Ground Water Monitoring&Remediation

Monitoring the Removal of Phosphate from Ground Water Discharging through a Pond-Bottom Permeable Reactive Barrier

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Abstract

Installation of a permeable reactive barrier to intercept a phosphate (PO_4) plume where it discharges to a pond provided an opportunity to develop and test methods for monitoring the barrier's performance in the shallow pond-bottom sediments. The barrier is composed of zero-valent-iron mixed with the native sediments to a 0.6-m depth over a 1100-m^2 area. Permanent suction, diffusion, and seepage samplers were installed to monitor PO_4 and other chemical species along vertical transects through the barrier and horizontal transects below and near the top of the barrier. Analysis of pore water sampled at about 3-cm vertical intervals by using multilevel diffusion and suction samplers indicated steep decreases in PO_4 concentrations in ground water flowing upward through the barrier. Samples from vertically aligned pairs of horizontal multiport suction samplers also indicated substantial decreases in PO_4 concentrations and lateral shifts in the plume's discharge area as a result of varying pond stage. Measurements from Lee-style seepage meters indicated substantially decreased PO_4 concentrations in discharging ground water in the treated area; temporal trends in water flux were related to pond stage. The advantages and limitations of each sampling device are described. Preliminary analysis of the first 2 years of data indicates that the barrier reduced PO_4 flux by as much as 95%.

Introduction

Many ground water contaminant plumes discharge to rivers and lakes, where they may have detrimental ecological and human-health impacts. An understanding of the characteristics of a discharging contaminant plume is critical to the evaluation of these impacts and to the design and implementation of effective remediation strategies. Contaminant-concentration profiles developed from high-resolution vertical pore water sampling can be used to delineate the extent of ground water contamination at the point of discharge to a surface water body, evaluate biogeochemical processes occurring in the lake or streambed sediment, and determine whether remediation at the point of discharge is a practical alternative.

One type of in situ remediation involves interception of a contaminant plume by a permeable reactive barrier (PRB). Zero-valent-iron (ZVI) geochemical barriers typically have been installed as a vertical wall to intercept an organic or inorganic contaminant plume in horizontally flowing ground water (Cantrell et al. 1995; O'Hannesin and Gillham 1998; Powell et al. 1998; McMahon et al. 1999; Puls et al. 1999; Blowes et al. 2000; Naftz et al. 2002). These barriers are designed to immobilize contaminants, produce less-soluble compounds, or reduce contaminants to nonhazardous or less toxic forms as they pass through the PRB (Powell et al. 1998). In August 2004, a PRB was emplaced subhorizontally on the bottom of a kettle-hole pond on Cape Cod, Massachusetts, where a contaminant plume containing phosphate (PO_4) discharges to the pond in a well-defined area near the shore (Air Force Center for Environmental Excellence [AFCEE] 2004). Monitoring the reduction by the barrier of the PO_4 flux to the pond near this interface required adapting sampling strategies and methods used in ground water/surface water interaction studies.

The difficulty of collecting representative pore water samples near the ground water/surface water interface in standing water has led to the development of many types of samplers. Suction samplers, including temporary drive points, microwell push points, and multilevel sampling devices, use suction pumping to draw samples to the water-body surface (Montgomery et al. 1981; Duff et al. 1998; Henry 2000; Berg and McGlathery 2001). Diffusion and dialysis samplers, including pore water peepers, gel samplers, and diffusion samplers, function by measuring equilibrated concentrations between water in the aquifer and various media in the sampling container (Hesslein 1976; Krom et al. 1994; Urban et al. 1997;

Paludan and Morris 1999; Savoie et al. 2000; Vroblesky et al. 2002; LeBlanc 2003). Seepage meters provide a means of directly measuring the exchange of water and solute mass between surface water and ground water (Lee 1977; Carr and Winter 1980; Zimmermann et al. 1985).

McCobb et al. (2003) describe a plume of dissolved PO_4 emanating from infiltration beds at a decommissioned wastewater treatment and disposal facility at the Massachusetts Military Reservation on Cape Cod. The PO_4 plume is part of a 6-km-long treated wastewater plume that has been studied extensively by the USGS Toxic Substances Hydrology Program (LeBlanc 1984; Parkhurst et al. 2003; Repert et al. 2006; USGS 2008). The plume discharges near the shore of Ashumet Pond, which is a ground water flow through kettle pond about 500 m downgradient from the infiltration beds (Figure 1A). In 1999, PO_4 concentrations were as great as 3 mg/L (as P) in shallow ground water sampled within 0.5 m of the pond bottom in the discharge area. The area of greatest concentrations was within 20 m of the shore along about 120 m of shoreline. In June 2004, the area of PO_4 discharge was delineated in detail using drive-point sampling (Figure 1B). In August 2004, a PRB was emplaced by AFCEE on the pond bottom to reduce PO_4 concentrations in ground water discharging to the pond and, therefore, to limit or reverse the adverse effects of PO_4 loading from the treated wastewater plume on the pond's ecological health. ZVI (Fe^0) was mixed into the pond-bottom sediment (3% ZVI by weight) to a depth of about 0.6 m in an area extending 12.2 m perpendicular to, and 91.4 m parallel to, the shore where the highest pore water PO_4 concentrations were observed (Figures 1B and 2). Iron hydroxides ($Fe(OH)_3$) formed by the oxidation of the ZVI have a high affinity for and capacity to adsorb PO_4 (Baker et al. 1998). The sediment/ZVI mixture was created by excavating the native pond-bottom sediment in 12-m-square sections while the pond was locally dewatered by using a temporary cofferdam and large pumps. An excavator with a mixing bucket was used to blend the native sediment and ZVI filings prior to placement of the mixture on the pond bottom (AFCEE 2004; Air Force Center for Engineering and the Environment 2008). Excavation of the pond bottom in the dewatered area provided a unique opportunity to install instrumentation within and below the barrier for future monitoring of PO_4 removal from shallow ground water near the ground water/surface water interface.

This paper describes the instrumentation that was developed and installed to monitor PO_4 concentrations as ground water discharges through the pond-bottom ZVI PRB. The operation of the permanently installed devices during several sampling events is evaluated with respect to the monitoring objectives, including the ability to produce representative, spatially distributed pore water samples in the PRB in an efficient, practical manner year-round. The effectiveness of PO_4 removal during the first 2 years of monitoring is also discussed briefly. A detailed assessment of the effectiveness of the PRB is given in Air Force Center for Environmental Excellence (2007).

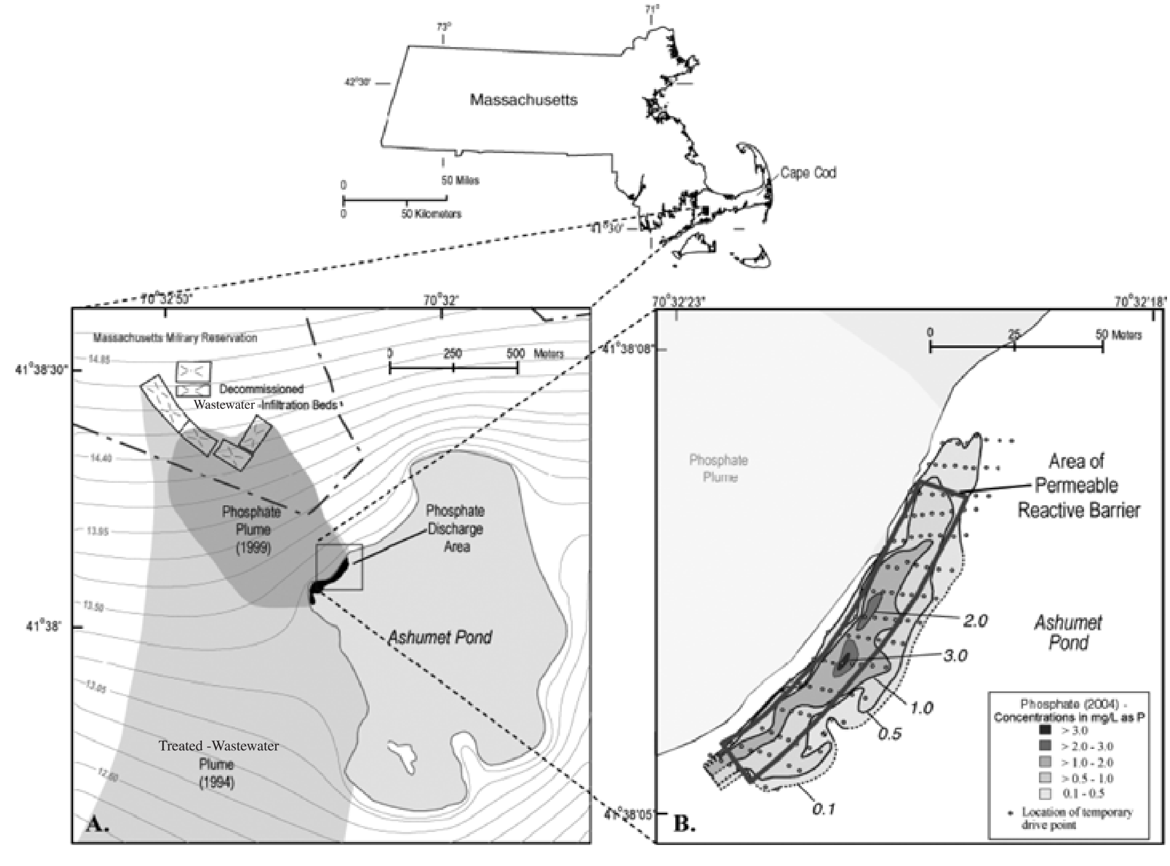

Figure 1. (A) Locations of Ashumet Pond and the phosphate ground water plume (1999) on Cape Cod, Massachusetts, water-table contours in meters above the National Geodetic Vertical Datum of 1929. (B) Areas of phosphate discharge (2004) and the PRB at the pond. Phosphate measured by field colorimetric analysis.

Design Criteria for Monitoring Devices

To evaluate changes in PO_4 concentrations in ground water flowing upward through the pond-bottom PRB, the monitoring approach needed to (1) include a dense vertical and horizontal distribution of sampling devices in and near the barrier; (2) provide for collection of representative pore water samples while minimizing pumped volumes during sampling; (3) protect the integrity of the PRB; and (4) use accessible, easy-to-use, aesthetically acceptable, and rugged equipment in the near-shore environment. Because it was uncertain which device or combination of devices would best meet these criteria, a variety of devices were installed at multiple locations to ensure that the monitoring network was sufficient to monitor the performance of the PRB.

Spatial Distribution of Sampling Points

A major consideration in designing the monitoring network was the need for a sufficient sampling density to determine spatial uniformity of the barrier and to measure PO_4 concentrations in and adjacent to the barrier at various distances from shore. The final iron-to-sediment ratio and thickness of the barrier varied spatially because of the challenges of emplacing the mixture in the 12-m^2 sections. Therefore, an array of well-distributed sampling locations was needed to monitor the barrier's performance throughout the treated area. The sampling locations had to extend deep enough to measure PO_4 concentrations below the influence of the barrier at a sufficient vertical spatial resolution to detect changes in PO_4 concentrations as ground water flowed upward through the reactive material. Sampling points also were needed just below the pond bottom where the treated ground water is about to discharge to the pond. In addition, previous sampling indicated that the spatial distribution of PO_4 concentrations below the pond bottom changed as the pond stage varied. Therefore, a sufficient sampling density was needed below the barrier to determine the distribution of PO_4 concentrations in ground water entering the barrier as the plume discharged to the pond.

Collection of Representative Samples

A major challenge to monitoring steep geochemical gradients within the PRB is that many pumped-sampling devices require extraction of substantial volumes of water during purging and sample collection, potentially compromising the ability to sample water from discrete, closely spaced intervals. The ability to collect a small volume was critical to limiting the mixing of targeted water with water, including surface water, from above or below the targeted depth interval. This was particularly important because fine-resolution vertical sampling of pore water near the ground water/surface water interface was needed to assess PO_4 concentrations in the ground water as it was about to cross this interface.

Integrity of Barrier

A consideration for the monitoring system was to enable collection of representative pore water samples without having to drive or dig devices repeatedly into the PRB. These invasive methods could provide preferential flow paths or low-iron zones through which the PO_4 plume might migrate untreated into the pond. In addition, the repeated use of temporarily installed devices, such as drive points and Lee-style seepage meters, is labor intensive. Therefore, instrumentation for this effort was designed to be permanently installed during barrier emplacement.

A further advantage of permanently installed devices was the improved ability to detect changes to the hydraulic properties of the barrier, including porosity and hydraulic conductivity, over time at fixed locations. Results of initial pilot tests using ZVI at Ashumet Pond (AFCEE 2004), applications at other sites (McMahon et al. 1999; Kamolpornwijit et al. 2003; Morrison 2003; Wilkin et al. 2003), laboratory column experiments (Gu et al. 1999; Mackenzie et al. 1999; Farrell et al. 2000), and reactive transport modeling (Liang et al. 2003; Li et al. 2005) indicated that flow paths can become clogged due to mineral precipitation and increased microbial activity in the barrier.

Aesthetically Acceptable, Rugged, and Accessible Instrumentation

Public access to the pond for boating, fishing, swimming, and wading precluded the use of devices that protrude above the bottom or are marked with surface buoys that interfere with boating or invite vandalism. The monitoring devices had to be rugged enough for installation during the excavation and backfilling by heavy equipment. The devices also had to be resistant to damage from pond ice during winter and corrosion in the chemically reactive environment in the PRB. Monitoring had to be possible when the pond was frozen or water levels were higher than average, thus submerging parts of the PRB in up to 5 feet of water.

Devices Installed to Monitor the PRB

Temporary cofferdams were used during emplacement of the PRB to isolate the area to be treated from the rest of the pond (AFCEE 2004). Once the area was dewatered and excavated, four types of permanent water-quality and water-flux monitoring devices were installed at locations within, outside, and below the zone containing the sediment/ZVI mixture. Horizontal multiport samplers (HMPS) were installed at two depths along two lines extending perpendicular to shore to monitor the spatial distribution of PO_4 concentrations in the discharge area relative to distance from shore (Figure 2). Ten vertical multilevel samplers (VMLS) and eight multilevel diffusion chambers (MLDCs) were installed to monitor PO_4 concentrations over small, discrete vertical intervals below the pond bottom and through the PRB. Pairs of permanent seepage meters were installed at various distances from shore to monitor water and PO_4 flux through the pond bottom at four locations inside and outside the barrier area (Figure 2).

Horizontal Multiport Samplers

Multiport sampling wells, also referred to as multilevel samplers, have been developed and used for monitoring ground water quality in a variety of investigative and remedial applications. Typically, these devices are installed vertically using standard drilling techniques (Pickens et al. 1978;

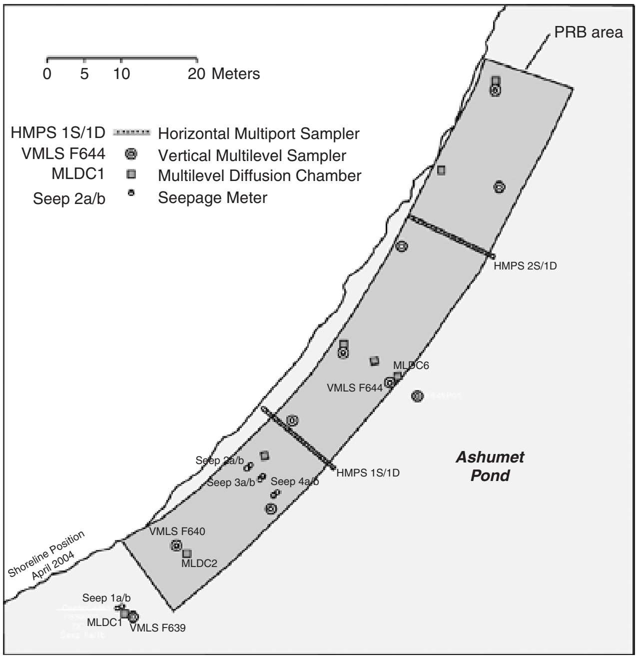

Figure 2. Locations of horizontal multiport samplers, vertical multilevel samplers, multilevel diffusion chambers, and seepage meters in and near the PRB at Ashumet Pond.

LeBlanc et al. 1991). In this effort, multiport samplers were set horizontally at two depths rather than vertically. One HMPS was set in the PRB material immediately below the sediment/water interface (0.15 m below the pond bottom), and a second HMPS was set directly beneath the first HMPS in the untreated sediment just below the PRB material (0.91 m below the pond bottom) (Figure 3). Each HMPS consists of a 3.05-cm-diameter polyvinyl chloride (PVC) pipe containing 15 color-coded 0.63-cm-diameter polyethylene tubes. The tubes exit through holes drilled in the PVC pipe at different distances from shore and are screened with nylon fabric held in place by stainless-steel wire. Two samplers were installed at each of two sites.

During installation of the PRB, the HMPS were assembled on the shore by coupling four 3.3-m-long prefabricated sections. The HMPS then were positioned so that they extended about 12-m perpendicular to shore, with the shoreward-most sampling ports set at the shoreline position at mean pond stage [13.5 m above sea level (NGVD29) based on records from a nearby pond-stage siphon gauge (McCobb et al. 1999)]. The deep HMPS of each pair was placed on the bottom of the excavated section (sampling ports facing downward), and untreated sediment was placed by hand on the PVC pipe. The excavation then was backfilled with the sediment/ZVI mixture to approximately the grade of the original pond bottom. The shallow sampler along each HMPS line was buried in the new pond-bottom material using a hand shovel. The sampling tubes for each HMPS were run landward from the shore along the bottom of a 1-m-deep hand-dug trench (below frost line) to flush-mounted road boxes. The road boxes were located about 8 m from the shoreline at mean pond stage, which placed them shoreward (on dry land) of the highest anticipated shoreline position.

Water samples were collected from the HMPS by using a suction peristaltic pump fitted with Norprene® (Cole Parmer, Vernon Hills, Illinois) tubing connected directly to the sampling tubes at the onshore road boxes. For this study, the water samples were analyzed in the field for specific conductance, pH, dissolved oxygen, and PO_4 by the methods described in McCobb et al. (2003).

Vertical Multilevel Samplers (VMLS)

Closely spaced vertical sampling was needed to characterize the steep geochemical gradients expected in the PRB. The VMLS used in Ashumet Pond were constructed from 1.27-cm-diameter, 1.24-m-long sections of Schedule 40 PVC pipe (Figure 4). Five 3.2-mm-diameter polyurethane tubes fitted with fiberglass screens were inserted in the PVC pipe. The screens were aligned to match 0.95-cm-diameter holes, or ports, drilled in the PVC pipe at expected depths of 0.02, 0.25, 0.49, 0.68, and 1.04 m below the pond bottom.

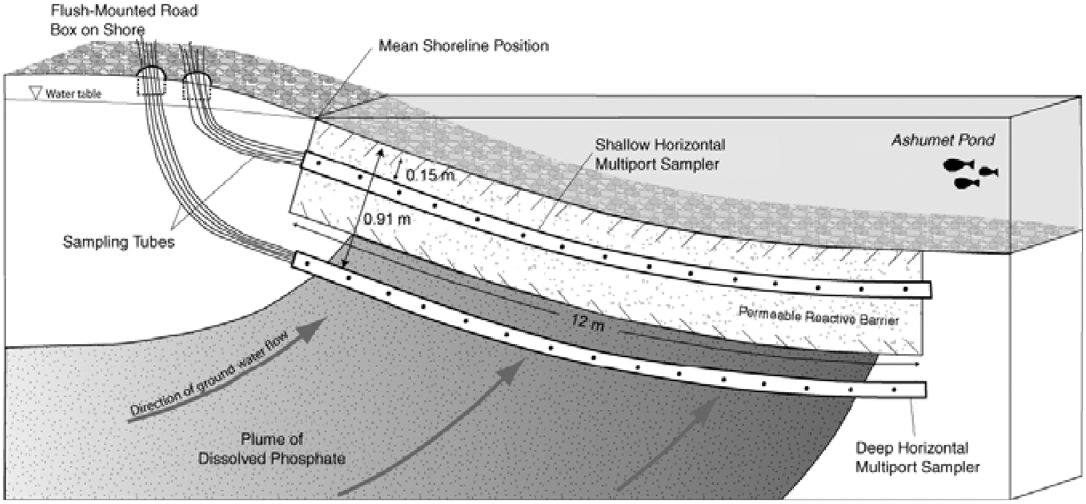

Figure 3. Schematic diagram of a pair of HMPS (not to scale).

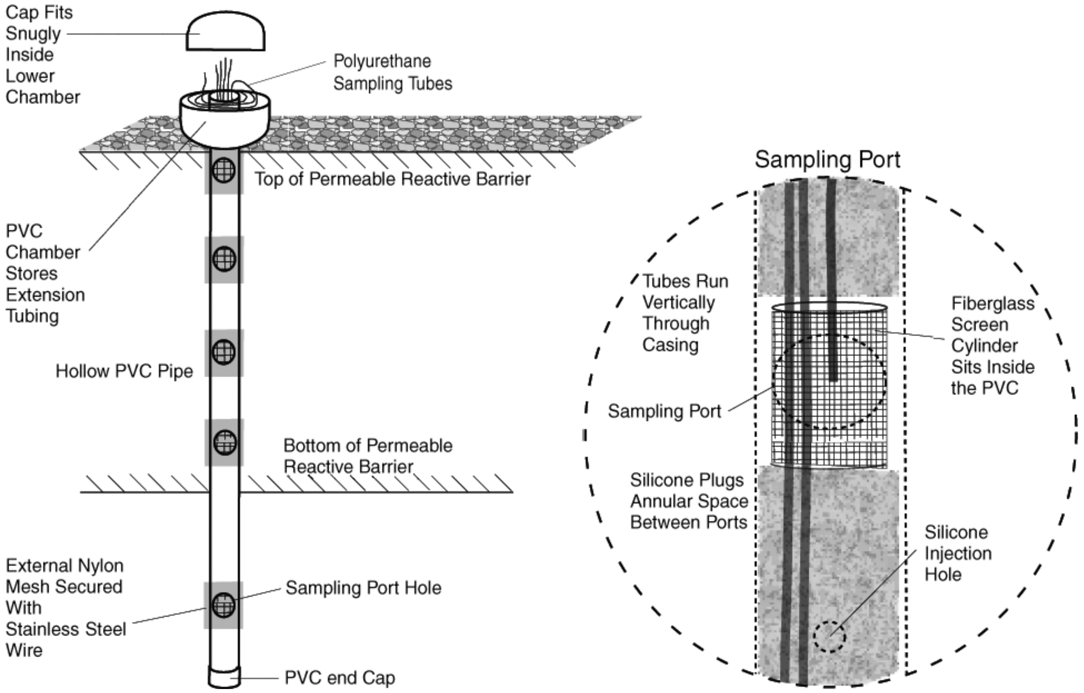

Figure 4. Schematic diagram of a VMLS (not to scale).

Silicone was injected between the ports through temporary holes in the PVC to isolate each screen, seal the annular space inside the PVC, and prevent vertical flow inside the PVC between the ports. Nylon mesh was wrapped around the outside of the PVC pipe at each port to act as a primary filter of large sediment particles.

During excavation of the pond bottom, each VMLS was positioned vertically at a targeted location so that the top port was set slightly below (0.02 m) the expected grade of the pond bottom after the sediment/ZVI mixture had been backfilled. The deepest port (1.04 m below pond bottom) was set below the PRB to allow monitoring of PO_4 concentrations in the upward flowing ground water before it entered the barrier. The final settings differed slightly from these targets as is discussed subsequently.

Samples from the VMLS were collected using Norprene tubing connected to a hand-operated plastic syringe. A small initial purge volume (100 mL) was removed and discarded prior to sample collection. For this study, water samples were analyzed in the field for pH, specific conductance, dissolved oxygen, and PO_4 and were preserved for laboratory analysis of total dissolved phosphorus by methods described in McCobb et al. (2003).

Multilevel Diffusion Chambers (MLDCs)

The diffusion-sampling method can be an efficient, cost-effective alternative to pumped-sampling methods for monitoring organic and inorganic compounds in wells (Vroblesky and Hyde 1997; Vroblesky et al. 2002). MLDCs were developed and used in Ashumet Pond to monitor the steep PO_4 concentration gradients in the PRB. The MLDCs consist of 1.22-m-long, square, hollow PVC posts with thirteen 3.8-cm-diameter holes, or ports, drilled on one face of each post (Figure 5). Nine ports were placed at 5.1-cm intervals to a depth of 40.1 cm below the expected pond bottom, and the remaining four ports were placed at 10.1-cm intervals to a depth of 81.3 cm. The outside of the post was wrapped with fiberglass screen to limit the entry of sand into the interior of the post. The MLDCs were installed during pond-bottom excavation and backfilling so that the top diffusion-sampler port would be aligned with the expected final grade of the pond and the two deepest sampling ports (0.71 and 0.81 m below the pond bottom) would be set below the PRB.

During a sampling event, a rack holding individual diffusion-sampler bottles is inserted into the vertical chamber. The internal rack is constructed of 3.8 × 8.9 cm plastic lumber. The plastic lumber was cut to the same length and drilled at the same intervals as the ports drilled in the hollow PVC posts. Each diffusion-sampler bottle consists of a 60-mL polyethylene bottle filled with deionized water. The bottle opening is covered with a 10-μm nylon-mesh fabric (part no. CMN-0010-D, Small Parts Inc., Miramar, Florida) that is held in place by a cap that has been drilled out with a 2.54-cm-diameter hole. A Minicel® (Sekisui Voltek L.L.C., Lawrence, Massachusetts) foam strip with holes cut for the caps of the diffusion-sampler bottles then is placed on the rack to prevent vertical leakage along the inside of the chamber. To load the chamber, the rack holding the diffusion-sampler bottles and foam strip is slipped into the chamber so that the foam seal is pressed tightly against the inside of the square PVC post. PVC wedges hold the rack assembly firmly against the wall of the chamber. Square stainless-steel covers fit snugly over each chamber top (Figure 5).

For this study, the diffusion-sampler bottles were set in the chambers and allowed to equilibrate with the formation water for 2 weeks, which had been determined from field tests to be a sufficient equilibration time. The water in the bottles was analyzed in the field for specific conductance and PO_4.

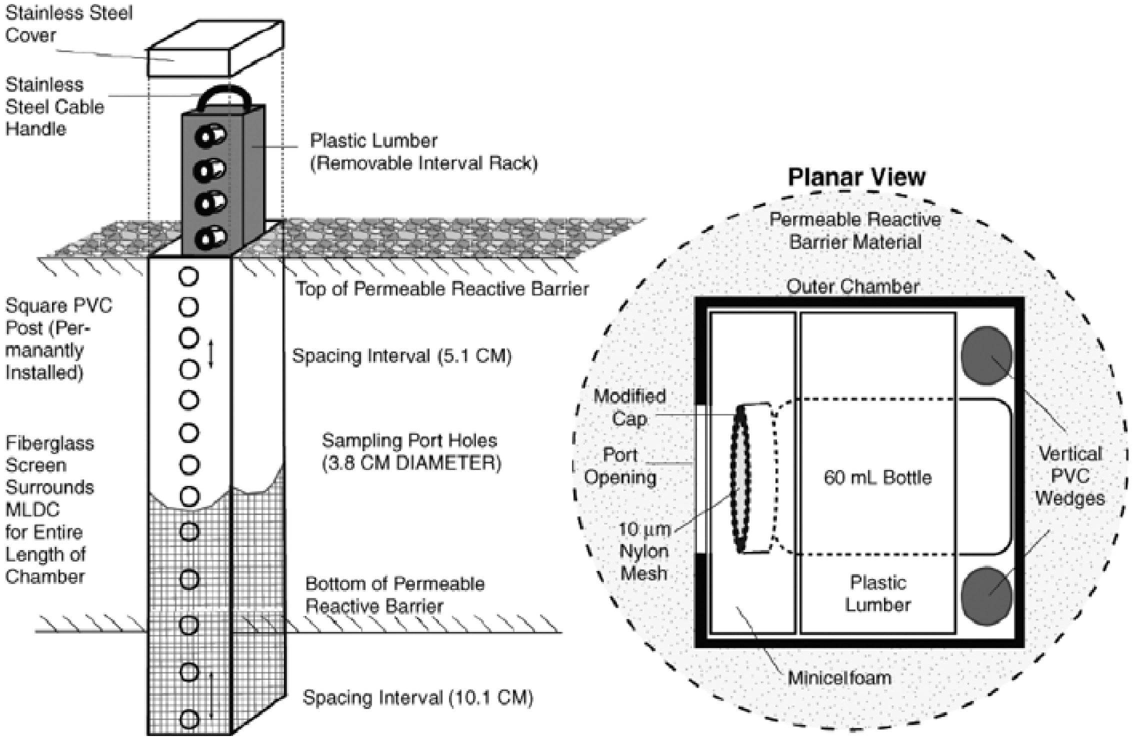

Figure 5. Schematic diagram of an MLDC (not to scale).

Seepage Meters

Seepage meters have been used in many studies to measure flow across the sediment water interface in lakes and streams (John and Lock 1977; Lee 1977; Sebestyen and Schneider 2001). Four pairs of permanent seepage meters were installed in or adjacent to the PRB during the backfilling operation; the meters in each pair were separated by about 1 m. Each meter consists of a 208-L polyethylene, corrosion-inhibiting drum cut to a length of 0.8 m and fitted with a removable 0.56-m-diameter lid. A 12.7-mm-diameter hole was drilled into each lid to allow outflow or inflow to be measured. During excavation of the pond bottom, each meter was placed in the open excavation with the top rim of the barrel positioned approximately at the expected grade of the pond bottom after backfilling. One pair of meters was installed outside the barrier and was filled with native sediments. The three pairs of meters installed in the barrier were backfilled by hand with the sediment/ZVI mixture.

To measure the discharge rate, the removable lid was secured to the rim. A thin-walled plastic bag that has been prefilled with a known volume of distilled water was attached to the measurement port for a known amount of time. The incremental volume that enters the bag was used to calculate the water-flux rate per unit area. In this study, the water in the bag was analyzed in the field to determine the PO_4 concentration in the ground water discharging into the bag. Between sampling events, the lids were removed so that the pond bottom enclosed by the seepage meters was exposed to the same environmental conditions as the pond bottom adjacent to the meters.

Field and Laboratory Analysis of Phosphate Concentrations

PO_4 concentrations were determined in the field or at the USGS National Water Quality Laboratory in Denver, Colorado. The analytical method depended on the type of sampling device and the volume of sample available for analysis. Field analyses of orthophosphate (PO_4) were made on unfiltered samples using a field spectrophotometer and reactive orthophosphate field test kit (Kit No. 8513, CHEMetrics, Calverton, Virginia). The colorimetric method uses the molybdenum blue method (APHA et al. 1998). Laboratory analyses of total dissolved phosphorus were made by alkaline persulfate digestion on water samples that had been filtered and acidified in the field. This analytical procedure hydrolyzes all forms of inorganic and organic phosphorus to orthophosphate, which is then determined using a photometric analyzer (Patton and Kryskalla 2003).

Although the field method measures only orthophosphate and the laboratory method measures total dissolved phosphorus, results from both methods are reported in this paper as PO_4 in mg/L as P because dissolved phosphorus under the geochemical conditions in the treated-wastewater plume is mostly in the inorganic orthophosphate (PO_4) form (Hem 1985). Also, a previously reported comparison of results from the laboratory and field analytical methods for samples from this site, when reported in mg/L as P, showed good correlation ($R^2 = 0.9667$, $n = 56$) for samples with concentrations greater than the detection limits of each method (McCobb et al. 2003).

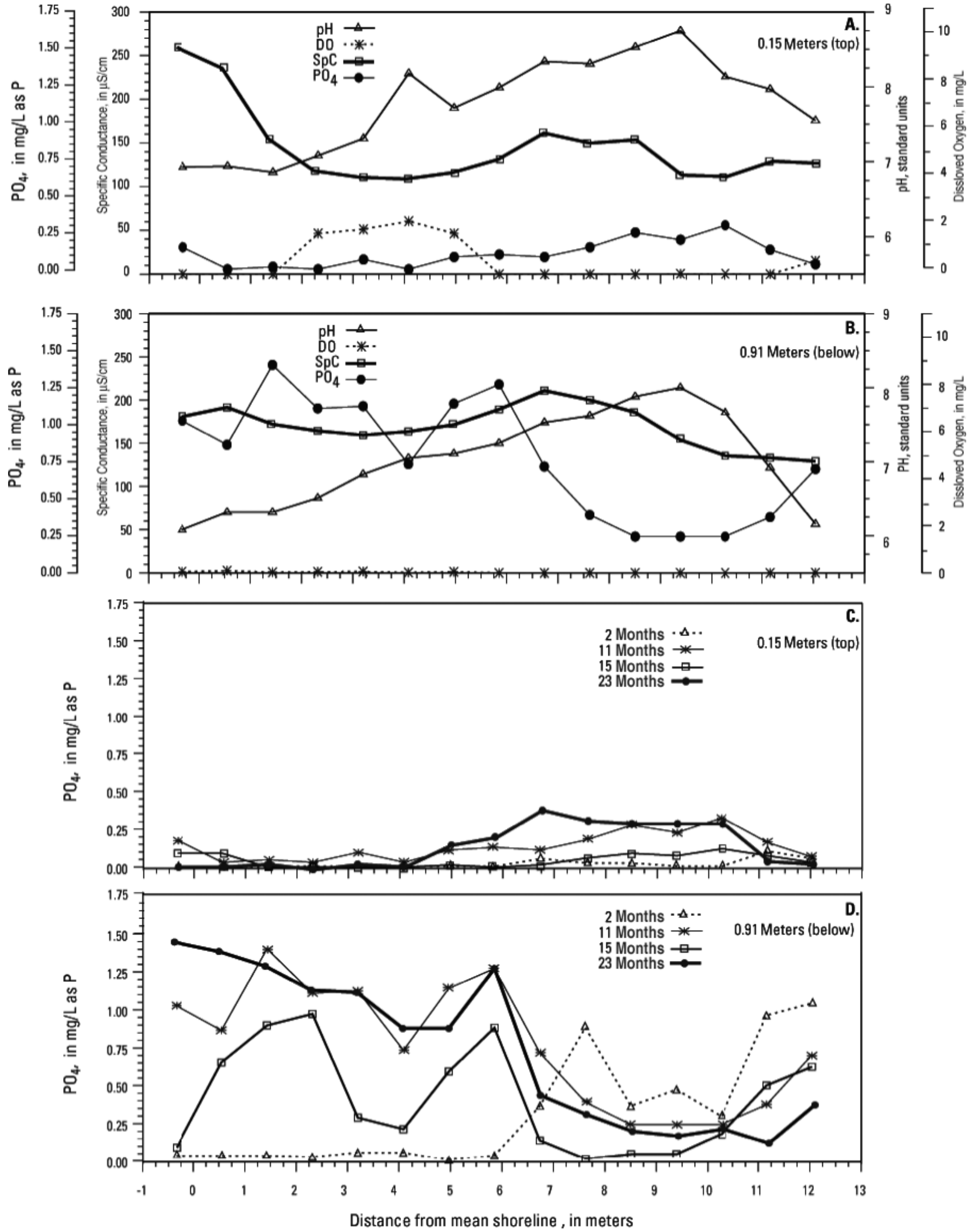

Figure 6. Distributions of (A-B) pH, dissolved oxygen (DO), specific conductance (SpC), and PO_4 11 months after installation of the PRB, and (C-D) PO_4 at 2, 11, 15, and 23 months after installation of the PRB, below and at the top of the PRB at HMPS 1S/1D. Landward edge of the PRB at 0 m. Pondward edge of the PRB at 12.2 m. Location shown in Figure 2.

Results from Monitoring of PRB

The HMPS provide data on the vertical and horizontal distributions of PO_4 and other chemical species along horizontal transects perpendicular to the shoreline below and near the top of the PRB. The horizontal distributions of specific conductance, pH, dissolved oxygen, and PO_4 11 months after PRB emplacement are shown in Figure 6A and B. The elevated specific conductance (greater than the background value of about 40 to 80 µS/cm [LeBlanc 1984]) in samples from the deep HMPS indicates the presence of the treated wastewater plume beneath the PRB. Spatial patterns in specific conductance in samples from the shallow HMPS closely replicate the patterns from the deep sampler. The similarity in spatial trends at the two depths is evidence that ground water flow paths curve upward as they approach the pond (Figure 3), and ground water flows nearly vertically upward through the PRB. Values of pH increase in an upward direction at all sampling points, with differences between the two depths ranging from 0.47 to 1.39 units. Little change in dissolved oxygen concentration between the deep and shallow samplers was observed, with the exception of a slight increase (up to 1.9 mg/L) for four adjacent sampling ports of the shallow sampler, most likely resulting from a small amount of pond water being pulled down into the port.

Monitoring results from the shallow and deep HMPS show a substantial reduction in PO_4 concentrations as ground water flows upward through the PRB (Figure 6C and D). PO_4 concentrations in water samples collected from the deep HMPS after emplacement of the PRB were similar to concentrations in samples collected from drive points prior to installation of the PRB, indicating that water below the PRB continues to contain elevated PO_4 concentrations. The mean PO_4 concentration for the deep HMPS 1S/1D (Figure 2) for the four sampling dates was 0.57 mg/L as P. In contrast, the mean PO_4 concentration for the shallow HMPS at line 1 for the four sampling dates was 0.08 mg/L; the maximum value was 0.36 mg/L.

The horizontal distribution of PO_4 concentrations with distance from shore for the deep HMPS (Figure 6D) is similar to the vertical distributions of PO_4 in monitoring wells located near the shore (McCobb et al. 2003; data not shown). Because ground water flow paths curve upward as the pond is approached (Figure 3), the vertical trends onshore are generally reflected as horizontal trends in the discharge area. The horizontal trends for the deep HMPS also indicate lateral shifts in the location of greatest PO_4 concentrations (about 1.5 mg/L) beneath the PRB due to changes in the shoreline position as the pond stage varies. For example, pond stage 2 months after the PRB was installed was at a near-historic low, and the pond stages at 11 and 15 months were substantially higher (91 cm) than the mean stage. The difference in shoreline position between the low and high stages resulted in a 5 to 6 m lateral shift in the location of the greatest PO_4 concentrations (Figure 6D).

The VMLS provide pumped samples at closely spaced vertical intervals through the PRB. PO_4 concentrations in water samples collected at the four depths between 25 and 104 cm below the pond bottom at site F639, the control site outside the PRB (Figure 2), are nearly equal, confirming that PO_4 concentrations do not change as plume water approaches the pond bottom outside of the PRB (Figure 7). PO_4 was not detected in water from the shallowest port (2 cm) because pond water apparently was drawn into the sampling port during pumping; the specific conductance of samples from this port was nearly equal to that of the pond water.

In contrast, PO_4 concentrations for VMLS at sites F640 and F644 in the PRB decreased from levels typical of the plume at the 104-cm ports (below the PRB) to less than 0.10 mg/L (as P) at the 25-cm ports (Figure 7). At these sites, PO_4 profiles developed prior to the PRB installation from drive-point samples showed no trend for PO_4 concentrations with depth. The results clearly indicate removal of PO_4 by the PRB.

The MLDCs also provide samples from closely spaced vertical intervals through the PRB. Detailed vertical PO_4 profiles were developed on the basis of data from the 13 ports over an 81-cm-long interval (Figure 8). The PO_4 concentration profiles from the MLDCs extend below the bottom of the PRB. At each MLDC site, a steep decreasing trend in PO_4 concentrations was observed as ground water flowed upward through the bottom 10 to 20 cm of the PRB.

The ability of the MLDC to obtain representative water samples, such as those obtained by pumping from the VMLS and HMPS, was unknown. Concentration results for samples from vertically adjacent sampling ports (elevation difference less than 3 cm) were compared for several adjacent MLDC and VMLS (less than 0.5 m apart laterally). The PO_4 concentrations for the two devices correlated strongly ($R^2 = 0.8907$, $n = 16$), confirming that the MLDC and VMLS yielded similar results. The results also verified field tests that established that a 2-week equilibration period was

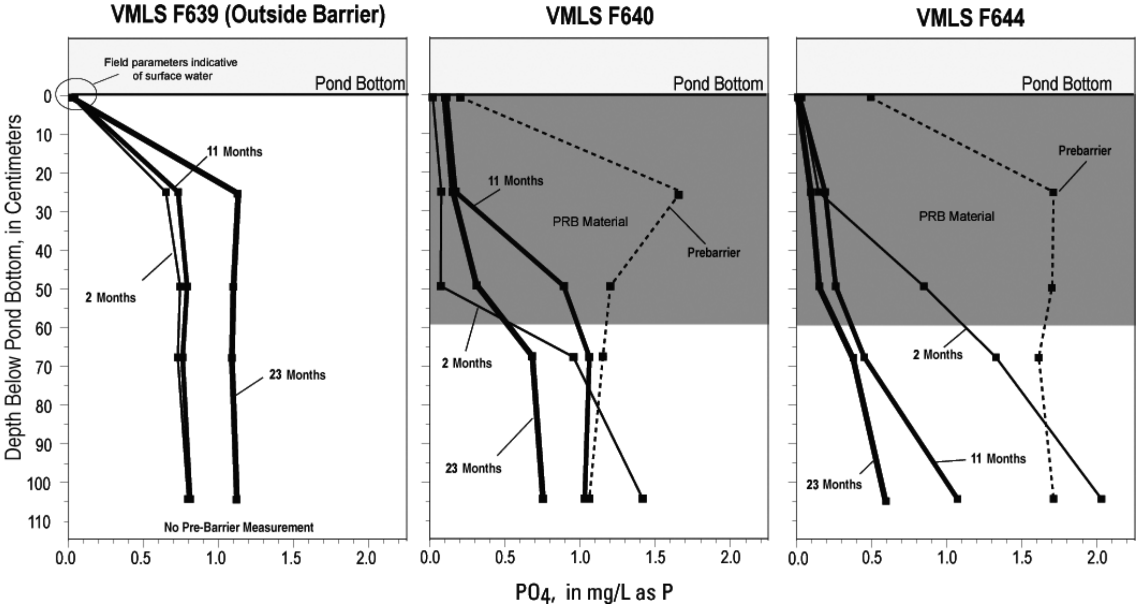

Figure 7. Phosphate concentrations in pore water samples collected from VMLS prior to and at 2, 11, and 23 months after installation of the PRB. Phosphate concentrations were reported by the USGS National Water Quality Laboratory as total dissolved phosphorus in mg/L as P. Locations of VMLS shown in Figure 2.

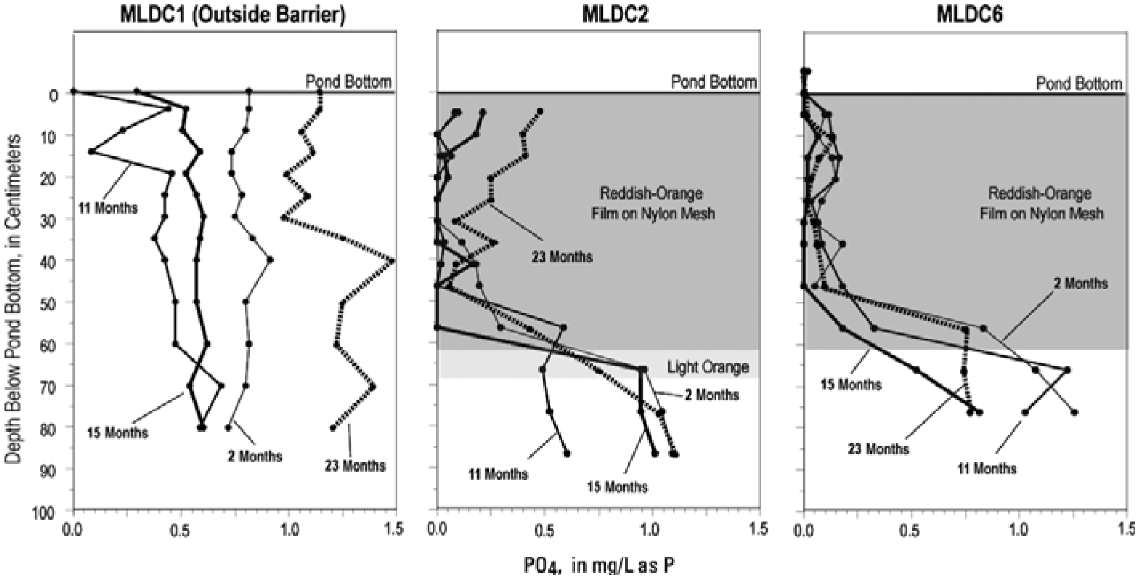

Figure 8. Phosphate concentrations in water samples collected from MLDCs at 2, 11, 15, and 23 months after installation of the PRB. Color observations from samples collected at 23 months from installation. Locations of MLDCs shown in Figure 2.

sufficient for diffusion methods to match pumped-sampling methods.

During the equilibration period, a reddish-orange film developed on the nylon mesh covering the openings on the diffusion-sampler bottles set opposite the ZVI/sediment mixture (Figure 8). The presence and color intensity of the film was used to estimate the thickness of the PRB at each MLDC location. Although the design thickness was 61 cm, the colored films indicated that the installed thickness ranged from 21 to 81 cm.

Seepage was measured during sampling events at 2, 11, and 23 months after installation of the PRB. At the control location outside the PRB and about 7 m from the mean shoreline position, one seepage meter (1a) with a high flow rate (mean 875 L/d/m^2) for all sampling events is adjacent to a meter (1b) with a consistently lower flow rate (391 to 512 L/d/m^2) (Table 1). Differences in water flux between seepage meters only about 1 m apart reflect the spatial variability in the rate of seepage through the pond bottom due to the heterogeneous nature of the sediments near and at the pond bottom.

Seepage results in Table 1 are mean rates from multiple measurements made at each meter during each sampling event; the multiple measurements varied an average of about 6.6% from the mean measurement for that event. Changes in seepage rates between sampling events were much greater and reflect changes in pond stage. With the exception of the control site, higher stage resulted in a lower water flux as the distance from shore of a given meter increased (Table 1). This effect is consistent with the general observation at lakes that seepage rates decrease exponentially with increasing distance from shore (McBride and Pfannkuch 1975). Water fluxes at the control site exhibited the inverse effect; water flux was greater as the distance from shore increased. PO_4 flux calculations, determined as a product of water flux and PO_4 concentration for each measurement, yielded values as low as 2.89 mg-P/d/m^2 in the barrier and as high as 1260 mg-P/d/m^2 at the control site (Table 1).

Discussion

The results from the first 23 months of monitoring demonstrate that the combination of devices was effective in providing the lateral, vertical, and temporal data on PO_4 concentrations needed for an initial evaluation of the PRB's performance. All of the devices were in good operating condition after being in place for 2 years. The sampling efforts generally transpired as expected, although unusually high water in 2006 required some modifications, such as the addition of extension tubes to the VMLS, the addition of handles to the tops of the MLDC to facilitate their retrieval in deeper water, and the installation of quick-connect fittings on the seepage meters. During the study period, the maximum depth of water encountered was 1.1 m, which was suitable for wading during sampling.

Installation of the devices, which were all constructed of PVC, to depths as great as 1 m below the pond bottom was possible because of the excavation to emplace the barrier. Although this project demonstrated the operation and effectiveness of the various suction, diffusion, and seepage devices, the designs and installation methods would have to be modified for applications not involving dewatering and excavation with heavy equipment. A prototype VMLS constructed with steel rather than PVC was successfully driven into the bottom sediments, although with great difficulty. An attempt to install an MLDC in about 1 m of water by driving and washing prior to emplacement of the PRB was not successful.

An unexpected challenge during installation of the devices was the vertical positioning of the VMLS and MLDC, which were designed so that the top sampling ports would be about the level of the pond bottom. They had to be set, however, after the site was dewatered and excavated. After the excavation was filled and graded to the approximate slope of the bottom, and currents and waves redistributed sediment to reform the natural bottom, some top sampling

Table 1

Observed Mean Water Flux and Calculated Mean Phosphate Flux at Seepage Meters inside (Meter Nos. 2a to 4b) and outside (Meters Nos. 1a to b) the PRB at 2, 11, and 23 Months after Installation of the PRB. Locations Shown in Figure 2.

	2 Months (Pond Stage = 13.26 m)				11 Months (Pond Stage = 13.83 m)				23 Months (Pond Stage = 14.05 m)			
Meter No.	Distance from Shore (meters)	Mean Water Flux (L/d/m^2)	Phosphate (mg/L as P)	Phosphate Flux (mg-P/d/m^2)	Distance from Shore (meters)	Mean Water Flux (L/d/m^2)	Phosphate (mg/L as P)	Phosphate Flux (mg-P/d/m^2)	Distance from Shore (meters)	Mean Water Flux (L/d/m^2)	Phosphate (mg/L as P)	Phosphate Flux (mg-P/d/m^2)
1a	3.96	804	0.44	354	8.17	853	0.80	682	10.4	967	1.3	1260
1b	3.96	391	0.57	223	8.17	483	0.82	394	10.4	512	1.3	666
2a	0.97	Meter dry	—	—	5.77	438	0.07	30.7	7.83	411	0.03	12.3
2b	0.97	Meter dry	—	—	5.77	441	0.03	13.2	7.83	395	0.02	7.91
3a	3.77	399	0.66	24.3	8.05	391	0.03	11.7	10.3	390	0.05	19.5
3b	3.77	729	0.27	197	8.05	402	0.05	20.1	10.3	384	0.07	26.9
4a	6.41	290	0.01	2.89	10.7	285	0.26	74.1	13.1	290	0.04	11.6
4b	6.41	250	nd	—	10.7	250	0.23	57.5	13.1	225	0.05	11.3

—, not measured: nd, not detected

Table 2

Mean Concentration, Total Dissolved Mass below and near the Top of the PRB Calculated for Hypothetical Cylinders with 2-cm Radius along the HMPS at 2, 11, 15, and 23 Months after the PRB's Emplacement, and Mass Loss of PO_4 at Each HMPS Pair. Locations shown in Figure 2.

		2 Months			11 Months			15 Months			23 Months		
	Depth (meters)	Mean Concentration (mg/L)	Total Dissolved PO_4 Mass (mg)	Mass Loss between Depths (%)	Mean Concentration (mg/L)	Total Dissolved PO_4 Mass (mg)	Mass Loss between Depths (%)	Mean Concentration (mg/L)	Total Dissolved PO_4 Mass (mg)	Mass Loss between Depths (%)	Mean Concentration (mg/L)	Total Dissolved PO_4 Mass (mg)	Mass Loss between Depths (%)
HMPS1 (South)	0.15	0.02	97.9	—	0.13	891.4	—	0.05	305.7	—	0.13	939.5	—
	0.91	0.31	1947	95.0	0.77	4878	81.7	0.44	2826	89.2	0.78	4841	80.6
HMPS2 (North)	0.15	0.01	53.0	—	0.11	629.7	—	0.03	174.1	—	0.19	1239	—
	0.91	0.15	1011	94.8	0.31	1653	61.9	0.17	1017	82.9	0.45	2558	51.5

ports were above the bottom and others were set deeper than intended.

The VMLS and MLDC produced comparable data on the steep vertical PO_4 concentration gradients that formed within the PRB (Figures 7 and 8). The closely spaced sampling ports on the MLDC allowed a finer resolution of the steep gradients (e.g., the decrease from 1 mg/L to less than 0.1 mg/L PO_4 [as P] at MLDC2 over less than 10 cm vertically; Figure 8); however, VMLS could be designed with more sampling ports than were used in this study. In general, the level of effort required during sampling and the relative costs between the VMLS and MLDC were comparable.

The MLDC had the additional advantage of passive sampling of the ground water, which avoided the mixing of water from different zones during pumping to purge and sample the VMLS. This advantage was especially evident in the samples from the top ports at the control site outside the barrier (VMLS F639 and MLDC1, Figures 7 and 8). PO_4 concentrations from the MLDC were elevated from about 100 cm below to the pond bottom, as expected in the untreated sediments, whereas the low PO_4 concentrations at the top of the VMLS indicated dilution with pond water drawn down to the top port during sampling.

A limitation of the MLDC was the 60-mL sample volume, which was sufficient for measurement of specific conductance and PO_4 concentration in the field but not for duplicate measurements or collection of additional samples for laboratory analysis. The VMLS, however, could be pumped to obtain sufficient volumes for measurement of other field parameters (e.g., pH) and collection of samples for laboratory analysis, although the pumping drew increasing amounts of water from the aquifer volume as purging and pumping proceeded.

The ports of the VMLS and MLDC set below the PRB confirmed the presence of the PO_4 plume but showed substantial variations in PO_4 concentrations over time (Figures 7 and 8). These variations had to be characterized to determine whether the PRB was reducing the PO_4 flux to the pond, but this would have been difficult using only the 18 widely distributed data points at the VMLS and MLDC. The pairs of HMPS at two locations (Figure 2) provided evidence that the PO_4 discharge area migrated toward and away from shore as a function of the pond stage, and at times of high stage, such as at 23 months after barrier emplacement, some PO_4 was presumed to have discharged landward of the PRB (Figure 6D). Temporary well points, VMLS, or MLDC would have been needed at 15 locations along each HMPS line to provide the same information. The HMPS also can be sampled from shore, which allows temporal monitoring of the PRB during winter when the pond is frozen or it is difficult to work in the water.

The data from the VMLS, MLDC, and HMPS indicated a substantial reduction in PO_4 concentrations as ground water flowed upward through the PRB. Data from the closely spaced sampling ports on the MLDC showed that much of the reduction in PO_4 concentrations occurred in the lower part of the barrier, indicating a rapid removal of dissolved PO_4 upon encountering the ZVI/sediment mixture.

The PRB was designed to reduce the phosphate solute-mass flux to Ashumet Pond. Direct estimation of a reduction in phosphate mass flux would require spatially distributed data on fluid flux and solute concentration; work is presently (2009) under way to measure the spatial distribution of fluid flux. The permanent seepage meters, although installed at only a few locations (Figure 2), provided direct evidence that PO_4 flux to the pond was reduced by emplacement of the PRB because the devices provide data on both fluid and solute-mass flux.

An indication of the effectiveness of the PRB can be obtained, however, by calculating the reduction of in situ solute mass between the deep and shallow sampling ports along the HMPS for the various sampling events. For these calculations, each HMPS was assumed to represent a horizontally oriented cylinder of aquifer with a 2-cm radius. The mass in the hypothetical cylinder spanning the entire HMLS can be estimated as

$$\text{Total Mass} = \sum_{i=1}^{14}\left[\frac{c_i + c_{i+1}}{2}\right][L][\pi r^2][n]$$

where c_i and c_{i+1} are the PO_4 concentrations at adjacent ports i and $i + 1$; L is the distance between ports; πr^2 is the cross-sectional area of the cylinder, and n is the porosity (0.39 from Garabedian et al. [1991]). The results indicate a decrease in dissolved PO_4 mass from the deep to the shallow HMPS of about 52% to 95% as the ground water from the treated wastewater plume flows upward through the PRB (Table 2).

The potential reduction in fluid flux through the barrier because of clogging by mineral precipitation or microbial growth could not be evaluated because of the temporal variability in measured water flux at each seepage meter caused by the changing pond stage. A long period of monitoring may be needed to establish a stage–seepage relationship for each meter to identify a trend in seepage rates because of possible changes in hydraulic properties of the PRB. The use of permanent meters at fixed locations would facilitate this analysis.

Summary

A PRB composed of a mixture of ZVI and native sediments was placed on the bottom of Ashumet Pond on Cape Cod, Massachusetts, to reduce the load of PO_4 to the pond from the discharge of a treated wastewater–ground water plume. Various suction, diffusion, and seepage devices were installed in and near the barrier to monitor its effectiveness. The devices met the design goals to provide spatially distributed monitoring points that were aesthetically acceptable, rugged, and easy to use; yielded representative pore water samples; and did not detrimentally affect the integrity of the barrier. Chemical analyses of pore-water samples collected from VMLS and MLDCs installed vertically through the PRB at 18 sites indicate a substantial decrease in PO_4 concentrations as ground water flows upward through the barrier. The MLDC worked best for delineating the steep concentration gradients through the barrier, whereas the VMLS provided greater sample volumes to allow measurement of several field water-quality parameters and collection of samples for laboratory analysis. Pairs of HMPS installed along two transects perpendicular to shore provided data on temporal variations in the discharge area of the PO_4 plume and could be sampled from shore even when the pond was frozen. Permanently installed Lee-style seepage meters with removable lids provided data on ground water and phosphate flux. Data collected during the first 2 years after emplacement of the PRB indicate that the barrier reduced PO_4 flux by as much as 95%.

Acknowledgments

The USGS Toxic Substances Hydrology Program and the Air Force Center for Engineering and the Environment (AFCEE) supported development and testing of the monitoring devices. The authors gratefully acknowledge the assistance of Megan Chaisson, Jessica Cochrane, Nicholas Geboy, Jonathan King, Luke Parsons, and Laura Strumness of the USGS in designing, installing, and sampling the devices. The authors would also like to thank Jon Davis, Jonathan Blount, and Spence Smith of AFCEE for their technical advice and support, and the staffs of Environmental Chemical Corporation and their subcontractors, who were extraordinarily cooperative as we installed the instrumentation during the barrier's emplacement.

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