controlling longevity by looking at failure rates. Rather, the existing information must be analyzed for factors that place a PRB "at risk," defined as an increased likelihood of compromised performance, based on reports of a decrease in permeability or in contaminant removal. In ZVI PRBs, high concentrations of dissolved solids, dissolved oxygen, carbonate, nitrate, and/or sulfate are expected to favor media corrosion and solids precipitation. This tendency would be exacerbated at high pH or low  $E_H$ . For example, to quantify the likelihood of precipitation, Liang *et al.*, (2003) argued that the saturation indices (SI) for calcite and iron (oxyhydr)oxides, defined as the difference between the actual pH and the pH at which solution ions would be in equilibrium with a solid phase ( $SI = pH_{\text{actual}} - pH_{\text{equilib}}$ ) (Köber *et al.*, 2002), may be a suitable parameter for predicting clogging, and thus reduced longevity. Using this approach, severe clogging over a 10-year period was predicted at the Monticello (UT) PRB, and, indeed, this PRB experienced a hydraulic conductivity loss of three orders of magnitude four years after installation (Mushovic *et al.*, 2006).

The objective of this research is to analyze the geochemical and performance data from existing *in situ* ZVI PRBs and determine whether certain geochemical parameters can indeed indicate a potential for reduced PRB longevity. In particular, three categories of parameters were considered: (1) master variables like pH and  $E_H$ , (2) parameters related to the quantity of precipitation [these precipitation parameters include total dissolved solids, dissolved oxygen and the concentrations, mass fluxes and cumulative fluxes of individual solutes (e.g.,  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$ ), and saturation indices]; and (3) parameters relating to reactivity promotion or inhibition (e.g., anions like

$\text{NO}_3^-$  and  $\text{Cl}^-$ ). It is recognized that these categories of parameters are not mutually exclusive: pH affects carbonate speciation, carbonate affects iron reactivity, etc.

## METHODS

Because of the limited comprehensive geochemical data available in the literature, the quantitative analysis was, of necessity, confined to 16 ZVI *in situ* field PRBs treating organics and/or metals for which extensive information was available (Table 3). *Ex situ* barriers were not included in the analysis, for they clearly operate under different conditions than *in situ* barriers, rendering them more prone to failure. Based on information provided in the literature and geochemical principles, 37 parameters were selected for consideration (Tables 4 and 5). Frequently, ranges of values, or values from several sampling events, or values from different monitoring wells were reported for a given parameter at a particular PRB. To distill this information to a single data point for the analysis, an arithmetic mean was used for all parameters except hydraulic conductivity, hydraulic gradient, and flow rate. Reported values of these parameters frequently ranged over several orders of magnitude, so a geometric mean was used. In some cases, geochemical parameters such as total dissolved solids and alkalinity were not reported and were calculated from the available information. Sites were assigned a 0 or 1 indicating failure, or 0 or 1 indicating at risk if a loss in permeability, a loss in reactivity, or some other indication of compromised performance was reported. The collated data are presented in Table 4 and the calculated parameters in Table 5.

Both graphical and statistical analyses were conducted to determine which geochemical parameters are correlated with potential decreased longevity. As a first cut, the data were plotted to give a rough indication as to whether the particular parameter had any relation to classifying PRBs as at risk. Statistical analyses included an assessment for collinearity, univariate and multivariate logistic regression, and maximization of odds ratios. The degree of linear correlation for all parameter combinations was calculated using the SPSS statistical software package (SPSS Inc., Chicago, IL). The sample correlation coefficient, also known as Pearson's correlation, is defined as (Myers, 1990):

$$r = \frac{S_{xy}}{\sqrt{S_{xx}S_{yy}}} \quad (6)$$

where  $S$  is the residual sum of squares (either for the interaction of 2 variables or each variable singly). Variables found to be correlated at the 95% confidence level

**Table 3.** Summary of PRBs analyzed.

<i>Name and location</i>	<i>Contaminants</i>	<i>Performance notes</i>	<i>Reference</i>
Beka Site; Tubingen, Germany	TCE; cDCE; VC	Despite the precipitation of calcium, iron, and magnesium carbonates, no changes in hydraulics were observed.	(Klein and Schad, 2000)
Canadian Forces Base, Borden; Borden, Ontario	TCE; PCE	Lower contaminant concentrations could have been achieved with higher Fe:sand ratio, or a more reactive Fe. Observed half-lives were ~6 times larger than those in bench tests, and rate constants decreased over time. Observations with time: 1 year—no visual or microbial fouling; 2 years—no precipitates or cementation; 4 years—precipitates observed; 5 years—no decline in performance.	(Nicholson <i>et al.</i> , 1983; O'Hannesin, 1993; O'Hannesin and Gillham, 1998; RTDF, 2001)
Chlorinated Solvent Manufacturing; Sydney, Australia	PCE; CTC	Estimated 1.3% porosity loss/yr (based only on precipitation of FeS).	(Duran <i>et al.</i> , 2000)
Copenhagen Freight Yard; Copenhagen, Denmark	TCE; cDCE; VC	Failure due to poor hydraulic characterization (1/5 of plume migrates around PRB) and precipitates. H <sub>2</sub> (g) production equiv. to 5% of pore space/day. TDS reduced by 600 mg/L through wall; most precipitates are in the upgradient part of wall. Precipitates reduced hydraulic conductivity from 5.2 m/day to 0.7 m/day during first year; loss stabilized after 1 year.	(Kiiricher <i>et al.</i> , 2000; Kjeldsen and Fulgsang, 2000; RTDF, 2001)
Denver Federal Center; Denver (Lakewood), CO	TCE; cDCE; 1,1-DCA; 1,1,1-TCA; 1,1-DCE	Hydraulic mounding and bypassing observed. Estimates of 0.35–0.5% porosity loss/year due to calcite and siderite—most at upgradient interface. Some cemented areas after 5 years; effects on hydraulic conductivity are expected. After 4 years, 10–50 µm layer of precip. at the upgradient interface (<20 cm into barrier). After 5 years, 50% of upgradient interface pore space is lost. H <sub>2</sub> (g) production decreases with time in Gate 2.	(McMahon <i>et al.</i> , 1999; RTDF, 2001; FRTR, 2002; Wilkin and Puls, 2003; Wilkin <i>et al.</i> , 2003)
Dover Air Force Base, Area 5; Dover, DE	PCE; TCE; DCE	Little precipitation observed after 18 months; no conclusions about long-term performance drawn. pH increases were not controlled by the pyrite-Fe mix, and the pyrite-Fe mix was not as effective at removing DO as pure Fe.	(Gavaskar <i>et al.</i> , 2000; Yoon <i>et al.</i> , 2000; Liang <i>et al.</i> , 2001; RTDF, 2001; FRTR, 2002)
Haardkrom Site; Kolding, Denmark	Cr	Failure attributed to heterogeneous loading of PRB, which has created “exhaustion of iron–chromate removal capacity in the wall” (RTDF, 2001).	(Kjeldsen and Fulgsang, 2000; RTDF, 2001; Kjeldsen 2006, personal communication)
Industrial Facility; Upstate New York	TCE; cDCE; VC	Expect 10% porosity loss over 2 years. 6% (wt) CaCO <sub>3</sub> at upgradient interface; <1% 15 cm into barrier. Calcite and aragonite dominate at upgradient interface. No adverse effects of precip noted: VOC removal constant; hydraulic conductivity close to fresh iron; water velocity constant. Expect H <sub>2</sub> -utilizing and sulfate reducing bacteria, but no microbial films observed. Suggest periodic scarification of upgradient face if necessary.	(Vogan <i>et al.</i> , 1998, 1999)
Intersil Semiconductor Site; Sunnyvale, CA	TCE; cDCE; VC	Pea gravel PTZ has resulted in precipitation of minerals and pretreatment of contaminants, and is therefore expected to increase life. Production of H <sub>2</sub> (g) (to near saturation) taken as indication of continued PRB operation (i.e., Fe corrosion continues).	(Warner <i>et al.</i> , 1998; RTDF, 2001; Sorel <i>et al.</i> , 2003)



Name and location	Contaminants	Performance notes	Reference
Lowry Air Force Base; CO	TCE	Estimate 9.7% porosity loss over 18 months. Groundwater flow has probably not been affected by porosity changes. "During a clogging study performed in May 1997, 18 months after installation, calcite, aragonite, "green rusts," amorphous iron hydroxides, and magnetite were observed. A porosity loss of 9.7% for the 18-month operational period was estimated from the investigation" (RTDF 2001).	(Vogan <i>et al.</i> , 1998; EPA, 1999; Jain <i>et al.</i> , 1999; RTDF, 2001; FRTR, 2002; ESTCP, 2003)
Moffett Field; Mountain View, CA	TCE; eDCE; PCE	Aragonite, calcite, iron carbonate hydroxide found at upgradient interface. Some precipitates found in well silt traps.	(Sass <i>et al.</i> , 1998; EPA, 1999; RTDF, 2001; Yabusaki <i>et al.</i> , 2001; FRTR, 2002; Gavaskar <i>et al.</i> , 2005)
Monticello Mill Tailing Site; Monticello, Utah	U; Mn; Mo; NO <sub>3</sub> <sup>-</sup> ; As; Se; V	Postulated that PTZ of gravel mix allows precipitation to occur upgradient of the reactive media. In contrast to column tests, effluent Fe concentrations are kept low by precipitation of Fe(OH) <sub>2</sub> 1 foot of upgradient mounding caused by 3 orders of magnitude hydraulic conductivity loss in pure ZVI; PTZ hydraulic conductivity remains unchanged.	(Ott, 2000; US DOE—Subsurface Contaminants Focus Area, 2000; Morrison <i>et al.</i> , 2001, 2002a; RTDF, 2001; Purdy <i>et al.</i> , 2002)
Somersworth, NH Landfill Superfund	PCE; TCE; 1,2-DCE; VC	Initial decrease in hydraulic conductivity due to settling.	(Sivavec <i>et al.</i> , 2003; O'Hara, 2006, personal communication)
USCG Support Center; Elizabeth City, NC	Cr; TCE	Estimate 1–2% porosity loss per year, but this should not affect the PRB permeability for 10 years. No hydraulic performance changes observed over 5 years.	(Puls <i>et al.</i> , 1999; RTDF, 2001; FRTR, 2002; Wilkin <i>et al.</i> , 2003, 2005)
Vapokon Site, Denmark	PCE, TCE, cis-DCE, VC, other chlorinated organics	No "pronounced" deterioration of chlorinated organic removal. Expect hydraulics change in future—limiting lifespan to 10 years. Tracer study reveals zones of low permeability and clogging that change flow path. 0.88% porosity loss per year between March 2000 and August 2003.	(Lai <i>et al.</i> , 2005, 2006)
Y-12 Plant; Pathway 2; Oak Ridge, TN	U, NO <sub>3</sub> <sup>-</sup>	Oxidation, precipitation, and cementation increased from 15 to 30 months (depends on depth). Akagenite transforms to goethite, and amorphous FeS into mackinawite. Fe oxy(hydr)oxides dominate precipitates; calcite not observed until 30 months. 30–80% of Fe filings are replaced by FeOOH corrosion rinds in cemented zones; Fe reactivity decreases. Based on corrosion, estimate lifespan of 5–10 years.	(Ott, 2000; Phillips <i>et al.</i> , 2000; Korte, 2001; Liang <i>et al.</i> , 2001; FRTR, 2002; Gu <i>et al.</i> , 2002; Phillips <i>et al.</i> , 2003; Gu, 2005a, 2005b)

**Table 4.** Reported geochemical data for PRBs.

Name	Run Time (year)	Flow Rate (m/day)	pH influent	pH internal	$E_H$ internal (mV)	TDS influent (mg/L)	DO influent (mg/L)	$Ca^{2+}$ influent (mg/L)	$Ca^{2+}$ internal (mg/L)	Alk influent (mg/L as $CaCO_3$ )	Alk internal (mg/L as $CaCO_3$ )	$CO_3T$ influent (mg/L as $CO_3^{2-}$ )	$Fe(T)$ internal (mg/L)	$SO_4^{2-}$ influent (mg/L)	$NO_3^-$ influent (mg/L)	$Cl^-$ influent (mg/L)	PTZ	$\Delta hydr.$	$\Delta perf.$	Failure	At risk
Beka Site, Germany	2	0.015	7.1	10.1	-310	800	1.0	150	20	338	711	464	0.25	88	7	75	1	0	0	0	0
Canadian Forces Base, Borden, Canada	10	0.082	8.1	8.7	-330	1065	3.4	278	102	140	82.0	170	7.5	609	0.6	2	0	0	0	0	0
Chlorinated Solvent Manufacturing, Australia	1	0.60	4.6	7.0	-217	1907	0.0	—	—	15.3	185	941	201	159	—	—	0	0	0	0	0
Copenhagen Freight Yard, Denmark	3	0.11	7.7	9.4	—	1222	0.2	130	3.6	503	299	625	0.2	110	0.2	180	1	1	0	0	1
Denver Federal Center, CO	7	0.07	7.5	9.7	-190	1100	0.61	107	2.7	440	350	560	0.04	260	2	64.5	1	1	0	0	1
Dover Air Force Base, Area 5, DE	4	2.5	5.1	10.8	-320	106	4.2	4.5	7.0	6	41.9	129	0.06	19.5	8	30	1	0	0	0	0
Haardkrom Site, Denmark	2	0.061	8.7	10.5	—	322	5.2	53.5	5	121	188	143	0.2	85.5	34.4	—	0	0	1	1	1
Industrial Facility, Upstate NY	4	0.45	7.4	9.5	-459	489	—	90.6	9.6	239	61.1	310	0.16	17.2	0.31	47.4	1	0	0	0	0
Intersil Semiconductor Site, CA	8	0.23	7.8	10.5	-350	686	2.0	—	—	235	7.4	291	0.05	400	—	—	1	0	0	0	0
Lowry Air Force Base, CO	8	0.30	6.9	10.0	-725	2900	0.66	290	—	530	—	795	—	1000	4	100	0	0	0	0	0
Moffett Field, Mountain View, CA	9	0.054	7.1	10.5	-372	820	0.1	158	10.9	288	20.2	400	0.02	350	2.4	40.9	1	0	0	0	0
Monticello Mill Tailing Site, UT	3	5.7	6.5	9.0	-388	1300	0.44	339	2.11	237	22.0	460	0.17	1170	118	123	1	1	1	1	1
Somersworth Landfill, NH	4	0.09	6.5	10.0	-750	400	2.0	82.7	37.5	338	175	660	0.0	13.7	0.5	84.3	0	0	0	0	0
USCG Support Center, NC	8	4.5	6.1	9.8	-400	290	1.1	12.5	5.3	50	38.0	155	0.05	49	1.1	40	0	0	0	0	0
Vapokon Petrochem. Works, Denmark	7	0.27	7.2	9.8	-133	754	3.4	179	42.7	314	64.5	422	2.5	120	—	46.0	1	1	0	0	1
Y-12 Plant; Pathway 2, TN	6	2.2	6.7	9.0	-166	887	2.8	190	93	360	868	604	14.9	92.5	85	50.5	1	1	1	0	1

“inf” and “int” indicate influent and values, respectively; “Run Time” is the time from a PRB’s construction to the most recently published information regarding that PRB; “ $CO_3T$ ” indicates total carbonate (the sum of carbonate, bicarbonate, and carbonic acid); “PTZ” stands for Pretreatment Zone; “ $\Delta hydr.$ ” and “ $\Delta perf.$ ” indicate reported changes in hydraulics and performance, respectively; “At risk” indicates a PRB for which either a hydraulic change, a performance change, or failure has been reported; DO, dissolved oxygen; TDS, total dissolved solids.

**Table 5.** Calculated geochemical data for PRBs.

<i>Name</i>	<i>Ca Flux</i> ( <i>g m<sup>-2</sup> day<sup>-1</sup></i> )	<i>Alk Flux</i> ( <i>g m<sup>-2</sup> day<sup>-1</sup></i> )	<i>CO3T Flux</i> ( <i>g m<sup>-2</sup> day<sup>-1</sup></i> )	<i>SO4<sup>2-</sup> Flux</i> ( <i>g m<sup>-2</sup> day<sup>-1</sup></i> )	<i>NO3<sup>-</sup> Flux</i> ( <i>g m<sup>-2</sup> day<sup>-1</sup></i> )	<i>Cl<sup>-</sup> Flux</i> ( <i>g m<sup>-2</sup> day<sup>-1</sup></i> )	<i>Ca<sup>2+</sup> Cumm. Flux</i> ( <i>kg m<sup>-2</sup></i> )	<i>Alk Cumm. Flux</i> ( <i>kg m<sup>-2</sup></i> )	<i>CO3T Cumm. Flux</i> ( <i>kg m<sup>-2</sup></i> )	<i>SO4<sup>2-</sup> Cumm. Flux</i> ( <i>kg m<sup>-2</sup></i> )	<i>NO3<sup>-</sup> Cumm. Flux</i> ( <i>kg m<sup>-2</sup></i> )	<i>Cl<sup>-</sup> Cumm. Flux</i> ( <i>kg m<sup>-2</sup></i> )	<i>SI Calcite</i>	<i>SI Aragonite</i>	<i>SI Siderite</i>	<i>SI Fe(OH)<sub>2</sub></i>	<i>SI Magnetite</i>	<i>SI Hematite</i>	<i>SI Ferrhydrite</i>	<i>SI Goethite</i> <i>At risk</i>	
Beka Site, Germany	2.2	5.0	6.8	1.3	0.10	1.1	1.6	3.6	5.0	0.94	0.075	0.80	2.8	2.6	1.1	0.23	2.5	2.0	0.66	1.7	0
Canadian Forces Base, Borden, Canada	22.8	11.5	13.9	49.9	0.049	0.16	83.2	42.0	50.9	182	0.18	0.60	1.5	1.3	1.9	0.27	2.1	1.4	0.11	1.2	0
Chlorinated Solvent Manufacturing, Australia	—	9.2	564	95.4	—	—	—	3.4	206	34.8	—	—	—	—	2.1	-0.72	1.4	0.80	-0.50	0.57	0
Copenhagen Freight Yard, Denmark	14.3	55.3	68.8	12.1	0.022	19.8	15.7	60.5	75.3	13.2	0.024	21.7	1.2	1.1	—	—	—	—	—	—	1
Denver Federal Center, CO	7.5	30.8	39.2	18.2	0.14	4.5	19.1	78.7	100	46.5	0.36	11.5	1.4	1.2	0.027	-0.42	2.5	2.1	0.78	1.8	1
Dover Air Force Base, Area 5, DE	11.0	14.7	317	47.8	19.6	73.5	16.1	21.5	463	69.8	28.6	107	1.3	1.1	-2.6	-0.42	2.2	1.7	0.40	1.5	0
Haardkrom Site, Denmark	3.3	7.4	8.7	5.2	2.1	—	2.4	5.4	6.4	3.8	1.5	—	1.7	1.6	—	—	—	—	—	—	1
Industrial Facility, NY	40.8	108	139	7.7	0.14	21.3	59.5	157	204	11.3	0.20	31.1	1.00	0.85	0.50	0.043	1.6	0.78	-0.52	0.55	0
Intersil Semiconductor Site, CA	—	52.8	65.4	90.0	—	—	—	154	191	263	—	—	—	—	-2.6	-0.26	2.1	1.5	0.24	1.3	0
Lowry Air Force Base, CO	87.0	159	239	300	1.2	30.0	254	464	697	876	3.5	87.6	—	—	—	—	—	—	—	—	0
Moffett Field, Mountain View, CA	8.5	15.6	21.6	18.9	0.13	2.2	28.0	51.1	71.0	62.1	0.43	7.3	1.1	0.95	-2.5	-0.45	1.9	1.3	-0.006	1.1	0
Monticello Mill Tailing Site, UT	1351	2620	6669	673	701	2116	1479	2869	7303	736	768	768	1.5	1.4	-0.065	-0.28	1.5	0.81	-0.49	0.58	1
Somersworth Landfill, NH	7.4	30.4	59.4	1.2	0.045	7.6	10.9	44.4	86.8	1.8	0.066	11.1	2.4	2.2	—	—	—	—	—	—	0
USCG Support Center, NC	55.6	223	690	218	4.7	178	162	650	2015	637	13.6	520	0.77	0.62	-0.37	-0.071	1.9	1.2	-0.15	0.92	0
Vapokon Petrochem. Works, Denmark	48.9	85.7	115	32.8	—	12.5	125	219	294	83.9	—	32.0	1.9	1.8	-0.12	-0.050	3.0	2.7	1.4	2.4	1
Y-12 Plant; Pathway 2, TN	418	792	1328	204	187	111	915	1735	2909	446	410	243	2.7	2.6	3.1	0.53	3.4	3.0	1.7	2.8	1

SI indicates, saturation index; CO3T indicates total carbonate (i.e., the sum of the carbonate species: carbonate, bicarbonate, and carbonic acid).

were discarded. Then, univariate logistic regression was carried out, following the approach outlined in Hosmer and Lemeshow (1989), using the SPSS software package. For the vector  $\mathbf{x}$ , a set of independent, predictor variables (the geochemical parameters), the conditional probability,  $\pi(\mathbf{x})$ , of a dependent variable outcome of at risk can be calculated from:

$$\pi(\mathbf{x}) = \frac{\exp(g(\mathbf{x}))}{1 + \exp(g(\mathbf{x}))} \quad (7)$$

using a linear predictor,  $g(\mathbf{x})$ , with coefficients  $\beta_i$ :

$$g(\mathbf{x}) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_p x_p + \dots + \varepsilon \quad (8)$$

where  $\varepsilon$  accounts for variations that are not covered by terms in the model. If the logistic regression considers only one variable, then this linear predictor reduces to  $g(\mathbf{x}) = \beta_0 + \beta_1 x_1 + \varepsilon$ . Continuously scaled variables (such as influent alkalinity), binary variables (such as the use of a pre-treatment zone), and combinations of variables may all be included in  $g(\mathbf{x})$ . The coefficients  $\beta_i$  are calculated through regression between the independent predictor variable vector  $\mathbf{x}$  and  $g(\mathbf{x})$ .  $g(\mathbf{x})$  is determined using Equation (7), assuming that  $\pi(\mathbf{x})$  may be calculated as:

$$\pi(\mathbf{x}) = P(\text{at\_risk}|\mathbf{x}) \quad (9)$$

where an estimate of  $P(\text{at\_risk}|\mathbf{x})$  is based on counts of PRBs that are at risk and those which are not (Hosmer and Lemeshow, 1989; Faraway, 2006).

In estimating each value of  $\beta_i$ , a standard error (SE) is estimated, and thus, the Wald statistic ( $\text{Wald}_i = \beta_i/\text{S.E.}(\beta_i)$ ) may be calculated. The Wald statistic tests the null hypothesis that  $\beta_i = 0$ ; if the significance (or  $p$ -value) associated with the regression is acceptably small (e.g.,  $\leq 0.25$ ), it may be assumed with the associated confidence level (for  $p \leq 0.25$ , this confidence level is 75%) that the null hypothesis may be rejected, and thus, the estimate of  $\beta_i$  is equivalent to  $\beta_i$ . Based on the recommendation of Hosmer and Lemeshow (1989), variables with significance  $\leq 0.25$  were considered further.

In addition to logistic regression, odds ratio maximization was used to identify geochemical parameters with a strong relationship to at-risk PRBs. The odds ratio estimates how much more likely it is for a certain out-

come (e.g., at risk) given an input (e.g., influent alkalinity concentration above a specified value). The odds ratio can be expressed as (Hosmer and Lemeshow, 1989)

$$\psi = \frac{\pi(1)/(1 - \pi(1))}{\pi(0)/(1 - \pi(0))} \quad (10)$$

where  $\pi(1)$  is the probability of being at risk, and  $\pi(0)$  is the probability of being not at risk.

If  $\pi(\mathbf{x})$  is not known, the probabilities may be estimated with a contingency table, a  $2 \times 2$  matrix that shows, for each possible outcome, the number of cases with each independent variable. For example, consider the parameter influent alkalinity concentration or  $\text{Alk\_inf}$  (Table 4). If 300 mg/L is defined as the cutoff value, then of the PRB sites with  $\text{Alk\_inf} \geq 300$  mg/L, 4 are at risk, and 3 are not at risk. Similarly, the cases with  $\text{Alk\_inf} < 300$  mg/L are divided into 2 at risk and 7 not at risk, yielding the contingency table shown in Table 6. The estimated odds ratio is then  $(4/3)/(2/7)$ , or 4.67. This result indicates that, for this dataset, sites with  $\text{Alk\_inf} \geq 300$  mg/L are 4.67 times more likely to be at risk than those with lower  $\text{Alk\_inf}$ .

The selection of a cutoff value is integral to the calculation of an odds ratio. In this study, the odds ratio for each parameter was maximized. Cutoff values for each parameter were systematically varied over 100 steps between the minimum and maximum values for that parameter, and the maximum odds ratio was recorded. A perfect predictor, a cutoff below which all sites were not at risk and above which all sites were at risk, would lead to the recording of zero values in the off-diagonal in the contingency table, and thus a value of zero in the denominator of Equation (10). In those cases, the zero value was replaced with 0.5, as recommended by Hosmer and Lemeshow (1989). To evaluate the importance of the calculated odds ratios, significance values were computed using the two-sided Fisher Exact test. This test, a form of the chi-square evaluation, is appropriate for sparse datasets and evaluates whether the tested variables are independent or associated (Faraway, 2006). In the current study, a significance ( $p$ -value) of 0.05 was used as the criterion for inclusion of variables for further consideration.

Finally, those parameters selected by the univariate logistic regression based on a significance  $\leq 0.25$  or an odds

**Table 6.** Example of contingency table using a cutoff value for influent concentration of alkalinity of 300 mg/L.

Total = 16	$\text{Alk\_inf} \geq 300$ mg/L	$\text{Alk\_inf} < 300$ mg/L
At risk	4	2
Not at risk	3	7

ratio Fisher Exact test significance  $\leq 0.10$  were incorporated into a multivariate logistic regression model. These variables were then used together in logistic regression [Eqs. (7–9)] in an attempt to judge the relative significance of the variables in determining longevity potential.

## RESULTS AND DISCUSSION

### Graphical analysis

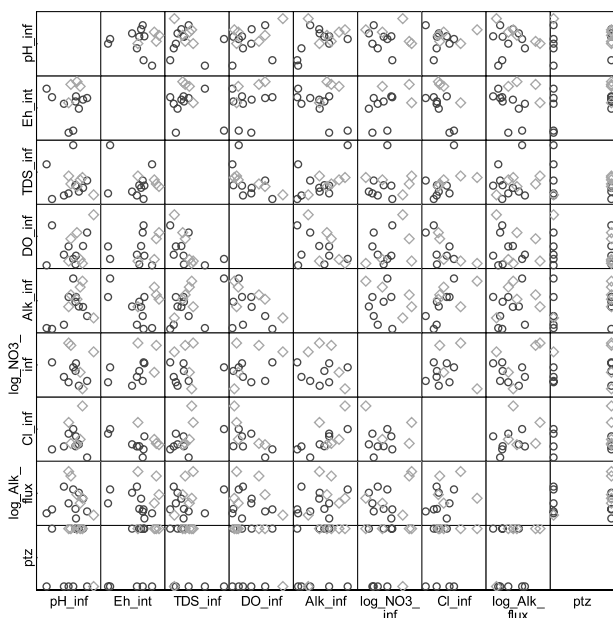
To determine which geochemical parameters correlate with compromised PRB performance, matrix plots of all the variables were constructed, an example of which is shown in Fig. 2. In this figure, PRBs classified as at risk are indicated by diamonds, while those PRBs not at risk are indicated by circles. Regions in these two-dimensional geochemical spaces where PRBs at risk and those not at risk tend to group may be indicative of important geochemical parameters; lack of grouping is suggestive of little correlation. For example, this figure suggests that dissolved oxygen (DO) and total dissolved solids (TDS) (shown enlarged in Fig. 3), although expected to strongly influence PRB performance based on the literature, do not do so. Column studies and theoretical calculations have clearly shown the possibility of deleterious effects of DO on barrier hydraulics (Liang *et al.*, 1997; Mackenzie *et al.*, 1999; Kjeldsen and Fulgsang, 2000; Ott, 2000;

Simon *et al.*, 2001; Morrison *et al.*, 2002b). DO is expected to corrode iron, increase pH, and promote the formation of (oxyhydr)oxide solids. If influent DO were a controlling factor, at risk PRBs should be grouped above some cutoff DO value. Yet Fig. 3a shows at-risk PRBs at extremely low DO values, suggesting that DO is not well correlated with PRB longevity.

Similarly, based on the literature, it seems likely that TDS is a good estimator of potential failure: high influent TDS concentrations generally lead to high quantities of mineral precipitation (Gillham *et al.*, 1993; Gu *et al.*, 1999; ESTCP, 2003; Wilkin and Puls, 2003). However, as seen in Fig. 3b, there are several PRB sites with high TDS that are not at risk. If solutes such as  $\text{Na}^+$  account for a large portion of the dissolved solids, TDS may not be a reliable indicator of the potential for precipitation.

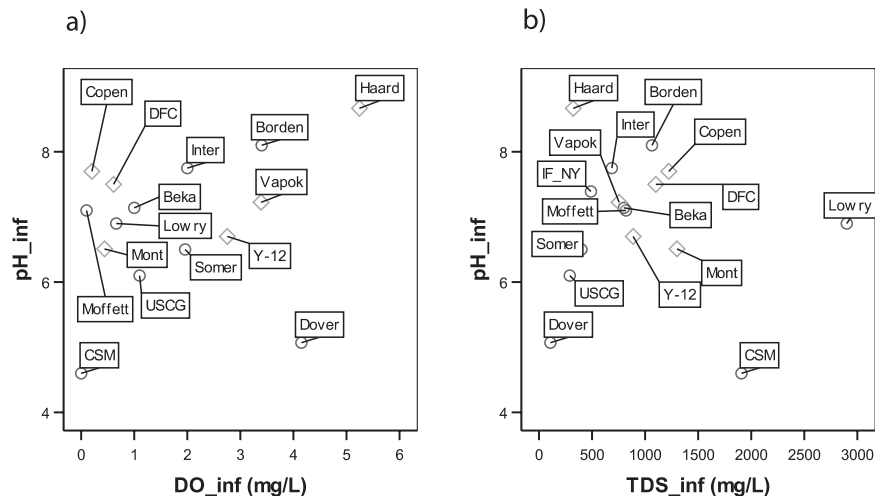
Besides suggesting parameters that may not correlate with the potential for reduced longevity, these matrix plots indicated other parameters that might be related to at-risk PRBs. Perhaps most evident were very high fluxes and cumulative fluxes of influent alkalinity, as well as influent concentrations and cumulative fluxes of nitrate (Fig. 4). Although these outliers were few in number, the extreme values appear to be strongly correlated with at-risk PRBs. Monticello (UT) and Y-12 (Oak Ridge, TN) PRBs have very high mass fluxes and cumulative fluxes for alkalinity and nitrate (as well as total carbonate and calcium); these PRBs are also classified as at risk. This finding makes conceptual sense, as exceptionally high mass loadings increase the possibility of high levels of precipitation (Wilkin and Puls, 2003). In addition, nitrate has been shown to inhibit corrosion (e.g., Köber *et al.*, 2002; Devlin and Allin, 2005). In most PRBs, nitrate values are generally quite low; only Monticello, Y-12, and Haardkrom (Denmark) have values above 10 mg/L, and of these three, two, Monticello and Haardkrom, have actually failed.

This analysis of the matrix plots also indicated some combinations of parameters that may be correlated with at-risk PRBs, including internal  $E_H$ , influent alkalinity, influent chloride concentrations, and the saturation indices of iron(III) solids. Two example plots are shown in Fig. 5. Figure 5a shows a complete separation of at-risk and not-at-risk PRBs using internal  $E_H$  and influent chloride concentration. In the upper right section of the graph, the at-risk PRBs are found, while the not-at-risk PRBs lie below and to the left. This PRB grouping makes sense: higher  $E_H$  values may lead to more oxidation and thus more potential passivation of iron (Stumm and Morgan, 1996; Johnson *et al.*, 1998; Wilkin and Puls, 2003). Chloride has been shown to increase corrosion of iron (Johnson *et al.*, 1998; Devlin and Allin, 2005), which would be expected to improve PRB performance; however,



**Figure 2.** Matrix plots of selected geochemical parameters. At-risk PRBs are indicated by diamond markers, not-at-risk by circles. Units are (mg/L) except for  $E_H$  (mV) and ptz (1 indicates use of a pretreatment zone).



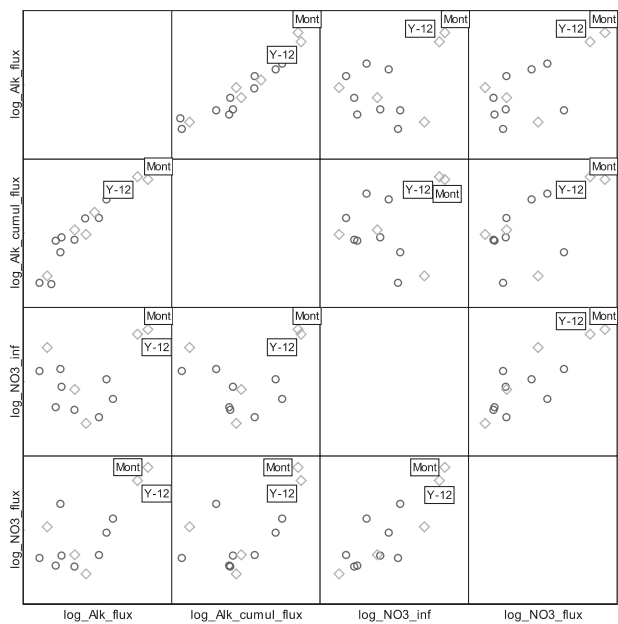


**Figure 3.** Plot of at-risk and not-at-risk PRBs with respect to influent pH and (a) influent DO, (b) influent TDS. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

Klausen *et al.*, (2001) showed that the reactivity-diminishing effects of nitrate may outweigh the corrosion-promoting effects of chloride. Figure 5b shows the data set plotted as a function of influent alkalinity and nitrate concentration. Although the separation of at-risk and not-at-risk PRBs is not as definitive as in Fig. 5a, Fig. 5b still suggests that higher alkalinity and higher  $\text{NO}_3^-$  concentrations correlate with being at risk. The PRB at Lowry AFB (CO), with low nitrate and high alkalinity, is an ex-

ception to this trend, but considering Fig. 5a, this may be attributable to its very low  $E_H$  value.

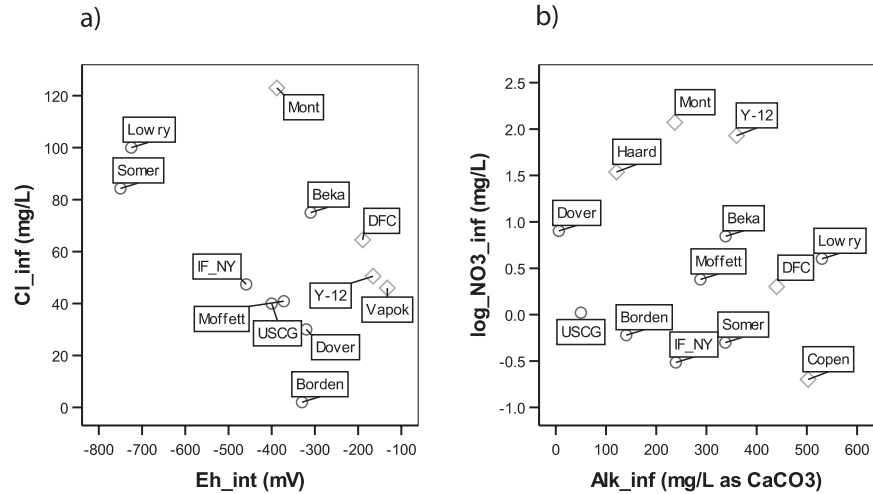
Finally, the matrix plots of the data indicated that many of the parameters, especially mass fluxes, cumulative fluxes, and saturation indices are strongly correlated with one another. The high degree of collinearity between mass fluxes ( $\text{g m}^{-2} \text{day}^{-1}$ ) and cumulative fluxes ( $\text{kg m}^{-2}$ ) (Fig. 6) suggests that variation in the flow rate dominates the parameter value rather than the variation in concentration. Similarly, the saturation indices of hematite, ferrihydrite, and goethite, all iron(III) species, and magnetite, an iron(II)/iron(III) solid, are collinear. This relationship stems from the fact that at the  $E_H$  values in the PRBs in this data set, aqueous iron(III) concentrations are negligible. Iron (III) concentrations may be calculated from reported values of iron (II), but it will be directly proportional to the reported  $E_H$  values. Because the saturation indices of these solids will vary with the aqueous iron(III) concentrations, all are collinear.



**Figure 4.** Significance of very high alkalinity and nitrate for prediction of at-risk PRBs. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

### Statistical analyses

To assess the degree of collinearity in the data, a Pearson correlation test was conducted. The results showed that three sets of variables had correlations significant at the 95% confidence level: (1) flow rate, mass fluxes, and cumulative fluxes; (2) the saturation indices of calcite and aragonite; and (3)  $E_H$  with saturation indices of iron(III) solids. Based on this analysis, it was deemed necessary only to include only one flux, one calcium carbonate solid, and one member of the third set. Based on its potential to diminish the hydraulic conductivity and reactivity of ZVI PRBs, the mass flux of alkalinity was chosen in the first category; calcite was chosen as the calcium carbonate



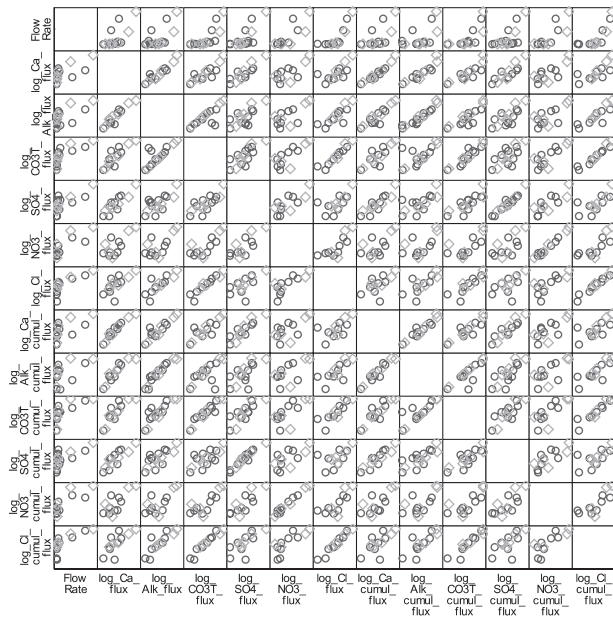
**Figure 5.** Geochemical parameters with relationship to at-risk and not-at-risk PRBs: (a) Influence chloride vs. internal EH; (b) influent nitrate vs. influent alkalinity. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

solid, and  $E_H$ , as a master variable, was chosen over the iron(III) solid saturation indices. In addition, it was found that influent alkalinity and chloride were linearly correlated at a 95% confidence level; however, both parameters were retained because they are not mechanistically related as the parameters in the other categories are.

Univariate logistic regression was carried out for each of the reported and calculated geochemical parameters in

Tables 4 and 5, with the exception of those parameters eliminated due to high collinearity, reducing the total number of parameters considered from 37 to 21. The results, presented in Table 7, include  $\beta_1$  [Eq. (7)] values, the S.E., the Wald value ( $\beta_1/S.E.$ ), and the  $p$ -value, or significance. Variables with a  $p$ -value  $\leq 0.25$  were considered to be significant: influent pH, internal  $E_H$ , influent alkalinity, mass flux of alkalinity, influent chloride, and the use of a pretreatment zone (ptz). Influent nitrate, with a significance of 0.258, is on the cusp of inclusion. These results agree well with the qualitative graphical analysis. With the exception of influent pH and ptz, the variables with  $p$ -values  $\leq 0.25$  were also identified visually. A reexamination of the influent pH data reveals that, while the pH data are tightly clustered relative to other variables, most at-risk PRBs have influent pH values  $>7$ ; on the other hand, there are several not-at-risk PRBs with lower influent pH values, while one, the PRB at Borden, Ontario has an influent pH  $>8$ . The probability of a PRB being at risk increases with the use of a pretreatment zone. Though counterintuitive, this appears to be a case of correlation, rather than causation. In cases where performance problems are anticipated, a PTZ is installed, which while undoubtedly useful, does not preclude loss of reactivity or permeability in the reactive zone.

To further corroborate the results of the graphical analysis and the univariate logistic regression, an odds ratio analysis was conducted using the same parameters as for the logistic regression. The results of this analysis are also shown in Table 7, which lists the maximum odds ratio achieved and the cutoff value corresponding to the maximum odds ratio. The two-sided Fisher Exact test was used to evaluate whether the tested variables are inde-



**Figure 6.** Matrix plot of fluxes, cumulative fluxes, and flow rate showing high degree of collinearity. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

**Table 7.** Univariate logistic regression analysis and maximized odds ratio results.

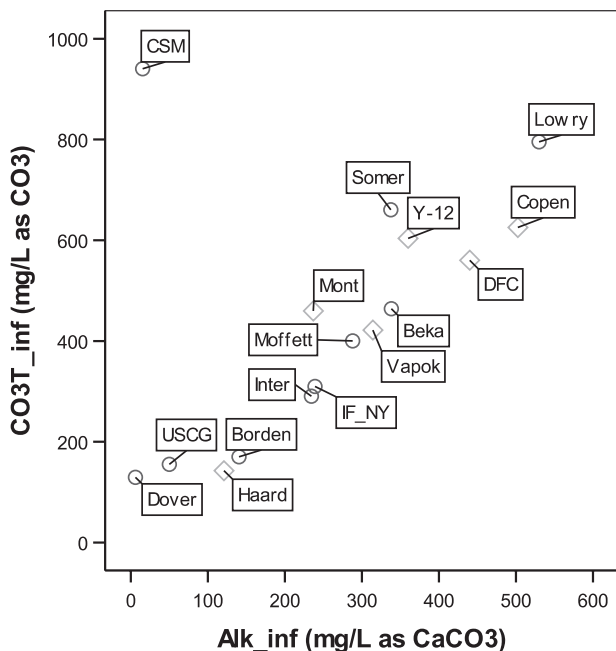
Parameter	Legend	Logistic regression				Odds ratio		
		$\beta_I$	Standard error	Wald significance	Max. odds ratio	Cutoff value	Fisher exact test significance	
Run Time (year)	RunTime	-0.1470	0.200	0.54	0.461	1.33	2.5	1.000
Flow Rate (m/day)	FlowRate	0.1806	0.302	0.36	0.550	2	1	0.604
pH influent	pH_inf	0.8910	0.700	1.62	0.203	4.67	7.2	0.302
pH internal	pH_int	-0.1315	0.564	0.05	0.816	3	8.9	0.500
$E_H$ internal (mV)	Eh_int	0.0161	0.009	3.32	0.069	60	-200	0.011
TDS influent (mg/L)	TDS_inf	0.0000	0.001	0.00	0.965	5	700	0.307
DO influent (mg/L)	DO_inf	0.2015	0.334	0.36	0.547	3.6	5	0.400
Ca <sup>2+</sup> influent (mg/L)	Ca_inf	0.0035	0.006	0.39	0.534	5	100	0.301
Ca <sup>2+</sup> internal (mg/L)	Ca_int	0.0106	0.012	0.84	0.359	6	40	0.266
Alk influent (mg/L as CaCO <sub>3</sub> )	Alk_inf	0.0050	0.004	1.70	0.192	9	350	0.118
Alk internal (mg/L as CaCO <sub>3</sub> )	Alk_int	0.0025	0.002	1.15	0.284	8	200	0.235
CO3T influent (mg/L as CO <sub>3</sub> <sup>2-</sup> )	CO3T_inf	0.0007	0.002	0.09	0.759	7.5	410	0.145
Fe(T) internal (mg/L)	Fe_int	-0.0180	0.035	0.26	0.610	1.75	1.3	1.000
SO <sub>4</sub> <sup>2-</sup> influent (mg/L)	SO4_inf	0.0003	0.001	0.04	0.840	8	75	0.234
NO <sub>3</sub> <sup>-</sup> influent (mg/L)	NO3_inf	0.1005	0.089	1.28	0.258	24	20	0.035
Cl <sup>-</sup> influent (mg/L)	Cl_inf	0.0246	0.018	1.93	0.165	10.67	110	0.128
Alk Flux (g/m <sup>2</sup> day)	Alk_flux	0.0040	0.003	1.37	0.242	5	25	0.307
SI Calcite	SI_calcite	0.5300	0.911	0.34	0.561	9	1.15	0.192
SI Siderite	SI_siderite	0.3483	0.377	0.85	0.356	8	-0.2	0.208
SI Fe(OH) <sub>2</sub>	SI_feoh2	0.9669	1.806	0.29	0.592	5.33	0.35	0.333
PTZ	ptz	1.6094	1.265	1.62	0.203	5	1	0.307

pendent or associated, with a cutoff significance of  $p \leq 0.10$ . Therefore, the geochemical parameters deemed to be most correlated with being at risk via odds ratio maximization were internal  $E_H$  and influent nitrate. While internal  $E_H$  was deemed highly significant by logistic regression, influent nitrate was on the borderline. Nitrate (Fig. 4) has outlying points; when fitting these data to the linear regressor equation  $g(\mathbf{x})$  [Eq. (7)], it is difficult to estimate an accurate  $\beta$  for this parameter, since there are outlying points and each point weighs heavily in the small data set. In contrast, when calculating the odds ratio, there is no weight associated with the extent that a point is an outlier (e.g., with an influent nitrate cutoff of 20 mg/L, the odds ratio treats values of 20.1 and 200 identically). Therefore, outliers do not affect the odds ratio in the same manner as in logistic regression.

Had a less stringent cutoff of, for example, a  $p$ -value  $\leq 0.15$  been chosen, the list of relevant parameters selected via odds ratio maximization would have included influent alkalinity, influent total carbonate, and influent chloride. With the exception of total carbonate, these additional parameters are a subset of those selected via logistic regression. Like influent nitrate, discussed above, the significance of total carbonate is very different when evaluated by logistic regression (significance = 0.76)

and by odds ratio maximization (Fisher's exact significance = 0.145). An inspection of the data, illustrated in Fig. 7, reveals that, although influent alkalinity and total carbonate are generally well correlated, there is one outlying point—that of the CSM PRB (Australia). This site has an unusually low pH, and hence, its low alkalinity does not correspond to low total carbonate. As in the case of nitrate, this outlier affects the fit such that the logistic regression using total carbonate predicts no at-risk PRBs for any of the total carbonate values in the data set. In contrast, the alkalinity values lack outliers, and hence, the estimated  $\beta$  value is more meaningful.

Both of the statistical approaches utilized here corroborated the qualitative graphical observations. TDS and DO are not major parameters in determining at-risk PRBs. However, influent pH, internal  $E_H$ , influent alkalinity, influent chloride, influent nitrate, mass flux of alkalinity, and use of a pretreatment zone are significant for describing at-risk PRBs. Despite the problems inherent with measuring  $E_H$  in the field (Sposito, 1989), both statistical approaches showed that this parameter has strong predictive power. While both approaches agreed on the significance of some parameters, influent nitrate was found to be more significant in the odds ratio analysis than in the logistic regression.



**Figure 7.** Differences between influent alkalinity and influent total carbonate; the CSM (Australia) PRB has unusually low influent pH. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

To better assess the relative significance and potential interaction of terms, multivariate logistic regression was performed with the combination of the parameters selected using the univariate logistic regression ( $p$ -value  $\leq 0.25$ ) and the maximization of the odds ratio ( $p$ -value  $\leq 0.10$ ): pH\_inf, Eh\_int, Alk\_inf, NO<sub>3</sub>\_inf, Cl\_inf, Alk\_flux, and ptz. Yet for this limited data set, internal  $E_H$  and influent chloride are “perfect predictors,” separating the data set completely into at-risk and not-at-risk groupings (Fig. 5a). Furthermore, the parameter subset influent alkalinity (or influent chloride, which is linearly correlated at the 95% confidence level), alkalinity mass flux, and influent nitrate perfectly predicted the data. Including perfect predictors into multivariate regression results in unstable parameter estimates (Faraway, 2006). Because of the limitations of the size of the data set, the best multivariate logistic regression that could be achieved included no interaction terms and only the parameters pH\_inf, Alk\_inf, and Alk\_flux. Even so, this model predicted at-risk PRBs with an 87.5% success rate, with Alk\_flux significant at a 90% confidence level and the other two at an 80% confidence level.

## CONCLUSIONS

PRBs, despite the lack of a thorough understanding of the processes therein, have worked well in most *in situ*

installations, as evidenced by the few PRBs reported to have failed. Indeed, nearly all *in situ* PRBs that use ZVI (i.e., rather than experimental media) and treat contaminants at field concentrations (i.e., not at the artificially high concentrations found in the laboratory) have met their design goals (Liang *et al.*, 2000). Furthermore, most PRBs continue to treat contaminants well despite the occurrence of potential problems such as porosity reduction. However, the current lack of understanding makes this apparent robustness seem fortuitous rather than designed.

The literature suggests that the major issue in PRB performance resulting in failure is design flaws (such as improper hydraulic characterization of a site), rather than depletion of media reactivity or media plugging. Predictions of severe plugging, usually based on laboratory work performed using conditions that are not representative of the field (elevated DO, abnormal concentrations and combinations of inorganic groundwater constituents, and high flow rates), are generally not borne out by field experience at *in situ* PRBs. *Ex situ* PRBs, on the other hand, experience conditions closer to the laboratory and suffer from high failure rates due to clogging, both from gas and precipitate production.

The quantitative analyses performed here suggest that high influent pH, internal  $E_H$ , high influent concentrations of nitrate, chloride, and alkalinity, are problematic for PRBs. Other parameters such as TDS, DO, and the SI of carbonate solids that have been suggested in the literature as controlling PRB longevity did not appear to have much predictive ability for classifying a PRB as at risk. Ideally, the parameters selected by univariate regression should be utilized in multivariate modeling to gain a better understanding of the relative significance of the parameters. However, the sparseness of the dataset made certain combinations of variables, like  $E_H$  and Cl<sup>-</sup>, perfect predictors, precluding their use in a multivariate analysis. Consequently, differentiating between reactivity and hydraulic changes as the dominant factor controlling PRB longevity with any certainty is not possible with the currently available data. Yet, the preponderance of variables selected as significant,  $E_H$ , alkalinity, and NO<sub>3</sub><sup>-</sup> influence PRB performance through their impact on ZVI reactivity. Thus, it appears that the inhibition of ZVI corrosion, rather than the loss of permeability, may determine PRB longevity.

As many PRBs begin their second decade of operation, they may be nearing the end of their estimated life spans (Table 2). Thus, it becomes critical that field PRBs are monitored more closely to determine the factors that control the time to failure. If it appears that precipitation at the upgradient face is dominant, lifetimes may be extended by the installation of a PTZ containing reactive



media, or by the periodic replacement of the first 20–30 cm of the PRB where the precipitates are concentrated. If media reactivity is the issue, then efforts should be directed toward developing methods for rejuvenating media *in situ* (Gavaskar, 1999; Gillham, 1999; Ott, 2000). Field experience suggests that PRBs are a more robust technology than one might anticipate based on laboratory column experiments. Thus, more detailed and comprehensive field monitoring is crucial to determining modes of failure and, in turn, PRBs' cost effectiveness as a long-term treatment technology.

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