

Figure 1. Location of study area, the extent of the phosphorus plume and discharge area in 1999, locations of monitoring wells and multilevel samplers, and the area of the pond-bottom permeable reactive barrier, Ashumet Pond, Cape Cod, Massachusetts. The inset map over the map of Massachusetts shows the location of the study area.

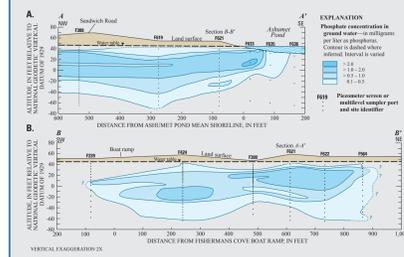


Figure 2. Vertical distribution of phosphate concentrations along sections A-A' and B-B' near Ashumet Pond, Cape Cod, Massachusetts, July-August 2004. Altitude is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29). Locations of sections shown in Figure 1.

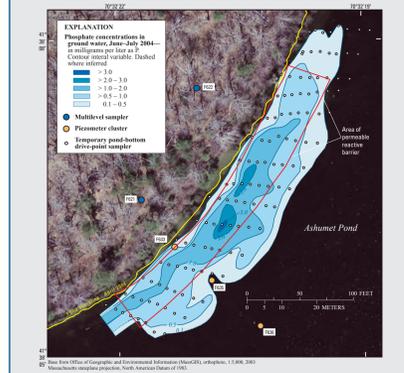


Figure 3. Areal distribution of phosphate concentrations in ground water near the pond bottom prior to installation of the permeable reactive barrier, Ashumet Pond, Cape Cod, Massachusetts, June 29-July 2, 2004. Phosphate concentrations were determined by using a field colorimetric method.

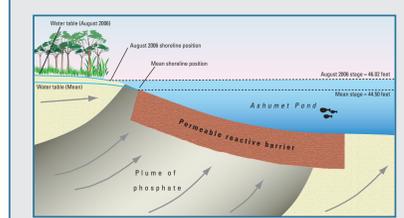


Figure 4. Conceptual cross section of the pond-bottom permeable reactive barrier. The barrier is composed of zero-valent iron mixed with native sediments to a 2- to 5-foot depth over an area of 10,200 square feet. At the highest pond stages (including August 2006), phosphate was detected near the shoreward edge of the barrier.

INTRODUCTION

Ground water contaminated with phosphate (PO₄) because of historical land disposal of treated municipal wastewater at the Massachusetts Military Reservation (MMR) is currently (2009) discharging into nearby Ashumet Pond (fig. 1; McCobb and others, 2003). Unlike the transport of many contaminants in ground water beneath the MMR, phosphate transport is greatly retarded because it adsorbs strongly to the aquifer sediments. Despite the removal of the wastewater source in 1995, phosphate concentrations in the ground water will remain elevated for many decades as natural flushing of the aquifer by uncontaminated ground water results in desorption of sorbed phosphate (Parkhurst and others, 2003).

The potential adverse effect of continued phosphate loading on the ecology of Ashumet Pond has prompted remedial actions by the Air Force Center for Engineering and the Environment (AFCEE), in August 2004, a permeable reactive barrier (PRB) was placed on the bottom of Ashumet Pond to reduce phosphate concentrations in ground water discharging to the pond to limit or reverse the adverse ecological effects of the phosphate.

In August 2006, the U.S. Geological Survey collected pore-water samples in and near the PRB from depths below, within, and at the top of the barrier. This report presents a series of maps showing constituent concentrations and values of physical properties, layered by depth, as a visual assessment of the effects of the PRB on the geochemistry of the pond water along the shoreline of Ashumet Pond.

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BACKGROUND

A plume of treated wastewater created by over 60 years of land disposal extends more than 3 miles south of the MMR toward the coast (LeBlanc, 1984; Savoie and LeBlanc, 1998). The eastern edge of this plume intersects Ashumet Pond, a kettle-hole pond about 1,600 feet (ft) southeast of the decommissioned infiltration beds in an area known as Fishermen Cove (fig. 1). Phosphate and other wastewater-related constituents discharge with the ground water to this area of Ashumet Pond (Walter and others, 1996; McCobb and others, 2003; Parkhurst and others, 2003).

Phosphate Plume

The distribution of phosphate in ground water upgradient of Ashumet Pond was measured in 1999 by using an extensive network of monitoring wells and multilevel samplers (fig. 1; McCobb and others, 2003). A subset of the wells and multilevel samplers was reinstalled in 2004. Phosphate concentrations used in this report for orthophosphate reported in milligrams per liter as phosphorus (mg/L as P). Results of analyses of samples collected along section A-A', extending from about 700 ft upgradient of the pond shoreline to about 160 ft offshore, indicate that elevated concentrations of dissolved phosphate (greater than 0.10 mg/L) were present in 2004 in a zone 80-120 ft thick immediately upgradient of the pond (fig. 2A). Phosphate concentrations along section B-B', which extends along the shoreline of Fishermen Cove, were greater than 0.1 mg/L along a shoreline length of greater than 900 ft (fig. 2B).

Phosphate Discharge to Ashumet Pond

The area through which the plume discharges into Ashumet Pond was mapped in September 1999 by using temporary drive points. Elevated phosphate concentrations (as great as 3 mg/L) were present in shallow ground water beneath the pond in an area within 60 ft of the shore along about 400 ft of shoreline (McCobb and others, 2003). Samples also were collected from temporary drive points from June through July 2004 prior to the installation of the PRB, and results of analyses indicated the area of elevated phosphate concentrations in the pore water beneath the pond (fig. 3) was about the same as that observed in 1999.



Figure 5. A temporary coffer dam system and large pumps were used to dewater the work area and expose the pond bottom before placement of the permeable reactive barrier, Ashumet Pond, Cape Cod, Massachusetts, 2004.

Table 1. Mean cell values of physical properties and constituent concentrations in the interpolation grid over the area of the permeable reactive barrier, by sampling depth, Ashumet Pond, Cape Cod, Massachusetts, August 3-21, 2006.

Depth of sample collection, in feet	Specific conductance, in µmhos/cm	Temperature, in °C	Dissolved oxygen, in mg/L	pH	Field-determined phosphate, in mg/L as P	Laboratory-determined phosphate, in mg/L as P	Nitrate, in mg/L as N	Ammonium, in mg/L as N	
0.50	Mean	147	20.5	0.372	7.21	0.215	0.116	0.080	0.232
	Std. Dev.	41.7	1.45	0.970	46.7	204	152	100	260
1.5	Mean	151	18.1	1.36	7.26	263	207	129	263
	Std. Dev.	40.8	1.42	1.42	530	296	253	157	293
3.0	Mean	145	16.4	2.99	6.56	862	872	488	243
	Std. Dev.	40.4	1.02	2.59	370	453	467	360	288

Pond-Bottom Permeable Reactive Barrier

The AFCEE installed a PRB on the bottom of Ashumet Pond in late August 2004 to intercept the phosphate plume as it discharges upward through the pond bottom (fig. 4). Thirty-seven tons of zero-valent iron (ZVI) were mixed into the pond-bottom sediment (1 percent ZVI by weight) to a depth of about 2.3 ft in an area extending 200 ft from the shore along 280 ft of shoreline, which is the area of highest observed pore-water phosphate concentrations. The ZVI-sediment mixture was created by excavating the sediment while the pond was locally dewatered by large pumps and a temporary cofferdam system (fig. 5). An excavator with a mixing bucket was used to blend the pond-bottom sediment and iron filings prior to placement of the mixture on the pond bottom (figs. 6 and 7) (AFCEE, 2004). This ZVI mixture reacts with oxygen and nitrate in the discharge plume and oxidizes to form ferrous hydroxide (Fe(OH)₂). Ferric hydroxide has a strong affinity for phosphate and, therefore, the capacity to adsorb and remove it from ground water. ZVI PRBs create strongly reducing conditions that also result in changes in ground-water chemistry, including pH, dissolved oxygen levels, and nitrate concentrations (Savoie and others, 2004). This PRB system was designed to reduce the load of phosphate to Ashumet Pond for at least 20 to 25 years (AFCEE, 2004).



Figure 6. The ZVI/sediment mixture was placed on the pond bottom, and the surface of the barrier was contoured to a slope similar to the original pond bottom, Ashumet Pond, Cape Cod, Massachusetts, 2004.

To collect samples at the 0.5-ft depth in the area between the PRB and the shore, the sample collection methods are described in detail in McCobb and others (2003, 2009). Specific conductance, pH, dissolved oxygen, temperature, and phosphate were measured and recorded in the field. Samples also were analyzed for phosphate and nitrogen at the USGS National Water-Quality Laboratory.

DATA INTERPOLATION AND DISPLAY

Values of physical properties and constituent concentrations are shown in maps (figs. 9-16) generated from concentration point data that were hand contoured and digitized using the ESRI ArcInfo program (Environmental Systems Research Institute, Inc., 2000). The ESRI TOPOGRID subroutine was used to rasterize each dataset into 0.82-ft by 0.82-ft cells by using an iterative fine-distance interpolation technique (Hutchinson, 1989). The boundary of the interpolation field was set as the outer extent of the sampling points for each sampling depth and, therefore, the shape of the concentration grid varies with depth. The mean and standard deviation of the grid-cell values were calculated for each constituent by depth over the area of the PRB; values are presented in table 1.

GEOCHEMICAL EFFECTS OF THE PERMEABLE REACTIVE BARRIER

Field values and laboratory results were used to characterize the geochemical effects of the barrier on the ground water beneath (3.0 ft), within (1.5 ft), and at the top (0.5 ft) of the PRB area. The distributions of specific conductance, dissolved oxygen, pH, temperature, field-determined phosphate, and laboratory-determined phosphate, nitrate, and ammonium are presented in figures 9-16 for the three depth intervals. Progressively shallower depths correspond to ground water flow along upward through the PRB. In general, the effects of the PRB on specific conductance at progressively shallower depths through the barrier were minimal. Temperature values increased at shallower depths as a result of conductive warming of shallow ground water by the warmer surface water above. Values of pH increased greatly as ground water flowed upward through the PRB. Dissolved oxygen concentrations were generally low (<1 mg/L) in the treated-wastewater plume water below the PRB and decreased to less than 0.1 mg/L at all shallow (0.5-ft depth) sampling points in the PRB.

In general, the field data showed a decrease in phosphate concentrations (from 2.2 mg/L to less than 0.1 mg/L) at progressively shallower depths in the barrier. During the 2006 sampling, however, the stage of Ashumet Pond (46.02 ft above mean sea level) was 1.5 ft above mean stage, and as a result, the phosphate discharge area temporarily shifted landward of the PRB, which resulted in a narrow zone of elevated phosphate concentrations between the shoreline and the near-shore edge of the barrier. Mean phosphate concentrations (laboratory) for each sampling depth over the extent of the PRB were reduced by more than 87 percent between the 3.0-ft and 0.5-ft sampling depths (table 1).

Laboratory results for phosphate confirmed field observations that concentrations decreased significantly with decreasing depth in the PRB. The limited nitrate that was present in ground-water samples collected at 3.0 ft, which is below the PRB, decreased to concentrations less than 0.1 mg/L (as N) in samples from all sampling locations in the PRB. However, ammonium concentrations remained constant and unaffected by the geochemical reactions occurring in the PRB.

CONCLUSIONS

The primary purpose of the temporary drive-point sampling was to characterize concentrations of phosphate and inorganic nitrogen in the treated-wastewater plume as it flows upward through the zero-valent iron permeable reactive barrier and to map the concentrations (August 2006) of phosphate at three depths in the area of the barrier. Field observations results indicated that the barrier was effective in reducing phosphate concentrations in the ground water passing through it. Results of laboratory analyses of ground-water samples from approximately 200 temporary drive-point locations indicated that the barrier was effective in reducing phosphate concentrations in the ground water passing through it. Results of laboratory analyses of ground-water samples from approximately 200 temporary drive-point locations indicated that the barrier was effective in reducing phosphate concentrations in the ground water passing through it.

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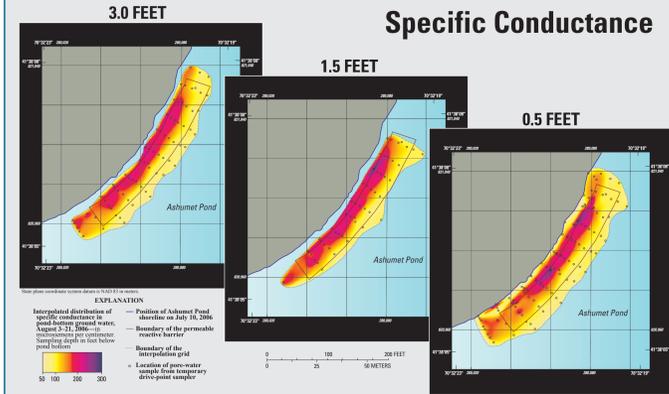


Figure 9. Specific conductance of ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. Specific conductance (SC) is a measure of how well water conducts an electrical current. SC increases with an increasing amount and mobility of ions. SC, therefore, is an indirect measure of the quantity of dissolved solids. At each sample depth in the barrier, SC was observed at values typically found in the treated-wastewater plume and was used as a general indicator of the presence of the plume. SC values in the discharge were ranging from 100 to 200 µS/cm (microsiemens per centimeter). SC data from the shallowest interval (0.5 ft) also were used as indicators of whether any shallow samples had been diluted by pond water during sampling. SC of the pond water was about 95 µS/cm.

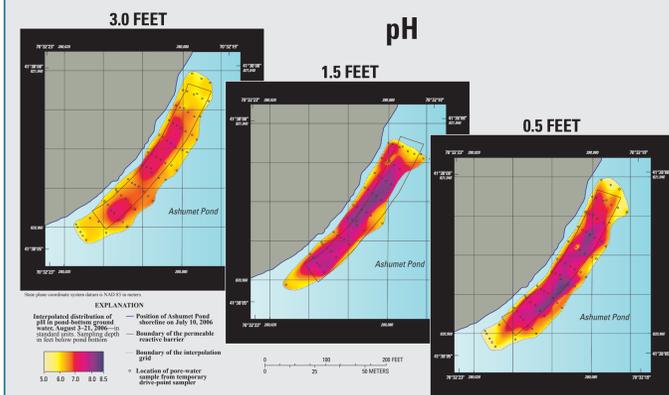


Figure 10. pH of ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. Pore-water sampling indicated that the pH of ground water increased (to values as high as 8.4) as the ground water flowed upward into the barrier. The iron-corrosion reactions (under both aerobic and anaerobic conditions) lead to the consumption of hydrogen and consequent increase in pH (Puls and others, 1998).

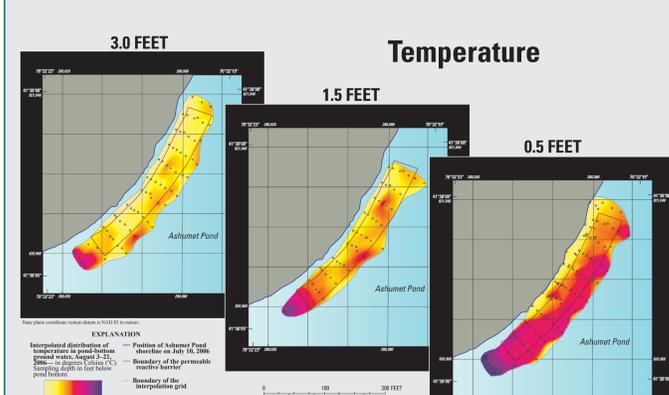


Figure 11. Temperature of ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. The temperature of ground water increased significantly between the 3.0-ft (mean = 18.4 degrees Celsius (°C)) and 0.5-ft (mean = 20.5 °C) sampling intervals. This change in ground-water temperature was not limited to the barrier area and can be attributed to conductive warming of shallow ground water by the warm (18 °C) pond water.

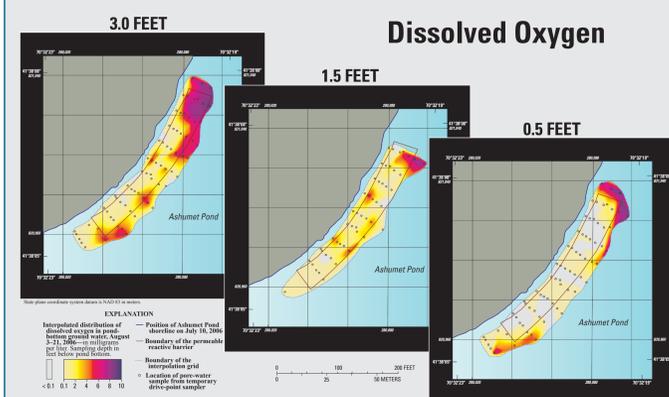


Figure 12. Concentrations of dissolved oxygen in ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. Dissolved oxygen (DO) concentrations in ground water immediately beneath the barrier were generally low (less than 0.1 milligrams per liter (mg/L)) and reflected low concentrations in the treated-wastewater plume (Repart and others, 2006). Once ground water entered the barrier, DO concentrations were generally reduced to less than 0.1 mg/L. This additional decrease in the already low DO concentrations can be attributed to the consumption of oxygen by aerobic corrosion processes in the barrier.

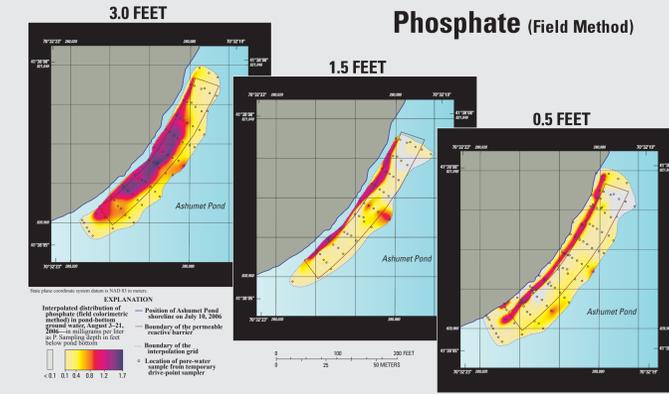


Figure 13. Concentrations of phosphate (field method) in ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. The field analyses of phosphate were conducted on unfiltered samples by using a colorimetric method that measures inorganic orthophosphate (PO₄). The field data generally showed a decrease in phosphate to about 0.1 milligrams per liter (mg/L) at progressively shallower depths in the barrier. The stage of Ashumet Pond (46.02 ft above mean sea level) was greater than 1.5 feet above mean stage (1992-2006). With the higher-than-average stage, the phosphate discharge area temporarily shifted landward. The thin zone of elevated phosphate concentrations between the shoreline and the near-shore edge of the barrier is a portion of the phosphate plume discharging to the pond during the high-stage period.

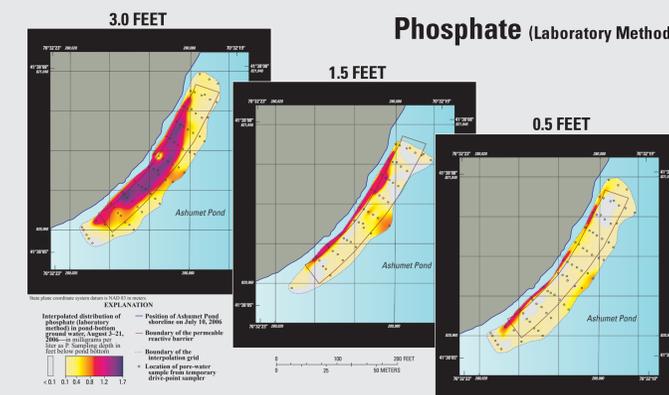


Figure 14. Concentrations of phosphate (laboratory method) in ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. Laboratory analyses were conducted on filtered and acidified water samples by using an alkaline persulfate digestion method that measures total dissolved phosphorus (as P). Because most phosphorus in the plume was present as orthophosphate, the field and laboratory methods gave similar results. Mean phosphate concentrations over the area of the permeable reactive barrier, as determined by using a geographical information system (GIS), were reduced more than 87 percent between the 3.0-ft and 0.5-ft sampling depths.

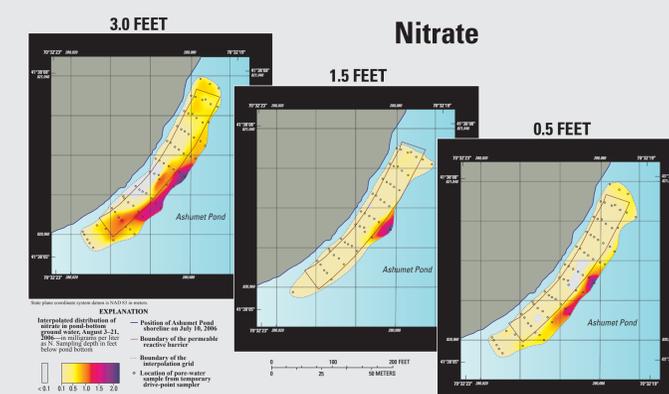


Figure 15. Concentrations of nitrate in ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. Inorganic nitrogen species are important nutrients in lakes. Samples were collected to evaluate the effects of the permeable reactive barrier on nitrate and ammonium. The results confirmed earlier observations (McCobb and others, 2003) showing that nitrate discharged farther offshore than the phosphate plume. For this reason, only a limited area of elevated nitrate concentrations was present in the sampling area near the barrier. Nitrate present at the 3.0-ft sampling depth was reduced to values less than 0.1 milligrams per liter as N at progressively shallower depths through the barrier. Further work would be needed to characterize the processes responsible for the decrease in nitrate concentrations in this complex geochemical zone.

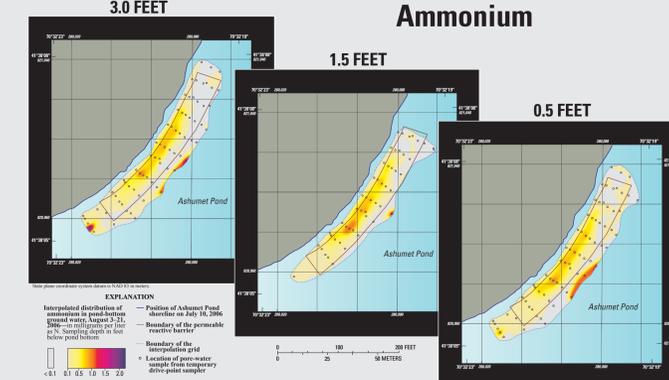


Figure 16. Concentrations of ammonium in ground water collected from drive-point samplers at 0.5, 1.5, and 3.0 feet, Ashumet Pond, Cape Cod, Massachusetts, 2006. Analytical results for ammonium showed little change in concentration at progressively shallower depths through the barrier. The mean concentrations at all the sampling depths were only about 0.2 milligrams per liter as N.

Distribution of Treated-Wastewater Constituents in Pore Water at a Pond-Bottom Reactive Barrier, Cape Cod, Massachusetts

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