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To Mike Jasinski/R1/USEPA/US@EPA, Gerardo Millan-Ramos/R1/USEPA/US@EPA, "Hoffman, Andrew" <ahoffman@des.state.nh.us>, Dick
cc "bbelmore@somersworth.com" <bbelmore@somersworth.com>, '"edward.jamison@ps.ge.com"'
bcc
Subject Somersworth Landfill - Response to Comments on 2006 Annual Report

Mr. Jasinski
Please find attached our Response to Comments from the EPA on the Annual Monitoring and Demonstration of Compliance Report for 2006, Somersworth Sanitary Landfill Superfund Site, Somersworth, New Hampshire. Please feel free to contact me our Tom Krug if you have any questions or require further information.
Thank you
Suzanne

Suzanne O'Hara
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TR0237 - Response to EPA Comments-2007-08-29.pdf

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August 29, 2007

Mr. Michael Jasinski, Chief
NH/RI Superfund Section
Office of Site Remediation and Restoration
U.S. Environmental Protection Agency
New England (Region I)
1 Congress Street (Suite 1100)
Boston, MA 02114-2023

Re: Response to Comments from NHDES and EPA on the Annual Monitoring and Demonstration of Compliance Report for 2006, Somersworth Sanitary Landfill Superfund Site, Somersworth, New Hampshire

Dear Mr. Jasinski;

On behalf of the Work Settling Defendants (WSDs) for the Somersworth Sanitary Landfill Superfund Site (the "Site"), Geosyntec Consultants (Geosyntec) has reviewed the comments, received in a letter dated June 13, 2007, from the United States Environmental Protection Agency (EPA) on the above referenced report and has prepared the following responses to the comments provided. The original comments are presented below along with our responses to comments. The responses to comments incorporate additional information on issues following our discussions during the conference call to discuss Comment Letter on August 16, 2007.

General Comments

1. ***EPA*** *- Thank you for laying out so clearly an overall summary of past events and their rationale, it was very enlightening.*

   Response - We will continue to maintain the summary of past events in future reports.

2. ***EPA*** *- In order to save paper and copying costs, for next deliverables, please send to EPA all the Appendices (data) on a CD-ROM. The rest of the report shall be delivered in a hard copy as usual. One copy shall suffice for EPA and please note that for NHDES you need to submit all deliverables following the procedures described in NH DES Waste Management Division Submittal Guidelines as posted at: http://des.nh.gov/orcb/doclist/Electronic_Submittal_Guidelines.pdf*

   Response - We would be happy to provide all of the appendices on CD in the future.

3. ***EPA*** *- On figures, 2.10c and 2.10d, what is going on at Wells FS-9A (?) and OB-17U? Do we have an explanation? If there are exceedances of CEs, what does it mean in terms of wall performance? Please discuss this in Section 4.1 (Summary and Conclusions of*

the Groundwater Monitoring Program). Have you considered the high concentrations observed, being the result of short residence times within the PRB, due to higher than anticipated GW flow velocities, or less iron thickness than the design criteria? Also, have you considered the precipitation of carbonate sulfide and hydroxide minerals within the PRB as performance parameters? Please refer to the EPA document titled "An In Situ Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water: Volume 2 Performance Monitoring" (EPA/600/R-99/095b, September 1999).

Response - OB-17U is upgradient of the PRB and is sampled to monitor the concentration of VOCs in the landfill waste. Data from OB-17U show that the landfill continues to act as a source of VOCs to groundwater. The concentrations of VOCs increased significantly in 2001. However, the concentrations of VOCs in OB-17U decline significantly in 2005 and again in 2006.

FS-9A was installed as a replacement for monitoring well FS-9 which was damaged during the construction of the CTW in 2000. FS-9 contained elevated concentrations of VOCs prior to construction of the CTW and it is believed that the concentrations at FS-9A likely reflect the prior existing elevated CE concentrations downgradient of the PRB (Appendix D Table D.1). As discussed in the report, the concentrations of cDCE and VC at FS-9A in have been declining since 2004.

It is possible that there is some connection between the elevated concentrations of VOCs that were observed in OB-17U at the landfill and the elevated concentrations observed at FS-9A in 2004 and 2005. We have considered the potential that the VOCs in FS-9A in 2004 and 2005 may be the result of: 1) short residence times within the PRB, due to higher than anticipated GW flow velocities; 2) less iron thickness than the design criteria; or 3) the potential impacts of operating parameters and precipitation on the performance of the PRB. We do not believe that any of these factors resulted in the VOCs observed in FS-9A in 2004 and 2005. We have not observed any changes in water levels that would indicate higher than anticipated groundwater velocities and we do not have any evidence that the PRB contains less iron thickness than the design. We have found no evidence that precipitation is occurring to a significant degree within the PRB and in fact a recent paper by Henderson and Demond (2007) evaluated the potential for performance problems at 16 ZVI PRBs including the one at Somersworth and concluded that the PRB at Somersworth was not "at Risk" for performance problems. What ever the cause of the elevated concentrations in FS-9A, the concentrations are exhibiting a decreasing trend.

4. ***EPA** - Both EPA and NHDES recognize there may be opportunities for cost savings if changes are made in the sampling frequency and/or methodology (e.g., reducing sampling frequency from three to two events per year). Please submit a proposal with any such changes and its rationale, for EPA and NHDES to review. Please add to this proposal one or more statistical analyses identifying seasonal and long-term variations that could help in optimizing the monitoring of natural attenuation.*

Response - We will evaluate the monitoring data from the Site using the MAROS software recommended by EPA during the August 16th, 2007 call as well as the methods mentioned in comment #4 and evaluate the potential for reduced monitoring at the Site. We received the MAROS software link from Richard Willey on August 23, 2007.

Specific Comments

1. ***EPA*** *- On page 12, 2nd paragraph, you assert that based on the PLFA data, biomass in the CTW has not increased and that it appears to be not significant; please explain the reasoning behind your conclusion. EPA and NHDES would like to confirm with you that this parameter (PLFA) is indeed the most economical and effective way of assessing the possibility of biofouling at the CTW. Please provide the rationale for your selection, including references to alternative methods that were not considered*

   Response - The PFLA measurement provides a quantitative estimate of the number of microbiological cells present in a groundwater sample by measuring the amount of phospholipid fatty acid. At the time that the SAP was developed for the Site, PLFA was one of two methods available to evaluate biological communities (the other was to culture the samples) and was by far the most cost effective method. Additional information on the PLFA analysis can be found at: <http://www.microbe.com/plfa.html>. If excessive biological growth were occurring in the PRB, we would expect to see an increase in the concentration of cells in the monitoring wells in the PRB. The PFLA measurements in nine monitoring wells within and in the vicinity of the PRB show either stable or decreasing concentrations suggesting that the amount of biological activity and therefore the degree of biofouling is not increasing. A review of long-term performance of ZVI PRBs conducted by Henderson and Demond (2007) also report that, "biofouling is unlikely at the high pH and low (E_H) values often observed in ZVI PRBs." Given the stable or declining values for the PFLA measurements and the fact that the pump testing within the PRB has not shown significant fouling of any kind in the PRB we believe that the monitoring for this parameter is not necessary in the future and recommend dropping this analysis form the monitoring program.

2. ***EPA*** *- On page 14, Section 2.2.2, please explain what value or values of mounding are considered excessive and provide references. Also, please clarify the purpose of this calculation.*

   Response - At the Denver Federal Facility it was reported (EPA, 1999) that there was ten feet of mounding of groundwater across a ZVI PRB. Ten feet of mounding was considered excessive and measures were taken to remedy the situation. While there are many differences in the configuration of the PRB at the Denver Federal Facility and the Somersworth Site, the degree of mounding observed at the Somersworth PRB is typically less that 0.2 feet and is not considered excessive. We are not able to resolve a difference in head of much more than about 0.05 feet. Excessive heads could result in diversion of groundwater flow around or beneath the PRB. We also look at: 1) the vertical gradients which would also be present if groundwater was being forced beneath the PRB by the presence of the PRB; and 2) the overall water table map for the site to see if there is diversion around the PRB. This other data do not indicate significant diversion of groundwater beneath or around the PRB. If we were to see the mounding increase significantly both laterally and vertically on a sustained basis relative to what we currently see we believe that further evaluation would be warranted.

3. ***EPA** - In Appendix D, please indicate somewhere that the bold figures are detectable levels.*

   Response - The following footnote will be added to the Notes section of these tables: "Bold values indicate the detection of a compound above the method detection limit".

4. ***EPA** - The scale for figures 2.10b through 2.18d, has not been changed as we previously requested via written comments (please see comment #5 from NHDES at the Response to Comments from NHDES and EPA on the Annual Monitoring and Demonstration of Compliance Report for 2005... you submitted to Mr. Michael Jasinski, Chief of NH/RI Superfund Section, on July 24, 2006). At the next report, please make the proper adjustments so that the graphs are more useful in depicting the changes in concentration levels. For example, on Figure 2.10c, it is impossible to see how much lower or similar were the October 2006 concentrations to the 2001 and 2003 concentrations.*

   Response - The scales on Figures 2.10b through 2.18d have been altered from the 2005 version of the Annual Report to allow for three different scales (0 to 300 µg/L, 0 to 800 µg/L and 0 to 2250 µg/L) versus the one scale used in 2005. The fixed scales were used to aid in the comparison of one graph to another on the figures. However, these figures will be generated in future with concentration-specific axes that will reflect the data plotted on each individual graph. Although this will make the direct comparison of one graph to another more difficult it will allow for all data plotted on one graph to be clearly displayed.

5. ***EPA** - On Appendix C, Table C-1, the Total CE concentration entering the CTW (Cinf) is based on the average total CE concentration for wells up gradient of the CTW, however, well CTW-50U is not up gradient of the CTW. Please explain why this well was selected, and whether the selection of this well poses limitations for flux calculations at Stream Tube C.*

   Response - Although CTW-50U is slightly transgradient to the CTW it is believed that it is representative of some of the water upgradient of Stream Tube C (see Figures 2.6, 2.7 and 2.8 – overburden flow maps). Since the calculation is on the basis of the total concentration and not an average concentration of CEs, using data from this well will not adversely affect the calculation.

6. ***EPA** - Figure 2.21, Panel ID should read Panel 1D, please make corrections throughout the figure.*

Response - This will be corrected.

7. ***EPA*** - *Page 26, Section 2.8.2, 1st paragraph; please explain why water elevation measurements were not taken at the CTW-1D transect, during the October 2006 event.*

   Response - The water elevation measurements were not collected at CTW-1D transect due to an oversight by the field crew.

8. ***EPA*** - *On figure 2.22, on the Vertical Gradient at Panel 1D graph, the y-axis should be labeled vertical gradient.*

   Response - This will be corrected on the Figure.

9. ***EPA*** - *Please clarify the discussion on 1st paragraph of page 28 and make reference to the appropriate map or figures. We could not locate HPA1-deep and HPA2-deep on figure 2.23.*

   Response – The locations where hydropunch samples HPA1 and HPA2 were taken are marked on Figure 2.23 as "A_1" and "A_2". We will clarify this in the text of future reports.

10. ***EPA*** - *Pages 29, last sentence, please expand on how well CTW-24U would determine if elevated concentration in CTW-23U may be the result of problems with this well. Also, please explain what kind of problems, and when the evaluation of the CTW performance at this location, would be considered complete.*

    Response – We have expanded on the text on page 29 to 30 as follows. It is possible that the shallow monitoring well on the downgradient side of the CTW (or PRB) at the CTW-20 transect (CTW-23U) does not contain groundwater representative of water that has passed through the CTW. The well is located in very close proximity to the PRB and may actually be located partially within the PRB (not downgradient of the PRB) and the well may be installed at an angle such that the water collected in the well screen is actually coming from further upgradient within the PRB than intended. A new monitoring well (CTW-24U) was installed along the CTW-20 transect further downgradient of the CTW than CTW-23U to determine if elevated concentrations in CTW-23U may be the result of problems with this well. The well is located far enough downgradient of the PRB that we are confident that the water in the well is from downgradient of the PRB. The concentrations of cDCE and VC in CTW-23U and CTW-24U have not been significantly elevated for the past two years and the performance of the CTW at this location has not been an issue. Unless we observe an increase in concentrations of VOCs in these wells and, therefore, an issue with the performance of the PRB at this location, we consider the evaluation complete.

11. ***EPA*** - *P. 36, objective 8, if water at CTW-23U is not representative of water passing through the CTW, where is it coming from? Please expand/clarify.*

Response – see additional text under specific comment #10.

12. ***EPA*** *- P. 37, Section 5 (Recommendations), objective 1A, please define single well-tests and clarify the frequency of their testing.*

    Response – The "single-well tests" are conducted to assess potential changes in the permeability of the PRB media that may be caused by inorganic or biological fouling in the PRB media. The tests involve pumping groundwater at different flow rates from a single well located within the PRB and monitoring the changes in water level in other nearby monitoring wells within and outside the PRB. In the past, the tests have been conducted in one monitoring well at each of three monitoring transects. These tests were conducted on an annual basis but the results show no significant changes in the permeability over time and we are recommending that these tests be conducted every second year rather than on an annual basis. We conducted the "single-well tests" in 2006 but have not yet conducted the tests in 2007.

13. ***EPA*** *– Volume Two of Two cover page has 2005 instead of 2006.*

    Response – We will correct this typographical error in our next report.

We trust that these responses address your comments. If you have any further questions, please do not hesitate to call me at (519) 822-2230.

Sincerely,

Thomas A Krug

Suzanne O'Hara, M.Sc.
Project Manager

Thomas A. Krug, M.Sc., P.Eng.
Associate

Encl: Henderson and Demond (2007)
Excerpt from EPA 542-R-99-002. Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers

cc: Gerardo Millan-Ramos, US EPA
Richard Willey, USEPA
Andrew Hoffman, NHDES
Norm Leclerc, City of Somersworth
Robert Belmore, City of Somersworth
Edward Jamison, General Electric Company

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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, NO_3^- and 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

TRADITIONAL 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 contaminants 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.

Factor	*Reference*
Loss of media reactivity caused by high TDS and high flow rates.	ESTCP, 2003
Loss of porosity—concentrated at influent interface.	Liang *et al.*, 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 *et al.*, 1999, 2002
Loss of media reactivity and decreases in hydraulic residence time.	Roberts *et al.*, 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 *et al.*, 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 *et al.*, 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^{2+} mass balance.	U; Mn; Mo; NO_3^-; As; Se; V	Morrison *et al.*, 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^{2+} measured in column tests.		
Y-12 Plant (Pathway 2), Oak Ridge, TN	>15 years	Visual inspection of corrosion of ZVI.	U; NO_3^-	Phillips *et al.*, 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 Locht, 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):

$$\mathrm{Fe^0 + RCl + H^+ = Fe^{2+} + RH + Cl^-} \qquad (1)$$

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):

$$\mathrm{CrO_4^{2-}} + \frac{3}{2}\mathrm{Fe^0(s) + 4\ H_2O = Cr^{3+}} + \frac{3}{2}\mathrm{Fe^{2+} + 8\ OH^-} \qquad (2)$$

$$\mathrm{(1-x)\ Fe^{3+} + (x)\ Cr^{3+} + 2\ H_2O = Fe_{(1-x)}Cr_xOOH(s) + 3\ H^+} \qquad (3)$$

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:

$$\mathrm{Fe^0(s) + 2\ H_2O = Fe^{2+} + H_2(g) + 2\ OH^-} \qquad (4)$$

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

$$\mathrm{2\ Fe^0(s) + O_2 + 2\ H_2O = 2\ Fe^{2+} + 4\ OH^-} \qquad (5)$$

The anaerobic oxidation of ZVI may also proceed abiotically through the reduction of nitrate to ammonia or nitrogen (Kielemoes *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 (Powel *et al.*, 1998). Wilkin and Puls (2003) showed that for iron redox couples [e.g., $\mathrm{Fe^{2+}}$ with $\mathrm{Fe(OH)_3(s)}$], 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, $\mathrm{Fe(OH)_2}$ 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; Ritter *et al.*, 2002; Phillips *et al.*, 2003; Su and Puls, 2004). Continued oxidation may produce poorly crystalline ferric oxyhydroxides such as ferrihydrite, which may age to more crystalline forms, such as goethite (α-FeOOH) and lepidocrocite (γ-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 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 nonreactive 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

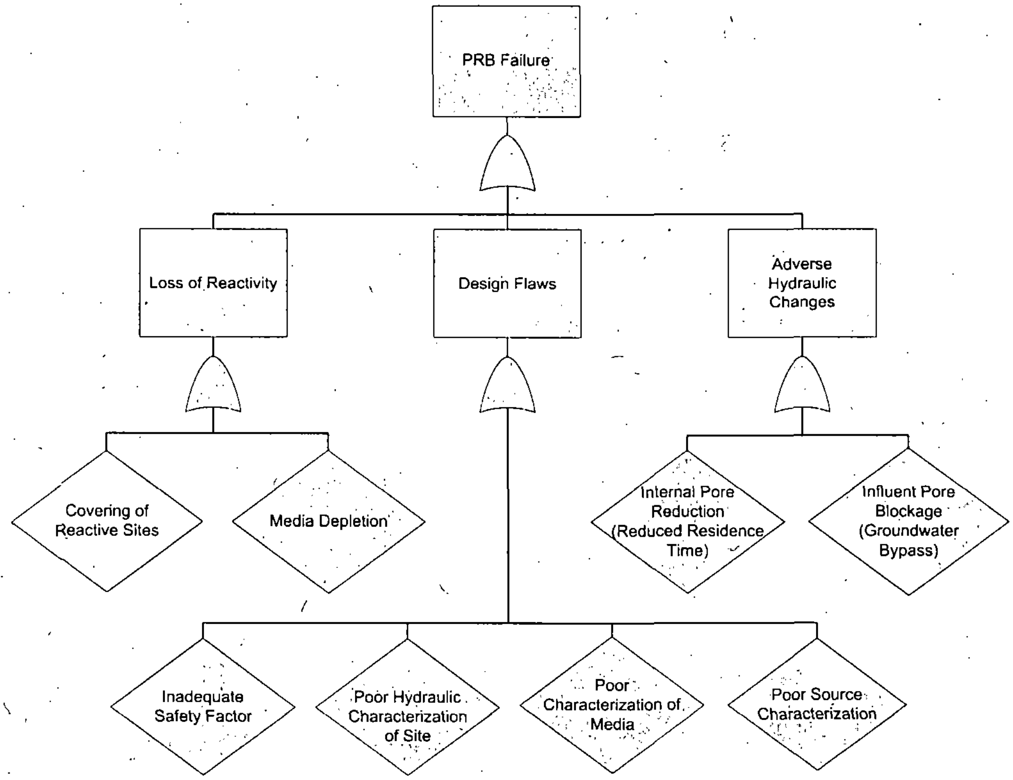

Figure 1. Fault tree showing events that contribute to PRB failure. Primary events (shown in diamonds) are combined with logical gates to create fault events (shown in rectangles) (McCormick, 1981).

(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, (Kamolpornwijit *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 ($SI = pH_{actual} - pH_{equilib}$) (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., CO_3^{2-}, Ca^{2+}), and saturation indices]; and (3) parameters relating to reactivity promotion or inhibition (e.g., anions like NO_3^- and 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 know 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.

Name and location	*Contaminants*	*Performance notes*	*Reference*
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 *et al.*, 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 *et al.*, 2000)
Copenhagen Freight Yard; Copenhagen, Denmark	TCE; cDCE; tDCE; VC	Failure due to poor hydraulic characterization (1/5 of plume migrates around PRB) and precipitates. $H_2(g)$ 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.	(Kiilerich *et al.*, 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. $H_2(g)$ production decreases with time in Gate 2.	(McMahon *et al.*, 1999; RTDF, 2001; FRTR, 2002; Wilkin and Puls, 2003; Wilkin *et al.*, 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 *et al.*, 2000; Yoon *et al.*, 2000; Liang *et al.*, 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) CaCO3 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_2-utilizing and sulfate reducing bacteria, but no microbial films observed. Suggest periodic scarification of upgradient face if necessary.	(Vogan *et al.*, 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 $H_2(g)$ (to near saturation) taken as indication of continued PRB operation (i.e., Fe corrosion continues).	(Warner *et al.*, 1998; RTDF, 2001; Sorel *et al.*, 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 *et al.*, 1998; EPA, 1999; Jain *et al.*, 1999; RTDF, 2001; FRTR, 2002; ESTCP, 2003)
Moffett Field; Mountain View, CA	TCE; cDCE; PCE	Aragonite, calcite, iron carbonate hydroxide found at upgradient interface. Some precipitates found in well silt traps.	(Sass *et al.*, 1998; EPA, 1999; RTDF, 2001; Yabusaki *et al.*, 2001; FRTR, 2002; Gavaskar *et al.*, 2005)
Monticello Mill Tailing Site; Monticello, Utah	U; Mn; Mo; NO_3^-; 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 $Fe(OH)_2$ 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 *et al.*, 2001, 2002a; RTDF, 2001; Purdy *et al.*, 2002)
Somersworth, NH Landfill Superfund	PCE; TCE; 1,2-DCE; VC	Initial decrease in hydraulic conductivity due to settling.	(Sivavec *et al.*, 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 *et al.*, 1999; RTDF, 2001; FRTR, 2002; Wilkin *et al.*, 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 *et al.*, 2005, 2006)
Y-12 Plant; Pathway 2; Oak Ridge, TN	U, NO_3^-	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 *et al.*, 2000; Korte, 2001; Liang *et al.*, 2001; FRTR, 2002; Gu *et al.*, 2002; Phillips *et al.*, 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 $CaCO_3$)*	*CO3T 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*	*Δ hydr.*	*Δ 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	211	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; "CO3T" indicates total carbonate (the sum of carbonate, bicarbonate, and carbonic acid); "PTZ" stands for Pretreatment Zone; "Δ hydr." and "Δ 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.

Name	*Legend*	*Ca Flux* (*g m*$^{-2}$ *day*$^{-1}$)	*Alk Flux* (*g m*$^{-2}$ *day*$^{-1}$)	*CO3T Flux* (*g m*$^{-2}$ *day*$^{-1}$)	SO_4^{2-} *Flux* (*g m*$^{-2}$ *day*$^{-1}$)	NO_3^- *Flux* (*g m*$^{-2}$ *day*$^{-1}$)	Cl^- *Flux* (*g m*$^{-2}$ *day*$^{-1}$)	Ca^{2+} *Cumul. Flux* (*kg m*$^{-2}$)	*Alk Cumul. Flux* (*kg m*$^{-2}$)	*CO3T Cumul. Flux* (*kg m*$^{-2}$)	SO_4^{2-} *Cumul. Flux* (*kg m*$^{-2}$)	NO_3^- *Cumul. Flux* (*kg m*$^{-2}$)	Cl^- *Cumul. Flux* (*kg m*$^{-2}$)	*SI Calcite*	*SI Aragonite*	*SI Siderite*	*SI Fe(OH)*$_2$	*SI Magnetite*	*SI Hematite*	*SI Ferrihydrite*	*SI Goethite*	*At risk*
Beka Site, Germany	Beka	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	Borden	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	CSM	—	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	Copen	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	DFC	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	Dover	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	Haard	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	IF_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	Inter	—	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	Lowry	87.0	159	239	300	1.2	30.0	254	464	697	876	3.5	87.6	—	—	—	—	—	—	—	—	0
Moffett Field, Mountain View, CA	Moffett	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	Mont	1932	1351	2620	6669	673	701	2116	1479	2869	7303	736	768	1.5	1.4	−0.065	−0.28	1.5	0.81	−0.49	0.58	1
Somersworth Landfill, NH	Somer	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	USCG	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	Vapok	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	Y-12	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 **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:

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

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

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

where ε 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 pretreatment zone), and combinations of variables may all be included in $g(\mathbf{x})$. The coefficients β_i are calculated through regression between the independent predictor variable vector **x** and $g(\mathbf{x})$. $g(\mathbf{x})$ is determined using Equation (7), assuming that $\pi(\mathbf{x})$ may be calculated as:

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

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 β_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., ≤ 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 β_i' is equivalent to β_i. Based on the recommendation of Hosmer and Lemeshow (1989), variables with significance ≤ 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 outcome (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)

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

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 × 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 Alk_inf (Table 4). If 300 mg/L is defined as the cutoff value, then of the PRB sites with Alk_inf ≥ 300 mg/L, 4 are at risk, and 3 are not at risk. Similarly, the cases with 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 Alk_inf ≥ 300 mg/L are 4.67 times more likely to be at risk than those with lower 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 ≤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	*Alk_inf ≥ 300 mg/L*	*Alk_inf < 300 mg/L*
At risk	4	2
Not at risk	3	7

ratio Fisher Exact test significance ≤ 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.

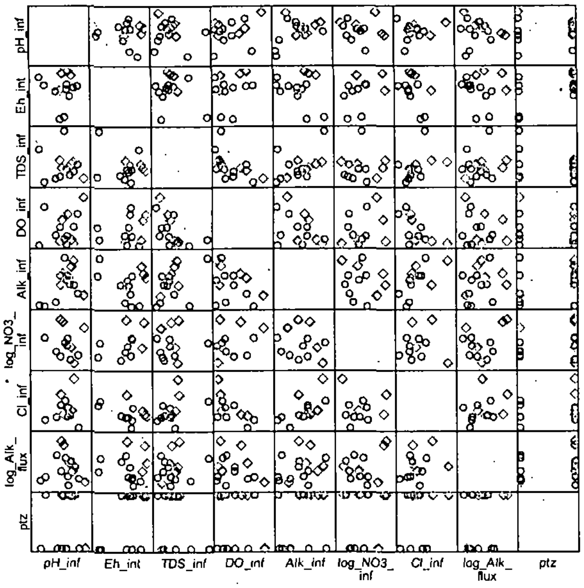

Figure 2. Matrix plots of selected geochemical parameters. At-risk PRBs are indicated by diamond markers, not-at-risk by circles. Units are (mg/L) except for E_H (mV) and ptz (1 indicates use of a pretreatment zone).

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 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,

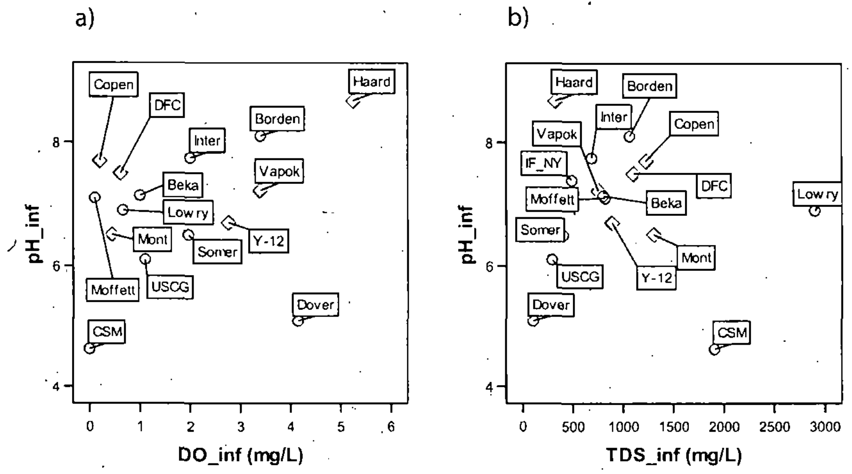

Figure 3. Plot of at-risk and not-at-risk PRBs with respect to influent pH and (**a**) influent DO, (**b**) influent TDS. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

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 NO_3^- concentrations correlate with being at risk. The PRB at Lowry AFB (CO), with low nitrate and high alkalinity, is an exception to this trend, but considering Fig. 5a, this may be attributable to its very low E_H value.

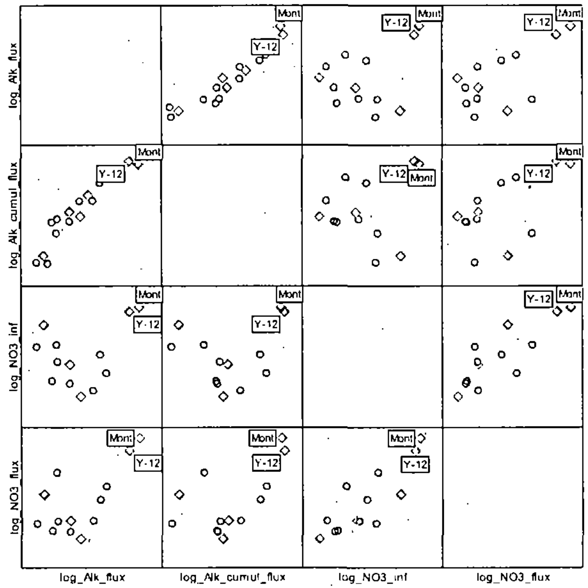

Figure 4. Significance of very high alkalinity and nitrate for prediction of at-risk PRBs. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

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 (g m^{-2} day^{-1}) and cumulative fluxes (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.

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

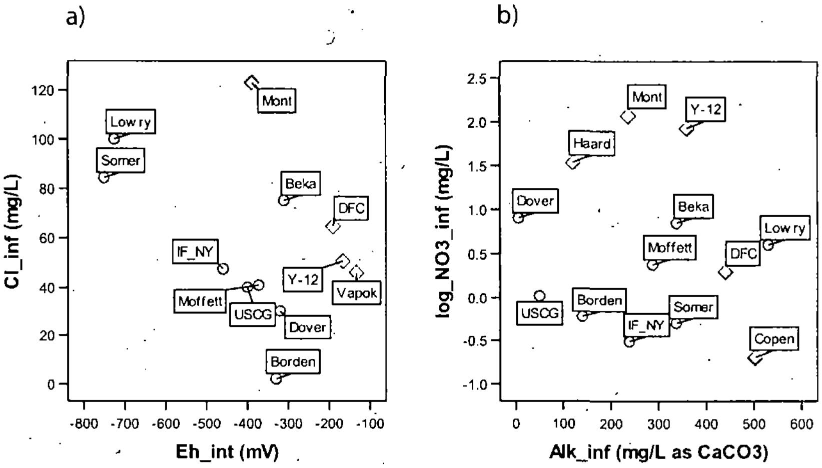

Figure 5. Geochemical parameters with relationship to at-risk and not-at-risk PRBs: (**a**) Influence chloride vs. internal EH: (**b**) influent nitrate vs. influent alkalinity. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

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 β_i [Eq. (7)] values, the S.E., the Wald value (β_i/S.E.), and the p-value, or significance. Variables with a p-value ≤ 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 ≤ 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.

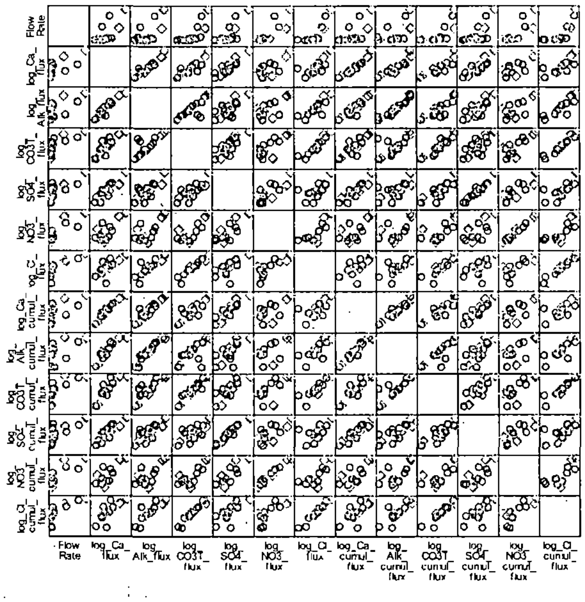

Figure 6. Matrix plot of fluxes, cumulative fluxes, and flow rate showing high degree of collinearity. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

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-

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

		Logistic regression				*Odds ratio*		
Parameter	*Legend*	β_l	*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^{2-} influent (mg/L)	Ca_inf	0.0035	0.006	0.39	0.534	5	100	0.301
Ca^{2-} internal (mg/L)	Ca_int	0.0106	0.012	0.84	0.359	6	40	0.266
Alk influent (mg/L as $CaCO_3$)	Alk_inf	0.0050	0.004	1.70	0.192	9	350	0.118
Alk internal (mg/L as $CaCO_3$)	Alk_int	0.0025	0.002	1.15	0.284	8	200	0.235
CO3T influent (mg/L as $CO_3{}^{2-}$)	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
$SO_4{}^{2-}$ influent (mg/L)	SO4_inf	0.0003	0.001	0.04	0.840	8	75	0.234
$NO_3{}^-$ influent (mg/L)	NO3_inf	0.1005	0.089	1.28	0.258	24	20	0.035
Cl^- influent (mg/L)	Cl_inf	0.0246	0.018	1.93	0.165	10.67	110	0.128
Alk Flux (g/m^{2}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 $Fe(OH)_2$	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 β 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 ≤ 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 β 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.

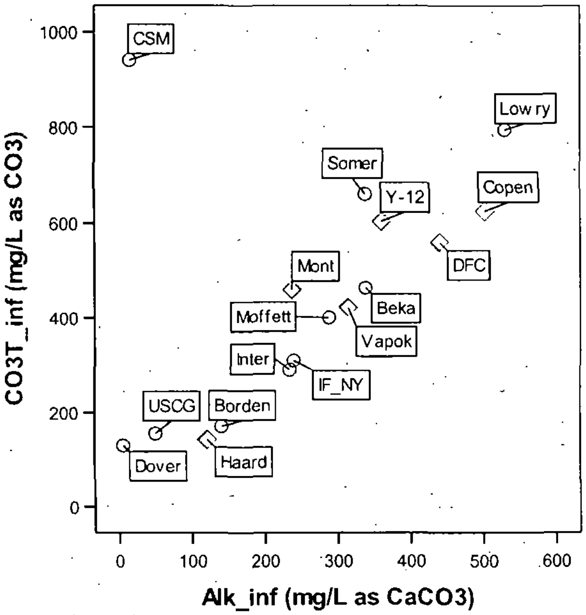

Figure 7. Differences between influent alkalinity and influent total carbonate; the CSM (Australia) PRB has unusually low influent pH. At-risk PRBs are indicated by diamond markers, not-at-risk by circles.

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 ≤ 0.25) and the maximization of the odds ratio (p-value ≤ 0.10): pH_inf, Eh_int, Alk_inf, NO3_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^-, 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_3^- 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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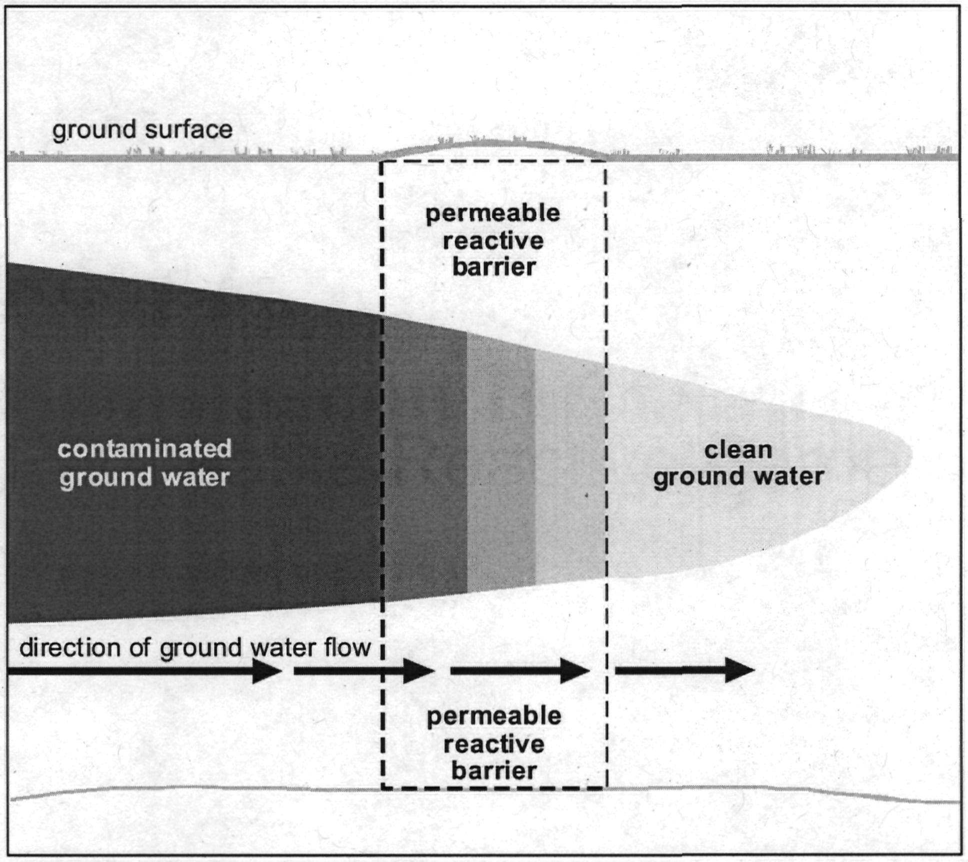
Field Applications of *In Situ* Remediation Technologies:

Permeable Reactive Barriers



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Field Applications of *In Situ* Remediation Technologies:

Permeable Reactive Barriers

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Technology Innovation Office
Washington, DC 20460
Walter W. Kovalick, Jr., Ph.D., Director

Contents

Full-Scale

Pilot-Scale

Full-Scale

Pilot-Scale

Federal Highway Administration (FHA) Facility, Lakewood, CO

Installation Date:
October 1996

Contaminants:
TCA; 1,1-DCE; TCE; cDCE

Reactive Media:
Fe^0

Installation Cost:
$1,000,000

Construction:
Funnel and Multiple Gate

Point of Contact:
Peter McMahon
U.S. Geological Survey
Denver Federal Center
(MS-415)
Denver, CO 80225
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A permeable reactive barrier (PRB) system was installed in October 1996 at a site in Lakewood, Colorado.

Site Background

Contaminants at the site included 1,1,1-trichloroethane (TCA), 1,1-dichloroethylene (1,1-DCE), trichloroethylene (TCE), and cis-dichloroethylene (cDCE). The contaminated area is an unconfined aquifer that is 15-25 ft thick and consists of unconsolidated gravelly sand overlying weathered (fractured) claystone. These units are in hydraulic connection and act as one aquifer. The geometry of the aquifer is irregular, with a local presence of clay lenses in the unconsolidated sand and sandstone lenses in the claystone. The aquifer is confined from below by unweathered (unfractured) claystone.

Technology Application

The PRB system is comprised of a 1,040-ft funnel section and four reactive gate sections, each 40 ft wide. This was the first funnel and multiple gate PRB system using granular zero-valent iron (Fe^0). A high degree of lateral geologic heterogeneity and variation in volatile organic compound (VOC) concentrations led to varying iron thicknesses in each gate. The gates were constructed using a sheet pile "box." Native material was excavated from the box and the reactive material installed, separated from the aquifer materials by a layer of pea gravel.

Cost

Installation cost of the PRB system was about $1,000,000. This includes the cost of design, construction, materials, and the zero-valent iron.

Results

Ground-water velocities through the gates were expected to range from 1 ft/day to 10 ft/day, depending upon the hydrogeologic conditions in the vicinity of the respective gates. Measurements in the cells using a heat-pulse flowmeter have ranged from < 0.1 ft/day to about 1.5 ft/day. Design concentrations include up to 700 µg/L of TCE and 700 µg/L of 1,1-DCE. Half-lives of about 1 hour or less were measured for these compounds in bench-scale design studies. The only VOC exiting the cells above the 5 µg/L reporting level is 1,1-dichloroethane, which has been measured up to 8 µg/L on the downgradient side of the cells. There is some evidence of the precipitation of calcite and siderite in the cells based on decreases in calcium and inorganic carbon in the treated ground water. This is estimated to result in a potential porosity loss of 0.5% of the porosity per year of operation.

Hydraulic head has increased upgradient of the barrier, with up to 10 ft of head difference measured across the barrier. This increases the possibility for contaminated water to move around the barrier. Indeed, VOC concentrations are increasing in ground water moving around the south end of the barrier and there is some evidence of VOCs moving under the barrier in one location.