Response Curves for Phosphorus Plume Lengths from Reactive-Solute-Transport Simulations of Onland Disposal of Wastewater in Noncarbonate Sand and Gravel Aquifers

By John A. Colman

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Conversion Factors, Datums, and Abbreviations

Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
foot per day (ft/d)	0.3048	meter per day (m/d)
foot per year (ft/yr)	0.3048	meter per year (m/yr)
gallon per day (gal/d)	3.785	liter per day (L/d)
gallon per square foot per day (gal/ft^2/d)	40.7	liter per square meter per day (L/m^2/d)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
mile (mi)	1.609	kilometer (km)
million gallons per day (Mgal/d)	3.785	cubic meter per second (m^3/s)
square foot (ft^2)	0.09290	square meter (m^2)
square mile (mi^2)	2.590	square kilometer (km^2)
ton per year (ton/yr)	0.9072	metric ton per year (ton/yr)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

kg/yr	kilogram per year
mg/g	milligram per gram
mg/L	milligram per liter
mL	milliliter
µmol/L	micromoles per liter

Response Curves for Phosphorus Plume Lengths from Reactive-Solute-Transport Simulations of Onland Disposal of Wastewater in Noncarbonate Sand and Gravel Aquifers

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Abstract

Surface-water resources in Massachusetts often are affected by eutrophication, excessive plant growth, which has resulted in impaired use for a majority of the freshwater ponds and lakes and a substantial number of river-miles in the State. Because supply of phosphorus usually is limiting to plant growth in freshwater systems, control of phosphorus input to surface waters is critical to solving the impairment problem. Wastewater is a substantial source of phosphorus for surface water, and removal of phosphorus before disposal may be necessary. Wastewater disposed onland by infiltration loses phosphorus from the dissolved phase during transport through the subsurface and may be an effective disposal method; quantification of the phosphorus loss can be simulated to determine disposal feasibility. In 2003, the U.S. Geological Survey, in cooperation with the Massachusetts Department of Environmental Protection, initiated a project to simulate distance of phosphorus transport in the subsurface for plausible conditions of onland wastewater disposal and subsurface properties. A coupled one-dimensional unsaturated-zone and three-dimensional saturated-zone reactive-solute-transport model (PHAST) was used to simulate lengths of phosphorus plumes. Knowledge of phosphorus plume length could facilitate estimates of setback distances for wastewater-infiltration sites from surface water that would be sufficient to protect the surface water from eutrophication caused by phosphorus transport through the subsurface and ultimate discharge to surface water.

The reactive-solute-transport model PHAST was used to simulate ground-water flow, solute transport, equilibrium chemistry for dissolved and sorbed species, and kinetic regulation of organic carbon decomposition and phosphate mineral formation. The phosphorus plume length was defined for the simulations as the maximum extent of the contour for the 0.015 milligram-per-liter concentration of dissolved phosphorus downgradient from the infiltration bed after disposal cessation. Duration of disposal before cessation was assumed to be 50 years into an infiltration bed of 20,000 square feet at the rate of 3 gallons per square foot per day. Time for the maximum extent of the phosphorus plume to develop is on the order of 100 years after disposal cessation. Simulations indicated that phosphorus transport beyond the extent of the 0.015 milligram-per-liter concentration contour was never more than 0.18 kilogram per year, an amount that would likely not alter the ecology of most surface water.

Simulations of phosphorus plume lengths were summarized in a series of response curves. Simulated plume lengths ranged from 200 feet for low phosphorus-concentration effluents (0.25 milligram per liter) and thick (50 feet) unsaturated zones to 3,400 feet for high phosphorus-concentration effluents (14 milligrams per liter) discharged directly into the aquifer (unsaturated-zone thickness of 0 feet). Plume length was nearly independent of unsaturated-zone thickness at phosphorus concentrations in the wastewater that were less than 2 milligrams per liter because little or no phosphorus mineral formed at low phosphorus concentrations. For effluents of high phosphorus concentration, plume length varied from 3,400 feet for unsaturated-zone thickness of 0 to 2,550 feet for unsaturated-zone thickness of 50 feet.

Model treatments of flow and equilibrium-controlled chemistry likely were more accurate than rates of kinetically controlled reactions, notably precipitation of iron-phosphate minerals; the kinetics of such reactions are less well known and thus less well defined in the model. Sensitivity analysis indicated that many chemical and physical aquifer properties, such as hydraulic gradient and model width, did not affect the simulated plume length appreciably, but duration of discharge, size of infiltration bed, amount of dispersion, and number of sorption sites on the aquifer sediments did affect plume length appreciably.

Because simulation of plume length in carbonate-mineral sediments indicated that the plume would be substantially longer than in noncarbonate-mineral sediments, the application of the response curves in locations with carbonate-mineral sediments would be inappropriate. The effect of carbonate minerals in sediments is to increase pH, which causes decreased sorption of phosphorus on aquifer sediments.

Phosphorus removal from solution by precipitation onto aquifer sediments is more efficient at high concentrations of disposed phosphorus than at low concentrations. At very low phosphorus concentrations, the solubility product of phosphorus minerals is not exceeded and no phosphorus mineral forms. An important consequence is that removal of dissolved phosphorus from the plume by processes in the subsurface is decreased the more that removal efforts are applied in treatment before wastewater is disposed.

Model simulations indicate that removal of phosphorus from wastewater disposed through septic systems would have the advantage of efficient phosphorus removal in the subsurface because phosphorus concentrations are high in septic-system effluent. Short plume lengths result from wastewater disposal through septic systems because of the efficient phosphorus removal and because of the low volume of wastewater involved. The simulation results for small-volume systems are not quantitative, however, because wastewater-infiltration rates are much lower than those of the higher-volume system that was used to calibrate the model and to create the plume-length response curves.

The response curves for phosphorus plume lengths, as defined by the maximum extent of the 0.015 milligram-per-liter concentration contour, is clearly defined in the model simulations, although the relation between simulated plume length and protective setback distance is subject to interpretation. Phosphorus does move beyond the point at which the simulated 0.015 milligram-per-liter concentration contour has stopped, so that a determination of protective setback distance must include a consideration of whether that continued flux, or some other flux amount, is appropriate. Also, simulations indicate that phosphorus plumes do not reach their full extent until 50 to 200 years after disposal cessation, depending on concentration of phosphorus disposed. No phosphorus plume has been monitored for that long after cessation, so there is no way to verify the long-term simulation results.

Introduction

Onland disposal of wastewater has been practiced for many years in Massachusetts at large and small wastewater-treatment facilities underlain by porous sediment deposits. Publicly owned facilities treating millions of gallons per day use onland disposal to stabilize waste further and lessen the effect of discharge on surface waters as compared to disposal through pipe outfalls. Smaller facilities, disposing on-site through septic-system leachfields, rely on waste stabilization processes that occur in the subsurface. Although generally environmentally beneficial to surface water, as compared to outfall discharge (Jantrania, 2000), onland disposal results in ground-water transport of wastewater constituents, including phosphorus, that may affect surface freshwater upon discharge from the aquifer.

Transport of phosphorus in the subsurface from onland disposal likely depends on physical and chemical properties of the aquifer that could remove phosphorus from the dissolved (mobile) fraction, and on volume and phosphorus concentration of the disposed wastewater. Quantitative knowledge of how these factors affect phosphorus would facilitate licensing of new onland disposal facilities. In 2003, the U.S. Geological Survey (USGS), in cooperation with the Massachusetts Department of Environmental Protection, initiated a project to simulate distance of phosphorus transport for plausible conditions of onland disposal and subsurface properties. The simulation model was based on data and a model developed for the sewage plume at the Massachusetts Military Reservation (MMR) (Parkhurst and others, 2003) and data from the septic-system leachfield at Walden Pond State Reservation, Massachusetts (Colman and Friesz, 2001). The simulation results are likely applicable to other noncarbonate sand and gravel aquifers in addition to the glacial outwash deposits of Cape Cod and eastern Massachusetts on which the model was based.

The multiple concerns regarding wastewater disposal include removal of solids, biological oxygen demand (BOD), bacteria, nitrogen, phosphorus, trace metals, and emerging contaminants (for example, pharmaceuticals and endocrine disrupters). Depending on degree of treatment, many of these materials are decreased before disposal at treatment plants. Onland disposal of wastewater through correctly functioning septic systems can also be effective in eliminating the polluting constituents of wastewater, because these materials degrade in the unsaturated zone or are immobilized by adsorption and precipitation in the unsaturated zone (the zone of the subsurface that is above the water table) and the saturated zone (the aquifer) (Robertson, 2003; Weiskel and others, 1996; Kent and others, 2000, Kolpin and others, 2003). Although less investigated than other constituents, the emerging contaminants may also be degraded effectively or removed from ground water onto the solid phase with onland disposal, because many of these compounds are biodegradable organic compounds and may also be surface reactive. Phosphorus, a cause of eutrophication in freshwater, and nitrogen, a potential contaminant of drinking-water supplies and cause of eutrophication of coastal marine ecosystems, are only partially removed in treatment plants and from the dissolved phase during transport in the subsurface. Subsurface transport of phosphorus, in addition to nitrogen, where drinking-water supplies or coastal marine resources are involved, is a concern for locating onland disposal systems.

Phosphorus is usually the limiting nutrient for plant growth in freshwater; therefore, supply to surface water can control eutrophication (Scheffer, 1998). Of the more than three-quarters of the lake and pond acreage surveyed in Massachusetts for an annual report to the U.S. Environmental Protection Agency and Congress described as "not supporting all beneficial uses," the most common reason for the unsupported use was excessive plant growth (U.S. Environmental Protection Agency, 1998). Introduction of nonnative species may have an effect; but overall, plant growth can continue only to the extent that plant nutrients, such as phosphorus, are available. Disposal of wastewater can result in substantial eutrophication of receiving waters because of the phosphorus contained in the effluents (Moore and others, 2003). Onland disposal of wastewater may partially or wholly mitigate the effects of phosphorus on surface water by phosphorus removal processes during transport through the unsaturated zone and in the saturated zone.

Quantifying the absorptive capacity of the unsaturated and saturated zones for phosphorus would allow this capacity to be used most effectively. The capacity of the subsurface to absorb phosphorus clearly depends on the phosphorus load applied, and there are examples of onland disposal systems that were overloaded resulting in substantial amounts of phosphorus transported to surface water (figs. 1 and 2), as well as examples where no appreciable transport of phosphorus has occurred (fig. 3). In addition to load, physical, chemical, and biological processes affect phosphorus retention in the subsurface.

Time-dependent effects of these processes affect absorptive capacity and must be considered because plumes of dissolved phosphorus may persist in the subsurface long after active discharge has ceased. Because persistence of phosphorus plumes in the aquifer is long in comparison to the lengths of investigations that have measured their effects, long-term effects must be determined by computer model simulations based on the known geochemistry and hydrology of the subsurface. Until recently, models have been inadequate to simulate the interacting three-dimensional flow (3-D) and chemical and biological reactions that determine phosphorus transport. However, PHAST, a USGS-developed 3-D reactive-solute-transport model, has become available (Parkhurst and others, 2004). By using PHAST simulations, engineering-response curves can be prepared that show how the length of the phosphorus plume in the aquifer relates to chemical, biological, and aquifer properties including phosphorus concentration in the effluent and thickness of the unsaturated zone.

This report describes the hydrology and geochemistry that affects phosphorus retention in the unsaturated and saturated zones of the subsurface. Computer models are described that simulate transport of phosphorus for onland disposal of wastewater primarily for large installations, with 20,000 ft^2 infiltration beds, infiltration rates of 3 $gal/ft^2/d$, and disposal duration of 50 yrs. Simulation results are summarized in graphical engineering response curves that show the relations among effluent phosphorus concentrations, thickness of the unsaturated zone, and length of the dissolved phosphorus plume in the aquifer. The dissolved phosphorus plume (hereafter called the phosphorus plume) is the zone in the aquifer characterized by above-background dissolved phosphorus concentrations. Use of the response curves can facilitate determination of the disposal location and the degree of phosphorus-removal treatment needed to meet low-impact disposal objectives. Sensitivity analysis is included to quantify the effects on the response curves of the number of phosphorus binding sites on the aquifer solids, duration of disposal, and other aquifer and disposal conditions.
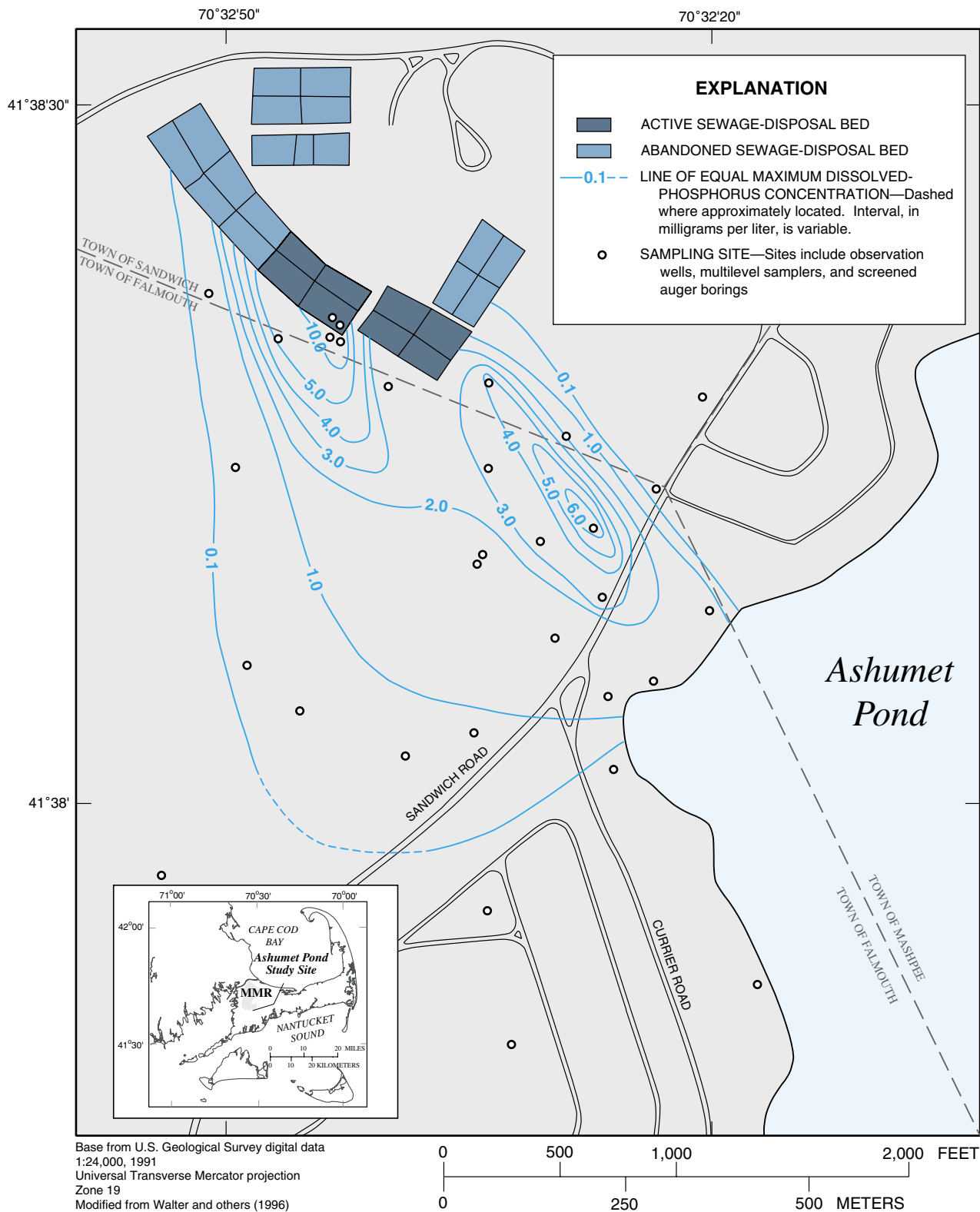
Figure 1. Measured dissolved phosphorus concentrations in the aquifer downgradient from sewage infiltration beds at the Massachusetts Military Reservation (MMR), Cape Cod, Massachusetts, 1993. Disposal ranged from 0.1 to 1.5 million gallons per day during 60 years of use.

Figure 2. Distribution of measured concentrations of dissolved phosphorus in ground water approximately 2 feet below the bottom of Ashumet Pond, 1999. The phosphorus derives from the sewage plume emanating from sewage infiltration beds at the Massachusetts Military Reservation, Cape Cod, Massachusetts.

Figure 3. Extent of nitrate plume emanating from the septic system of the Walden Pond State Reservation, Massachusetts. Dissolved phosphorus concentrations were at background values and are not shown. Essentially no phosphorus from the septic system disposal site has been transported to the pond during the 25 years of system operation. Disposal rate averages 0.001 million gallons per day.

Approach to Computer Simulations of Phosphorus-Plume Length

The approach to simulations uses a conceptual model to define conditions of wastewater disposal, phosphorus plume formation, and safe setback distances for locations of disposal from surface water. The conceptual model is quantified by use of computer models based on chemical and physical principles of subsurface flow and transport.

Conceptual Model

Typically, onland disposal of wastewater at treatment plants involves application of treated sewage effluent to infiltration beds excavated into the ground. A recent installation of infiltration beds for onland disposal of treated sewage has been completed in Acton, MA. The beds were set next to a 0.25 Mgal/d treatment facility, initially running 0.1 Mgal/d; effluent will be treated to decrease phosphorus concentrations to 0.15–0.2 mg/L; monitoring wells were installed 50 to 100 ft downgradient from the beds (Acton Department of Health, oral commun., 2003; fig. 4). Alternatively, onland disposal of sewage can be through septic-system leachfields

without pretreatment other than settling in septic tanks with effluent phosphorus concentrations of 10–15 mg/L. Common for the small scale of individual homes with effluent volume of 300–400 gal/d, septic systems can also be used to dispose of sewage at larger facilities such as the Walden Pond State Reservation, Concord, MA (up to 5,500 gal/d; Colman and Friesz, 2001; fig. 3).

Wastewater disposed to the ground infiltrates vertically through the unsaturated zone to the water table where it flows as ground water through the aquifer and eventually discharges to surface water (fig. 5). The required safe setback of the infiltration beds from downgradient surface-water bodies depends on whether, or at what point downgradient, the continued movement of dissolved phosphorus is effectively limited by interaction with the solid phase so that transport of phosphorus to a surface-water body is not a problem. Phosphorus transport in the unsaturated and the saturated zones is affected directly by processes of phosphorus precipitation and adsorption to the solid phase and indirectly by geochemistry that alters the rates or amounts of precipitation and adsorption. Simulation of phosphorus plume length to facilitate determination of protective onland disposal setback distance as a function of disposal and aquifer conditions is the objective of the modeling effort and can be quantified once the computer model has been developed.

Figure 4.   Sewage-infiltration beds at a new (2002) treatment plant in Acton, Massachusetts, permitted for a disposal rate of 0.25 million gallons per day.
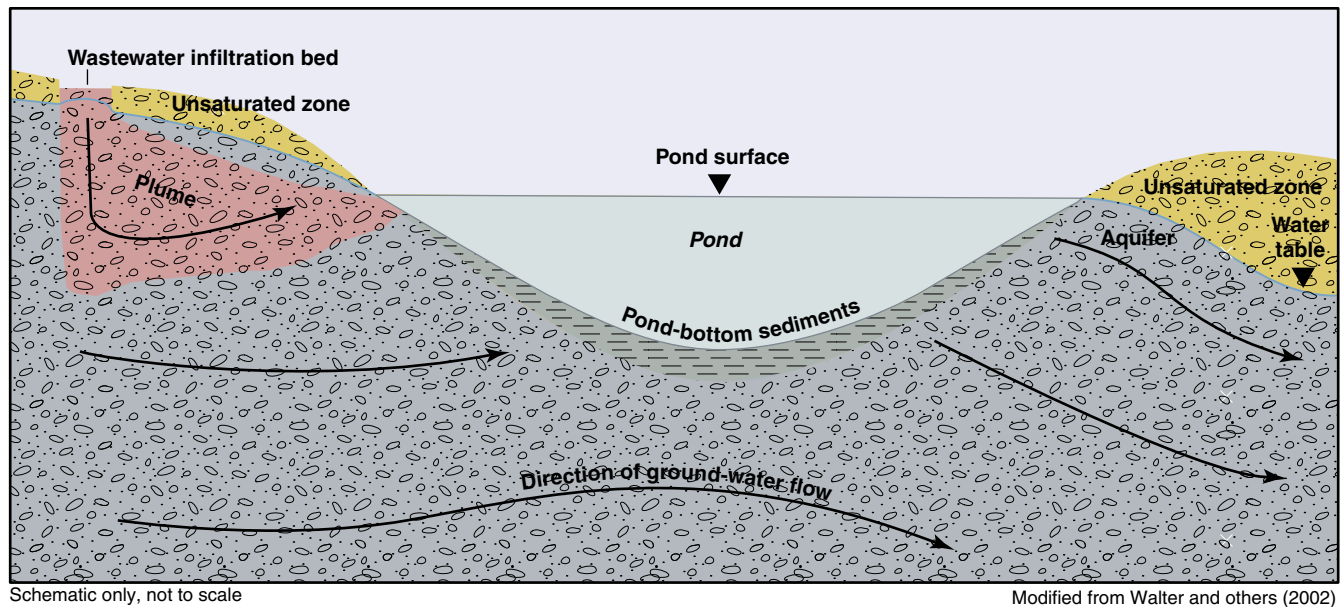
Figure 5. Conceptual model of wastewater infiltration through the unsaturated zone from an infiltration bed and transport down-gradient through the aquifer.

Processes Affecting Phosphorus Transport

Phosphorus transport in the subsurface depends on physical and biogeochemical processes. The complex interactions of these processes that affect phosphorus transport are best accounted for by computer simulations.

Physical Properties

Ground-water velocity, which refers to speed and direction of ground-water flow, determines where a plume will migrate from a given wastewater-disposal location. The effect of physical properties on flow direction can be simulated with computer models (MODFLOW) in a useful way for water-supply development. Many MODFLOW models for aquifers in Massachusetts are available (for example, Masterson and Barlow, 1997). These models incorporate the effects of recharge, withdrawals, porosity, hydraulic conductivity and simulate hydraulic head, ground-water velocities, and water flux. By using available flow-model results, determination of flow direction may be made, for example, in the vicinity of a proposed infiltration bed and a nearby kettle-hole pond. In the absence of a ground-water-flow model, determinations of flow direction may be derived from ground-water-level information, such as available water-table maps.

Physical properties of the aquifer also affect chemistry. Flow rate and dispersion affect the contact time of water with aquifer solids and the volume of aquifer solids encountered by a ground-water phosphorus plume, and thus, the progress of kinetically controlled reactions and the size of the reaction surface area for reactions between dissolved phosphorus and the solid phase. The reaction surface area also depends on grain size—for a given weight of sediment, the smaller the grain size, the greater will be the surface area. The effect of physical properties on both ground-water flow and chemistry can be evaluated by simulation with PHAST, the computer model used in this study.

The range of possible values for physical properties investigated in this study is limited by practical considerations for wastewater disposal: at installations treating tens of thousands of gallons per day, a conductive aquifer is required so that infiltration rates will be in the range of 2–3 gal/ft^2/d, and the area required for infiltration beds can be kept reasonably small. Aquifer sediment, such as a sand or fine sand, will accept 2–3 gal/ft^2/d; these materials are present throughout Cape Cod and southeastern Massachusetts as glacial outwash deposits. Valley-fill deposits in central and western Massachusetts are also often relatively coarse-grained and will accept infiltration at a high rate. Commonly, infiltration is sufficiently high in the same kinds of geological deposits as are suitable for public ground-water-supply development; maps are available for these deposits (for example, Frimpter, 1980; Friesz, 1996).

Biogeochemical Processes

Knowledge of geochemical controls and field observations indicate that phosphorus infiltrating the ground as a consequence of sewage disposal does not biodegrade, as organic contaminant compounds might, or change into benign forms, such as nitrate conversion into unreactive nitrogen gas. Rather, inactivation of phosphorus in the subsurface with respect to transport and discharge to surface water can occur only through phosphorus removal from the dissolved phase by adsorption on the aquifer solids or precipitation in mineral phases.

Phosphorus adsorption and precipitation can account for substantial amounts of phosphorus removal from the dissolved phase of wastewater plumes; these processes greatly retard the transport of phosphorus with respect to ground-water velocity. Retardation of phosphorus transport in the subsurface is clearly demonstrated at the decommissioned sewage-disposal site at the MMR, Cape Cod, MA, by comparison of the sewage-plume extent, determined by elevated conductance, and the phosphorus-plume extent, determined by elevated phosphorus concentration, downgradient from the infiltration beds (fig. 6). During 60 years of sewage disposal at the site, from 1936 to 1995, the estimated 516 metric tons of phosphorus disposed (Parkhurst and others, 2003) has been transported about 2,500 ft downgradient in dissolved concentrations greater than 0.1 mg/L, whereas more mobile constituents of the contaminant plume have progressed 15,000 ft, possibly to discharge at the wetland head of a coastal embayment (fig. 6) (Walter and others, 1996). Although the bulk of the sewage plume moved toward the coast, a portion of the phosphorus plume discharged to the kettle hole Ashumet Pond, only 1,600 ft downgradient from the beds (fig. 2), and contributed to the eutrophication of that water body (McCobb and others, 2003).

In another location, Walden Pond, Concord, MA, phosphorus attenuation associated with onland disposal of sewage has been so great as to render phosphorus concentrations in a sewage plume indistinguishable from background concentrations. At Walden Pond, where the unsaturated zone is 40 ft thick, untreated sewage from a visitor center and bathhouse has been discharged to a septic-system leachfield since 1975 at an average rate of 0.001 Mgal/d. Phosphorus concentrations above background levels have not been detected in wells screened at the water table as close as 10 ft downgradient from the leachfield (Colman and Friesz, 2001). Attenuation of dissolved phosphorus plumes also has been measured in noncarbonate-mineral aquifers studied in Canada (Robertson, 2003).

Phosphorus is present as an amphoteric oxyanion in water (dihydrogen or monohydrogen phosphate ion) that, depending on pH, may bind strongly with metal hydroxides of aluminum and iron at aquifer-solid surface sites. Unconsolidated deposits and deposit surface coatings in much of Massachusetts are formed from crystalline bedrock of metasediments and granite. As the deposits weather, ferrous iron is released, oxidized, and precipitated as iron oxyhydroxide coating on aquifer solids. This surface, and similar aluminum oxyhydroxide surfaces, interact electrostatically, because of the charged solids and charged anions, and through covalent bonding to adsorb anions like phosphate.

The descriptive sorption chemistry of oxyanions on pure metal hydroxide surfaces is well known (Dzombak and Morel, 1990). Because aquifer-solid surfaces contain hydroxides of various metals, their sorption characteristics may be similar, but not the same, as measured for the pure systems. Several adsorption-desorption experiments have been completed on overburden sediments from eastern Massachusetts: column experiments involving sorption and desorption with uncontaminated sediments, and column and batch experiments using wastewater-contaminated sediments (Walter and others, 1996; Parkhurst and others, 2003). Estimates of the logarithm of the equilibrium constant (log K) for the reaction

$$SiteOH + PO_4^{3-} + 2H^+ = SiteHPO_4^- + H_2O, \qquad (1)$$
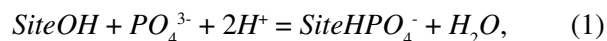
where *Site* represents a phosphorus-sorption site on the aquifer solids, are 25.39 for purely iron hydroxide sites (Dzombak and Morel, 1990), and 26.7 for sites present on aquifer solids (Parkhurst and others, 2003). The number of sites can be computed by fitting experimental data from column experiments with the double-layer model of Dzombak and Morel (Parkhurst and others 2003). The estimated number of phosphorus sorption sites measured for the aquifer sediments present at the MMR is 3,450 μmol/L (Parkhurst and others, 2003).

Because hydrogen ion binds at both cation and anion sorption sites, phosphorus sorption can be affected by changes in pH and in cation concentration. These effects were observed during column experiments when a spike in phosphorus desorption occurred coincident with a change in the eluent from an ionic composition similar to treated sewage to that of background aquifer water (Walter and others, 1996). The results indicate that phosphorus release may occur from sorption sites in the aquifer when uncontaminated ground water moves into the plume after cessation of wastewater discharge. This effect is important to include in models that simulate phosphorus transport in the aquifer.

Less is known about the reactions of chemical precipitation that include phosphorus—the rates of formation and the types of materials that form—than is the case for sorption of phosphorus. Mineral-forming constituents of the iron-phosphate minerals vivianite and strengite (Parkhurst and others, 2003) and the aluminum-phosphate mineral variscite (Robertson, 2003) typically are supersaturated in wastewater plumes, so formation is under kinetic rather than solubility control.
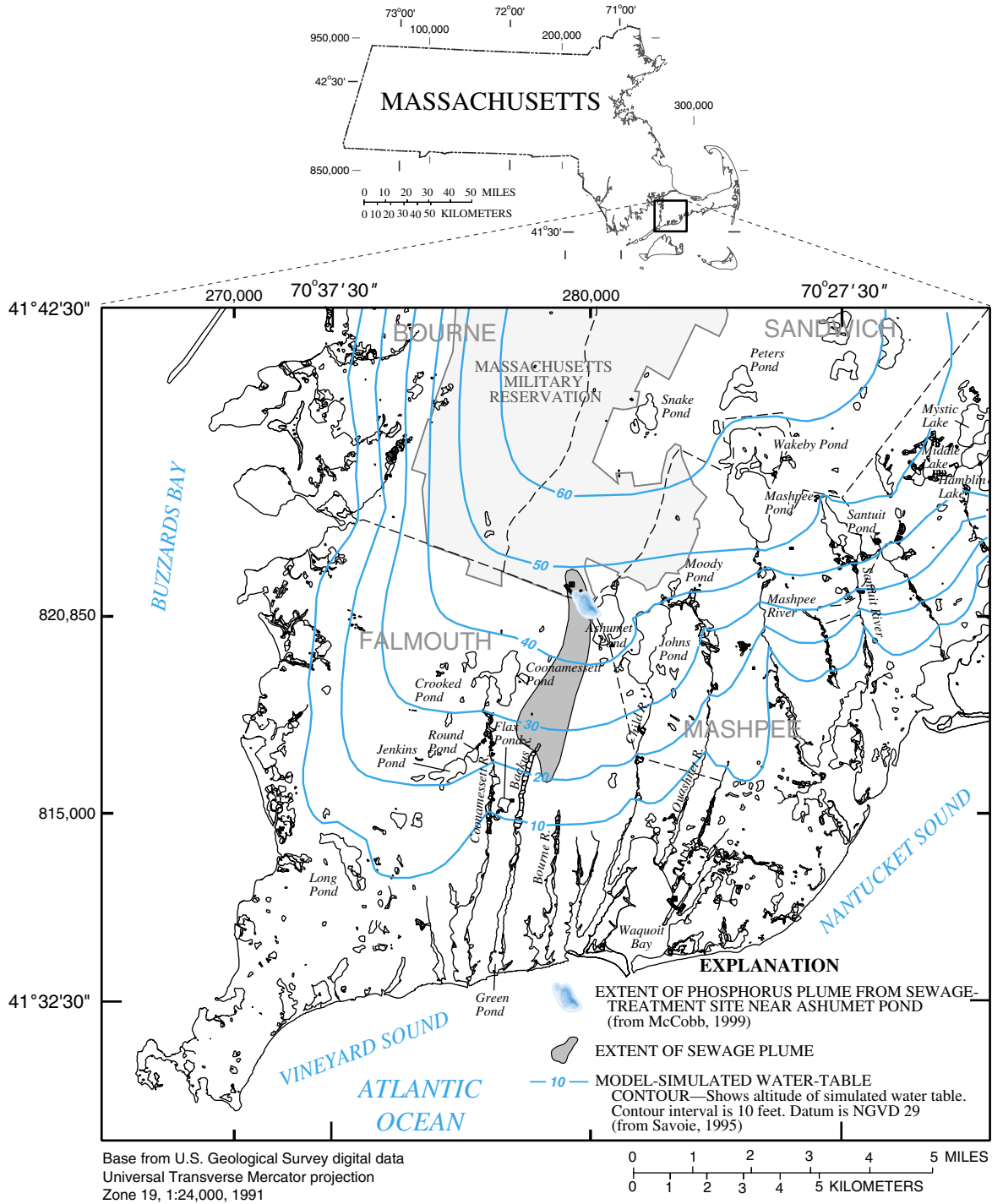
Figure 6.   Comparative transport of phosphorus and other sewage-derived constituents in the ground-water contaminant plume from wastewater disposal at the Massachusetts Military Reservation, Cape Cod, Massachusetts.

Sediment investigation has demonstrated that substantial retention of phosphorus occurs by processes other than sorption. During experimental work at the MMR, sediments from the contaminated zone were washed repeatedly with pH 10 water. This washing released the sorbed fraction of sediment phosphorus. Total nondesorbable phosphorus that remained after the washing ranged from about 0.015 to 0.25 mg/g of sediment (Parkhurst and others, 2003), whereas background phosphorus concentration is consistently about 0.02 mg/g of sediment (Walter and others, 1996). Apparently, the nondesorbable phosphorus was deposited in mineral form and had accumulated to concentrations as much as 10 times greater than background concentrations. Evidence from another site, Walden Pond, indicates that substantial amounts of phosphate minerals form in the unsaturated zone as well. At Walden Pond, essentially all of the phosphorus discharged through the septic-system leachfields during 25 years has been sequestered in the unsaturated zone (Colman and Friesz, 2001), whereas mass-balance calculations using the number of sorption sites available indicate that breakthrough of phosphorus to the saturated zone would be expected if sorption alone were involved. Other evidence for mineral formation has been obtained by microprobe analysis of phosphorus-aluminum-iron compounds in authigenic coatings on sand grains collected by coring beneath septic-system disposal tiles (Robertson, 2003).

Although phosphorus in natural waters has only one important oxidation state, other constituents that precipitate with phosphorus, such as iron, change oxidation state according to redox conditions in the aquifer. Because other redox-sensitive species, such as nitrogen, manganese, carbon, and oxygen, will determine the redox environment of iron, the biogeochemistry of all of these constituents needs to be included in a comprehensive phosphorus-transport simulation. Accounting for all the factors that could affect phosphorus transport, therefore, requires a model that simulates many chemical constituents and reactions simultaneously.

Carbonate aquifers, such as those in the Housatonic and Hoosic River Valleys, may retard phosphorus less than the noncarbonate aquifers, which are present in the rest of Massachusetts. The higher pH in ground water from aquifers that are present in carbonate regions would cause phosphorus to sorb less readily than in noncarbonate aquifers. Also, comparison of septic-system plumes in carbonate and noncarbonate aquifers indicates that phosphorus is transported in the former but not the latter (Robertson, 2003). Phosphorus retardation in noncarbonate aquifers is attributed by Robertson (2003) to aluminum dissolution from gibbsite, under acidic conditions that develop in noncarbonate-aquifer plumes, and reprecipitation with phosphate. In contrast, less aluminum would dissolve under the near-neutral conditions that prevail in carbonate aquifers.

Three-Dimensional Reactive-Solute-Transport-Model for the Saturated Zone

The computer model of the saturated zone was based on previous computer models of phosphorus transport at the MMR on Cape Cod, MA. These models include a one-dimensional (1-D) model (Stollenwerk, 1996; Stollenwerk and Parkhurst, 1999) and a 3-D model (Parkhurst and others, 2003). The previous models were created to simulate transport of phosphorus in the aquifer after 60 years of wastewater disposal in infiltration beds at the MMR. Investigation of the aquifer downgradient from the infiltration beds has been conducted for 25 years with a network of hundreds of well clusters and multilevel samplers (Walter and others, 1996; LeBlanc, 1984). Data from the network were used to verify the models. The more recently developed 3-D model used new estimates of organic-matter decay rates, phosphorus sorption, and phosphorus precipitation and included the effect of 3-D ground-water flow in shaping the plume.

Despite the variable wastewater loadings associated with large fluctuations in population as military efforts changed at the MMR, the 3-D model accurately simulated distribution of 1993 and 1999 dissolved-phosphorus concentrations in the aquifer downgradient from the infiltration beds (Parkhurst and others, 2003). Because of the mechanistic geochemical and flow features built into the model for simulation of future phosphorus transport resulting from past variable disposal rates of wastewater, the model can be adapted for predicting phosphorus plume length as a function of loading rate in other similar situations.

The computer model used in this investigation to simulate 3-D transport in the saturated zone is a finite-difference code developed by the USGS called PHAST (Parkhurst and others, 2004). PHAST is a combination of the geochemical code PHREEQC (Parkhurst and Appelo, 1999) and the finite-difference flow-and-transport code HST3D (Kipp, 1997). PHAST is a general-purpose code that can accurately simulate flow, transport, and chemical processes controlled by chemical equilibrium or by reaction kinetics.

The principal modifications to the previous 3-D saturated-zone PHAST model of Parkhurst and others (2003) involved simplifying the ground-water-flow-system geometry and decreasing the number of infiltration beds to one. Geometry of the base-case model grid includes 100-ft node spacing in the horizontal directions, extending 5,300 ft in the direction of flow by 1,100 ft in the lateral direction, and 10-ft node spacing in the vertical direction, extending 150 ft in depth (fig. 7). At each time step (0.5 yr), the model solves for hydraulic head and constituent concentrations at each point of intersection in the grid (the model nodes), and for ground-water and chemical-constituent flux across each cell face. Cell faces extend from halfway between adjacent nodes to halfway to the next node or to the node if the node is on the boundary.
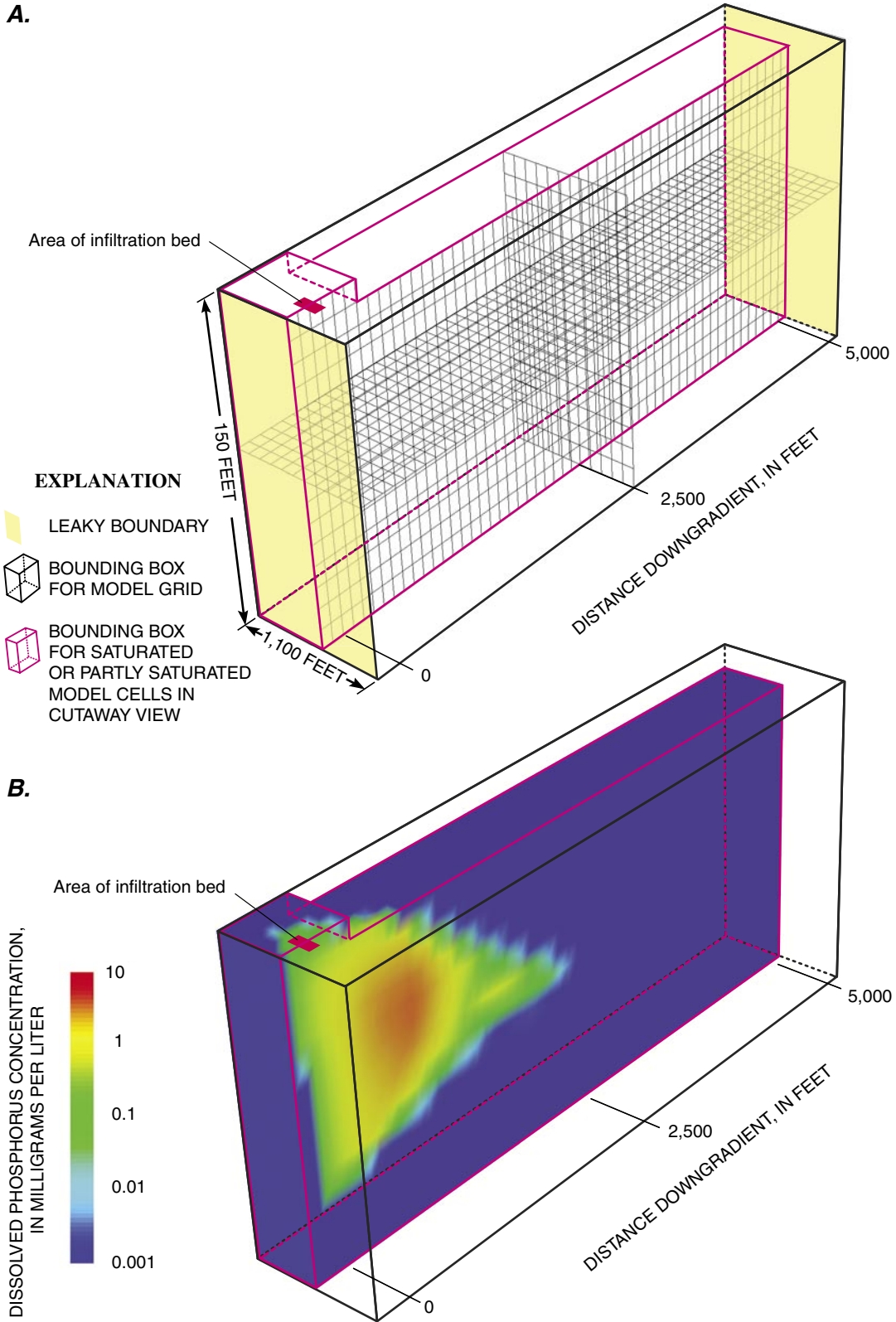
Figure 7.   *A,* Saturated-zone PHAST model grid used in this study. Boundaries are constant-flux on top, leaky boundaries on ends as indicated by yellow shading, and no-flow on other sides; and *B,* The modeled extent of the dissolved phosphorus plume at year 70 for base case—50 years of continuous discharge—with dissolved phosphorus concentrations shown on a log scale.

Hydraulic boundaries of the model are no-flow boundaries on the long sides and the bottom, leaky boundaries on the short ends, and flux boundary on the top (fig. 7). The flux boundary allows recharge from rainfall, 0.0059 ft/d (26 in/yr), except in the area of the infiltration bed, where recharge from wastewater flux was 0.40 ft/d (3 gal/ft^2/d). The sewage-infiltration bed, 200 by 100 ft, was set transverse to the direction of flow with its center 200 ft from the upgradient leaky boundary and midway between the lateral no-flow boundaries (fig. 7). The leaky boundaries, which allow flow in or out of the model domain, are constrained by remote fixed heads outside of the model grid—50 ft above an arbitrary datum upgradient and 30 ft above the datum downgradient, 7,000 ft distant from, and parallel to, the leaky boundaries. The average hydraulic gradient established by the fixed heads is 0.001 ft/ft. Water generally flows in through the upgradient leaky boundary and out through the downgradient leaky boundary as determined by the fixed heads of the leaky boundaries and recharge through the top of the model. Hydraulic properties of the saturated-zone model include the hydraulic conductivity of 300 ft/d in the horizontal directions and 85 ft/d in the vertical direction, and a porosity of 0.39. These model parameters result in an average ground-water velocity of about 1.5 ft/d. The hydraulic properties were taken from the previous MMR model (Parkhurst and others, 2003) based on measurements made on Cape Cod.

Although the model can simulate dispersion, it is effective only when dispersivity, the dispersion coefficient, is greater than the inherent numerical dispersivity of the model. Numerical dispersivity is a function of model-cell size and time step approximately according to the relation

$$D = \Delta X/2 + V\Delta T/2, \qquad (2)$$

where D is the numerical dispersivity, ΔX is the cell dimension in the X direction, ΔT is the time step and V is the velocity (Fletcher, 1991). In the saturated-zone model, dispersivity in the principal direction of flow is approximately

$$100/2 + 1.5(180)/2 = 185 \text{ ft.} \qquad (3)$$

This dispersivity is much greater than the longitudinal dispersivity of 3 ft estimated in tracer-test experiments in the aquifer at the MMR (Garabedian and others, 1991). In the simulations, dispersivity was set to the small value of 0.0003 ft, so that the effective longitudinal dispersivity would be the numerical dispersivity alone.

Initial solution conditions for the saturated-zone model are the solute concentrations measured in uncontaminated ground water at the MMR (table 1). Initial conditions of the reactive surfaces were set to be in equilibrium with the uncontaminated (background) ground water. The composition of water moving into the model through the upgradient leaky boundary was set to uncontaminated ground water (table 1) as was the composition of water recharged as rainwater.

Table 1. Solution compositions for uncontaminated ground water and treated sewage effluent.

[Modified from Parkhurst and others, 2003. Concentrations are milligrams per liter, unless otherwise noted. TDIC, total dissolved inorganic carbon; °C, degrees Celsius]

Constituent or physical property	Uncontaminated ground water	Secondary treated sewage effluent
pH, standard units	5.6	6.0
Temperature, °C	14	14
Oxygen	4.0	4.0
Calcium	1.2	13
Magnesium	.75	4.1
Sodium	4.6	48
Potassium	.39	9.3
Sulfate, as SO_4	8.3	27.9
Chloride	[1]5.6	[1]48
Nitrate, as N	0	15
Ammonium, as N	0	2.5
Phosphate, as P	0	5.9
Iron	0	.18
Manganese	.035	.022
Total organic carbon, as C	0	19
Total dissolved inorganic carbon, as C	.34	14

[1]Chloride was adjusted to achieve charge balance in the solution.

Rainwater was assumed to be altered to the composition of uncontaminated ground water during passage through the soil and unsaturated zones. Chemical composition of wastewater effluent recharged through the infiltration bed was the same as that measured in wastewater at the MMR (table 1).

The chemical reactions simulated in the saturated-zone model were the same as those in the MMR sewage-plume investigation (Parkhurst and others, 2003). These included reactions relating directly to dissolved phosphorus concentration, such as sorption on metal oxyhydroxide surfaces and precipitation, and those relating indirectly through redox, pH or ionic-strength effects. Ionic-strength effects were included in all equilibrium reactions.

Equilibrium was assumed for homogeneous aqueous reactions including protonation, ion-pair formation, and redox reactions as found in the database to PHREEQC (Parkhurst and Appelo, 1999). In addition, equilibrium and kinetic reactions involving sorption, mineral equilibria, organic carbon, and dissolved nitrogen gas were included (table 2).

Table 2.   Major chemical reactions used in reactive-transport simulations.

[Modified from Parkhurst and others (2003); *C*, concentration; *k*, rate constant; *SI*, saturation index—log ion activity product divided by the solubility product; *DOC*, dissolved organic carbon; │ │ indicates absolute value]

Reaction number	Reaction	Reaction type	Equation
1	Phosphorus sorption	Equilibrium	$SiteOH + PO_4^{3-} + 2H^+ = SiteHPO_4^- + H_2O$
2	Phosphorus-sorption site protonation	Equilibrium	$SiteOH + H^+ = SiteOH_2^+$
3	Phosphorus-sorption site deprotonation	Equilibrium	$SiteOH = SiteO^- + H^+$
4	Cation sorption	Equilibrium	$Cation\_siteOH + Cat^{x+} = Cation\_siteOCat^{x-1} + H^+$
5	Cation-sorption site protonation	Equilibrium	$Cation\_siteOH + H^+ = Cation\_siteOH_2^+$
6	Cation-sorption site deprotonation	Equilibrium	$Cation\_siteOH = Cation\_siteO^- + H^+$
7	Fe(OH)$_3$(amorphous)	Equilibrium	$Fe(OH)_3 + 3H^+ = Fe^{+3} + 3H_2O$
8	Pyrolusite	Equilibrium	$MnO_2 + 4H^+ + 2e^- = Mn^{+2} + 2H_2O$
9	Decomposition of dissolved organic carbon (DOC), reactant is CH$_2$O	Kinetic	$Rate = -kC_{DOC}$
10	Decomposition of sorbed organic carbon, reactant is CH$_2$O (applies after cessation of wastewater disposal)	Kinetic	$Rate = -k_{O_2}C_{O_2,\,aq} - k_{NO_3}C_{NO_3,\,aq}$
11	Vivianite precipitation and dissolution, reactant is Fe$_3$(PO$_4$)$_2$	Kinetic	$Rate = -kC_{PO_4}\left(\dfrac{SI_{vivianite}}{1+|SI_{vivianite}|}\right)$
12	Strengite precipitation and dissolution, reactant is FePO$_4$	Kinetic	$Rate = -kC_{PO_4}\left(\dfrac{SI_{strengite}}{1+|SI_{strengite}|}\right)$
13	Removal of dissolved N$_2$ (prevents N$_2$ reoxidation to nitrate), reactant is N$_2$	Kinetic	$Rate = -kC_{N_2,\,aq}$

Sites for the sorption reactions were of two types—for cations (*Cation_site*, table 2) or for phosphate (*Site*, table 2)—except for hydrogen ion, which was allowed to react at both types of sites. Cations allowed to sorb were ammonium, calcium, magnesium, sodium, iron, and manganese. A single equilibrium constant was applied to all cation-sorption reactions because insufficient data were available to distinguish individual equilibrium constants for each cation (tables 2 and 3). Phosphate and hydrogen ion were the only chemical species allowed to sorb at the phosphate sites. The surface complexation mass-action equation used to simulate sorption includes an electrostatic term to account for the work done in moving a charged species to a charged surface (Parkhurst and Appelo, 1999, p. 14–15).

Kinetics were assumed to control formation and dissolution of strengite and vivianite, decay of organic carbon, and removal of nitrogen gas. The rate or equilibrium-constant values used in the reactions, method of determination, and reference for calibration are summarized in table 3. The kinetic formulation for precipitation of minerals involved the saturation index so that the reaction rate would approach zero as equilibrium was established. Denitrification of nitrate was under thermodynamic control, and kinetic removal of nitrogen

gas (reaction 13, table 2) was included to prevent reoxidation to nitrate. Sorption of organic carbon was under kinetic control during the active discharge period. After cessation of wastewater discharge, decay of the sorbed carbon was also expressed by kinetic reaction (reaction 10, table 2).

One-Dimensional Reactive-Solute-Transport Model for the Unsaturated Zone

Flow in the unsaturated-zone model was simulated as 1-D transport. The 1-D model is a simplification of the complex processes of unsaturated flow. Nevertheless, the time of transport, ratio of solution to reactive surfaces, and exposure to oxygen of actual unsaturated flow can be approximated with a 1-D model so that kinetic, equilibrium, and redox reactions are simulated as accurately as possible. For the base case, 15 column cells were used to cover a vertical distance of 50 ft (fig. 8), so that each cell was 3.33 ft thick. Simulations of the unsaturated zone with different thicknesses were accomplished by adding or subtracting column cells to produce the required unsaturated-zone thickness. Vertical flow was simulated with the TRANSPORT option of PHREEQC, included in PHAST,

Table 3. Base-case values for the three-dimensional reactive-transport model and the unsaturated zone model.

[Modified from Parkhurst and others (2003); P, phosphorus; μmol/L, micromole/liter; s^{-1}, per second]

| Property or process	Saturated-zone model	Unsaturated-zone model	Source	Reference
P sorption constant (log K, eq. 1)	26.7	26.7	Column sorption/desorption experiments	Walter and others, 1996; Parkhurst and others, 2003
P sorption sites, μmol/L	3,450	3,450	Column sorption/desorption experiments	Walter and others, 1996; Parkhurst and others, 2003
Cation-sorption constant (log K, reaction 4, table 2)	-1.8	-1.8	Column sorption/desorption experiments	Parkhurst and others, 2003
Cation-sorption sites, μmol/L	18,000	18,000	Column sorption/desorption experiments	Parkhurst and others, 2003
First-order rate constant for dissolved organic carbon, s^{-1}	1.0×10^{-7}	1.0×10^{-7}	Fit to field data for O_2 and NO_3	Parkhurst and others, 2003
Rate constant for strengite, s^{-1}	2.3×10^{-8}	1.6×10^{-7}	Fit to data for accumulation of nondesorbable phosphate	Parkhurst and others, 2003
Rate constant for vivianite, s^{-1}	2.3×10^{-8}	1.6×10^{-7}	Fit to data for accumulation of nondesorbable phosphate	Parkhurst and others, 2003

wherein water is shifted from one cell to the next down the column of cells. The shifts occur according to a specified time-step, and concentrations of all constituents are computed after each shift according to the chemical reactions specified in the model. At the base-case infiltration rate, 3 gal/ft²/d, downward velocity in the infiltration pond would be 0.401 ft/d, equivalent to 1.02 ft/d vertical velocity in the unsaturated zone, based on an aquifer porosity of 0.39. With 3.33-ft column cells, the number of cell volumes, or shifts, required per year to achieve the given infiltration rate is 114.

The unsaturated-zone model generally is based on the same chemistry as that developed for the saturated-zone model. In the unsaturated-zone model, as in the saturated-zone model, phosphorus is retained by the solid phase through sorption and mineral precipitation. One difference between models, however, is that oxygen is introduced in the unsaturated-zone model to account for oxygen in soil gas to which the water would be exposed during infiltration. Thirty-percent saturation with oxygen was specified for a zone beginning 6.7 ft below the surface and extending down to the water table. Thus, oxygen was available for reactions in the unsaturated zone and in the saturated zone because effluent entering the aquifer at the water table also contained dissolved oxygen.

Whereas the saturated-zone calibration can be based on that used for the MMR, unsaturated-zone transport needs to be calibrated in this study because no investigation of the unsaturated zone was included in the previous investigation. Calibration data are available from total amounts of solid-phase phosphate measured in the sediment cores from the unsaturated zone under the sewage beds at the MMR (Walter and others, 1996).

Background concentration of phosphorus in the solid phase was 0.02 mg/g (Walter and others, 1996), whereas solid-phase phosphorus concentrations below an infiltration bed at the MMR ranged from 0.1 to 0.4 mg/g (fig. 9), with the highest concentrations immediately below the bed. Concentrations in the rest of the unsaturated zone and the top 20 ft of the saturated zone were about 0.1 mg/g. The maximum amount of sorbed phosphorus can be calculated from the number of anion sorption sites (Parkhurst and others 2003). Given anion sorption sites of 3,450 μmol/L of pore water, occupied entirely with phosphorus, the maximum concentration of sorbed phosphorus is 0.025 mg/g of aquifer solid, assuming pore volume of 0.39 and rock density of 2.7 (Parkhurst and others, 2003). Thus, the sum of background and sorbed phosphorus concentrations is about 0.05 mg/g, which leaves 0.05 to 0.35 mg/g that is attributable to mineral forms built up during 60 yr of discharge. Such mineral formations are described by Robertson (2003) in his investigation of septic plumes with a conceptual model that iron is reduced near the beds and infiltrates to lower levels in the unsaturated zone, where it is oxidized and redeposited as $Fe(OH)_3$ or $FePO_4$. For the unsaturated-zone model to produce the appropriate concentrations of solid-phase phosphorus, the rate constant for formation and dissolution of strengite was increased from the saturated-zone value of 2.3×10^{-8} to 1.6×10^{-7} s^{-1} (table 3).
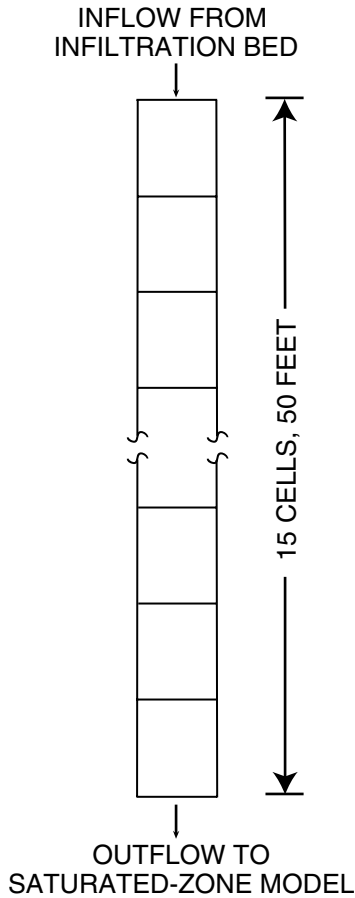
Figure 8. Base-case unsaturated-zone PHAST model boundaries and grid.
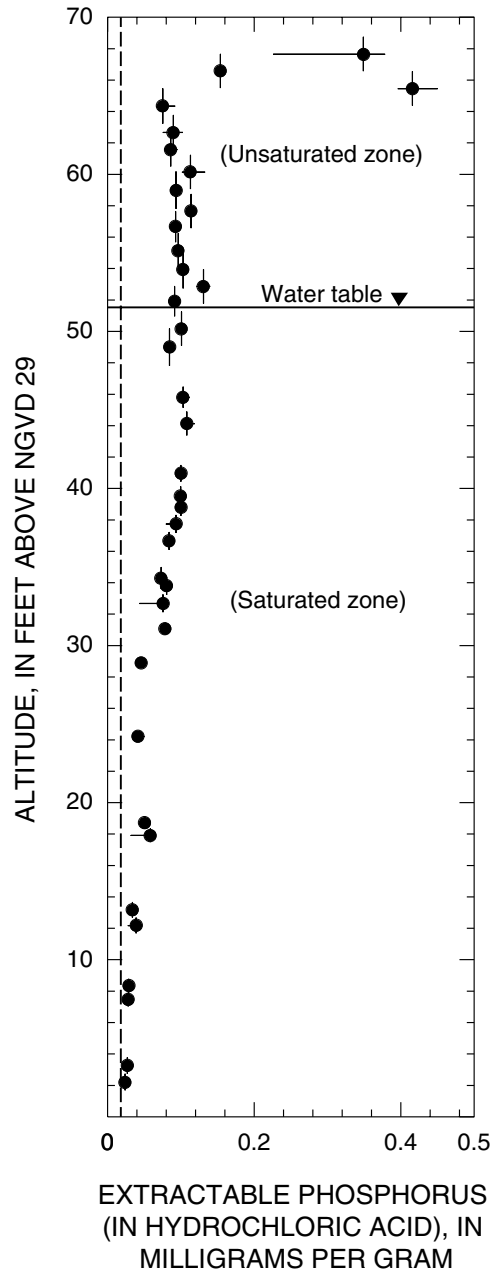
Figure 9. Solid-phase phosphorus concentrations beneath the infiltration beds at the Massachusetts Military Reservation, Cape Cod, Massachusetts (Walter and others, 1996). Vertical bars represent cored interval. Horizontal bars represent variability among replicate extractions. Dashed line represents background extractable phosphorus concentrations collected from extractions at an upgradient sampling site.

Combined Unsaturated- and Saturated-Zone Models

Because the reactive constituents—phosphorus, organic carbon, and nitrogen species—are altered as a function of time in the unsaturated zone as well as of the duration of disposal, the inputs to the saturated-zone model require a direct coupling of the two models. The output of the unsaturated-zone model becomes the time varying input to the saturated-zone model. The last concentration emerging from the unsaturated zone after each year was used as input concentration to the saturated-zone model for that year. The combined model was used to produce the plume-length response curves that are the product of this project.

Combining the models could potentially alter the calibration relation between source loads and aquifer transport of phosphorus of the model constructed for this project, relative to the MMR model, because the MMR model did not include the unsaturated zone. At the phosphorus calibration

concentration of the MMR model, however, the effect on phosphorus concentrations of the unsaturated-zone model through sorption is small because the sorption sites rapidly reach a steady state relative to the effluent phosphorus concentration, after which the input phosphorus concentration is not affected

by sorption. With respect to formation of phosphorus minerals, the unsaturated-zone chemistry results in continuous removal of about 20 percent of the phosphorus from the input under base-case conditions, such that the phosphorus concentration entering the saturated zone is constant at about 80 percent of the effluent phosphorus concentration.

Simulation Results for the Saturated- and Unsaturated-Zone Models

The saturated-zone model can be used to define the approach to estimating phosphorus plume length by indicating stages of plume development and phosphorus transport during and after disposal. The unsaturated-zone model output modifies the input to the saturated zone, but not the qualitative aspects of plume transport stages.

Base-Case Saturated-Zone Model and Stages of Plume Development

The base-case saturated-zone model has one infiltration bed (100 by 200 ft) with a constant loading rate of 3 gal/ft^2/d for 50 yr of wastewater with a composition of that of the secondary treated sewage at the MMR (table 1). This model simulates how phosphorus plumes might be distributed during discharge, immediately after discharge cessation, and long after discharge cessation. During a 200-yr simulation, progression of the leading edge of the phosphorus plume during active discharge (0–50 yr) is slow, about 12 ft/yr (fig. 10). After discharge cessation (at year 50), when the aquifer is beginning to receive clean water, plume progression almost triples to 34 ft/yr, and the highest concentration zone leaves the area under the infiltration beds and moves toward the leading edge of the plume (fig. 10). The counter-intuitive increase in plume speed following cessation of discharge results from desorbed phosphorus responding to changes in pH and ionic strength; the same effects were apparent in the column experiments that were used to calibrate the model (Parkhurst and others, 2003). The desorbed phosphorus increases the dissolved phosphorus concentration, which moves downgradient with ground-water flow to the front of the plumes where unoccupied sites are present. After the fast-progression period (year 50 to year 70), the plume slows again, and by year 100, forward movement has stopped, as best seen by plume cross-section plots of dissolved phosphorus concentrations in the 0 to 0.015 mg/L range (fig. 11). Change after year 100 is a slow decrease in dissolved phosphorus concentration throughout the model cross section (fig. 11).

Even after downgradient progression of dissolved phosphorus in the 0 to 0.015 mg/L cross-section plot appears to stop, dissolved phosphorus transport continues, but at low rates. The continued phosphorus transport associated with low concentrations can be determined at an arbitrarily chosen contour of low concentration, for example, 0.015 mg/L, approximately the dissolved concentration of phosphorus measured at background locations in the aquifer of Walden Pond (Colman and Friesz, 2001). For the base-case simulation, the longest extent of the 0.015 mg/L phosphorus contour is 2,500 ft (indicated by the leading edge of the red zone, fig. 11), and transport of phosphorus through a plane at that location varies between 0 and 0.17 kg/yr during a period of 0 to 200 years after initiation of effluent discharge (fig. 12). For reference, the annual phosphorus input load from all sources for an oligotrophic lake, Walden Pond, was estimated as 32 kg/yr (Colman and Friesz, 2001). The phosphorus load to Walden Pond is greater by a factor of 190 than the highest rate of transport through the downgradient edge of the base-case plume, and greater by a factor of 670 than the average downgradient transport rate in the first 200 years. The simulations indicate that the association of phosphorus with the aquifer solids is substantial and that phosphorus is released to the dissolved phase slowly. If ground-water movement through an aquifer is considered as a nutrient-removal process for wastewater, the calculated phosphorus-removal efficiency for the base-case model over the first 200 years is greater than 99.9 percent.

Phosphorus fluxes were also evaluated at distances closer than the 0.015 mg/L contour and increased sharply with decreasing distance to the infiltration beds (fig. 12). An 8-percent decrease in distance (from 2,500 ft to 2,300 ft) corresponded to a 380-percent increase in the maximum phosphorus flux. Although a greater phosphorus flux might be deemed protective for surface water than that which continues past the 0.015 mg/L contour, fluxes quickly become large (and likely not protective) as distances downgradient are decreased from that of the 0.015 mg/L contour.

In summary, the model simulates the stages of plume evolution during and after cessation of wastewater disposal. Although phosphorus migrates quickly immediately after cessation, the dissolved phosphorus plume eventually is characterized by low concentrations of dissolved phosphorus at the leading edge. The position of the contour for 0.015 mg/L stops advancing, and phosphorus flux at the leading edge is small by comparison with that entering oligotrophic lakes. Therefore, the distance from the beds to a selected low-concentration contour may help to indicate a protective setback distance from receiving surface water for an onland wastewater-disposal location. The simulation effort of this project will focus on predicting the phosphorus plume length, defined as the distance from infiltration beds to the 0.015 mg/L phosphorus contour, for a range of wastewater loading and aquifer properties.
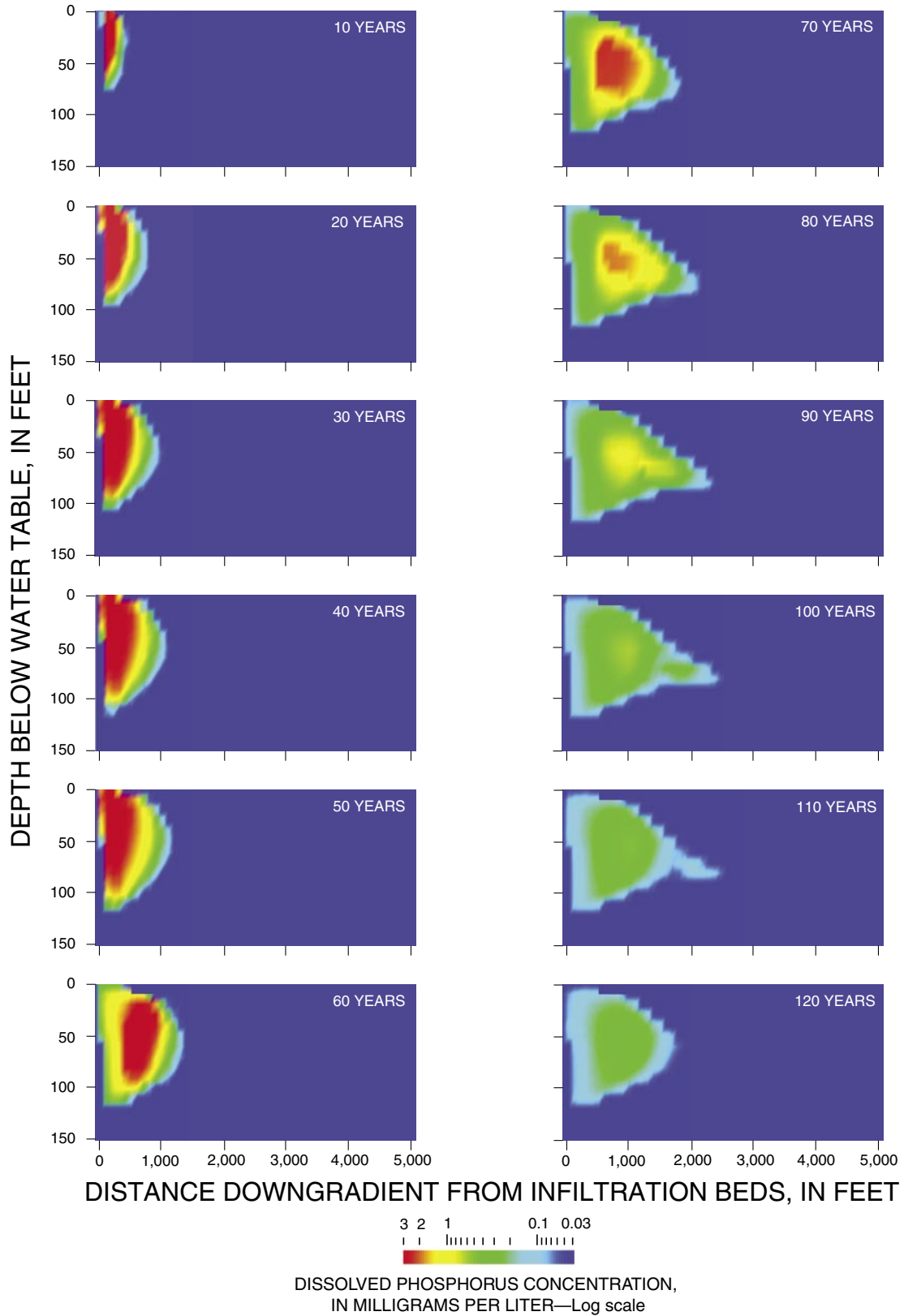
Figure 10. Base-case simulations of the stages of phosphorus plume development in the saturated zone.
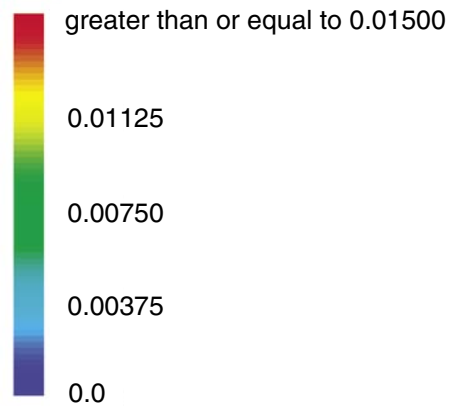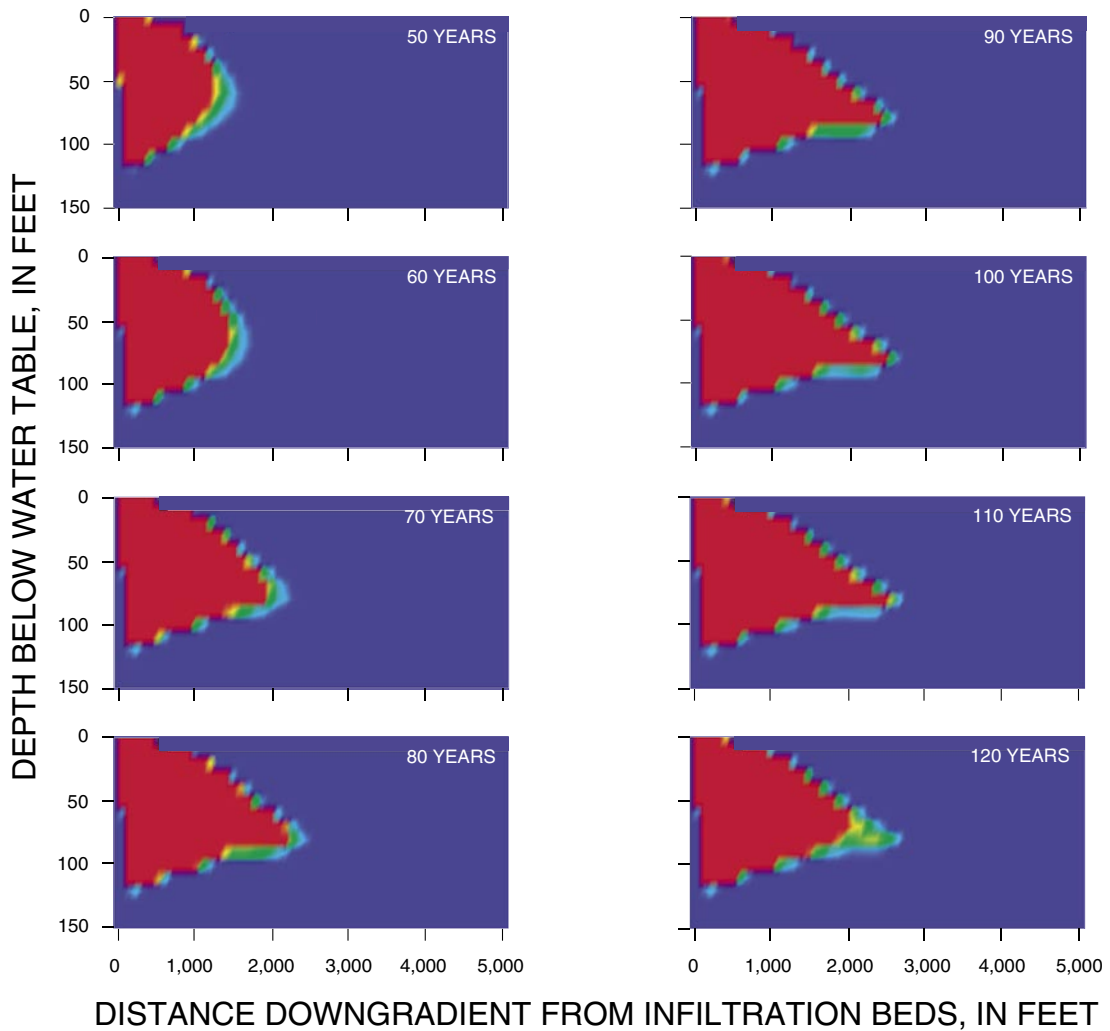
Figure 11.   Simulated stages of development of the base-case phosphorus plume length (defined as the extent of dissolved phosphorus equal or greater than 0.015 milligram per liter) in the saturated zone.
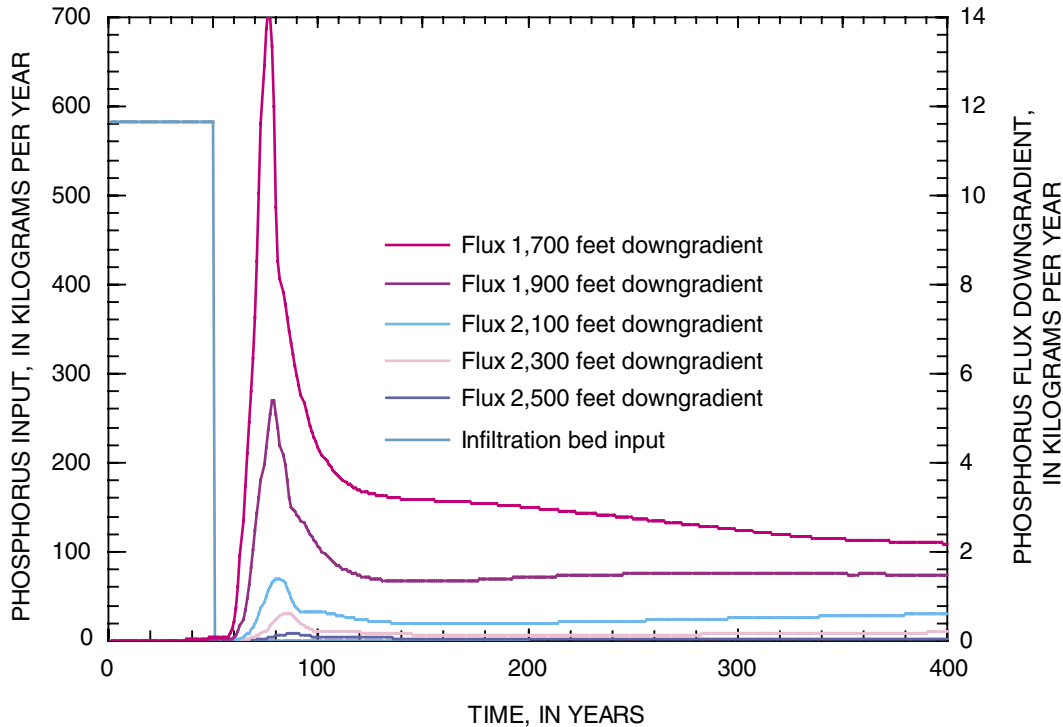
Figure 12.   Comparison of flux of effluent phosphorus into the infiltration bed and output through the model boundaries from 1,700 to 2,500 feet downgradient. Input and output are plotted at different scales.
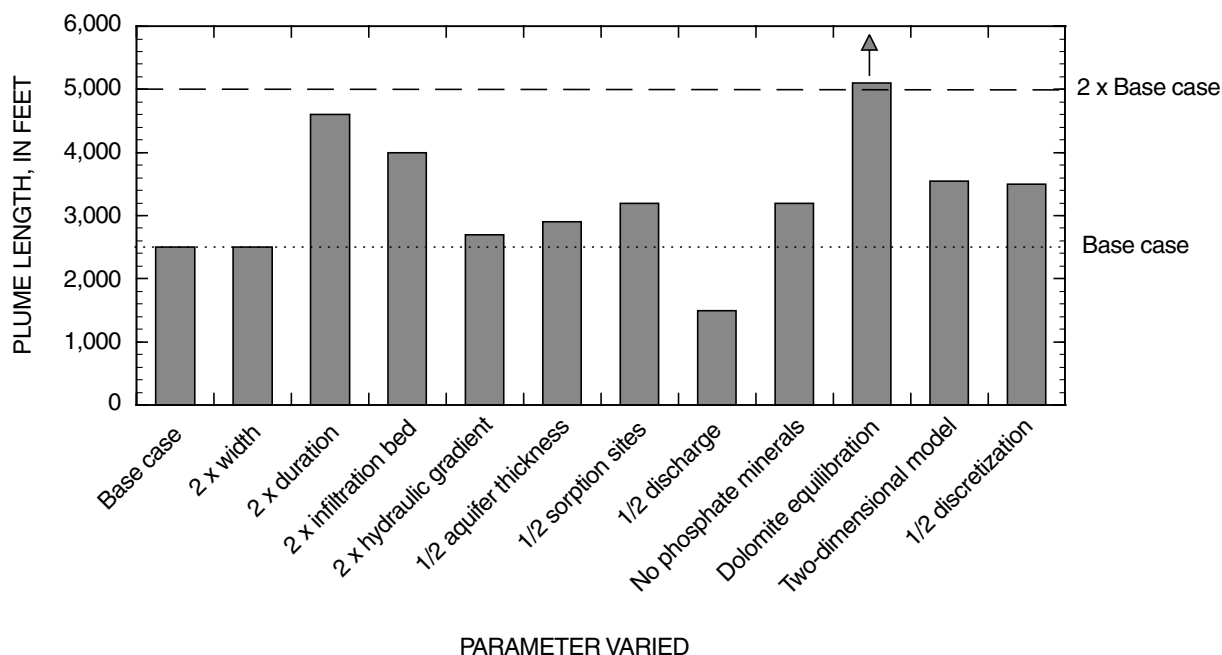
Sensitivity Analysis

A sensitivity analysis was conducted to determine the relative dependence of phosphorus transport on aquifer properties and other model parameters. For sensitivity testing, only the base-case saturated-zone model was used. The unsaturated zone was omitted, in part, to save computer run time and also because the most sensitive variable in the unsaturated-zone model is unsaturated-zone thickness, which is one of the parameters varied in runs of the combined model. To test model sensitivities, parameters were usually increased or decreased by a factor of 2. Parameters increased by a factor of 2 were aquifer width (model width), duration of discharge, width of the infiltration bed, and hydraulic gradient. Parameters decreased by a factor of 2 were aquifer thickness, number of phosphorus sorption sites per liter of pore water, and effluent discharge rate. Other factors tested were elimination of iron-phosphate mineral precipitation, equilibration with dolomite (which buffers the pH at about 7.5), conversion of the model to two dimensions (2-D), and use of a finer mesh grid and shorter time step. The latter decreased dispersivity, in the longitudinal direction, for example, from 185 to 93 ft.

The sensitivity analysis of the base-case saturated-zone model indicated that the largest changes in plume length were in response to equilibration with dolomite, a carbonate rock (plume length reached the model length, 5,100 ft, at 260 years and was still increasing). Equilibration with dolomite

increased pH, which substantially decreased the sorption of phosphorus on the metal-hydroxide surfaces of the aquifer. This result was in agreement with observations in the field of extended transport of phosphorus plumes from small septic systems in carbonate as compared to noncarbonate aquifers (Robertson, 2003).

None of the factor-2 parameter changes caused a proportional change in plume length (fig. 13), although response to increased discharge duration was nearly so (plume length increased by 92 percent), and the response for decreased effluent discharge was also substantial (plume length decreased by 40 percent). The less-than-proportional response between parameter change and the size of the response was caused by chemical precipitation kinetics. When the dissolved phosphorus concentration is increased, such as by increased discharge or decreased sorption sites, the precipitation kinetics (reaction 12, table 2) are faster. When the result of the parameter change is lower dissolved phosphorus concentrations, precipitation occurs at a slower rate. Thus, the effects on plume length of both increased and decreased dissolved phosphorus concentrations are compensated.

Increasing the width of the model decreased the plume length only 2 percent, indicating that the no-flow lateral boundaries of the model were not causing elongation of the plume. Changing the model to 2-D (in effect, to one cell width), however, caused the plume to lengthen by 48 percent. Increasing hydraulic gradient by a factor of 2 increased

Figure 13.   Model sensitivity analysis showing base-case phosphorus plume length and plume lengths altered in response to perturbation of the input parameters. The arrow over the response for dolomite equilibration indicates that the plume was still increasing when the model boundary at 5,100 feet was reached.

plume length by only 13 percent. Decreasing the number of sorption sites by half caused a 33-percent increase in the plume length. When mineral precipitation of phosphorus was eliminated, plume length increased 33 percent; lack of greater response indicates that sorption, rather than chemical precipitation, is the dominant phosphorus-removal mechanism. Finally, decreasing the numerical dispersion by decreasing the grid mesh and time step caused the plume length to increase 48 percent. Decreasing the dispersion caused the plume to become more narrow and to be exposed to less aquifer sediment.

Unsaturated-Zone Model

Some of the constituents of wastewater change concentration during simulated percolation through the unsaturated zone, and the degree of change varies over the period of simulation. The concentration of dissolved phosphorus eluting from the unsaturated zone decreased from the base-case input concentration of 5.9 mg/L to nearly 0 during the first 1.5 years. After 1.5 years, phosphorus breakthrough occurred. After breakthrough, concentrations eluting from the unsaturated zone increased to 4 mg/L but never reached the base-case input concentration (fig. 14). The difference between dissolved phosphorus concentrations after breakthrough and in the input is caused by precipitated phosphorus, which builds

up continuously in the unsaturated zone (fig. 15). All sorption sites in the unsaturated zone are filled by the beginning of dissolved phosphorus breakthrough at 1.5 years (fig. 14). As the sorption sites fill, dissolved phosphorus concentrations increase, and precipitation of iron-phosphate minerals begins, continuing thereafter for the duration of the wastewater disposal. In the unsaturated-zone model, iron phosphate is formed by a kinetically controlled reaction (reaction number 12, table 2) whose rate is dependent on the phosphorus concentration. Thus, the minerals form slowly, or not at all, while soluble phosphorus is filling sorption sites on the solid surfaces but at a greater rate after the sites are filled and dissolved phosphorus concentrations increase.

Generally, the unsaturated-zone model was run for just the 50 yr of active disposal. A model simulation continued past active disposal, however, indicated that, as in the saturated case, dissolved phosphorus concentrations are higher when disposal stops and background water (rainwater) moves through the unsaturated zone. In the unsaturated zone, however, the flux of water decreases after disposal cessation by a factor of 88, unlike in the aquifer, where water flux is controlled substantially by regional gradients in groundwater heads. In the unsaturated zone, water flux is limited to recharge only. The decreased flow of water in the unsaturated zone when disposal of wastewater ceases causes transport of all constituents, including phosphorus, to decrease greatly.
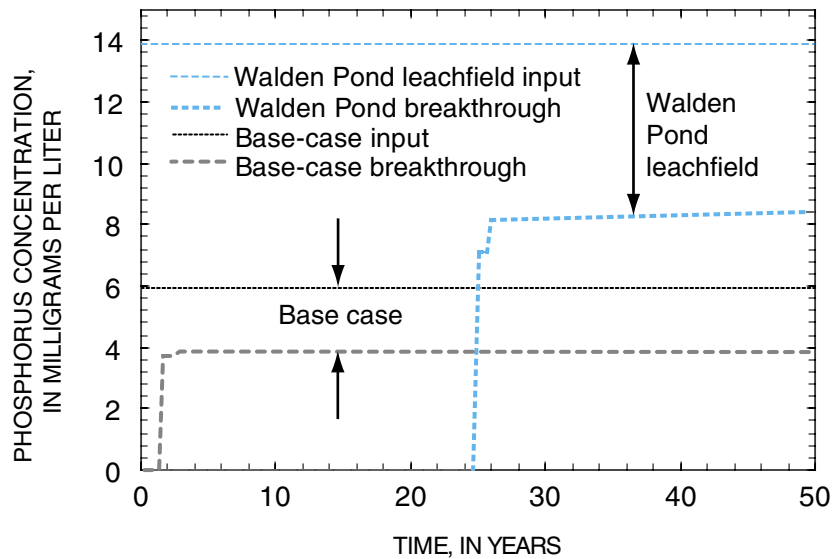
Figure 14.   Phosphorus concentration of effluent entering and exiting the unsaturated zone for simulations of the Walden Pond, Massachusetts, leachfield and for the base-case conditions. Differences between input and exiting concentrations are caused by continuous phosphate mineral formation in the unsaturated zone. Delay of breakthrough is caused by adsorption.

Response Curves of Phosphorus Plume Length as a Function of Unsaturated-Zone Thickness and Effluent Phosphorus Concentration

Plume lengths, as represented by the 0.015 mg/L dissolved phosphorus contour, were simulated as a function of unsaturated-zone thickness and effluent phosphorus concentration using the combined model (fig. 16). Plume length ranged from 200 ft for the greatest unsaturated-zone thickness (50 ft) and lowest phosphorus concentration (0.25 mg/L), to 3,400 ft at the lowest unsaturated-zone thickness (0 ft) and highest phosphorus concentration (14 mg/L). The relation was nonlinear with respect to both phosphorus concentration and unsaturated-zone thickness. At low phosphorus concentrations (less than 2 mg/L), plume length is essentially independent of unsaturated-zone thickness, whereas at higher concentrations, plume lengths are shorter for greater unsaturated-zone thicknesses. For a constant unsaturated-zone thickness, plume length increases less rapidly as phosphorus concentrations increase. The cause of the nonlinear response to unsaturated-zone thickness is the variable rate of precipitation of strengite (iron phosphate) in the unsaturated zone; the rates depend on the phosphorus concentration. Large amounts of strengite form in the unsaturated zone when the phosphorus concentration is

high, but precipitation slows or even ceases when the phosphorus concentration is low and the solubility product for iron-phosphate formation is not exceeded.

Model Verification

Verification of the combined model was difficult because no disposal system has been monitored long enough to provide accurate time histories of effluent phosphorus concentration and effluent flux rate, required inputs for the model. Likewise, phosphorus plumes from onland disposal have not been monitored for the length of time (greater than 50 years after cessation) necessary for maximum length of plumes to be developed. Comparison of simulation results with available data at the MMR and a small system at Walden Pond, however, is still of interest to determine if the model is generally in agreement with available data.

At the MMR, a range of effluent disposal rates was used during the discharge period from 1936 to 1995, from 0.32 to 3.1 gal/ft^2/d. The number of infiltration beds and total discharge also fluctuated resulting in disposal areas that varied from 107,600 to 538,000 ft^2 and total discharge from 0.1 to 1.5 Mgal/d. The discharge in the base-case model, by comparison, is 3.0 gal/ft^2/d at 0.06 Mgal/d, so that the base-case discharge was over a smaller infiltration area. Effluent
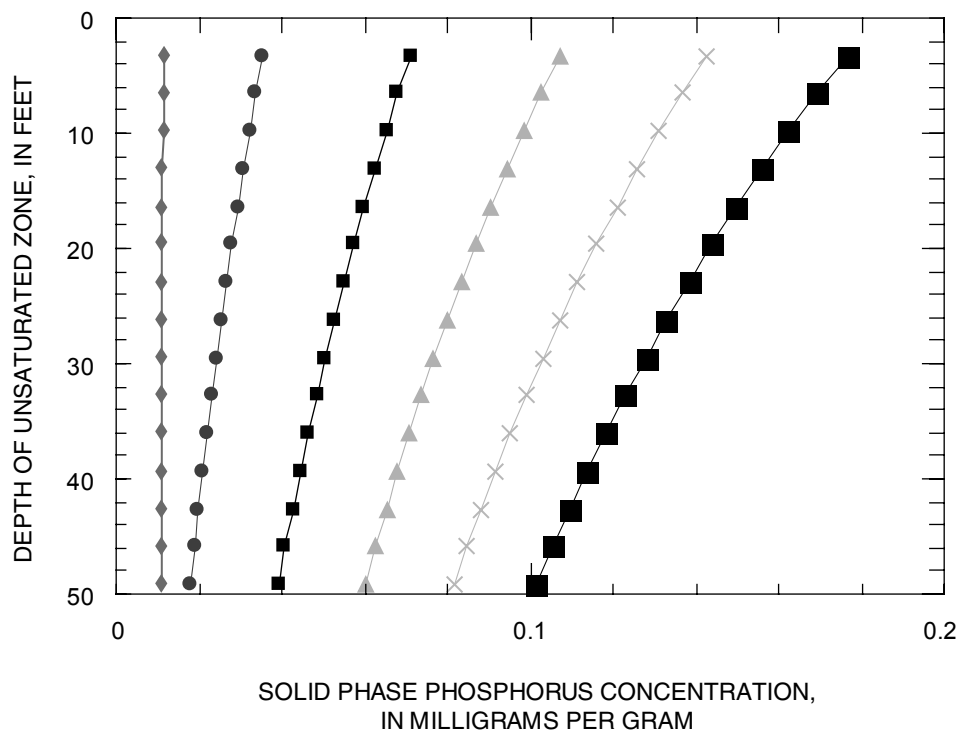
Figure 15. Simulated unsaturated-zone concentrations of phosphorus minerals in the solid phase at 10-year intervals during active discharge of wastewater, and of sorbed phosphorus after 10 years. The simulated sorbed concentration remains constant during the 10-to-50-year interval.

phosphorus concentration at the MMR was estimated to be 11.8 mg/L before a treatment-plant upgrade in 1983 and 5.9 mg/L after the upgrade until discharge cessation in 1996. Plume-length results from the combined model (fig. 16) for 12 mg/L phosphorus, which applied for the first 50 years of discharge at the MMR, and 20 ft of unsaturated zone present at the MMR is 2,500 ft. The measured plume length at the MMR in 1993, plotted as the 0.1 mg/L contour, (fig. 1, Walter and others, 1996) also was 2,500 ft. Measured plume length as represented by the 0.015 mg/L contour would likely be longer than 2,500 ft and might have increased since 1993 because

only 10 years had passed since cessation of wastewater discharge supplying the long axis of the plume. The longer MMR plume results are compatible with the simulation base-case results because wastewater was applied to a greater area in the measured case than in the base case. Simulations run for the sensitivity analysis indicated that the use of expanded infiltration bed size with the same flux resulted in longer plumes.

Data from the septic-system leachfield at Walden Pond provide information on transport through the unsaturated zone rather than information about plume length. After 24 years of operation of the leachfield, phosphorus had not arrived in the
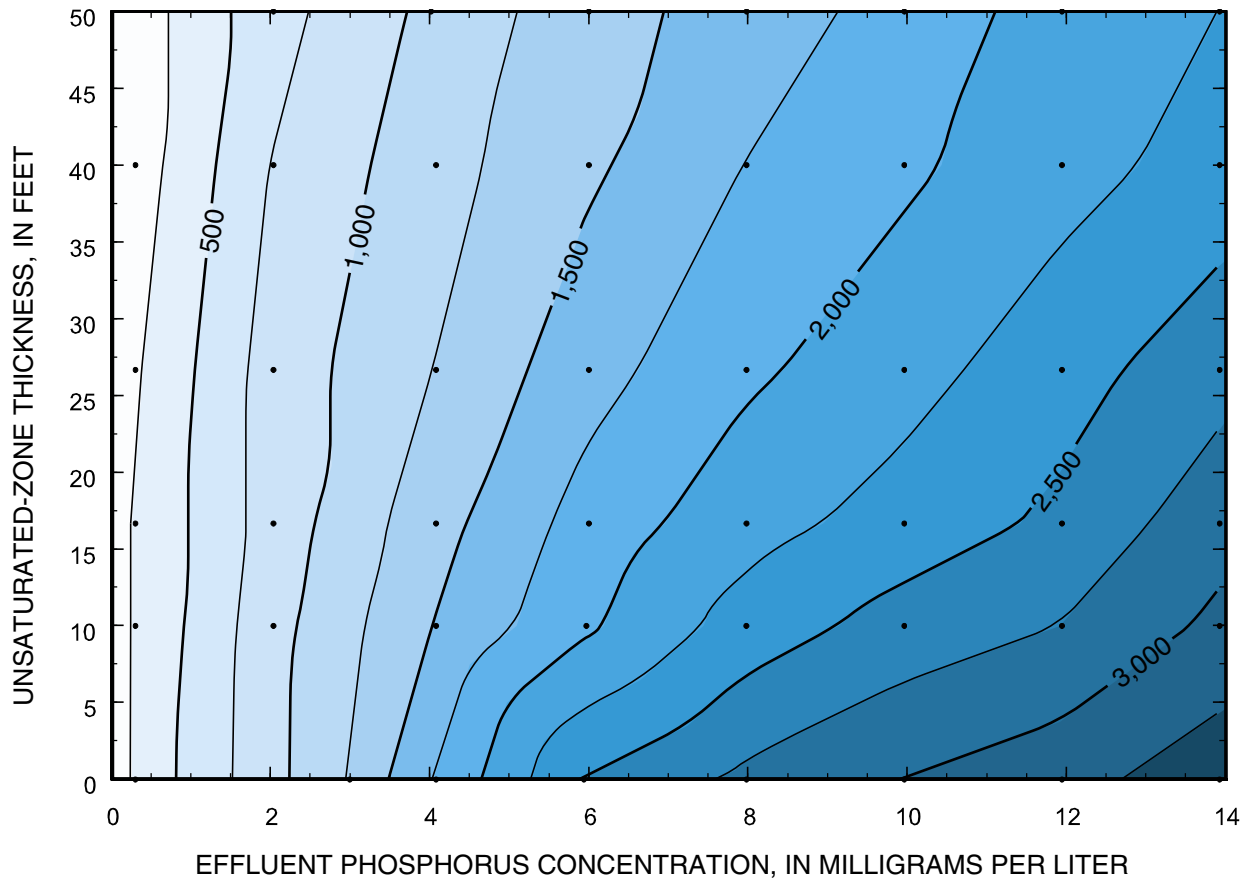
Figure 16.   Simulated dissolved phosphorus-plume length, as a function of unsaturated-zone thickness and phosphorus concentration in the discharge. Plume length (illustrated with the contours; contour interval is 250 feet) is defined by the extent of the 0.015 milligram per liter dissolved phosphorus contour after 50 years of discharge at the rate of 3 gallons per square foot per year onto a 20,000 square foot infiltration bed. Dots indicate the values of unsaturated-zone thicknesses and phosphorus concentrations of effluent used in the model runs.

saturated zone (Colman and Friesz, 2001). By comparison, the simulation for the Walden Pond leachfield with discharge of 14 mg/L phosphorus concentration to the 40-ft thick unsaturated zone indicated that breakthrough would occur at 25 years (fig. 14). Thus, the measured and simulated results are compatible, although the results imply that phosphorus breakthrough to the saturated zone might occur in the near future. Note that the plume lengths represented in figure 16 are not appropriate for the septic system at Walden Pond because the disposal rate at Walden Pond in terms of gallons per day is 60 times less than that used in figure 16.

Evaluation of Simulation Results

The relation among unsaturated-zone thickness, effluent phosphorus concentration, and phosphorus plume length (fig. 16) can be used to help plan setbacks between onland disposal sites and surface-water bodies that are long enough to protect the surface water from phosphorus eutrophication.

The simulated plume lengths can be used for planning and cost-benefit analysis of alternative disposal designs, such as treatment removal of phosphorus as compared to acquisition of land with characteristics favorable to phosphorus removal in the subsurface.

Application of Simulation Results

The model simulations can be used appropriately to simulate plume length where parameters other than phosphorus load and unsaturated-zone thickness (explicitly tested in this investigation) are similar to those used in the model, or differ only with respect to parameters determined in the sensitivity analysis not to affect plume length (fig. 13). The sensitivity analysis indicated that the tested parameters, other than those associated with load and with carbonate rocks (pH), changed the plume length less than 33 percent. Thus, although the calibration data used were for the MMR, the model results are expected to apply more generally to sand and gravel aquifers, with the exception of regions with carbon-

ate rocks. The simulations were made with a thick aquifer (150 ft), although plume length increased only 21 percent when the aquifer thickness was reduced by half (75 ft). The model was run for porous, hydraulically conductive material that is likely to allow infiltration rates of 3 gal/ft^2/d. The model would not be applied for hydraulically unconductive material because onland disposal would not be selected at sites where infiltration would be much less than 3 gal/ft^2/d.

Whether the application of simulation results (fig. 16) is for a specific location or for comparison of alternative sites, knowledge of the direction of flow, downgradient distance to surface water, and unsaturated-zone thickness is required. Ground-water-flow direction can be determined from results of previous regional-flow simulations or from hydraulic-head measurements for at least three wells screened at the water table (McCobb and others, 1999). Unsaturated-zone thickness can be determined as the difference between land-surface elevation and the water table by using methods established by Frimpter (1981). Once unsaturated-zone thickness and down-gradient distance to surface water have been established, the effluent phosphorus concentration corresponding to a plume length equal to the downgradient distance at that site can be obtained from figure 16. The phosphorus concentrations and plume lengths shown in figure 16 represent model simulations; their use as protective combinations for onland disposal upgra-dient of surface water may require additional interpretation by the regulating agency.

Monitoring downgradient from onland disposal instal-lations allows the predictions to be checked and knowledge of phosphorus mobility to be improved for further refine-ments of model-simulated estimates of phosphorus plume length. Monitoring wells installed downgradient of onland disposal installations that have intercepted plumes of effluent-associated constituents (conductance, nitrate) would be appro-priate to monitor for eventual breakthrough of phosphorus.

Effluent constituents in addition to phosphorus can be important at an onland disposal facility. Nitrogen transport in ground water is a concern, for marine areas, where nitrogen supply may control growth of aquatic plants, and for local drinking-water supply. Increasing the setback distance so that the aquifer is used efficiently in phosphorus removal may expose a larger zone of ground water to high nitrogen con-centrations, rendering it unfit for water supply. In near-shore areas, a substantial fraction of nitrogen disposed onland may be transported to the coast. Some nitrogen removal in the aqui-fer or in the sediments at the point of discharge to the marine environment is likely, however. As a result, onland disposal of nitrogen-containing waste may be preferable to direct dis-charge of an equivalent waste to surface water. A satisfactory onland disposal balancing requirements of phosphorus and nitrogen pertains for the septic-system leachfield at Walden Pond. Setback is sufficient to eliminate phosphorus transport to the pond. Nitrogen is transported to the pond, but apparently without appreciable effect on water quality because phos-

phorus, not nitrogen, controls the growth of aquatic plants. No water-supply wells are present near in the plume between the leachfield and Walden Pond (Colman and Friesz, 2001).

Model Strengths, Weaknesses, and Reliability

The strengths (accuracy in simulating plume length) of the reactive solute-transport model derive from the coupling of full chemistry with flow in the 1-D unsaturated and in the 3-D saturated zones—a model structure that is state-of-the-art. The model accounts for the complex dilution that results as infiltrated water interacts with ground water in the aquifer, and for the deepening of the plume downgradient because of recharge (fig. 10). Chemical reactions are treated with the full set of equilibrium and kinetic reactions available from PHREEQC (Parkhurst and Appelo, 1999). The sequestra-tion of phosphorus in both unsaturated and saturated zones, rather than just the latter can be important. Chemical effects relating to control of sorption by pH and control of pH by ion exchange and redox chemistry are included explicitly in the model simulations. These explicit reactions represent the important chemical effects that have been observed in column studies, where more phosphorus is released because of pH and ionic-strength effects when ground water enters the plume area after cessation of discharge.

Model weaknesses (uncertainties in simulating plume length) are related primarily to difficulty in simulating chemi-cal reactions controlled by kinetics rather than by equilibrium conditions and in specification of sorption properties of the solids. Rates of reaction for organic-carbon degradation and phosphate-mineral formation are important, but only a few calibration points are available, from laboratory data from the MMR for carbon oxidation and from the observed buildup of phosphate minerals in the unsaturated and saturated zones at the MMR for phosphate minerals. The formation of iron-phosphate minerals is not certain, but a similar result would pertain for other possible precipitates, such as aluminum phos-phate. Dissolution rates for the phosphate minerals that likely occur after disposal cessation are also uncertain. Because rates in kinetically controlled processes may depend in a complex manner on pH, bacteria populations, temperature, and con-centrations of reactive species, the limited calibration data available from the MMR studies are probably not sufficient to provide robust simulations. Nevertheless, the reactions have been confirmed to proceed and the relations used in the kinet-ics have been shown to be adequate in simulating phosphorus transport at the MMR.

The amount of iron-phosphate mineral precipitated is a larger percentage of the total phosphorus removed when onland wastewater discharge is low and phosphorus concen-tration in the effluent is high, such as is the case for septic systems (not covered in figure 16). Thus, the predictions for a septic system with a small plume length are more highly dependent on mineral formation than are predictions for the

base-case model, which apply to high disposal rates. Whereas phosphate-mineral formation has been observed in analysis of the unsaturated zone below septic systems (Robertson, 2003), the rate of formation has not been quantified.

Efficient Use of Phosphorus Removal in the Subsurface

The curvatures of the response curves in figure 16 provide an important conclusion regarding the efficacy of treatment of phosphorus before disposal onto infiltration beds; phosphorus removal in the sewage-treatment plant before discharge onto the beds results in little or no removal by precipitation of mineral phases in the subsurface because of the low phosphorus concentration in the effluent. The reactions in the subsurface, precipitation of phosphorus with iron, are actually among those applied for phosphorus removal in treatment plants. If phosphorus removal is carried out in the plant, however, the resulting effluent is too dilute for precipitation reactions to occur in the subsurface.

Summary and Conclusions

Phosphorus loading to surface freshwater can be the principal environmental problem associated with disposal of domestic wastewater. Onland disposal of wastewater results in less phosphorus transport to surface water than does direct discharge through an outfall pipe because of geochemical-loss processes in the subsurface. Quantification of the loss processes, which may occur in the saturated and unsaturated zones, could be used to plan onland disposal systems. In 2003, the U.S. Geological Survey, in cooperation with the Massachusetts Department of Environmental Protection, initiated a project to simulate distance of phosphorus transport for plausible conditions of onland disposal and subsurface properties.

The report summarizes the hydrology and geochemistry that controls phosphorus retention in the unsaturated and saturated zones of the subsurface. Computer models are described that simulate transport of phosphorus for onland disposal of wastewater primarily for large installations—3 gal/ft^2/d to a 100 by 200 ft infiltration bed. Although disposal at lower rates, such as rates pertinent to septic systems, are discussed, plume lengths are not simulated because the septic-system disposal rates are too small by comparison with rates used to calibrate the combined model. Simulation results are summarized in graphical engineering response curves that show the relations among effluent phosphorus concentrations, thickness of the unsaturated zone, and length of the phosphorus plume in the aquifer. The response curves can facilitate determination of the disposal location and the degree of phosphorus-removal treatment needed to meet low-impact disposal objectives.

Sensitivity analysis is included to quantify the effects on the response curves of the number of phosphorus binding sites on the aquifer solids, duration of disposal, and other aquifer and disposal conditions.

The dependence of phosphorus plume length on unsaturated-zone thickness and wastewater phosphorus concentration was simulated by combining 1-D unsaturated zone and 3-D saturated-zone PHAST computer models. Grid-element sizes were 3.33 ft in the unsaturated zone and 100 by 100 ft by 10 ft in the saturated zone. The simulations gave estimates of phosphorus plume length for use in determining setback distances for onland disposal of wastewater required for protection of surface water from eutrophication by subsurface transport of phosphorus. Base-case disposal conditions were 3 gal/ft^2/d of effluent disposed in a 100- by 200-ft infiltration bed for 50 yrs. The length of the phosphorus plume was defined as the maximum extent of water with 0.015 mg/L or more dissolved phosphorus downgradient from the infiltration bed during discharge and after discharge cessation; the plume may take more than 100 years to reach its maximum length. For the base case, phosphorus transport beyond the extent of this contour did not exceed 0.18 kg/yr, an amount expected to have little or no effect on the aquatic plant growth of most surface water.

Simulations of phosphorus plume lengths were summarized in a response-curves graph. Simulated plume lengths ranged from 200 ft for low-concentration (0.25 mg/L) effluent and thick (50 ft) unsaturated zones to 3,400 ft for high-concentration (14 mg/L) effluent discharging directly into the aquifer (unsaturated-zone thickness of 0 ft). Plume length was nearly independent of unsaturated-zone thickness at low values of phosphorus concentration in the wastewater because little or no phosphorus mineral formed at low dissolved phosphorus concentrations. At high concentrations of effluent, plume length varied from 3,400 ft for 0-ft unsaturated-zone thickness to 2,250 ft for 50-ft unsaturated-zone thickness. Plume-length dependence on the concentration of phosphorus in the wastewater was also variable, with diminished increase in plume length as wastewater phosphorus concentration increased. The diminished response was caused by the phosphate-mineral precipitation rate, which increases with increase in phosphorus concentration.

Model treatments of flow and equilibrium controlled chemistry were likely more accurate than were assumed properties of sorption surfaces and assumed rates of kinetically controlled reactions, notably precipitation of phosphate minerals. A sensitivity analysis indicated that many chemical and aquifer properties, such as hydraulic gradient and model width, did not affect the simulated plume length appreciably; but duration of discharge, size of infiltration bed, and number of sorption sites on aquifer sediments did appreciably affect plume length.

An important result from the simulations is that phosphorus removal by aquifer sediment is more efficient at high effluent concentrations of phosphorus discharged than at low

concentrations. High-concentration phosphorus is removed more efficiently because the rate of phosphorus removal by precipitation of phosphorus minerals is a function of phosphorus concentration; at low phosphorus concentrations, the solubility product of minerals is not exceeded, so no mineral forms. A consequence of the dependence of mineral formation on phosphorus concentration is that extent of phosphorus removal processes in the subsurface is decreased as more complete removal efforts are applied in treatment before wastewater disposal. The relation between phosphorus concentration and phosphorus removal rate means that removal of phosphorus in the subsurface from small volumes of wastewater, such as are disposed through septic systems, may be highly efficient. Phosphorus concentrations and removal rates are high in septic-system effluent; volume of wastewater disposed is low; consequently plume lengths are short. Less efficient is phosphorus removal from effluents with phosphorus concentration that has been decreased by treatment before disposal. If phosphorus removal is carried out in the treatment plant, the resulting effluent may be too dilute for precipitation reactions to occur in the subsurface.

Whereas the results of this investigation are expected to have wide application to noncarbonate glacially deposited sediments of Massachusetts, simulation of plume length in carbonate-mineral sediments indicated that plumes would be much longer. Thus, the model results would be inappropriately applied to locations containing carbonate-mineral sediments. The simulations indicate that less phosphorus is removed in carbonate or other high-pH ground-water environments.

Even with the simulations of the response curves for phosphorus plume lengths, as defined by the 0.015 mg/L concentration contour completed, the relation between plume length and protective setback distance is subject to interpretation. Phosphorus does move beyond the point at which the 0.015-mg/L-concentration contour has stopped, so that a determination of protective setback distance must include a consideration of whether that continued flux, or some other flux amount is protective. Also, model simulations indicate that phosphorus plumes do not reach their full extent until 50 to 200 yrs after disposal cessation, depending on concentration of phosphorus disposed. No phosphorus plume has been monitored for that long a period after cessation so that there is no way to verify the long-term simulation results.

Acknowledgments

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