ESTIMATION OF THE CONTRIBUTION OF PHOSPHORUS FROM ON-SITE SEWAGE DISPOSAL SYSTEMS TO LAKES

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By D.H. Waller, S.C. Sauveur and J.D. Mooers
Centre for Water Resources Studies (CWRS)
1360 Barrington Street
Halifax, Nova Scotia B3J 2X4

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CMHC Project Officer: A.J. Houston

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ABSTRACT

The objective of this research was to develop a modelling methodology that could be used to more accurately estimate phosphorus loads to lakes from on-site sewage disposal systems. Approaches that have been used to estimate phosphorus loads to lakes were reviewed. These approaches do not include explicit consideration of factors and processes that control phosphorus removal in soils. These factors and processes, and commonly available computer models that have been used to describe them, were explored in detail, based on a thorough review of the relevant literature. These reviews led to identification of models—CHEMFLO for the unsaturated zone, and MODFLOW and MT3D for the saturated zone—that offered the capability of representing the factors and processes involved in phosphorus removal. Exploration of the use of these models began with sensitivity analyses, based on a range of typical soil parameters; the results suggest responses, in terms of phosphorus removal, to variations in significant model parameters. Field and laboratory studies provided evidence about possible phosphorus removal under a variety of site and oil conditions. They also provided data for model calibration and verification. Modelling results reported here include the application of field data from one site to calibrate the unsaturated zone model for phosphorus removal, and application of the calibrated model to other sites. Also included are results of groundwater flow modelling in the saturated zone. Continuing work to apply project data to modelling phosphorus movement in the saturated zone is described. This study focused on phosphorus movement at the scale of single properties. Further work is necessary to determine the most effective manner in which this information can be incorporated into watershed-scale estimates of phosphorus loads. Analytical problems that were encountered and resolved are described. The significance of phosphorus detection limits of alternative analytical procedures is discussed.

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ESTIMATION OF THE CONTRIBUTION OF ON-SITE SEWAGE DISPOSAL SYSTEMS TO LAKES

1. INTRODUCTION

Phosphorus is considered in most situations to be the nutrient most responsible for eutrophication of freshwater lakes.

Planning for control of lake eutrophication involves application of models that identify and quantify sources of phosphorous that originate in a watershed. Some sources, such as untreated municipal sewage, are easy to identify and quantify.

But in some situations, such as those where these sources do not exist, or phosphorus is not discharged to a lake because of diversion or treatment, on-site sewage disposal systems may be the greatest single source of phosphorus.

Methods that have been used to estimate the phosphorus contribution from on-site systems have either assumed that all or some fraction of on-site phosphorus from the total watershed, or from the portion within an assumed distance from a lake or its tributaries, reached the lake, These approaches do not account directly for effects of factors such as soil type, groundwater depth, or chemical processes in the soil.

The objective of this research was to develop a modeling methodology that can be used to more accurately estimate annual phosphorus loads to lakes from on-site sewage disposal systems.

The report begins with a review of approaches that have been used to estimate phosphorus loads to lakes. Factors and processes that control phosphorus movement, and commonly available computer models that have been used to describe them, are explored in detail, based on a thorough review of the relevant literature. These reviews led to identification of models that offer the capability of representing these factors and processes. Exploration of the use of these models begins with sensitivity analyses that suggest responses, in terms of phosphorus removal, to variations in significant model parameters. Field and laboratory studies—which provide evidence about phosphorus removal under a variety of site and soil conditions, and provide data for model calibration and verification—are described. Modelling results are reported and discussed, and continuing work to apply project data is described. The need for further work is indicated. This report also describes analytical problems that were encountered and resolved, and the potential significance of phosphorus detection limits of alternative analytical methods.

2. ESTIMATION OF ON-SITE CONTRIBUTIONS TO PHOSPHORUS LOADS

2.1 Phosphorus Loadings From On-Site Systems

The amount of phosphorus discharged from an on-site system depends on the phosphorus loading from the source (usually a single family dwelling), less any phosphorus removed in the septic tank and disposal field before the effluent enters the soil below the field.

Throughout this report phosphorus concentrations and loads are taken to be total phosphorus. Vollenweider, 1969, and Dillon and Kitchner, 1975, are among those who have reported that chlorophyll a concentrations in lakes correlate best with total phosphorus loadings. The latter authors illustrate how use of total phosphorus can lead to erroneous results if biologically unavailable phosphorus is included in particulate matter; this concern should not apply if on-site phosphorus is transported in groundwater in soluble form. Section 3.1.2 of this report relates project experiences in analyzing for low concentrations of total and soluble phosphorus.

Brandes, 1976, estimated that a septic tank removes 4 percent of phosphorus from sewage. Hardistry, 1974, quoted by Dillon *et al.* 1986, found removals of 20-30 percent. Dillon and Rigler, 1975, and Dillon *et al.* 1986, make no allowance for phosphorus removal in the tank or disposal field.

Porter, 1975, in a study of New York lakes, assumed that domestic sewage prior to June 1, 1973 (when phosphate detergents were banned in New York State) contained about 1.5 kg/cap/yr of phosphorus, and about 0.9 kg/cap/yr after that date. No reference is made to removal of phosphorus in the disposal system; these values apparently reflect the phosphorus loading to the soil.

Dillon and Rigler, 1975, estimated that the phosphorus contribution from domestic sewage was 0.8 kg/cap/yr; this value was confirmed by Dillon *et al.* 1986, based on values of septic tank P concentrations and water use from the literature. Brandes, 1976, reported the phosphorus contribution from a single septic tank as 0.84 kg/cap/yr.

Other estimates of phosphorus contributions have been smaller or greater than those cited above. Brandes, 1976, estimated the annual phosphorus contribution as 1.5 kg/cap/yr. McGrail *et al.* 1976, used a value of 0.6 kg/cap/yr. Laak, 1986, used a phosphorus load entering a septic tank of 3.65 kg/cap/yr.

Dillon and Rigler,1975, and Dillon *et al.* 1986, modify annual per capita loadings by a index that reflects the average household size and fraction of a year that dwellings are occupied —expressed in units of capita-years/year.

2.2 Phosphorus Contributions to Lakes

All references considered here have recognized that the potential loads estimated in the previous section may not reach a lake. Factors cited by Dillon and Rigler, 1975, include:

- Dwellings distant from a lake or its tributaries may not contribute to a lake.
- Phosphorus loads may be reduced by phosphorus retention in soils, which may alter over time.
- Malfunctioning systems may contribute more phosphorus than those that function properly.

Jones and Lee, 1979, identify the following factors:

- There may be no relationship between surface topography and groundwater flow to a lake: if the groundwater table slopes across the lake, dwellings on the downstream site will not drain to the lake, and especially in glaciated regions an impervious layer can exist beneath the lake and prevent groundwater input.
- The potential for phosphorus removal by aquifer materials increases with distance between a septic tank and a lake.
- If phosphorus is transported to the lake via a stream it frequently becomes associated with particulate matter and is removed from solution.
- If phosphorus is transported to the lake via an upstream lake part of the phosphorus will be retained in the upper lake.
- Phosphorus removal in some on-site systems may be deliberately enhanced through system design.

Of the factors identified above, only those associated with system design or soil processes are considered in this report; other factors are included in procedures, such as those described by Dillon *et al.* 1986, for estimating the impact of phosphorus inputs on lake systems.

Jones and Lee, 1979, refer to removal of phosphorus by inclusion of limestone or aluminum oxide in the disposal field or in a dyke that is constructed between the field and a watercourse. Brandes, 1975, 1976, 1977, demonstrated significant removals of phosphorus by incorporation of red mud (a by-product of aluminum extraction from bauxite) or limestone in disposal fields, and by direct dosing of alum to a septic tank. Laak, 1986, summarizes design of a sand filter, based on the phosphorus adsorption capacity of the filter medium, that would remove phosphorus for a 20 year period. Results of experiments using porous reactive walls containing iron oxide and limestone are summarized by Ptacek *et al.* 1994.

Dillon *et al.* 1986 state that the removal of phosphorus by septic systems depends on proper system design and maintenance. They indicate that an average of 61 percent of systems in Ontario were not properly designed, constructed or maintained. Porter, 1975, indicates that a proportion of on-site systems work imperfectly and allow some considerable fraction of the effluent to be discharged to a stream before the soil has removed phosphorus. Neither reference indicates those design, construction, or maintenance factors that affect phosphorus removal.

2.2.1 Phosphorus Concentration in Groundwater

A number of studies have examined phosphorous concentrations in groundwater below or downstream of on-site systems.

Robertson *et al.* 1991, describe a site at Muskoka, Ontario, in poorly buffered carbonate-depleted sand. After one year in operation no detectable phosphorus (>0.02 mg/l) was found in groundwater. The geochemistry suggested that attenuation was controlled by presence of sparsely soluble phosphate minerals (iron or aluminum based), or by sorption. pH of groundwater was much lower than at Cambridge.

Robertson *et al.* also described results at a site at Cambridge, Ontario, which were updated by Ptacek *et al.* 1994. This system discharged to a carbonate-rich sand aquifer. Robertson *et al.* found that after 12 years of operation, very little phosphorus attenuation occurred in the unsaturated zone, but concentrations were reduced to less than 0.02 mg/l after several meters of flow in the groundwater zone. The geochemistry suggested that attenuation was controlled by hydroxylapatite complexing. Results in year 17 indicated advancement of the phosphorus plume at a rate of about 1 m/year. The phosphorus concentration in the plume was 5 mg/l, about 70 percent of the concentration of 7 mg/l in septic tank effluent. The plume behaviour suggested that phosphorus mobility was controlled primarily by sorption.

Ptacek *et al.*, 1994, also described a site at Peelee, Ontario, where the tile bed operated for 30 years. Soil below the bed was 7-8 m of poorly graded coarse sand, underlain by dense clay. The winter groundwater table was less than 1 m below the ground surface. Concentrations near the bed were about 0.3 mg/l, decreasing to <0.05 mg/l at a distance of 38 m. The authors suggest that different phosphorus removal mechanisms may be active at this site, where incomplete oxidation of effluent is suggested by elevated NH_4 and COD concentrations, compared with the Cambridge site, where the effluent is extensively oxidized.

2.2.2 Phosphorus Loading Estimates

Two approaches to estimating the potential phosphorus contributions from on-site systems to lakes have been recorded. Dillon and Rigler, 1975, consider contributions to a lake only from dwellings within 300 m of the lake or tributary streams. Hart *et al.* 1978, who followed the Dillon and Rigler procedure, used the same assumption. McGrail *et al.* 1976, recognized contributions from dwellings within 100 m of a lake. These authors do not explain the rationale for limiting consideration to dwellings close to a lake, or for the distance selected.

The alternate approach, adopted by Dillon *et al.*, 1986, and Porter, 1975, is to consider potential contributions from all dwellings in a watershed.

Systems studied by Dillon and Rigler, 1975, were located in Precambrian areas typically having very shallow, coarse-textured sandy or muck soils. In the absence of satisfactory evidence to indicate that phosphorus is retained in these soils they assumed that all phosphorus discharged from an on-site system into sand, gravel, or muck soils eventually reaches a lake. Dillon and Rigler, 1975, and Dillon *et al.* 1986, suggest that where information on soil types is available, phosphorus retention values determined by Brandes *et al.* 1974, in soil column studies could be used; representive values from that source are included in Table 2.1.

A number of studies have examined phosphorous concentrations in groundwater below or downstream of on-site systems.

Aitkens, 1977 found that in soils of the Precambrian Shield soil depth was the main limitation on phosphorus retention.

Brandes, 1975, described results of field experiments to determine phosphorus transport from 15 on-site systems. The phosphorus concentration in the effluent from one system was 15 mg/L. For three systems where imported fill containing stones and boulders was used, phosphorus concentrations at a distance of about 10 m were about 3 mg/l. For the other 12 systems concentrations were between 0.12 and 0.39 mg/l. Most of the phosphorus was removed within a short distance from the disposal system. Downstream concentrations dropped with distance from the bed and with the proportion of clay and silt in the soil. In these systems phosphorus removals—based on loads leaving the systems and those in groundwater entering the lakes—ranged from 50 to 98 percent. Extraction of phosphorus from the soil of these systems showed that phosphorus was retained mostly within the upper layers of soil below the disposal beds.

Snodgrass and O'Melia, 1975, applied their predictive model for phosphorus in lakes to data reported by other investigators. They concluded that phosphorus concentrations predicted by Imboden, 1973, were too high because all phosphorus from the watershed—assumed at 0.9 kg/cap/yr—was assumed to reach the lake.

Hart, *et al.*, 1978, in applying the approach of Dillon and Rigler, 1975, found that an estimated on-site loading of 0.4 kg/cap/yr—i.e. 50 percent of the potential loading assumed by Dillon and Rigler—best explained the trophic status of a series of lakes in Nova Scotia.

Porter, 1975, cites an initial estimate that 50 percent of phosphorus in household wastes from the watershed was contributed to lakes, based on consideration of

- proximity of most dwellings to lakes;
- old systems that overflow into storm drains;
- small lot sizes.

This estimate is compared with results of measurements from a rural watershed, with more dispersed dwellings on larger lots, which indicated a loss of 10 percent of on-site phosphorus to the lake.

Dillon *et al.* 1986, found agreement between observed and calculated lake phosphorus levels for three lakes when all of the potential on-site load entered the lake. Estimates for a fourth lake agreed when 19 percent of the potential load was included. Possible explanations for the difference were differences in the phosphorus retention capacities of soils, and the fact that cottages surrounding the fourth lake are newer, implying a better state of repair and a greater proportion of the binding capacity of soils remaining available to remove phosphorus.

2.2.3 Malfunctioning Systems

Several authors have identified malfunctioning systems as a phosphorus source. A malfunctioning system is assumed here to mean one that permits escape of effluent to the ground surface or a ditch or drain.

The amount of phosphorus from a malfunctioning system that reaches a lake or stream may depend on opportunities for biological processes to attenuate phosphorus in ditches and lakes. The effects of the latter process could be seasonal, and should depend on travel time. A conservative approach to estimation of loads from such systems, if their numbers can be estimated, might be to assume that all phosphorus from malfunctioning systems within 300 m of a lake or its tributaries (the distance used by Dillon and Rigler, 1975) contributes to the lake.

2.3 Discussion

The potential phosphorus loading to lakes can be estimated based on the total number of dwellings in the watershed, subject to:

- care in definition of the hydrologic regime that determines how the surficial watershed relates to the area of groundwater discharge to the lake;
- estimation of the extent of occupancy of dwellings, especially where cottage properties are included.

Per-capita phosphorus loadings can be estimated from assumed or measured values of hydraulic loads and effluent concentrations. Recorded values of both of these parameters vary markedly. Phosphorus concentrations range from lows of 7 and 8 mg/l reported by Ptacek *et al.*, 1994 and Robertson *et al.*, 1991 for a site at Cambridge, Ontario, to 19.6 reported by Brandes, 1976. Brandes estimates a phosphorus load of 0.84 kg/cap/yr based on

19.6 mg/l and 117.6 l/cap/day; Dillon *et al.*, 1986, estimate almost the same load, 0.8 kg/cap/day, based on 13.2 mg/l and 164 l/cap/day.

Removal of phosphorus by a septic tank and disposal field is generally considered to be insignificant.

Figure 2.1 is a conceptual representation of pathways of phosphorus movement from an on-site system to a lake. The basic routes are (a) from the disposal system into the unsaturated soil below the bed, through the unsaturated layer to the groundwater table, and through the saturated layer, with the groundwater, to the lake, and (b) from a malfunctioning system to the soil surface, from which the wastewater may flow or be carried by stormwater to the lake (unless it first re-enters the soil system). Real systems are obviously more complex than the figure suggests, including wide variations in soil properties, topography, and groundwater characteristics.

As Figure 2.1 suggests, phosphorus may be removed in the unsaturated zone below a disposal field, or during passage of groundwater from the field to a lake. If effluent from a malfunctioning system escapes to the surface it may reach a lake directly via ditches and drains. If the phosphorus enters a stream or upstream lake tributary to a lake some phosphorus will be trapped in these systems; these effects, which apply to phosphorus from any source, are commonly considered in lake loading models, and are not considered further in this discussion.

The references cited here assume or describe removals that range from nil in shallow, coarse-textured soils, to removal to less than 0.02 mg/l. Factors that have been identified or suggested by these references are:

- degree of oxidation of the effluent reaching the soil
- texture and composition of soils beneath the disposal bed
- depth of unsaturated soil
- texture and composition of soil below the groundwater table
- travel distance in the saturated zone
- age of the system, which may determine both system design and construction, and the distance of phosphorus movement from the system.
- concentration of dwellings, if cumulative phosphorus loads may contribute to saturation of phosphorus attenuation sites in the direction of groundwater movement.

Some of these factors are a function of system design and location; others depend on local soils and hydrogeology, and time.

Distance from a shoreline or tributary stream will be a factor if phosphorus removal is primarily a function of lateral flow in the groundwater. In this case, drainage density in the watershed will be a variable; this parameter plus shoreline length, multiplied by the distance within which systems are assumed to contribute, will define the area that includes systems that are considered to contribute phosphorus to lakes.

If, on the other hand, phosphorus attenuation is solely a function of processes in the unsaturated zone, or if systems, soils and geology are such that no phosphorus attenuation should be assumed, distance of systems from shorelines or watercourses will not be a factor.

It should perhaps be noted, in considering the results of those studies that report phosphorus movement in soils, that the detection limit commonly stated is 0.02 mg/l; it might be inferred that if phosphorus is not detected at this level no significant amount is present. Phosphorus loads that can impact on lake water quality are not large when expressed in terms of concentrations in groundwater or tributary streams: concentrations in most samples from streams tributary to Nova Scotia lakes impacted by on-site systems are usually well below 0.02 mg/l in both base flow and wet weather periods. Using an analytical procedure with a reporting limit of 0.001 mg/l. Hart, *et al.* 1978 estimated that the mean concentrations of groundwater total phosphorus attributable to on-site systems in two lakes were 0.03 and 0.005 mg/l. Calculations based on a phosphorus detection limit of 0.02 mg/L may therefore under estimate phosphorus loadings.

This discussion suggests the following questions, which are intended to be addressed—by field results and mathematical modelling—in the following sections:

- How do variations in the depth of the unsaturated zone, and soil properties affect the attenuation of phosphorus?
- How do variations in soil properties and composition, and groundwater chemistry and hydraulics, affect the attenuation of phosphorus in the saturated zone?
- How do variations in effluent flow and composition affect attenuation of phosphorus in the unsaturated or saturated zone?
- How does the extent of phosphorus attenuation and travel of the phosphorus plume vary over time?
- Are results of modelling and field work in this project consistent with results reported in the literature?
- How can results of modelling and field work in this project be applied in estimating phosphorus loadings contributed to lakes by on-site systems?

3. MODELING SUBSURFACE PHOSPHORUS REMOVAL PROCESSES - LITERATURE REVIEW

3.1 Introduction

This section reviews literature related to mathematical relationships that describe phosphorus removal processes in soils.

Terms used in this section are defined in Appendix C.

3.2 Principle Processes

Phosphorus may exist in the soil in one of three possible forms. These include phosphorus dissolved in soil water, phosphorus adsorbed onto soil particles, or discrete phase precipitates which contain ions such as aluminum, calcium, or iron in association with the phosphorus.

Adsorption and precipitation are considered the main two processes by which phosphorus is removed from solutions flowing through the subsurface (Shah *et al.*, 1975; Tofflemire and Chen, 1977; Wilhelm *et al.*, 1991; and others). In addition to these processes, other methods of phosphate removal include uptake by plants and biological immobilization (Tofflemire and Chen, 1977). However, in the case of on-site disposal systems it is felt that these two processes are insignificant, due to the fact that disposal fields lie below the biologically active upper soil horizons. Reneau *et al.* (1989) agree with the four processes outlined above, except they subdivide the adsorption and precipitation processes as follows. Adsorption is considered to include physical adsorption, chemical adsorption (chemisorption), and anion exchange processes, while precipitation may occur on the surface of soil particles or as discrete solids within soil pore spaces.

In its simplest form the process of phosphorus removal is one in which some of the phosphorus is quickly adsorbed onto soil particles at rates which are typically measured in hours. Minerals such as calcium, iron, and aluminum will react with some of the remaining solution phosphorus to form highly insoluble phosphorus. The rates for these precipitation reactions are much slower than those for adsorption and are usually on the order of weeks to months. Some of the literature dedicated to phosphorus attenuation in soil states that adsorption is the dominant reaction with some of the adsorbed phosphorus eventually forming precipitates (Reneau *et al.*, 1989; Wilhelm *et al.*, 1991; and others). Other researchers however, have concluded that these two processes do not necessarily occur in series. Tofflemire and Chen (1977) and Barrow and Shaw (1975) are among some of the researchers who developed models that assume the two processes occur simultaneously, so their models contained terms to represent the loss of phosphorus from the solution pool by both processes. Barrow (1983) agrees with an initial reaction involving adsorption, however he concludes that the reaction which occurs next is one in which the adsorbed phosphorus diffuses (penetrates) into vacancies in the soil particles.

Finally, some researchers have noted a correlation between phosphorus concentrations in the soil solution and the relative importance of adsorption and precipitation reactions. Van Riemsdijk *et al.* (1984) observe adsorption to become relatively insignificant when the phosphorus concentration is above 1 mmol/l (~31 mg/l). They also note that, in some cases, precipitation has become the dominant reaction after only 5-15 minutes, much less time than most workers assume. Reneau *et al.* (1989) seem to agree with the relative importance of precipitation at higher phosphorus concentrations when they state that precipitation reactions only occur if the concentration of phosphorus is in the moles per liter range.

Much of the early research dealing with phosphorus attenuation in soil (e.g. Saini and MacLean, 1965; Saunders, 1965) merely recognizes that it is attenuated without giving much attention to the processes involved. Rather than considering the two separate processes of adsorption and precipitation, these papers attempt to correlate the degree of phosphorus attenuation with various soil parameters such as pH, clay, iron, aluminum, or calcium contents, or other characteristic soil properties.

Later workers who have considered actual attenuation mechanisms (e.g. Reneau and Pettry, 1976; Khalid *et al.*, 1977; Kuo and Mikkelsen, 1979; and others) have reported that sorption reactions are controlled by environmental properties such as oxygen supply, soil water content, and temperature as well as soil properties such as pH, the amount and types of clays present, and the presence of organic matter and extractable iron and aluminum oxides.

3.3 Environmental Properties

The effects of oxygen supply and water content noted in the literature are often cited together due to the fact that flooding of unsaturated soils tends to lead to reducing conditions. Hill and Sawhney (1981) report that the onset of reducing conditions due to flooding increases the mobility of phosphorus in soils. Patrick and Khalid (1974) also discuss the effects of oxygen supply on phosphorus adsorption. In this study they observed the differences between anaerobic and aerobic conditions for two solutions, one with no phosphorus and the other with a phosphorus concentration of 100 mg/l. They found that at low solution phosphorus concentrations anaerobic conditions led to the release of phosphorus from the soil to the solution and thus to an increase in phosphorus mobility. On the other hand anaerobic conditions favored an increase in adsorption for the high concentration solution. They make no conclusion as to the concentration at which the observed difference in the effect of oxygen supply would occur, however it is likely that septic system effluent would behave much like the lower concentration solution due to its relatively low phosphorus concentration.

Another paper which describes the effects of soil flooding on phosphorus adsorption is Kuo and Mikkelson (1979). In this case they note that seasonal flooding of rice fields leads to the conversion of crystalline iron minerals to amorphous forms. The higher surface area of the amorphous iron minerals results in an increase in adsorption due to the greater abundance of sorption sites. They are unclear however, as to whether this increase was noted after re-drying of the soils or whether it occurred while the soil was still flooded.

One further comment regarding soil water content deals with variations in hydraulic conductivity as saturation levels vary. It is well established that hydraulic conductivity increases with the level of saturation. Increasing flow rates may lead to greater phosphorus mobility as the phosphorus may be moved through the soil at a rate too great for attenuation reactions to occur. This would likely have a greater effect on precipitation reactions than adsorption reactions due to the fact the former occur at much slower rates.

The effect of temperature has been reported on by Barrow and Shaw (1975). They looked at how the rate of change in the phosphorus concentration of a solution varied in response to temperature when the solution was mixed with various soils. They found that each 10°C increase in temperature results in a tripling of the observed rate of change in phosphorus concentration. Based on this observation they conclude that higher temperatures result in an increase in initial adsorption. However, they report that higher temperatures also affect the equilibrium between adsorbed phosphorus and that still in solution by favoring the solution side of the reactions. Therefore it appears that the effects of temperature may cancel each other out to a certain degree. It should be noted temperature fluctuations of 10°C in the subsurface below a septic field would be unusual and thus the effects of temperature variations for a particular site would not be as significant as those discussed here.

3.4 Soil Properties

Tofflemire and Chen (1977) report on a study conducted in New York State which found that soils with increased levels of iron and aluminum, or those with a greater proportion of silts and clays exhibited greater capacity for phosphorus adsorption. This study also concluded that acidic soils had better adsorption capabilities than calcareous ones and that tills performed better than outwash deposits. The latter is not surprising given that tills tend to have a greater proportion of silt and clay sized particles. Barrow (1983) observed the same correlation between pH and phosphorus adsorption in which he noted a decrease in sorption as pH increased. This relationship was only valid, however, for situations where the pH was high to start with. Ptacek *et al.* (1994) state that the cause of the observed effect of pH on adsorption has to do with the surface charge of the soil minerals. They define the zero-point of charge of a mineral as the pH at which the mineral surface has equal negatively and positively charged sites. Below this pH positive sites dominate while negatively charged sites become dominant as pH increases. Since HPO_4^{2-} and $H_2PO_4^-$ are the dominant forms of phosphate in the typical pH range of groundwater, positively charged surfaces will be better phosphorus adsorbents. They state further that since the neutral phosphate species, $H_3PO_4^0$, dominates when pH is below 2.2, very low pH conditions do not favor adsorption.

The role of particle size has also been supported by Sawhney and Starr (1977) who conclude that finer grained soils allow less movement of phosphorus than coarser grained soils. Tofflemire and Chen (1977) also report a negative correlation between phosphorus adsorption and the amount of quartz, plagioclase and potassium feldspar present in a soil. This can most likely be attributed to the fact that soils abundant in these minerals tend to be coarser grained due to their greater resistance. Many workers (e.g. Enfield, 1974; Hill and Sawhney, 1981) feel that that portion of the soil which can pass through a 2mm sieve is the critical fraction for phosphorus attenuation.

The importance of clays and iron has been questioned by some workers. Saini and MacLean (1965) correlate phosphorus retention to the proportion of clays, iron, and aluminum present in a soil. They found that, although iron and clay content plays a minor role, aluminum exhibits the most significant correlation. They conclude that the role attributed to clays is more likely due to the fact that most clays consist of aluminum minerals. In contrast to this view of the significance of iron, Barrow (1983) concludes that iron (particularly disturbed iron oxides) and aluminum both play a significant role in phosphorus retention.

One study which mentions the factors controlling precipitation is Reneau et al. (1989) who indicate that these reactions are governed by factors such as pH, the concentrations of phosphorus, iron, aluminum, and calcium, the presence of competing ions and the reaction rates. Although they do not discuss these parameters in detail, it would appear that the following would hold true:

- greater concentrations of aluminum, iron, and calcium, would result in greater precipitation since these are the minerals which form precipitates with phosphorus;
- the presence of competing ions would, on the other hand, discourage phosphorus precipitation since these ions would react with the minerals in place of some of the phosphorus;
- the pH of the system may not play that great a role in the level of phosphorus retention, but it may control the precipitates which form. Generally calcareous precipitates form in neutral to basic conditions while iron and aluminum are important under acidic conditions.

As mentioned above adsorption reactions are generally assumed to proceed at much higher rates than those involved in precipitation. Reaction rates, especially those for precipitation reactions, are important because the phosphorus is also being moved through the subsurface by flowing groundwater. If the rate at which phosphorus precipitates is very low, it may be likely that the phosphorus moves through the soil too quickly for the reactions to occur.

3.5 Regeneration of Phosphorus Adsorption Sites

Many workers have indicated that adsorption sites may be regenerated over time thereby making a soil's retention capacity infinite. Sawhney and Hill (1975) concluded that repeated wetting and drying of a soil brings fresh calcium, aluminum, and iron as well as other minerals into equilibrium with the soil resulting in new adsorption surfaces. However they were unsure of the mechanism through which this resulted. Laak (1980) felt that the precipitation of phosphorus frees up adsorption sites to be reused. One problem with this conclusion is that, if the view that adsorption occurs at much faster rates is followed, it seems unlikely that precipitation would free up adsorption sites at a rate fast enough to maintain adsorption indefinitely. In contrast to the above observations, Goodrich and Monke (1971) conducted column experiments which showed that, upon introducing a phosphorus solution into a soil column, the concentration of adsorbed phosphorus was seen to rise until a certain level was reached and then no further increase was observed. After this point, the phosphorus concentration in the column effluent increased dramatically. They concluded that once all adsorption sites were occupied no further adsorption could occur and thus any phosphorus in solution was free to move further along the direction of flow. This conclusion is likely a simplistic view of the process. Even if one ignores the possibility of adsorption site regeneration, some of the phosphorus in solution will be attenuated through precipitation.

3.6 Adsorption Isotherms

A soils capacity to adsorb a particular substance can be described using experimentally derived isotherms. Although isotherms may be employed for any number of substances which undergo adsorption, the discussion which follows will be limited to studies involving phosphorus. Phosphorus adsorption isotherms are graphical plots of solution phosphorus concentration against it's adsorbed concentration for a given soil at given pressure and temperature (hence the term isotherm) (Ghadiri and Rose, 1992, §3.3). Typically isotherms are derived using either column experiments or batch tests in which a given quantity of soil is mixed with a number of solutions of varying phosphorus concentrations. The effluent phosphorus concentration (column experiments) or solution concentration (batch tests) is then analyzed at various time intervals to determine how much phosphorus has been lost to the soil. Graphs plotting adsorbed concentration against solution concentration at equilibrium may then be constructed (e.g. figure 3.1). The overall purpose of plotting isotherms is to derive coefficients which may be used to describe the observed relationship between a soil and a particular substance in solution. Ghadiri and Rose (1992) present some general isotherms commonly used. The use of isotherms assumes equilibrium conditions exist between the sorbed species and that still in solution. It should be noted also that isotherms are merely an empirical representation of observed data and they do not indicate the mechanisms by which sorption occurs, although they are usually developed with a somewhat mechanistic approach (Sposito, 1989).

The two most common isotherms used are the Langmuir Isotherm and the Freundlich Isotherm, with many of the ones developed later being extensions of either of these. One problem often pointed out regarding the Langmuir isotherm was that it did not consider the fact that a particular soil has a finite sorption capacity. The modified Langmuir isotherm presented by Sposito (1989) however, accounts for finite capacity. This isotherm is described mathematically as:

$$S = \frac{bKC}{1+KC} \qquad \text{Equation 3.1}$$

Barrow (1983) states that the Langmuir equation seldom describes actual conditions for phosphorus. He goes on to say that the Freundlich approach is better over limited ranges of conditions or that a modified Freundlich isotherm (after Shayan and Davey, 1978) will provide accurate predictions over larger ranges. Sposito (1989) provides a criteria for determining the suitability of either of these isotherms for a particular soil as well as a fairly simple method for measuring a soils' adsorption capacity and determining the coefficients used in the isotherm equations. Not withstanding the concerns raised by these workers regarding the use of the Langmuir isotherm for describing phosphorus adsorption, many recent workers (e.g. Shah *et al.*, 1975; Novak *et al.*, 1975; Enfield *et al.*, 1981, van der Zee *et al.*, 1989) consider its use to be valid.

The discussion thus far has focused on the process of adsorption but it is also necessary to bear in mind the possibility that desorption may occur. The desorption process is inherently accounted for by the assumptions that equilibrium exists between solution and adsorbed phosphorus, and that the adsorption reactions proceed very quickly relative to overall groundwater flow. Any phosphorus returned to the solution through desorption will quickly be replaced through the adsorption side of the reaction. Adsorption-desorption reactions may be considered 'gradient driven'. Initially the relatively higher phosphorus concentration in the solution results in adsorption. With time the concentration gradient between solution and soil particles decreases and the equilibrium is reached. As long as the system remains at a steady state (i.e. no drastic changes in things like effluent or groundwater phosphorus concentrations) desorption need not be considered. Desorption should be kept in mind, however, especially in situations where solution phosphorus concentrations later decrease for one reason or another. Such a situation would result in a change in the concentration gradient possibly resulting in the movement of phosphorus to the solution phase until a new equilibrium is reached.

3.7 Non-Equilibrium Reactions

The foregoing discussion assumes that equilibrium conditions exist between the adsorbed species and that still in solution. If equilibrium does not exist, then a method which considers reaction kinetics must be used. Any equation used to describe non-equilibrium conditions must take into account the rates at which both adsorption and desorption of a particular species occur. Basically the difference between these two rates will determine whether adsorption, desorption. or neither occurs as well as how quickly either will proceed. Mathematically this can be written as:

$$\frac{\partial \Delta C}{\partial t} = R_f - R_b \quad \text{(Sposito, 1989)} \qquad \text{Equation 3.2}$$

where:

$$R_f = k_f C \qquad \text{Equation 3.3}$$

$$R_b = k_b S = k_b \Delta C \qquad \text{Equation 3.4}$$

The use of the equations presented for describing the reaction rate terms assumes that these reaction follow first order kinetics. The value of either k_f or k_b may be found by plotting graphs of the natural log of the concentration in solution over time (Sposito, 1989), however the conditions of the experiment must be such that rate of the reaction not being considered must be negligible. For example, if one were to conduct adsorption experiments to determine the value of k_f, the experiment must be carried out under conditions such that desorption did not occur or was insignificant. One of the major reasons for the occurrence of non-equilibrium conditions is that the reactions involved with adsorption are often different from those which lead to desorption, and thus the rates of the two are different.

3.8 Modeling Phosphorus Movement

Most attempts to model phosphorus movement in the subsurface have been based on the conventional advection-dispersion equation which has the following form:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - V\frac{\partial C}{\partial z} \qquad \text{Equation 3.5}$$

The first term on the right hand side of the equation accounts for loss of a species from a particular location due to dispersion while the second term accounts for losses due to physical movement via flowing water. The velocity term is a function of a given soil's hydraulic conductivity. When considering flow rates, soil water contents must also be considered. This is because a given soil's hydraulic conductivity will vary as the water content of the soil changes. Mansell *et al.* (1977) account for this by including a volumetric water content term in their advection term. Another approach to this problem is to develop a hydraulic conductivity function which accounts for changes in conductivity over the range of expected volumetric water contents. This function can then be used in place of the flow velocity variable. This will be discussed further with the discussion of models which vary from the conventional advection-dispersion approach. Since the velocity term in the above equation is described by a variable rather than a function, use of the equation implies conditions of saturated flow.

Any attempt to reduce complex natural systems to a simple numerical expression must be based on a number of assumptions. The equations presented thus far assume that the area of interest is homogeneous with one conductivity and uniform groundwater flow. Although some of the more complex models available (e.g. MODFLOW) have provisions for describing non-uniform conditions, it is impractical to describe actual conditions on a detailed scale due to spatial variations that are the result of differences in such factors as grain size distribution, soil compaction, or the presence of structures such as root channels. For this reason data is used which represents average conditions for the area of interest. This assumption becomes more critical when dealing with the unsaturated zone due to the likelihood that spatial and temporal variations will exist in the level of saturation of the soil.

When considering phosphorus another term is required, that being one to describe losses due to adsorption and precipitation. Table 3.1 lists some of the variations on this equation put forward by earlier workers to attempt to model phosphorus movement. Note that some workers use the term flux of water (q) in place of velocity of flow (V), however the two terms are basically interchangeable in this case.

The irreversible removal term (Q) can be used to simulate processes such as biological phosphorus uptake or precipitation reactions. In the case of septic system effluent, uptake of phosphorus by soil organisms or plants may be considered insignificant as the area of interest is generally below the biologically active upper soil horizons. Precipitation processes are considered irreversible due to the extremely low solubilities of the precipitates formed.

It is obvious from Table 3.1 that there is little significant difference between any of these equations. The equation used by Tim and Mostaghimi (1989) will account for flow in two directions, but it is based on the same theory as the others. All of these equations assume steady flow rates, uniform water contents, and uniform media along the flow path. The real difference in these equations is the approach taken in defining the adsorption term ($\partial S/\partial t$) or the loss term (Q, ϕ).

The various approaches taken will be discussed below, but first some comments regarding some of the other terms are warranted here. The velocity of flow is considered in all of these equations because this is the major mechanism by which solute is transported in the subsurface. Apart from this, however, there are two other processes by which solute transport occurs, dispersion and diffusion. It is quite difficult to distinguish between these two processes so most workers tend to combine the two into one term and refer to it as apparent dispersivity. In simple terms dispersion refers to the variation in rate of movement between solute particles due to the fact that flow lines exhibit tortuosity as the water molecules move around individual soil particles. Diffusion, on the other hand, is solute movement on a microscopic scale in response to a gradient.

Some of the workers noted in Table 3.1 (Enfield *et al.*, 1981, for example) drop the dispersivity term from subsequent modifications of their equation. They rationalize this by concluding that movement by advection (bulk flow) typically renders dispersion insignificant. Since dispersion is a function of flow length, the possibility of introducing errors by dropping this term becomes greater as distances increase. Diffusion, on the other hand, is relatively insignificant and therefore can usually be ignored with little concern for error.

3.9 Modeling Phosphorus Attenuation

As mentioned in a previous section, the approaches taken towards modeling the rate of change in adsorption can be divided into those based on equilibrium between adsorbed and dissolved species and those which assume non-equilibrium conditions. Tim and Mostaghimi (1989) assume that equilibrium exists between the two forms and support this conclusion by the fact that, due to the relatively low flow rates in the subsurface, abundant contact time exists between the soil and the solution for equilibrium to be established. They cite earlier workers who also reached this conclusion. Referring back to Table 3.1, their general equation was:

$$\frac{\partial(\theta_w C)}{\partial t} = \frac{\partial}{\partial x}\left[D_x \frac{\partial(\theta_w C)}{\partial x}\right] + \frac{\partial}{\partial z}\left[D_z \frac{\partial(\theta_w C)}{\partial_z}\right] + q_x \frac{\partial C}{\partial_x} + q_z \frac{\partial C}{\partial_z} - \rho \frac{\partial S}{\partial t} \pm \phi$$

Equation 3.6

In addition to a term to describe attenuation processes ($\partial S/\partial t$), this equation also contains a transformation term (ϕ). Since they choose to assume equilibrium conditions for adsorption, their attenuation term is:

$$S = K_D C$$

Equation 3.7

Where K_D is the distribution coefficient and is found from isotherms. They also present a term for retardation (R) which is described by:

$$R_d = 1 + \frac{\rho}{\phi} K_D$$

Equation 3.8

Although they choose to assume the existence of equilibrium conditions, they also apply a term to represent the loss or addition of phosphorus. They state that this term is used to describe any change of phase which occurs in the phosphorus. These processes are assumed to follow first order kinetics and are described as follows:

$$\phi = \frac{-(k_4 + k_5)}{\theta_w C} \qquad \text{Equation 3.9}$$

The negative term in the numerator of this equation signifies a loss of phosphorus from the solution pool. If necessary, it would also be possible to include a term to describe the addition of phosphorus due to remineralization of organic phosphorus. Tim and Mostaghimi (1989) choose not to include such a term due to a lack of available data at the time.

Although the above model assumes the establishment of equilibrium between solution phosphorus and that which is adsorbed, it also assumes phosphorus is lost directly from the solution pool through precipitation and organic processes. As mentioned earlier, the importance of biologic activity at depths associated with on-site sewage disposal systems is questionable and, as pointed out by Saini and MacLean (1965), most phosphorus retention associated with organics is the result of the formation of organometallic complexes rather than the conversion of inorganic phosphorus to organic forms.

Tim and Mostaghimi (1989) were not the first to employ a model which considered both equilibrium and non-equilibrium conditions. Cameron and Klute (1977) determined the value of their rate term ($\partial S/\partial t$) in the convection-dispersion equation (see Table 3.1) using a combined equilibrium and kinetic approach. They felt that such an approach will 'average out the total ensemble of reactions occurring in a large number of pores'. Based on this, their rate term was expressed as:

$$\frac{\partial S}{\partial t} = \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \qquad \text{Equation 3.10}$$

They further define each rate term on the right hand side of the equation as follows:

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\theta_w}{\rho} C - k_2 S_1$$ Equation 3.11

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\theta_w}{\rho} C$$ Equation 3.12

Thus:

$$\frac{\partial S}{\partial t} = k_1 \frac{\theta_w}{\rho} C - k_2 S_1 + k_3 \frac{\theta_w}{\rho} \frac{\partial C}{\partial t}$$ Equation 3.13

They applied this model to case studies of earlier workers who had used only an equilibrium or kinetic approach and found their model to predict the actual observations of these earlier workers better than the earlier models. However, they did not determine the various rate constants experimentally, but rather through a trial and error process until the predicted results best fit the observed conditions. There would appear to be two problems with this approach. One, there is no basis for the values of the adjustment parameters other than the fact that they were the values that worked. Also the fact that their sorption term ($\partial S/\partial t$) is composed of three parameters rather than two (for the non-equilibrium approach) or even one (for equilibrium) would make it possible to get a better fitting curve.

Another variation of the combined approach is provided by Mansell *et al.* (1977). Again their overall model is based on the convection-dispersion equation with an adsorption term incorporated. Their first step was to develop equations to describe both linear and non-linear equilibrium as well as non-equilibrium conditions. These equations were as follows:

Linear: $S = KC$ Equation 3.14

Non-linear: $S = KC^N$ where $N > 1$ Equation 3.15

Kinetic: $\frac{\partial S}{\partial t} = \frac{\theta_w}{\rho} k_a C^N - k_d S$ Equation 3.16

These models were used to try to describe observed phosphorus attenuation in two soils from one particular site. These soils were very similar with the only differences being a slight increase in organic matter, iron, and aluminum in one of them. They conclude that the kinetic based model most accurately reproduced their observations for both soils, however they felt that the predictions were not acceptable for the soil with the higher organics and exchangeable iron and aluminum. They note that not all the applied phosphorus was recovered in the effluent and assume some to be irreversibly lost within the soil. Thus, in order to improve the model predictions they added a sink term (Q) as shown in Table 3.1. Irreversible attenuation is assumed to occur through precipitation or chemisorption from either solution phosphorus or from the physically adsorbed phosphorus. They present the following equations to describe this loss:

$$Q = k_c(\theta_w C \qquad \text{Equation 3.17}$$

$$Q = k_s(\rho S) \qquad \text{Equation 3.18}$$

Although the use of a sink term improved the model predictions, they conclude that the model still did not accurately portray the conditions observed for the soil with higher organic, iron, and aluminum contents.

Enfield (1974) uses two variations to describe the sorption term in the convection-dispersion equation. One is based on first order kinetics and has the form:

$$\frac{\partial S}{\partial t} = \alpha(\kappa C - S) \qquad \text{Equation 3.19}$$

The other is an empirical formula expressed as:

$$\frac{\partial S}{\partial t} = aC^{b'}S^{d} \qquad \text{Equation 3.20}$$

The various adjustment parameters are determined with batch sorption experiments. Graphs of sorbed phosphorus versus equilibrium solution phosphorus concentrations are plotted using the results of the batch tests. Regression analyses are then performed on the data in these graphs to determine the value of the various parameters. This process is described in detail in Enfield (1974). Enfield concludes that the equation derived empirically produces better results, however neither produced precise reaction rates. In a later comparison of the two equations (Enfield and Shew, 1975) the superiority of the empirical approach was reaffirmed.

As mentioned in a previous section, Mansell *et al.* (1985) developed a model based on the assumption that physical adsorption and chemisorption (precipitation) occur in series rather than concurrently. This may be expressed as:

$$\theta C \underset{k_2}{\overset{k_1}{\Leftrightarrow}} \rho S_i \underset{k_4}{\overset{k_3}{\Leftrightarrow}} \rho S_{ii}$$

As with most models, this one is also based on convection-dispersion theory with the only real difference being the approach taken towards the rate term for adsorption ($\partial S/\partial t$). This particular model assumes equilibrium conditions exist between the moving solution and the non-moving sorbed phosphorus. This assumption is based on the slow flow rates relative to the reaction rates for sorption. In this case the use of the Freundlich isotherm is deemed appropriate. This isotherm has the form:

$$S = Kc^{n} \qquad \text{Equation 3.21}$$

The variable K is further defined as:

$$K = K_i + K_{ii} = \frac{\theta_w}{\rho}\frac{k_1}{k_2}\left[1 + \frac{k_6}{k_7}\right] \qquad \text{Equation 3.22}$$

As with some of the previously discussed approaches, the expression used to describe the rate term for sorption is made up of two parts, one describing physical adsorption, the other for the second reaction in the series, chemisorption.

$$\rho\frac{\partial S}{\partial t} = \rho\frac{\partial S_i}{\partial t} + \rho\frac{\partial S_{ii}}{\partial t} \qquad \text{Equation 3.23}$$

Where the terms S_i and S_{ii} represent physical adsorption and chemisorption respectively and are defined as:

$$\rho\frac{\partial S_i}{\partial t} = [k_1\theta_w C^n - k_2\rho S_i] - [k_6\rho S_i - k_7\rho S_{ii}] \qquad \text{Equation 3.24}$$

$$\rho\frac{\partial S_{ii}}{\partial t} = [k_6\rho S_i - k_7\rho S_{ii}] \qquad \text{Equation 3.25}$$

Combining these three equations yields:

$$\rho\frac{\partial S}{\partial t} = k_1\theta_w C^n - k_2\rho S_i \qquad \text{Equation 3.26}$$

The various rate constants (k_1, k_2, k_3, k_4) are determined using batch sorption experiments and isotherm theory.

Mansell *et al.* (1985) conclude that the model predictions were close but that the fit could have been better. They attribute the inaccuracy to errors resulting from the use of batch experiments. Overall they conclude that an approach which assumes adsorption and precipitation occur in series is better than one based on simultaneous reactions.

3.10 Differences Between Attenuation in the Unsaturated and Saturated Zones

Much of the existing research dealing with phosphorus attenuation has been conducted by workers in agricultural settings. As a result the available data and resulting conclusions are typically for the unsaturated zone. Studies directly involving septic system research pertaining to phosphorus also tend to mainly consider the reactions that occur above the water table, most likely due to the fact that phosphorus is usually highly attenuated in this zone.

In all likelihood the processes that are responsible for phosphorus attenuation above the water table—adsorption and precipitation—are also the major processes by which it is retained in the saturated zone The following discussion will be directed towards the differences between these processes in each zone. Direct comparisons of similar soils above and below the water table are rare in the literature due to the fact that individual researchers tend to consider only one zone or the other. Generally workers who studied the unsaturated zone look at differences in solid phase soil phosphorus concentrations as one progresses downgradient from a septic field. Workers who consider the saturated zone tend to compare soil water phosphorus concentrations along the direction of flow. Based on this, the comparisons outlined below will tend to be inferred from earlier workers rather than descriptions of actual research.

One major difference between the unsaturated and saturated zones is the level of oxygen in each. The fact that not all of the pore spaces in the unsaturated zone are filled allows for the relative ease of oxygen diffusion throughout this horizon. Oxygen diffusion into the zone below the water table is severely hampered by the presence of water in the pore spaces of the soil. This, along with the very low solubility of oxygen in water at typical groundwater temperatures, acts to limit the availability of oxygen in the saturated zone. A result of this would be lower concentrations of oxidized mineral forms, often cited as a major control in phosphorus adsorption (e.g. Ptacek *et al.*, 1994).

Another significant difference between the two horizons is the rate at which water will move through each. The hydraulic conductivity of a soil decreases dramatically with the level of saturation (Brooks and Corey, 1966 and others). As discussed in section 3.3, the rates at which reactions between phosphorus, soil particles, and other soil-water system constituents must be considered. This is due to the fact that as phosphorus moves with the water, it may move through the system fast enough that reactions cannot occur to a great degree. Thus differing flow rates above and below the water table will result in differences in the significance of these reactions.

Another possibility that must be considered is that the soil near the location of the mean water table depth will actually experience repeated episodes of complete and incomplete saturation in response to water table fluctuations. This would result in periods of low oxygen availability interspersed with periods of abundant oxygen. The effects of this will be discussed below.

As mentioned, Ptacek *et al.* (1994) indicates that oxidized mineral forms (such as Mn(IV)—and Fe(III)—bearing solids) are the strongest phosphorus adsorbents. She also mentions that any process that leads to reduction of these oxidized minerals will also lead to a decrease in the soil's phosphorus adsorption capacity. Further, the movement of incompletely oxidized effluent out of the unsaturated layer and into the saturated zone may lead to the loss of such minerals. Such minerals will be used as an oxidant by the effluent due to the low oxygen concentrations below the water table as compared to those in the unsaturated zone. Based on this it is quite possible that, although the same basic processes lead to adsorption above and below the water table, adsorption may be less efficient under saturated conditions. It should be noted that Ptacek *et al.* refers to complete loss of the oxidized mineral forms via reductive dissolution, rather than their conversion to less stable forms.

As discussed in section 3.3, Kuo and Mikkelsen (1979) conclude that adsorption actually increases in flooded soils. This increase is attributed to the conversion of crystalline iron to amorphous forms as well as a lowering in soil pH, both of which are brought about by flooding .

The difference between the above conclusion and that reached based on Ptacek *et al.* (1994) may be attributed to the conditions which each considers. Kuo and Mikkelsen (1979) look at drastically changing conditions (repeated flooding and drying) which results in periods of high oxygen availability. Ptacek *et al.* (1994), on the other hand, assume fairly uniform conditions under which oxygen availability is quite limited. The availability of sufficient oxygen in the former case would help maintain, and even increase, the phosphorus adsorption capacity of the soil. Greater oxygen availability would result in an increase of oxidized minerals forms which in turn would permit greater phosphorus attenuation.

The approach taken here is that adsorption occurs at a fast enough rate compared to overall flow that the reactions may be considered at equilibrium. Precipitation, on the other hand, is assumed to be a very slow process and thus is described mathematically using a coefficient with the term of inverse time. Since hydraulic conductivity increases with increasing water content, flow rates below the water table would be significantly higher than those in the unsaturated zone. Higher flow rates would move dissolved phosphorus through the system quicker, also resulting in lower precipitation rates.

From the foregoing discussion, it is plausible to expect overall phosphorus attenuation to be lower, for identical soil conditions, under conditions of continuous saturation (as opposed to repeated cycles of saturated and unsaturated conditions). More detailed comparisons between the two horizons would require the collection and analyses of soil samples from each zone. Soils representative of saturated conditions would need to be kept isolated from the atmosphere in order to maintain the low oxygen levels. Conversely, analyses would have to be carried out quickly so that what little oxygen is there does not become depleted prior to the analysis. Comparisons of adsorption and precipitation data could then be made between the two environments.

The approach taken towards modeling phosphorus attenuation and movement in the saturated zone would be much the same as that described for unsaturated conditions with a few exceptions. Obviously differences in precipitation rates and adsorption capacities would be accounted for in different values for each of these parameters. As well equations for determining hydraulic conductivity from soil water contents (such as the Richards Equation) would not be required. Under saturated conditions flow rates would simply be described by the saturated hydraulic conductivity value.

3.11 Summary

The two main processes by which phosphorus is removed from solution in the subsurface include adsorption and precipitation. Adsorption occurs on the surface of soil particles. These reactions occur fast enough that equilibrium is established between the adsorbed phosphorus and that still in solution. Adsorption reactions are described mathematically using isotherms such as the Langmuir Isotherm. Precipitation reactions, on the other hand, proceed very slowly and do not reach equilibrium. These reactions follow first order kinetics and may be described mathematically using a first order rate constant.

Many environmental and soil related factors control how effective the above processes attenuate phosphorus. Environmental factors include such parameters as oxygen levels in the subsurface, soil water saturation levels, and temperature. Soil properties such as grain size distribution, pH, and soil mineralogy.

Decreasing oxygen levels tend to result in lower phosphorus attenuation since both adsorption and precipitation proceed best in the presence of oxidized minerals. Water content may also indirectly affect these reactions because as saturation levels increase oxygen levels decrease. This is because atmospheric oxygen has less chance to enter the soil zone under saturated conditions. Water levels may also increase phosphorus adsorption, however this usually requires repeated wetting and drying of a soil. Weathering of soil minerals in the presence of water breaks them down resulting in greater surface area per unit volume of soil. Upon the return of unsaturated conditions and increased oxygen levels, this greater surface are will provide more adsorption sites. Many workers have referred to this as the regeneration of adsorption sites.

The most critical soil property is pH. In the pH range of typical groundwater systems, lower pH values result in more positively charged surfaces on minerals present in the soil.

The dominant phosphate forms in this pH range are anions, thus positively charged mineral surfaces play a significant role in adsorption.

Iron, aluminum, and calcium figure prominently in both adsorption and precipitation reactions. Thus soils with higher concentrations of these minerals will be more effective at attenuating phosphorus.

A soil's ability to adsorb phosphorus is also a function of its grain size distribution. Finer grain soils contain more surface area per unit volume of soil than coarser soils. This increased surface are provides more potential adsorption sites. Some workers have, however, attributed the increased adsorption seen in finer soils to the fact that finer soils particles, such as clays, tend to be aluminum rich.

A soils' hydraulic conductivity will be important to precipitation reactions. Due to the very low rates of these reactions it may be possible for water to move the phosphorus through the system quickly enough that the reactions may not be able to proceed as effectively as they could at slower flow rates.

In addition to these attenuation reactions, it is possible for opposing reactions to result in the remobilization of phosphorus. Adsorbed phosphorus may become mobile through desorption reactions. Drastically changing conditions, such as increased hydraulic loadings, higher water table elevations, lowering of oxygen levels in the soil system, or increasing phosphorus concentrations can lead to the onset of desorption. Such conditions may also result in dissolution of previously precipitated phosphate minerals, although here the effects may be less drastic due to the very low solubility of these minerals.

All of these factors must be considered in any attempt to accurately simulate the processes using computer simulation models. Other than water table fluctuations, environmental and soil properties are not likely to vary significantly. Therefore these parameters will be accounted for in laboratory experiments designed to quantify the precipitation and adsorption rate terms, provided these experiments are carried out under conditions which accurately portray the actual field conditions. In addition to these reaction rate terms, properties such as soil grain size distribution, bulk density and porosity, and hydraulic loads and phosphorus loads to the septic field must also be defined for the models described in this section. Finally the relationship between the level of saturation of a soil and its corresponding hydraulic conductivity must be described in order to accurately simulate unsaturated zone conditions.

4. COMPUTER SIMULATION OF SOIL PHOSPHORUS REMOVAL

4.1 Introduction

Section 3 describes results of attempts by many researchers to represent the complex processes of phosphorus movement and removal by mathematical relationships. Some of these relationships have been incorporated into computer simulation models that are generally available and have the potential to represent the systems that are of interest in this study. This section describes models applied in this work, and indicates how these have been used here. Section 5 describes the modeling and modeling results.

Each of these models is available commercially, or from the US Environmental Protection Agency (EPA) or the US Geological Survey (USGS). All are widely used in a variety of applications related to groundwater flow and chemistry. They are not believed to have been applied in the manner described here.

Section 3 indicates that phosphorus is attenuated by reactions involving adsorption or precipitation. Cameron and Klute (1977) suggest that phosphorus is attenuated by a suite of reactions intermediate between these two extremes and that the use of a term for adsorption and one for precipitation will average out the results of these various reactions. It is assumed that adsorption processes quickly reach equilibrium and that precipitation follows first order kinetics.

As the effluent from a septic system migrates through the subsurface it passes through two distinct environments: the unsaturated zone until it encounters the water table, whereupon it enters the saturated zone. In the unsaturated zone water will move predominantly in the vertical direction in response to gravity. Upon reaching the saturated zone the effluent will then migrate along the direction of groundwater flow. Due to the similar densities of septic system effluent and the groundwater little mixing will occur across the direction of flow. The tortuous flow path which the groundwater and effluent follows as it moves around individual soil particles will result in some movement across the flow direction through dispersion.

Each of these zones must be modelled separately due to the differences that exist between them. The first step taken in this study is to model the movement and attenuation of phosphorus as the effluent travels between the septic field and the water table. This involves modeling unsaturated flow over distances of a few meters or less. Once steady state conditions are achieved, the output of this modeling, consisting of phosphorus concentration and water flux at the bottom of the unsaturated zone, becomes inputs to the saturated zone model.

The next step is to model the horizontal movement of phosphorus under saturated conditions.

The movement of water will vary within each zone, because hydraulic conductivity varies with the degree of saturation. This variation will affect precipitation reactions in particular as these reactions proceed at a slow rate. If the solute is quickly carried through the system it will have less chance to react with the soil particles and form precipitates. Adsorption reactions will be less affected as they are assumed to reach equilibrium quickly.

Other changes will also be brought about by the constant presence of water below the water table. For example, oxygen is abundant in the unsaturated zone due to the ease with which air can diffuse into the pore spaces. This supply of oxygen will usually be in excess of what is required by the attenuation reactions. In the saturated zone however, water filled pore spaces will inhibit oxygen diffusion thereby reducing its availability to chemical reactions. This reduction in oxygen availability would also limit the presence of oxidized mineral forms, often cited as a major control in phosphorus adsorption.

It should be noted that the coefficients commonly used in models to describe adsorption and precipitation characteristics of soils are derived from experiments that use fresh soil samples. These characteristics do not necessarily represent results of changes in soil properties over time, as a result of processes discussed in Section 3 (Ptacek, *et al.*, 1994), and the models discussed here cannot simulate these processes.

4.2. Modeling the Unsaturated Zone

After careful consideration, the model CHEMFLO (Nofziger *et al.*, 1989) was chosen for modeling phosphorus removal in the unsaturated zone. This model was developed as a tool for simulating chemical and water movement in groundwater, and allows chemical processes to be modelled in a straightforward and simple manner. The model has many positive attributes including its ease of use, its ability to be used with even very low level personal computers, and the fact that it comes as a ready to use package. CHEMFLO will allow simulation of the movement of any chemical in both the unsaturated and saturated zone.

4.2.1 CHEMFLO Structure

The model is based on two partial differential equations. These consist of an equation for describing water movement, coupled to one that describes chemical movement and attenuation along the flow path. The movement of water in the unsaturated zone is modeled using the equation of Richards (1931):

$$B_{(h)}\frac{\partial h}{\partial t}=\frac{\partial}{\partial z}\left[K_{(h)}\left(\frac{\partial h}{\partial z}-\cos(A)\right)\right] \qquad \text{Equation 4.1}$$

$B_{(h)}$ is the specific water capacity. $K_{(h)}$ is the hydraulic conductivity as a function of matric potential, h, which is a measure of the degree of soil saturation; i.e., the rate of flow through the soil is a function of the degree of saturation. A is the angle of flow direction relative to the vertical

Equation 4.2, describing chemical movement, is derived from the convection-dispersion equation (Equation 3.5).

$$\frac{\partial}{\partial t}(\theta C+\rho S)=\frac{\partial}{\partial z}\left[\theta D\left(\frac{\partial C}{\partial z}-qC\right)\right]-\alpha\theta C-\beta\rho S+\gamma\theta$$

Equation 4.2

The model is based on the assumption that equilibrium exists between the sorbed and dissolved phases of a chemical (see Section 3..9, Tim and Mostaghimi, 1989); thus the sorbed concentration at any time and place is determined by $S = K_D C$, where S and C are concentrations of sorbed and dissolved contaminant, and K_D is a phosphorus partition coefficient.

Combining this equation with Equation 4.2 yields:

$$\frac{\partial}{\partial t}(\theta RC)=\frac{\partial}{\partial z}\left[\theta D\left(\frac{\partial C}{\partial z}-qC\right)\right]-(\alpha\theta+\beta\rho K)C+\gamma\theta$$

Equation 4.3

where the retardation factor is defined as:

$$R = 1+\frac{\rho K}{\theta}$$

Equation 4.4

and l= bulk density, q=soil water content, D= dispersion coefficient, and α and β are first order degredation rate constants for the liquid and solid phases.

Although the model does not consider precipitation explicitly, the process may be simulated using the degradation rate terms, assuming the process follows first order kinetics. The zero order constant γ is not required for phosphorus modelling. The way in which the equations are written allows for the exclusion of any of the rate terms α, β, or γ. This allows the user to apply the conclusion of Reneau *et al.* (1989) or van Riemsdijk *et al.* (1984) that precipitation becomes insignificant at low phosphorus concentrations. Precipitation from the adsorbed phosphorus phase was ignored in this study, by assigning a value of zero to β. This follows the method of earlier workers such as Mansell *et al.* (1977), and Tim and Mostaghimi (1989), who consider this process unimportant for phosphorus.

4.2.2 CHEMFLOW Model Inputs

The model allows the user to choose from a variety of boundary conditions for both the water and the chemical. These conditions include such things as constant water potentials (heads) or constant fluxes (flow) at both the upper and lower boundaries. The most useful boundary conditions for the chemical consist of a constant concentration of inflowing solution at the upper boundary and a situation of mass flow without dispersion (the chemical moves out of the soil with the flowing water) at the lower boundary. The boundary conditions may be altered at any time during the running of the model. This feature allows the user to simulate such things as pulse inputs of water and/or chemical.

The inputs required for modeling water movement consist of the length of the soil column (thickness of soil layer for problems of vertical flow), the direction of flow relative to the vertical direction, the specific boundary conditions (either potentials or fluxes), and the matric potential throughout the soil. The matric potential may be set as uniform throughout the soil column or individual values may be entered at any interval along the direction of flow. Among the inputs for modeling chemical movement are the bulk density of the soil, the water-soil partition coefficient for the chemical, diffussivity and dispersivity terms, and the various rate constants as described above.

Nofziger *et al.* (1989) list a number of limitations associated with this model. One of the most significant is that the soil is assumed to be homogeneous, but this assumption is common to most models.

4.2.2.1 Determining the Phosphorus Partition Coefficient

Other problems are related to the attenuation equation used in the CHEMFLO model. The equation, cited in section 3.9, is

$$\frac{\partial S}{\partial t} = K_D \frac{\partial C}{\partial t} \qquad \text{Equation 3.14}$$

This linear equation establishes no upper limit on the amount of adsorbed chemical. In addition, limited information is available to establish values of the phosphorus partition coefficient K_D .

These limitations were overcome by establishing a relationship between Equation 3.14 and the Langmuir Isotherm. Much of the available literature (e.g. Shah *et al.*, 1975; Novak *et al.*, 1975; Enfield *et al.*, 1981, van der Zee *et al.*, 1989) represents phosphorus adsorption using the Langmuir Isotherm.

The partition coefficient may be determined from the Langmuir Isotherm equation, which was introduced earlier as:

$$S = \frac{bKC}{1+KC} \qquad \text{Equation 3.1}$$

where b is the maximum amount of sorbed phosphorus, and K relates to the energy with which the phosphorus adsorbs onto soil particles.
Combining the previous two equations yields:

$$K_D = \frac{bK}{1+KC} \qquad \text{Equation 4.5}$$

Applying this equation with the Langmuir Isotherm variables, the CHEMFLO partition coefficient can may be determined.

In addition, the Langmuir Isotherm variable b establishes the limiting value of sorbed phosphorus.

To apply the preceding information with CHEMFLO, advantage can be taken of the model's ability to allow the user to view the amount of chemical adsorbed over time; thus the model can be run until the maximum capacity of the soil is reached.

To verify this approach, a series of CHEMFLO runs were conducted, using K_D values based on literature values of Langmuir Isotherm K and b, and corresponding soil properties. In every case the mass of sorbed phosphorus in CHEMFLO, when steady state conditions were defined by the point in time at which phosphorus concentrations no longer increased at any point in the soil column, corresponded to the Langmuir b value.

4.2.2.2 Hydraulic Conductivity and Water Content Functions

CHEMFLO provides a choice of four separate equations for describing the water content function and five choices for the hydraulic conductivity function. These equations are based on the results of earlier workers (Brutsaert, 1966; Haverkamp *et al.*, 1977, van Genuchten, 1980; Brooks and Corey, 1964).

For this study the approach used by van Genuchten (1980) was chosen, because it widely used, and because the adjustment parameters required in the equations can be determined from soil properties as an alternative to laboratory experiments.
The water content function is:

$$\theta_h = \theta_r + \frac{\theta_s - \theta_r}{\left\{1 + \left(a|h|\right)^b\right\}^m} \qquad \text{Equation 4.6}$$

and the hydraulic conductivity function is:

$$K_h = K_{sat} \frac{\left\{\left[1 - \left(a|h|\right)^{b-1}\right] * \left[1 + \left(a|h|\right)^b\right]^{-m}\right\}^2}{\left[1 + \left(a|h|\right)^b\right]^{m/2}} \qquad \text{Equation 4.7}$$

where: $m = 1 - 1/b$

In the above equations the term q denotes the volumetric water content for a given condition, K refers to hydraulic conductivity, and h is the matric potential. The subscript h refers to the specific matric potential in question, s indicates saturated conditions, and r indicates residual water levels. In all cases $\theta_h = \theta_s$ and $K_h = K_{sat}$ when the matric potential is greater than or equal to zero (matric potential = 0 at the point of saturation). The parameters a and b are adjustment parameters derived by fitting curves to observed water retention data from laboratory experiments.

If the approach of either Brooks and Corey (1964) or van Genuchten (1980) is deemed valid for a particular situation the model SOILPROP[1] may be used to estimate the adjustment parameters from grain size distribution data, soil bulk density, and porosity, rather than through the use of water retention experiments.

4.2.3 Verification of CHEMFLO Prediction

The suitability of this model for predicting the movement and attenuation of phosphorus was determined by attempting to use it to reproduce the observations of Mansell *et al.* (1977). All of the inputs to the model, such as hydraulic conductivity, hydraulic loading rate, solution phosphorus concentration, partition coefficient for phosphorus, and the precipitation rate constant, were input as supplied by Mansell *et al.* (1977). The exception was the value of the van Genuchten adjustment parameters, which were determined with SOILPROP using the physical soil properties (grain size distribution, soil bulk density, porosity) also supplied in the earlier paper. As shown in Figure 4.1 the model accurately reproduced the conditions in the earlier column experiments.

4.2.4 CHEMFLO Model Inputs

The first requirement for defining a problem is to describe the soil. This information consists of the saturated and residual water contents, saturated hydraulic conductivity, and selection of functions for describing the hydraulic conductivity and water content.

Once a soil is defined the various other parameters required to run the model must be input. For a problem involving the movement of water and chemical, the following data is required:

- length of soil column and orientation Z(vertical, horizontal, or specified angle)
- boundary conditions for water at upper and lower column boundaries (specified flux rates or matric potentials)
- matric potential within soil column at start of simulation
- boundary conditions for chemical at upper and lower column boundaries and concentration profile of chemical within soil prior to start of simulation
- bulk density of soil
- dispersivity coefficient for water in the soil system

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[1] Environmental Systems and Technologies, Blacksburg, Virginia, USA.

- soil:water partition coefficient for chemical, diffusion coefficient of chemical in water, first order degradation rates for chemical in both liquid and solid phases within the soil system
- time to be simulated and mesh sizes for grid in both time and depth.

4.3 Modeling The Saturated Zone

A review of models currently available for simulating the transport of solutes under saturated conditions led to selection of MT3D (Zheng,1990), a module designed to be used with the USEPA-supported flow model MODFLOW. The model is applicable to saturated conditions only. MT3D can simulate water and chemical movement in three dimensions,.

Although CHEMFLO can be used to model the saturated zone, it has limitations when compared with MT3D: it is limited to a column length of 10 meters, and it can represent only one contamination source.

For the preliminary analyses reported here, Two-D (MacQuarrie and Sudicky, 1991), a simpler but easier to use alternative to MT3D, was applied.

4.3.1 MT3D

Zheng (1990) presents the underlying equations on which MT3D is based. The equations used to describe flow, adsorption, and precipitation are very similar to those used in CHEMFLO.

Describing flow mathematically in the saturated zone is much simpler than in the unsaturated zone, because the volumetric water content of the soil does not have to be considered. Although MT3D is applicable to any chemical, in the following discussion all concentrations are shown as relating to phosphorus.

The overall equation on which the model is based has the form:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) - \frac{\partial}{\partial x}(vC) + \frac{q}{\theta}\overline{C_s} + \sum R \qquad \text{Equation 4.8}$$

The equation includes terms for describing the loss or gain of contaminant from sources or sinks in the area of interest. This allows the user to introduce a contaminant solution to the area of interest (such as a septic system) or to remove some of the solution from the area (such as a withdrawal well). Apart from the terms representing advection and dispersion, the other significant term is the chemical reaction term. If the chemical reactions are assumed to include only adsorption, which reaches equilibrium, and precipitation, which follows first order kinetics, the reaction term (R) may be further defined as:

$$\sum R = \frac{\rho}{\theta}\frac{\partial \bar{C}}{\partial t} - \lambda\left(C + \frac{\rho}{\theta}\bar{C}\right) \qquad \text{Equation 4.9}$$

Although the above equation shows only a single reaction rate term for precipitation from both the dissolved phase and the adsorbed phase, Zheng (1990) indicates that the model will accept input for two different rate terms to describe the loss of solute from each phase separately.

As with CHEMFLO, the only reactions that can be simulated with MT3D are equilibrium controlled sorption and first order irreversible reactions, such as chemical precipitation. This model differs from the approach of CHEMFLO in that it will recognize non-linear sorption reactions described by either Langmuir or Freundlich isotherms. This avoids the need to estimate a linear phosphorus partition coefficient as required by CHEMFLO (Section 4.2.2.1). The equations describing the various sorption and precipitation reactions are similar to those already introduced.

This model is similar to CHEMFLO in that all of the variables such as hydraulic conductivity, soil bulk density, hydraulic loading rates, contaminant (phosphorus) concentration, and the terms describing the various reactions are input into the model. It is necessary to provide a thickness for the aquifer. The top of the area of interest can be set as the water table.

The models MT3D and MODFLOW look for certain input files when solving a problem and expect to find the data in these files in a very rigid format. The use of the preprocessor MODELCAD[2] makes defining the problem much simpler than manually entering the data into these input files.

4.3.2 Two-D

To obtain a first approximation to a solution a simpler model, Two-D (MacQuarrie and Sudicky, 1991), can be used. The equations on which this model is based are similar to those described above for MT3D and, for the chemical reactions, CHEMFLO. Two-D models in only two dimensions.

This model has a few limitations compared to MT3D. These include the assumptions that the geometry of the contaminant source is regular, contaminant concentration is constant, that the aquifer is thin with no vertical variations in concentration, and that there is only one contamination source.

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[2] Gerharty and Miller, Inc., Reston, Virginia, USA.

5. APPLICATION OF COMPUTER SIMULATION MODELS - SENSITIVITY ANALYSES

5.1 Introduction

Section 4 outlines a modelling approach, using CHEMFLO and MT3D, for simulation of phosphorus movement and removal in the subsurface. This approach would be applied by using CHEMFLO to represent unsaturated zone effects on one or more representative on-site sources, with any variations in soil properties or depth. The saturated zone of the watershed discharging to a lake or its tributaries would be represented by MT3D; the output(s) from CHEMFLO would be added at appropriate locations in the watershed.

In anticipation of the application of this approach, sensitivity analyses were undertaken, to explore the response of a range of hypothetical soils, representing soils in which septic systems might be installed, to variations in input parameters. CHEMFLO was used to represent the unsaturated zone. Two-D was used to examine the saturated zone, because of its capability to rapidly examine a variety of input scenarios.

Inflow from the unsaturated zone from a single on-site system, simulated by CHEMFLO, was added to the saturated zone, and assumed in Two-D to move in a thin layer at the top of the aquifer. As mentioned earlier it is assumed that mixing of effluent and groundwater is limited to a few meters at most due to their similar densities.

Similar values for all of the variables describing the soil and the chemical reactions were used for both the unsaturated and saturated zones.

The initial soil phosphorus concentration was set equal to zero. Soil phosphorus concentrations are typically in the 1 ppm range (e.g. Paul and Clark 1989). It was found that these values resulted in no change to the steady state solution to the model due to the insignificance of the levels as compared to the phosphorus concentration in septic tank effluent.

5.2 Unsaturated Zone

The assumed depth of the unsaturated zone was 90 cm., the minimum separation distance between disposal field and groundwater that is specified by the Nova Scotia Department of Health, 1988.

In light of the success which was achieved using CHEMFLO to simulate the conditions reported by Mansell *et al.* (1977), this soil was chosen as one of the hypothetical soils. The soil is very sandy (Soil 1 - Table 5.1) and is in the upper grain size range for material acceptable for septic fields. A silty clay (Soil 2 - Table 5.1) described by McCallister and Logan (1978) was chosen to represent the finer grained extreme of suitable material. The hydraulic loading rates used for each soil were based on the guidelines of the Nova Scotia Department of Health, 1988.

Sufficient information to make predictions using the sandy soil was available in Mansell *et al.* (1977), or in Tim and Mostaghimi (1989), who also used the soil described in the earlier paper. In the case of the silty clay however, some of the parameters had to be estimated or assumed, for example the bulk density of the soil was assumed using a value provided in another study (Dethier, 1988) for a soil with similar grain size distribution. Although this parameter will vary with soil mineralogy, the estimate does provide a possible value. The porosity and hydraulic conductivity were estimated using the model SOILPROP described earlier. The porosity is determined using the grain size data and bulk density assuming the individual particles have a density of 2.65 g/cm^3.

The coefficients for describing the chemical reactions in the sandy soil were taken from Mansell *et al.* (1977) and Tim and Mostaghimi (1989), while those for the silty clay were determined using the information provided or were assumed. The partition coefficient was calculated using the Langmuir Isotherm coefficients, as described in Section 4.2.2.1, using the Langmuir data supplied by McCallister and Logan (1978).

It is not possible to use the data supplied by McCallister and Logan (1978) to estimate a value for the first order rate constant that describes the precipitation of phosphorus from solution, because this term is highly dependent on the types of minerals present in the soil and their concentrations. Tim and Mostaghimi (1989) present a value of 0.1 hr^{-1} for the sandy soil and this value was also applied to the silty clay soil. Additionally, a value of 0.25 hr^{-1} was assumed for the silty clay based on the fact that finer grained soils typically have a greater concentration of iron and aluminum bearing clays than coarser grained soils. Since these minerals play a significant role in phosphorus precipitation, their increased concentration would result in a larger value of the precipitation rate constant.

The data presented in Table 5.1 was input into CHEMFLO for each of the two soils. For each soil one run was conducted assuming no phosphorus precipitation occurred (Figures 5.1 and 5.2).

The assumption of no phosphorus precipitation always resulted in a steady state situation in which the phosphorus concentration leaving the unsaturated zone equaled that entering the soil in the effluent. This agrees with the conventional wisdom, which states that if adsorption were the only mechanism operating, a solid phase concentration would eventually be reached after which no more phosphorus is attenuated. The phosphorus concentration entering the groundwater equals that in the effluent after approximately 1125 hours (46 days) for the sandy soil and almost 105,000 hours (about 12 years) for the silty clay. The slow rate of phosphorus movement in the silty clay as compared to the sandy soil can be attributed to the much lower loading rate in the former as well as its higher partition coefficient.

In addition to the run assuming no precipitation, another run was conducted for the sandy soil assuming a first order precipitation rate constant of 0.1 hr^{-1}. The addition of this term drastically reduced the steady state phosphorus concentration leaving the unsaturated zone. As can be seen in Figures 5.3 and 5.4, this concentration decreases from just under 1 mg/L at a depth of 30 cm below the trench to about 0.009 mg/L (9µg/L) at a depth of 90 cm.

For the runs described in Figures 5.5 to 5.7 phosphorus concentrations at the 30 cm and 90 cm levels were equal to or less than 0.001 mg/L (1 µg/L). Results of these runs have therefore been expressed as the variation of the steady state phosphorus concentration with depth.

Since no precipitation rate term was available for the silty clay, two values were assumed, one set equal to that given for the sandy soil (0.1 hr^{-1}) and one equal to 0.25 hr^{-1}. Figures 5.5 and 5.6 show that, regardless of which of these two values is used, no phosphorus reaches the groundwater for this situation. In fact neither case produces phosphorus concentrations above 0.001 mg/L (1 µg/L) at the 30 cm depth.

An additional run was conducted for the silty clay, this time setting the upper flux boundary for water at 0.10 cm/hr. This was done to see what effect an increase in the hydraulic load due to rainfall might have on phosphorus movement. The lower phosphorus precipitation rate constant of 0.10 hr^{-1} was used here. The results (Figure 5.7) show that even though the phosphorus migrates further in response to the higher hydraulic load, there is still no phosphorus reaching the water table.

Figure 5.8 indicates the effect on phosphorus removal of variations in the phosphorus precipitation rate constant K_l for the sandy soil. The value assumed for Run 2 was 0.1 hr^{-1}. The run was repeated with larger and smaller values of K_l. The figure also indicates the effect of soil depth on phosphorus removal, and suggests that above a K_l value of 0.05 hr^{-1}, removal at the 90 cm level approached 100 percent for this particular situation.

5.3 Saturated Zone

The values for water flux and phosphorus concentration provided by CHEMFLO for the bottom of the unsaturated zone were used as the initial conditions for the saturated zone modeling.

Because no dissolved phosphorus remained at the bottom of the unsaturated zone in the silty-clay soil., the only soil for which further modeling could be carried out was the sandy soil. The results of the unsaturated zone modeling for this soil (Figure 5.9) indicate that, once steady state conditions are achieved, the phosphorus concentration in the partially treated effluent reaching the groundwater is 0.009 mg/l. The flux rate at this point (neglecting additions from sources other than the septic system, such as rainfall) is 0.17 cm/hr; this is the same as the effluent loading rate because no change in water storage occurs within the unsaturated zone.

Results are shown in Figure 5.9. Assumed values for the retardation factor, R_f (a measure of adsorption, c.f. equation 4.4) and the precipitation rate term, K_l are indicated on each graph.

Comparing A. and B., with the same value of K_l, the phosphorus movement is significantly reduced—to a concentration after 20 years of 1 μg/L at 20m instead of 120 m—when K_l is increased from zero to the value reported by Mansell *et al.* (1977).

In C, it can be seen that a small change in R_f makes no appreciable reduction in phosphorus movement.

In D, it can be seen that to achieve the same effect achieved by consideration of phosphorus precipitation, the value of R_f must be increased by more that 1700 times.

In light of the very short distance over which phosphorus is seen to move under these assumed conditions, further modeling of the cumulative effects of a number of septic systems was deemed unnecessary, due to the fact that the phosphorus did not move far enough for interaction to occur.

5.4 Discussion

The results support the conclusion, often reached in the literature, that although the movement of phosphorus is very restricted in the unsaturated zone, there is potential for its migration to the saturated zone under appropriate conditions. This further supports the site-specific nature of phosphorus attenuation problems and reinforces the need for a general, easy to apply model capable of predicting its movement. At the very least this exercise indicates that the general assumption that all phosphorus within 300m of a lake will reach the lake is not a valid one to make.

Modeling of these hypothetical situations also shows that precipitation is by far the more important of the two processes involved in phosphorus attenuation. Fairly modest changes in the value of the term used to describe this process result in drastic changes in the distance of phosphorus migration. It is possible that situations reported in the literature in which phosphorus is seen to migrate over great distances are cases where factors such as soil chemistry result in less efficient precipitation. Based on this observation, studies involving actual soils must determine this variable as accurately as possible.

It should be remembered that the terms used to describe adsorption are determined empirically from relatively small soils samples which are assumed to be representative of the overall field conditions.

6.0 EXPERIMENTAL AND FIELD RESULTS

6.1 Methodology

6.1.1 Data sources

An ongoing applied research program conducted by CWRS provided a source of both experimental and field results related to phosphorus removal from on-site effluents. In addition, plans were made to obtain samples from a number of field sites, intended to provide information about phosphorus contributions from on-site systems in conditions representative of Atlantic Canada.

6.1.2 Analytical Procedures

All project samples were analyses for dissolved phosphorus, assuming that in a groundwater environment all phosphorus would be in this form. Dissolved phosphorus was determined as total dissolved phosphorus (TDP) or soluble reactive phosphorus (SRP). SRP is considered to be the proportion of TDP that is more readily available to plants. TDP is generally used in modeling of lake response to phosphorus loads, because it correlates better with chlorophyll a concentrations, and produces more reliable results.

Initial project field samples were analyzed for both TRP and SRP, with the expectation of determining if or how these phosphorus forms changed in groundwater. The analytical procedure in each case was based on a very sensitive ascorbic acid technique used by CWRS for determination of low concentrations of phosphorus in surface waters. Initial samples from this project, analyzed by this technique, produced anomalous results for groundwater, in that soluble phosphorus concentrations in some samples exceeded total phosphorus results. Exchange of reference samples with local laboratories produced similar results using this technique.

Discussions with Environment Canada laboratories at Moncton and the Canada Centre for Inland Waters led to evaluation and adoption of the stannous chloride method[3]. This method produced consistent results for groundwater samples, and is equally sensitive; the lowest reporting limit is 0.001 mg/L. Project field samples after 1992 were analyzed using this method.

The change from one method to the other is not considered to invalidate earlier TDP results obtained using the ascorbic acid method; results by both methods are comparable. The change is intended to eliminate inconsistencies that arose when some SRP results were somewhat higher than TSP values for the same samples. The inconsistencies were not apparent when the new method was used.

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[3] Canada Centre for Inland Waters, National Centre for Environmental Testing, Stannous Chloride Technique for Total and Soluble Reactive Phosphorus.

Some results cited here are from laboratory model samples that were analyzed by a commercial laboratory that uses the ascorbic acid method, for SRP, with a lower reporting limit of 0.01 mg/L.

6.1.3 Soil Analyses

6.1.3.1 Physical Soil Properties

During installation of piezometers (discussed in the next section) soil samples were collected at each site. Samples were either collected when a change in the nature of the soil was noted or, if no change was noted, representative samples were collected approximately every metre. Physical descriptions of each soil are described in the sections dealing with each site.

The chemical transport models (Chemflo and MT3D) chosen for this study require inputs such as soil bulk density and porosity. Porosity was determined using the equation $n = \left(1 - \frac{\rho_s}{\rho_b}\right)$ where n is porosity, ρ_s is the density of the soil particles, and ρ_b represents the overall soil bulk density. The latter two parameters were determined for each soil using standard soil analytical procedures such as those described by Bowles (1978).

Unsaturated zone modeling with the Chemflo model requires terms for describing flow under unsaturated conditions as well as the residual water content of the soil (the amount of water which the soil will retain under drainage by gravity only). For this study it was decided that the equations described by Van Genuchten (1980) would be used to describe unsaturated water movement. The computer model Soilprop (Environmental Systems and Technologies) was used to estimate each of these terms. The inputs to this program consist of grain size distribution data, porosity and soil bulk density. Grain size distributions were determined through sieve analyses following the procedure outline by Bowles (1978) for the grain size fraction with diameters greater than 0.075mm. The distribution of particles with diameters smaller than 0.075mm was determined using a Melverne Particle Analyzer at the Department of Mining and Metallurgy of The Technical University of Nova Scotia. The combined results of the grain size analyses are shown in Table 6.1 and Figures 6.1 to 6.4.

Once the grain size distribution data, bulk density, and porosity were known for each soil, the residual water content and van Genuchten coefficients describing unsaturated flow were determined using the Soilprop program.

The method used for construction of piezometers interfered with attempts to determine the saturated hydraulic conductivity of the various soils, therefore another approach was deemed necessary. One method for estimating hydraulic conductivity is to use the Hazen formula (e.g. Freeze and Cherry, 1979) which has the form $K_s = cd_{10}$ where K_s is the saturated hydraulic conductivity, d_{10} is the grain size diameter at which ten percent of the particles are finer, and c is the Hazen coefficient. This equation is most valid for soils consisting predominantly of sand and the Hazen coefficient typically varies between 0.8 and 1.2 but is generally assumed to be 1.0 (Freeze and Cherry, 1979). This approach produced what were felt to be unrealistically high hydraulic conductivities, most likely due to the fact that the soils in this study are predominantly silt and clay sized particles outside of the range most suitable to the Hazen formula. Attempts to determine in-situ hydraulic conductivity at each site using a falling head permeameter ('Guelph Permeameter') met with limited success for two reasons. Firstly the use of a falling head permeameter is not possible below the water table or for horizons deeper than 50cm at most (due to the size of the permeameter). Secondly many of the sites studied here contained abundant cobbles and boulders which interfered with attempts to use the permeameter. As shown in Table 6.2 for those sites where the permeameter could be employed, hydraulic conductivities were determined which were an order of magnitude lower than those estimated using the Hazen approach. The lower conductivities are more in line with typical literature values for material containing abundant silts and clays (e.g. Freeze and Cherry, 1979) are deemed to be more accurate. Based on this the hydraulic conductivities used in this study are all an order on magnitude lower than those predicted using the Hazen approach.

6.1.3.2 Phosphorus Adsorption Isotherms

Phosphorus adsorption isotherms were determined for each soil using a slight modification of the approach presented by Ballaux and Peaslee (1975). This approach consists of adding a known quantity of soil to a known volume of solution at a given concentration. Any phosphorus lost from the solution is assumed to be adsorbed by the soil. The experiments are carried out over a short enough time span that adsorption is allowed to proceed but precipitation remains insignificant.

For this study 1 gram of soil was added to 20ml of solution containing 0, 25, 50, 100, 200 or 250 mg/l of phosphorus. The solution was buffered to maintain a pH of 7.0. Samples representative of saturated conditions were purged with nitrogen to represent conditions below the water table in respect to oxygen levels. The samples were then shaken continuously for 23 hours at a temperature of 10°C. This temperature differs from most previous studies which were typically conducted at 20°C. It appears that the higher temperature is often used since most early research into phosphorus adsorption was conducted by agricultural scientists concerned about soil fertilization requirements. A temperature of 20°C would more closely represent the average temperature of a surface soil during the growing season. In contrast measurements taken during this study show a temperature of 10°C to be more representative of conditions below the surface layer. Groundwater temperatures were measured using a Solinst T4 temperature probe.

After 23 hours the samples were centrifuged and then filtered. This differs from the approach of Ballaux and Peaslee (1975) who only used centrifugation to separate the soil from the supernatant. In this study the abundance of clays in the soils reduced the effectiveness of centrifugation alone and thus the samples were filtered through 1 μm glass fiber filters. Prior to filtration the soil-solution mixture was centrifuged for approximately 5 minutes to remove as much of the soil as possible and minimize clogging of the filters.

The supernatant was then analyzed using the stannous chloride routine described earlier.

All equipment and sample bottles used were acid washed using a solution of 10% sulphuric acid and rinsed with de-ionized water to assure no extraneous phosphorus was introduced during the procedure. Duplicates, blanks, and control samples of known phosphorus concentration were employed to assure the reliability of the analyses.

The results of the adsorption experiments are shown in Table 6.3. The exact location of each soil and a description of each is presented in section 6.2.2 which discusses the field sites in more detail The mass of phosphorus lost to the soil can be calculated as the difference between the initial and final concentration of each solution multiplied by the volume of solution used. The solution at the end of 23 hours is assumed to be at equilibrium with the soil and this concentration is used to determine the Langmuir adsorption coefficients. These coefficients were determined by fitting curves to the observed data using the commercial curve fitting software package Easyplot.

6.1.3.3 Phosphorus Precipitation Rate Terms

No straightforward approach could be found in the literature for determining the rate terms for describing the precipitation of phosphorus in a soil environment. The few papers which deal with this subject (e.g. van Riemsdijk *et al*, 1984) use elaborate column experiments and analytical equipment beyond the scope of the study. It was decided therefore, that precipitation rate terms would be estimated through model calibration.

6.1.4 Field Methods

6.1.4.1 Piezometer Installation

The project design assumed use of a lightweight and inexpensive hand auger to provide holes for piezometer installations. It became apparent that this device was not capable of drilling in the glacial tills that characterize most of the proposed field sites. Heavy duty drilling equipment capable of this task was well beyond the project budget. With assistance from another source, CWRS acquired a lightweight power drilling rig . This equipment is capable of drilling in sites that can not be drilled by the hand auger, but can not handle boulders in glacial till. Selection of field sites was therefore limited by the capability of this equipment.

Piezometer installation was accomplished by first drilling a hole approximately 10cm in diameter to the desired depth using the solid stem augers of the above mentioned drill. Immediately following withdrawal of the augers from the hole, a one inch I.D. piezometer was installed. Piezometers consist of a 70cm long 20 slot PVC screen with schedule 40 PVC pipe as the casing. Each screen is wrapped with at least three turns of geotextile secured with plastic wire ties to minimize the fine soil material which may enter the piezometer. No glue was used in the construction of the piezometers to avoid potential contamination.

The annulus around the screen was filled with clean #2 silica sand up to a level just above the top of the screen and #8 granular bentonite was placed to form a plug approximately 30cm thick above the sand pack. A separate length of PVC casing was used as a rod to ensure no bridging occurred in the sand pack or bentonite plug and to check on the thickness of material placed in the borehole. The annulus above the bentonite plug was backfilled with native soil material and a second bentonite plug was placed at the top of the casing.

Clear PVC tubing was placed in each piezometer for sampling purposes. Each piezometer contained dedicated sample tubing to minimize the risk of cross contamination during sampling.

6.1.4.2 Piezometer Sampling

All piezometers were purged a number of times before and sampling was carried out at each site. The goal of this was to remove any fine material present in the well as a result of well construction. During each sampling event piezometers were again purged before sample collection to assure that the sample was representative of the true groundwater conditions. When possible purging consisted of pumping the well dry and allowing it to recover. If it was not possible to pump the well dry, three well volumes were purged from the well. Purging was accomplished by attaching a hand vacuum pump to the dedicated tubing in the well.

Samples were collected directly into 125ml plastic lab bottles. This was accomplished by placing a two hole rubber stopper on the bottle. One side of the stopper was attached to the vacuum pump while the other was connected to the dedicated piezometer tube. To avoid the presence of fines in the samples, an in-line filter was used before the sample bottle. Due to the high cost of suitable disposable filters, the filter used consisted of a plastic housing which would accept standard 50mm diameter glass fiber filters. 1 μm filters were used for this purpose. With the exception of approximately 30cm of sample tubing, the filter apparatus, and the inside surface of the rubber stopper, no equipment came into contact with more than one sample. This equipment was rinsed thoroughly with distilled water between samples, and was then flushed with water from the well to be sampled prior to collecting the actual sample.

Immediately upon return to TUNS (usually within 1 hour of sample collection) duplicate 10ml aliquots of each sample were withdrawn. These aliquots were then acidified with 100µl of a 30% sulphuric acid solution. Once acidified the samples were stable for many weeks. After a suitable quantity of samples had been collected they were analyzed using the stannous chloride procedure outline earlier.

Numerous control samples were used to assure quality control and the reliability of the results. These included the use of lab control samples (samples which did not leave the lab), trip control samples (samples filled in the lab and brought into the field but left unopened) and field control samples (actually filled in the field). Solutions of known concentration as well as distilled water were passed through the sample apparatus while in the field to ensure that rinsing between samples was effective.

6.2 Experimental Results

Ultimately four sites were selected for detailed study in this project. These consist of a two private homes, a provincial recreational facility, and a school which relies on a lateral sand filter for treatment of its septic tank effluent. In addition to these sites a number of field sites as well as laboratory models were investigated to a lesser degree. The latter sites are discussed briefly in the next section followed by more detailed discussions of the sites which received more intensive study.

6.2.1 Preliminary Sites

6.2.1.1 Laboratory Model of Contour Trench System

The contour trench model, which is shown in Figure 6.2, represents a full scale section of a contour trench system, including unsaturated and groundwater systems below the trench. The model was loaded with septic tank effluent at field rates. Samples from the outlet represent vertical unsaturated flow of 0.3 m, and approximately 1 m of horizontal flow after mixing with tap water in the saturated zone. The soil in the model is a silty sand, with an hydraulic conductivity of 1.5×10^{-5} m/s.

All samples were analyzed by the ascorbic acid method, except the final set, which used the stannous chloride technique.

Phosphorus results are summarized in Table 6.4. Phosphorus removals in every case exceeded 93 percent; most exceeded 99 percent.

6.2.1.2 Laboratory Model of Lateral Sand Filter

The model, which is shown in Figure 3.2, represents a full scale longitudinal section of a field system. Three parallel channels compared results for different sand characteristics. The model was loaded with septic tank effluent at rates corresponding to field conditions. Samples were withdrawn at the mid point and the outlet, representing saturated travel distances of about 2 and 4m through the sand after vertical flow through about 0.35m of sand. Analyses of these samples used the ascorbic acid method.

Results shown in Table 6.5 are mean values of three monthly samples, beginning 3 months after system start-up. Percentage removals ranged from 40 to 99 percent.

6.2.1.3 Individual Home Lateral Sand Filters, Halifax County, N.S.

Check, 1992, reported on the performance of three lateral sand filters. These systems have been in operation since 1990.

Mean effluent SRP concentrations, based on periodic sampling over 1 year that began about 6 months after the systems were installed, were 0.53, 0.04, and 0.19 mg/L. Apparent removals, assuming typical septic tank effluent concentrations of 12 mg/L, are 95 to 99 percent. These removal efficiencies do not account for unmeasured effects of dilution by surface infiltration into these systems.

6.2.1.4 Small Community Contour Trench System, Port Maitland, N.S.

This system was installed in 1982. It has been monitored periodically since its installation (Porter Dillon Ltd., 1985; Charles, et al., 1990), but no phosphorus results were included.

As indicated by Figures 3.3 and 3.4, the system includes two parallel contour trenches (one of which is in operation at any time, alternated at about 6 month intervals), and an upstream interceptor trench that is intended to collect and divert surface water. Soils are described by Charles, et al. 1990, as moderate to highly compact silty till, underlain by a compact sandy till. The contact between the two horizons is about 2.5 m below the surface. The hydraulic conductivity is low, about 4.5×10^{-6} m/s. The surface slope is 5 to 10 percent.

Sampling arrangements at this site do not allow for collection of septic tank effluent or of background groundwater quality samples.

For this study samples were obtained from the system on June 5, 1992, and November 3, 1993. Sample locations, relative to the trench, are shown in Figures 6.6 and 6.7. Piezometer numbers are those assigned in Porter Dillon Ltd., 1985.

Groundwater levels were recorded on the first sampling date, and are included in Table 6.6. Levels were not recorded on the second date because of an equipment malfunction, but visual comparison indicated that levels were at least 0.5 m higher than those at the time of the first sampling.

TDP for the first sample set was determined using the ascorbic acid method; the second set was analyzed by the stannous chloride method. Chloride analyses were carried out on the November, 1993 samples to provide an indication of dilution by groundwater.

Results are presented in Table 6.6, and illustrated on Figures 3.3 and 3.4. Phosphorus concentrations suggest that trench #2 was operating at the time of both visits. The high phosphorus concentrations at piezometer 4 at the second visit are consistent with higher groundwater at that time, and with a finding by Porter Dillon Ltd., 1985, that the interceptor trench is too close to the contour trenches, and may intercept effluent from them.

Phosphorous levels are clearly higher at the time of the second sampling. The difference is consistent with the higher groundwater table at the time of the second visit, if it is considered that phosphorus removal in the unsaturated zone is significant. During the June 1992 sampling, the unsaturated zone below the septic field was about 70cm thick. In November 1993 this zone was, at most, 20 cm thick.

At the first visit phosphorous concentrations in the saturated zone immediately below the bed were as high as 0.021 mg/L. The maximum value at the second visit was 0.16 mg/L.

If we assume that septic tank effluent at this site is similar to that collected at other sites in this study then concentrations of 10-15 mg/L for phosphorus and 50-100 mg/L for chloride would be expected. Travel distance from the lower trench (Trench #2) to the furthest downgradient piezometer was about 6.5m. Based on these values, it appears that more than 99% of the phosphorus was removed in the unsaturated zone at the time of the November 1993 sampling. Phosphorus concentration reductions in the saturated zone appear to be the result of dilution by natural groundwater only. Conclusions regarding the June 1992 samples are harder to make in the absence of chloride samples, however even greater reductions in the unsaturated zone appear to be occurring due to its greater thickness at this time. Saturation of previously unsaturated sediments appears to result in the dissolution of previously precipitated phosphate minerals.

Interpretation of the 1993 sample results is limited to only those piezometers below trench #2. Looking at relative concentrations between piezometers 8 and 14, there is an overall decrease in both phosphorus and chloride downgradient of the lower trench. However, if one looks at only the area between piezometers 8 and 10, changes in phosphorus concentrations do not coincide with those in chloride concentrations. If we assume that the decrease of approximately 50% in chloride levels is the result of dilution, a mechanism is needed to account for the fact that phosphorus does not decrease over this same distance. One possible explanation is that previously precipitated phosphate minerals are being re-dissolved in order to maintain chemical equilibrium with the groundwater. These minerals would have been precipitated under unsaturated conditions while the water table was at a lower elevation. They would become more soluble when this region becomes saturated. Phosphate precipitates will be more abundant closer to the trench thus any lowering of solution phosphorus concentrations through dilution would be buffered by dissolution of these minerals. Further from the trench less phosphorus has been precipitated. In this region phosphorus precipitation would be the dominant reaction.

6.2.1.5 Summary of Preliminary Sites

The data collected from the above sites indicates that phosphorus removal processes are, for the most part, very effective for the conditions noted here.

A comparison of the laboratory contour trench model and the lateral flow sand filter models indicates that soils with low hydraulic conductivities are better suited to phosphorus removal. The contour trench model, with a low conductivity soil, and the finer grained lateral sand filter models exhibited removals in the range of 98% to over 99%. In contrast removal of only 40% of the phosphorus load was observed in the coarsest grained sand filter model.

The results from the Port Maitland site indicate that the depth of the unsaturated zone plays a significant role in phosphorus attenuation. As shown above much more phosphorus remained in solution during the period characterized by a higher water table. Also fluctuations in the position of the water table may lead to the re-dissolution of previously precipitated phosphate minerals.

6.2.2 Detailed Field Sites

6.2.2.1 Individual Home System, Waverly, N.S.

This home had been the focus of an earlier study at the Centre for Water Resources Studies (Waller and Charles. 1990). The system consists of a contour trench which has been in continuous operation since 1987. The trench bottom appears to be 30 cm below the ground surface. A secondary chamber with easy access located after the septic tank allows for collection of raw effluent samples. Four piezometers from the earlier study were still in place at the site. Additional piezometers were installed for this study as shown in Figure 6.8. The pre-existing piezometers are designated P1, P3, P4, and P5. These pre-existing piezometers consist of 2 inch I.D. PVC pipe. Although construction details are not available for these piezometers it is believed they were constructed by cutting slots in the lower end of the pipe with a hacksaw and then wrapping this section with geotextile. The material used to backfill the borehole is unknown.

Two different types of soil were noted during drilling at this site. These soils have been designated WAV-1 and WAV-2 for the purposes of this study. The change from one soil type to the other occurs in a lateral direction rather than vertically. The lateral change coupled with the similar appearance of these soils when viewed in the field makes the contact shown in Figure 6.8 somewhat arbitrary.

Soil WAV-1 consists of a light to medium brown coloured poorly sorted till. Grain sizes range from clay to cobble sized particles with approximately 25% of the particles being gravel sized or larger. The coarser material suggests a variety of parent material including granite; quartzite and silicified sandstone of the Goldenville Formation; and slates of the Halifax Formation. Soil WAV-2 was similar to WAV-1 except that it was slightly darker in colour and contained significantly more clay and less coarser material. Regional soil maps categorize the area as Stewiacke Till.

Early in the study one set of samples was collected from the pre-existing piezometers and from four temporary boreholes created with a hand auger. Analyses of these results suggested that, after accounting for dilution, phosphorus loads were reduced by 94% and 99.5% within a few meters of the trench and 22m from the trench respectively.

During the project it was decided to install the newer piezometers at this site. Due to the fact that this was accomplished later in the study only two more sets of samples were collected at this site. The analytical results for these samples are shown in Table 6.8. As can be seen in Tables 6.7 and 6.8 static water levels in the piezometers and raw effluent chloride and phosphorus concentrations are available for more occasions. This was possible because the site was visited on numerous occasions as part of another project at CWRS, however time and resources did not allow for the collection of piezometer samples on these occasions. Raw effluent samples were collected as part of the other project and have been made available to this study. Chloride analyses have been conducted to aid in determining the amount of dilution. Due to the fact that the phosphorus and chloride concentrations fluctuate somewhat over time and because the concentration of the effluent at a particular time has little bearing on the concentration some distance form the trench at the same time, it was decided that it would be best to use average concentrations for data analyses.

Attempts to determine the effects of dilution in the saturated zone directly below the trench using a mass balance approach that considers the chloride concentration in the effluent and background concentrations were unsuccessful. A mass balance approach assumes perfect mixing between the effluent leaving the unsaturated zone and the groundwater. It is highly unlikely that this is occurring due to the fact that the effluent plume actually displaces some of the groundwater rather than mixes with it. The major difficulty then becomes determining the volume of groundwater that would mix with the effluent directly below the trench. Ultimately it was decided that dilution immediately below the disposal trench would be determined as the ratio of the chloride concentration in the effluent to that directly below the trench (i.e. background chloride concentrations are deemed insignificant for samples collected directly below the trench). Only P3 and P4 sample the area directly below the trench and they yielded the following 'dilution factors' (DF):

Piez. 3 $$DF = \frac{\overline{[Cl]}_{EFF}}{\overline{[Cl]}_{P3}} = \frac{56.8mg/l}{40.5mg/l} = 1.40$$

Piez. 4 $$DF = \frac{\overline{[Cl]}_{EFF}}{\overline{[Cl]}_{P4}} = \frac{56.8mg/l}{24.0mg/l} = 2.37$$

where: $\overline{[Cl]}_{EFF}$ = Average chloride concentration of effluent

$\overline{[Cl]}_{Px}$ = Average chloride concentration in piezometer

As can be seen in Table 6.8, the average phosphorus concentrations observed in Piezometers 3 and 4 are 3.9mg/l and 0.94mg/l respectively. Multiplying these concentrations by their respective dilution factor yields undiluted phosphorus concentrations of 5.46mg/l below the trench at piezometer 3 and 2.22 mg/l at piezometer 4. Based on an average raw effluent phosphorus concentration of 14.2 mg/l it appears that phosphorus loads have been reduced by 61% after 25cm of movement in the unsaturated zone (piez. 3) and by 84% after 35cm (piez. 4). It is interesting to note that at both piezometers the rate of reduction in phosphorus loads works out to be approximately 0.34mg/l (or 2.4%) per centimetre of travel in the unsaturated zone.

The conclusion reached above is tentative due to the lack of samples and the large variation in concentrations. The first sample from piezometer 3 was collected when the water table was only 1cm below the trench while the water table was 42cm below the trench during the second sampling. From Table 6.8 it can be seen that there is a difference of two orders of magnitude between the two samples. These results would suggest that phosphorus removal mechanisms become less efficient further from the trench bottom. This agrees with the observation that phosphorus retention processes (in particular adsorption) are gradient driven, becoming more efficient as solution phosphorus concentrations increase. Finally it should be noted that the agreement between observed phosphorus load reductions, on a per centimetre of travel basis, in piezometers 3 and 4 may be due to the fact that the water table is located a similar distance below the trench in both cases.

It is difficult to explain the measured results in the saturated zone due to difficulties in estimating the effects of dilution. The chloride concentrations observed in piezometers 8 to 11 suggest that solute concentrations have been diluted to, or very close to, background levels. Phosphorus levels on the other hand are still significantly above background suggesting that this has not occurred. One possible explanation for this is that chloride diffusion occurs to a greater extent than phosphorus and that this diffusion has resulted in a chloride plume of greater extent than that of phosphorus but with lower concentrations relative to the initial load. Phosphorus and chloride levels in piezometers 6 and 7 support this conclusion. In this case chloride concentrations are above background whereas phosphorus is still at background levels. Both of these piezometers sample the deeper horizon. It would appear that closer to the trench diffusion has resulted in a deeper migration of chloride while the phosphorus plume remains above these piezometer screens and is therefore not sampled at either location.

An anomaly in the results is the fact that the phosphorus concentration at the location of piezometer 5 is lower than further downgradient as seen in piezometers 8 to 11. It is possible that piezometer 5 intersects the plume more towards the fringe as it is near one end of the trench. Again the somewhat elevated chloride concentrations in piezometer 5 may be the result of diffusion.

Overall it would appear that reductions in phosphorus levels after nearly 20 metres of travel in the saturated zone are significant. The sampling conducted using the pre-existing piezometers and the temporary drive point holes had suggested that, after considering dilution, phosphorus load reductions of 99.5% were occurring after 20m of travel. These earlier results also indicated that levels were approaching background values by this distance. In contrast, sampling of the newer piezometers suggests that 20m from the trench phosphorus concentrations remain up to ten times greater than background levels, even after dilution. Quantifying dilution is difficult here due to the possible effects of chloride diffusion as discussed above. It is possible, however, to define a range for dilution. As a minimum we could assume that no dilution occurs while the maximum potential dilution would assume that what we are seeing in piezometer 11 is entirely diluted effluent (i.e. the effects of diffusion and background chloride are ignored). As shown in Table 6.8 the average raw effluent chloride concentration is 56.8 mg/l while at piezometer 11 the average concentration is 7.8 mg/l. Therefore the maximum potential dilution is about seven times, or alternatively dilution has reduced solute concentrations by 86%. Phosphorus load reductions would thus vary from over 99.5% assuming no dilution to about 97.5% if maximum dilution were occurring.

In conclusion a few comments regarding this site should be considered. First, although there is a significant reduction in phosphorus loads after only 20m of travel, the vast majority of this reduction appears to be occurring in the unsaturated zone below the trench. The results of the phosphorus adsorption experiments agree with this observation. The Langmuir coefficients for soil WAV-1 from the unsaturated and saturated zones show that soil in the unsaturated zone has a maximum adsorption capacity of 491 mg of phosphorus per gram of soil. In comparison soil in the saturated zone only has a maximum capacity of about 7mg phosphorus per gram of soil. Two explanations are put forward for this observation. One possible explanation relates to the pH of the groundwater at this site. The pH of the groundwater here is about 5.0 while most other sites studied for this project have pH levels of 7 or slightly more. It is possible much of the phosphorus adsorption metals (mainly iron and aluminum) have been leached from the soil below the water table resulting in a lower phosphorus adsorption capacity. However similar contrasts in adsorption capacities were noted above and below the water table at the elementary school site described in section 6.2.2.4 but the pH of this site is around 7. The soils at both of these sites have similar parent materials therefore it is possible that the chemistry of these soils is such that adsorption capacities become severely limited under saturated conditions, possibly in response to lower oxygen levels.

A second comment worth noting is that even though phosphorus loads are being reduced significantly, they are still well above background concentrations at the furthest downgradient point sampled in this study. Unfortunately the lot size at this site limited our ability to install piezometers further from the disposal bed, and in any event the presence of a septic system on the next lot would interfere with any results. Therefore conclusions regarding phosphorus removal after significant distances cannot be made on the basis of the samples collected at this site alone. It is hoped that computer modeling will have the ability to make accurate predictions regarding phosphorus levels at distances greater than those studied here.

6.2.2.2 Individual Home System, Near Bridgewater, N.S.

This site was instrumented for another project currently in progress at the Centre for Water Resources Studies. Therefore the design and location of the piezometers were dictated by the needs of this other study. In this case a total of four piezometers were installed. One piezometer was installed directly in the gravel portion of the disposal field. This piezometer was dry on every visit to the site and was therefore never sampled. The remaining piezometers were installed in a line perpendicular to the trench and spaced approximately 5, 10, and 15 metres from the trench. The piezometers are screened over their entire depth, thus any samples collected from them represent the vertically averaged concentration of the groundwater over this depth.

The disposal trench at this site receives effluent which has been treated by an alternative design on-site disposal system being studied by the above mentioned project. The bottom of the trench is approximately 0.6m below grade. The location of the piezometers here does not allow for measurement of the static water level directly below the trench, however it appears that there is a least 1m of unsaturated soil below trench.

During drilling two distinct soil horizons were encountered. These soils have been labelled BH-1 and BH-2 for the purposes of this study. Soil BH-1 occurs to a depth of approximately 2.5m at all piezometer locations. This soils is a poorly sorted till material which exhibits a medium orange brown colour. Soil particles from clays and silts to material with a diameter of over 5cm. Over 50% of the particles are gravel size or larger and are subrounded to subangular in shape. The coarser material indicates a diverse origin for the soil including granites, moderately to highly silicified siltstones, and slates.

The lower horizon encountered during drilling, soil BH-2, consists of sediments which exhibit a grey colour. The composition of this soil is similar to BH-1 however the coarser grained material is less abundant and rarely exceeds 1cm in diameter. Occasionally clasts were noted which crumbled very easily, suggesting that they had weathered in-situ. while drying the soil in an oven a sulphur smell was noted. The stark contrast between the two soil types at this site makes the location of the contact in Figure 6.9 very precise.

The phosphorus adsorption experiments conducted using these soils indicate that, under saturated conditions, soil BH-2 has a much greater potential maximum phosphorus adsorption capacity than BH-1. The phosphorus adsorption capacity of soil BH-1 does appear to differ greatly between unsaturated and saturated conditions. The adsorption data generated for these soils suggests they have better adsorption capabilities than the soils encountered at the Waverly site or at the school site discussed below. One possible factor influencing these differences is the pH at the Waverly site. As mentioned in the previous section, pH may play a role in these differences, however differences in soil chemistry is a more likely cause.

The home at this site is a new construction and was first inhabited in late September or early October of 1994. Sampling was carried out between February and June of 1995. As can be seen in Table 6.10, there had been insufficient time for phosphorus to migrate to even the closest piezometer by the time sampling ceased. The higher reported phosphorus concentration in piezometer 3 on June 29, 1995 cannot be explained. Since this piezometer is the furthest from the trench it is unlikely that this apparent increase in phosphorus is effluent related since no increases were noted in the closer sample locations.

6.2.2.3 Provincial Recreational Facility System

The septic system at this facility was installed during the late winter of 1994. Wastewater is directed through a series of two septic tanks with a combined capacity of 5000 imperial gallons (~22,700 litres) and is then pumped up to the disposal trenches. Due to space limitations at the site, two parallel trenches have been installed separated by a minimum distance of 12m. Each trench is 3.05m wide and the together have a combined length of 167.5m. Each trench receives effluent on an alternating basis each time the pump operates.

The facility operates from early May to late October each year and the only contribution to the septic system is from public washrooms. The system is designed to handle a peak two day attendance at the facility of 5000 people giving a design flow of 15,500 l/day over this time. Attendance figures indicate the maximum number of annual visitors should not exceed 300,000. Therefore, during a typical operating season an average of 10,000 visitors per week can be expected. Using the same assumptions and data that were used for designing the system, the average flow to the system becomes 62,000 l/week or ~8800 l/day.

Test pits performed at the site during preliminary system design indicate that the soil in the area consists of an average of 0.61m of silty sand underlain by an impermeable clay till. The location of water table appears to be controlled by this contact. Analyses of soils encountered during drilling confirm this observation. As shown in Figure 6.10 four soil types were described for the site. Detailed analyses, however indicate there to be little difference between the soils designated PF-1, PF-2, and PF-4, which can be all classed as clay tills. Soil PF-3 is characteristic of the silty sand. Descriptively soils PF-1, PF-2, and PF-4 are brown to reddish brown clays with trace gravel clasts composed of slate and silicified sandstone. The clasts have diameters up to 2cm across and are generally flat. Soil PF-1 appears to have a minor sand component whereas PF-2 is finer grained. PF-4 contains a significantly greater proportion of clay sized particles and the included clasts rarely exceed a few millimetres in diameter. The greater clay component of PF-4 allows it to be formed into thin continuous ribbons. The silty sand, soil PF-3, exhibits a lighter colour than the other soils and contains minor clasts with diameters of up to 5mm. The clasts are composed of highly weathered slate. The sand component of this soil appears to increase downslope from the trench and locally the sand component is very high. As well the thickness of this silty sand layer increases downslope. As shown in Figure 6.10 the trenches are located at the upper end of the area characterized by the coarser grained soils.

A saturated hydraulic conductivity of $2.5\text{x}10^{-3}$ cm/s ($2.5\text{x}10^{-5}$ m/s) was estimated for the silty sand based on test pit analyses. Later tests conducted using a falling head permeameter indicated a similar conductivity of $1\text{x}10^{-3}$ cm/s. A saturated hydraulic conductivity one order of magnitude less has been determined for the clay till based on the results of one test conducted with the falling head permeameter.

Phosphorus adsorption tests carried out on these soils confirm the similarity of soils PF-1, PF-2 and PF-4 (Table 6.3). Overall these soils exhibit a greater phosphorus adsorption capacity than soil PF-3, likely due to the greater clay, and therefore iron and aluminum, content of the clay till. The much greater adsorption capacity of soil PF-1 under unsaturated conditions is surprising. As can be seen in Table 6.3, this soil appears to have a sorption capacity under unsaturated conditions over two order of magnitudes greater than for saturated conditions. The most likely reason for this increase would be the nature of the minerals present in each case. As discussed earlier, iron and aluminum minerals are present in oxidized forms above the water table whereas reduced forms dominate in the saturated zone. Oxidized minerals tend to have better adsorption capabilities than reduced forms.

A total of seven piezometers were installed at this site, placed to allow for the collection of samples from above the trenches, immediately downgradient of each trench, and at distances up to 50m from the lowermost trench. Water level data was recorded and samples collected a total of four times over the 1994 operating season of the facility. This data is presented in Tables 6.11 and 6.12.

Raw effluent chloride and phosphorus concentrations differ markedly from those found in effluent from a typical private dwelling septic tank. Phosphorus concentrations are about one tenth those seen at the private homes in this study while chloride levels are double those for the site with no water softener. This would indicate that the majority of the phosphorus seen at the other sites is derived from sources such as dish washing. The higher chloride concentrations, on the other hand, are derived from the use of chemicals used to clean and disinfect the washrooms at the facility.

Data analyses suggests that, in the relatively short time during which this system has been operating, very little plume migration has occurred. Chloride concentrations in piezometer 2 were elevated above background levels by the time of the first sampling and continued to increase over the summer. Once again attempts to characterize dilution using chloride data were unsuccessful based on a mass balance approach which assumes perfect mixing of the effluent and the groundwater. Chloride levels in piezometer 2 suggest that a greater proportion of the water in this piezometer is derived from effluent and that the effluent displaces the groundwater somewhat as it leaves the unsaturated zone. Chloride in the other piezometers remained at background concentrations throughout the study period. The higher chloride concentrations noted in piezometer 7 in October and November do not appear to be related to effluent migration due to the fact that no increases were noted in the closer piezometers. The timing of this chloride increase coincides with the period of increased rainfall. Piezometer 7 is located within 10m and downslope from a small paved access road located in the park. Although no salt would have been used on the road at this time (if ever) it is possible that deposits on the road surface are being transported to the groundwater during periods of rain.

Phosphorus concentrations in the piezometers indicate that no phosphorus reached the groundwater during the course of this study. The consistently higher phosphorus levels in piezometer 5 should be discounted. Even after purging this well numerous times, the water from it contained a significant amount of fine sediments which would often plug the filter paper used during sample collection making it necessary to change the paper one or more times. The high levels likely reflect this problem. It should be noted that since the phosphorus concentration of the raw effluent is so low, only low levels of phosphorus would enter the groundwater. These concentrations may be to low to make any observable impact on the groundwater after dilution occurs. This fact is compounded by the relatively high ambient phosphorus concentrations in the groundwater at this site. Two possible explanations can account for these elevated levels. In the past this site was agricultural land which would have likely been fertilized. Also the area surrounding the disposal trenches is mowed regularly quite likely fertilized. Finally the overall higher phosphorus concentrations seen in samples collected on November 25 may reflect a change in the saturated environment around this time. While collecting these samples a faint sulphur smell was noted, particularly in piezometers 1 and 5. This smell may indicate that conditions had become more reducing which would result in increased phosphors mobility. The reason for such a change in reducing conditions is unknown, however it does not appear to be related to the operation of the disposal trenches since piezometer 1, located quite far upgradient of the trenches, also exhibited these conditions.

6.2.2.4 School System, Hants County, N.S.

This site consists of an elementary school at which a new disposal system was installed in the fall of 1994 due to a failure of the existing system. The installation consisted of removing the original material in the disposal bed and then backfilling the entire area with sand to a maximum depth of approximately 1.2m. A new disposal bed consisting of crushed stone was then installed within the imported sand. The disposal bed itself is approximately 90m long by 3m wide. The imported fill extends a minimum of 7.6m downgradient from the lower edge of the trench and at least 4.5m above the top edge. An stone filled interceptor trench above the upper edge of the imported fill diverts surface runoff away from this sand filter. Another stone filled trench constructed in the native soil at the lower edge of the imported fill ensures that the partially treated effluent does not break out at the contact between the native soil and the imported sand. This installation is similar to the sand filters discussed in sections 6.2.1.2 and 6.2.1.3.

A total of approximately 175 students and staff are present at the school during the school year. The system has a design flow rate of 9087 l/day (2000 IGPD).

A total of four piezometers were installed at the site as shown in Figure 6.11. Piezometer 1 samples the area upgradient of the disposal bed. The borehole for piezometer 3 was stopped just below the water table at the time of drilling, however the screen for this piezometer was below the contact between the imported sand and the native soil. It is likely however that any effluent from the disposal bed would remain above this contact in the higher permeability zone and would therefore remain above the screened section of piezometer 3. For this reason another piezometer, piezometer 2, was installed with its screen just above this contact. Unfortunately this piezometer rarely contained any water and on the rare occasions when it did, it did not recover after purging thus no samples were ever collected from it.

Three types of material were encountered during drilling. These consisted of two horizons within the native soil and the imported fill. The imported fill is a typical fine to medium grain light brown sand. The uppermost horizon in the native soil, referred to as soil RS-1 in this study, consists of a brown poorly sorted till. Particle sizes range from clays to cobbles with diameters up to 5cm. The coarser material represents a diversity of parent materials including granite, quartzite, and highly silicified slates. The coarser material becomes less abundant with depth and by approximately 3m depth, the soil contains predominantly clay sized particles. This lower horizon, soil RS-2, contains only minor sand size particles and forms continuous ribbons upon squeezing.

As can be seen in Table 6.3 both of the native soils at this site exhibit similar phosphorus adsorption capacities under saturated conditions. Under unsaturated conditions the adsorption capacity of soil RS-1 is seen to increase two orders of magnitude.

Sample results from this site are presented in Tables 6.13 and 6.14. Background chloride and phosphorus levels are similar to those seen at Waverly. The higher phosphorus concentration reported in piezometer 1 on January 28 is likely a result of fine soil material in the well. As can be seen later samples showed lower concentrations suggesting well development had occurred. The relatively low phosphorus concentrations are typical of situations such as this where most of the effluent load is derived from blackwater. The concentrations are slightly higher than at the provincial park, possibly due to the presence of a cafeteria at the school. The chloride concentrations are extremely high in the effluent. Again these are likely the result of the use cleaning agents used for disinfecting purposes.

The phosphorus concentrations in the piezometers below and downgradient of the trench are similar to those recorded at Waverly in spite of the fact that initial concentrations were at least five times greater at Waverly. It is believed that the phosphorus seen in these piezometers was derived from the earlier, failed disposal bed. As mentioned above it is expected that downward migration of the effluent at this site will be impeded by the presence of the low permeability native material. This will cause the effluent to move laterally following this contact which would keep it above the piezometer screens. Another possibility is that effluent if reaching the screens through the material used to backfill the piezometer during construction. Care was taken during placement of the bentonite plug to ensure a good seal, however it is possible that effluent is bypassing this plug. This appears unlikely however since we would expect phosphorus and especially chloride levels in the piezometers to be closer to those in the raw effluent if this was the case.

If we assume the elevated phosphorus levels to be the result of the older disposal bed, a few possibilities exist to explain the differences between this site and the Waverly site, even though both have similar adsorption capacities. First the system at the school would have been much older than the Waverly system. It is possible that over time the phosphorus plume migrated further outward from the trench. The slope at this site is also much greater than at Waverly and it is possible that this has resulted in higher rates of flow which in turn resulted in greater phosphorus transport. However the most plausible explanation is the fact that the original system had failed. A system failure here refers to the fact that effluent had begun breaking out at the ground surface. This suggests that the area surrounding the disposal bed had become saturated due to the low permeability of the original soil. As shown in Table 6.3 this soil loses most of its adsorption capacity under saturated conditions therefore little phosphorus would have been attenuated under these conditions. This conclusion is further supported by the fact that chloride levels in the lower piezometers are more representative of ambient groundwater than the effluent. Given the extremely high effluent chloride concentrations, we should expect much higher levels in the groundwater below the trench. However upon remediation of the disposal bed effluent loads would no longer be reaching the groundwater below the trench, therefore the source of both chloride and phosphorus would be cut off. The new trench was installed in the early fall of 1994 and sampling began in January 1995. Over this period the higher mobility of chloride would allow it to be quickly removed from the site however the adsorbed phosphorus would remain for a longer period of time. It is expected that, given enough time, phosphorus levels in the native soil below and downgradient of the trench would return to, or close to, background values.

6.2.2.5 Summary of Field Observations

The most significant observation noted during the analyses of the soils and water samples is that, for the sites studied here, phosphorus attenuation in the unsaturated zone is much more effective than under saturated conditions. As can be seen in Table 6.3 every soil for which the adsorption experiments were carried out for both conditions show much higher adsorption capacities for unsaturated conditions. This conclusion is also reached from the field data for the Waverly site where significant reductions in phosphorus loads were noted over distances much less than 1m in the unsaturated zone while reductions were not as great after a further 22m of travel in the saturated zone.

Although lower groundwater pH levels at the Waverly site may be responsible for the lower attenuation in the saturated zone, difference in chemistry below the water table are a more likely cause. This conclusion is based on the similar observations made for the elementary school site where pH levels are higher. It is more likely that lower oxygen levels below the water table result in a greater proportion of reduced iron and aluminum forms which have been shown to be less effective at phosphorus attenuation as discussed in chapter 3. The last set of samples collected at the recreational facility also lead to this conclusion. At this time a sulphur smell, suggesting reducing conditions was noted in most piezometers. Sample results show phosphorus levels were higher at this time than at any previous time, even above the disposal field.

Samples collected during different water table elevations at the Waverly site would indicate that phosphorus reductions increase exponentially with the thickness of the unsaturated zone (Table 6.8).

A comparison of phosphorus concentrations below the disposal fields at the Waverly and elementary school sites indicates less attenuation at the latter, even though both sites have soils with similar adsorption capacities. A number of reasons were put forward for this including - an older system at the school resulting in further migration of the effluent plume; a steeper slope resulting in increased flow rates and greater phosphorus transport; or failure of the soil to accept the effluent loads resulting in saturated conditions in or directly below the field which in turn led to a much lower adsorption capability.

Finally it must be noted that although phosphorus concentrations appear to be reduced to very low levels within tens of metres of the disposal beds, the resulting concentrations are still significantly elevated over natural groundwater levels and may represent a threat to surface water supplies.

7.0 MODELING RESULTS

7.1 Introduction

As discussed earlier this project will attempt to simulate effluent migration and phosphorus attenuation by first modeling vertical movement in the unsaturated zone below the disposal trench and then by modeling sub-horizontal movement in the saturated zone. The model Chemflo will be used for the former while Modflow and MT3D will be used for the latter. What follows will be a discussion of the results of modeling with Chemflo using the various soil parameters determined in Chapter 6. Model predictions will be compared to field observations whenever possible.

7.2 Individual Home System, Waverly, N.S.

The inputs required by Chemflo and values for soil WAV-1 are summarized in Table 7.1. No values are given for soil WAV-2 because this soil does not need to be modeled under unsaturated conditions since the trench is not located in it. The methods used to determine the value for most of these terms are described in section 6.1.

The value for the apparent dispersivity term has simply been estimated. As discussed in the section which introduced the model, Nofziger *et al.* (1989) suggest values greater than 10cm are suitable for field conditions. In light of the short flow lengths between the bottom of the disposal trench and the water table at this site a value of 5 was chosen. Again, as discussed earlier, sensitivity analyses show that altering the dispersivity input has little effect on model predictions in regard to steady state solute concentrations.

The partition coefficient has been estimated from the Langmuir Isotherm coefficients as discussed in section 4.2.2.1.

Previous studies of this system conducted at CWRS show the daily hydraulic loading rate to be 0.745 m^3/d. The trench covers an area of approximately $30m^2$, therefore an areal loading rate of 0.025m/d or approximately 0.10m/hr is used here.

The phosphorus concentration of the effluent is based on the average of 11 samples collected over a period of more than 2½ years.

One critical input missing from Table 7.1 is the rate term for describing precipitation reactions. As discussed previously, attempts to find a suitable method to determine this parameter in the lab were unsuccessful therefore it was decided that the model would be calibrated for this term. In this case it is also possible to verify the term due to the fact that there are two piezometers located below the trench with a different unsaturated flow length at each piezometer. The bottom of the trench is located 30cm below the surface thus Table 6.7 indicates that there is, on average, an 18cm thick unsaturated zone below the trench at piezometer 3. Likewise the unsaturated zone at piezometer 4 averages 35cm in thickness. It should be noted that the unsaturated zone below the trench at this site is much thinner than suggested in the Nova Scotia guidelines for septic fields.

After assembling all of the required input data, the next step in modeling was to determine the expected 'undiluted' phosphorus concentrations in piezometers 3 and 4. As mentioned earlier attempts to estimate dilution using a mass balance between groundwater and effluent chloride concentrations proved difficult and so it is assumed that any decrease in chloride concentrations in the piezometers over raw effluent concentrations is due to dilution. Calculations using this assumption indicate that the model should predict an undiluted phosphorus concentration of 5.52 mg/l at piezometer 3 and 2.40 mg/l at piezometer 4.

Initial attempts to calibrate and verify the model using results from one particular sample event were unsuccessful. It was then decided that average concentrations and static water levels should be employed since these values are seen to fluctuate over time and the effluent concentration at any given time would not effect groundwater concentrations at the same time.

For the conditions described here, Chemflo predicted a phosphorus concentration of 5.51mg/l after 18 centimetres of travel through the unsaturated zone when the first order rate term for precipitation equals 0.017hr^{-1}. This value compares very favourably with the expected concentration of 5.52mg/l. Changing only the travel length to 35cm, the average unsaturated zone thickness at piezometer 4, resulted in a model prediction of 2.38mg/l. Again this correlates very well with the expected concentration of 2.40mg/l observed in piezometer 4. Therefore it can be concluded that the model can be calibrated and verified for the average conditions seen in the field. This appears to lend strength to the interpretation of dilution effects based on chloride data as discussed in section 6.2.2.1.

7.3 Individual Home System, Near Bridgewater, N.S.

Table 7.2 list the Chemflo inputs for soil BH-1 from this site, the only soil in which flow occurs under unsaturated conditions. Once again dispersivity has been estimated and the Langmuir Isotherm coefficients were used to estimate a linear partition coefficient.

Water usage, as indicated by a water meter installed in the house, has increased during the period of the study. Initially an average of just over 0.42m^3 (92 Imperial gallons) of water was being used each day. Observations recorded on April 27, 1995 indicate this had increased to 0.48m^3/d (105 IGPD) and by October 5, 1995 it had increased to 0.84m^3/d (100 IGPD). One possible explanation for this increase is the installation of a water softener just prior to April 27, 1995. The occupants indicated that they had been purchasing bottled water prior to this. The switch from bottled water to well water coupled with the increase in water demand for reactivating the water softener is the most likely reason for the increased water usage. Ultimately a loading rate of 0.45m^3/d (100

IGPD) was chosen for modeling purposes. Given a trench area of approximately 25m^2, an areal loading rate of 0.018m/d or 0.08cm/hr was determined.

Samples of raw effluent indicate an average phosphorus concentration of 21.0 mg/l.

Model runs were conducted assuming a 100cm thick unsaturated zone. Water levels measured at the site suggest this to be a minimum value, however direct measurements of the position of the water table directly beneath the trench were not possible due to the location of the piezometers as discussed in section 6.2.2.2. Using the inputs presented in Table 7.2, an undiluted phosphorus concentration of 0.071mg/l is predicted for the effluent when it reaches the saturated zone. This concentration is much lower than that which is seen at Waverly reflecting the thicker unsaturated zone at this site and the higher adsorption capability of this soil as indicated by the Langmuir Isotherm values.

Finally it should be noted that the precipitation rate term determined for the Waverly site may not be truly representative of this site. It is possible that the higher adsorption capacity of the soil here as compared to the Waverly site may indicate that precipitation reactions would also be more efficient at this site.

7.4 Provincial Recreational Facility System

The drilling conducted at this site during piezometer installation indicates that the trenches here are actually installed in the clay material immediately above the contact between the clays and the silty sand soil. For this reason all modeling using Chemflo was based on soil PF-1.

Determining a hydraulic loading rate for the septic system at this site required a little more effort than at the private homes as no provision has been made to monitor flow rates. Ultimately the same assumptions made during design of the system were made to estimate a loading rate. The design process assumed a peak two day attendance at the park of 5000 people with annual attendance not exceeding 300,000. In this case the annual attendance figure was divided by the approximate number of weeks the park is opened, 30 weeks. This yields an average weekly attendance of 10,000 people. Further the assumption that each visitor uses the facilities and washes their hands is maintained here. The use of ultra low flow toilets and metered taps at the facility would result in the use of approximately 5.12 litres of water per flush and 1 litre for hand washing. Multiplying these figures yields an average weekly flow of 61,200 litres or approximately 8.74m^3/day. The two trenches cover an area of 511m^2 (5500ft^2). From this an areal loading rate of 0.017m/d or 0.07cm/hr was determined as the input to the Chemflo model.

Other parameters used for this modeling exercise are listed in Table 7.3. Each has been determined from observed data, lab analyses, or estimated as described in the preceding sections and section 6.1. As before the term used to describe the first order phosphorus precipitation reactions will be that which was determined through calibration of the Waverly site.

An unsaturated thickness of 30cm was modeled below the trench. This depth was determined from the cross section in Figure 6.10.

Model runs conducted using the above inputs predicted an undiluted phosphorus concentration of 0.200 mg/l at the bottom of the unsaturated zone. The model also indicated conditions approach steady state after approximately 500 hours (~21 days). This suggests that effluent derived phosphorus should in fact have reached the water table by the end of the sampling period. The fact that this predicted concentration is so much lower than that predicted for the Waverly site, coupled with the fact that there is a few meters of flow in the saturated zone between the upper trench and piezometer 2, may explain why dilution is masking these increases at this site.

The length of unsaturated flow here is similar to that at Waverly as are the Langmuir Isotherm coefficients at the two sites. Thus it appears that the difference in phosphorus loads reaching the water table at these sites is due to difference in the raw effluent concentrations. For the conditions observed in piezometer 4 at Waverly, the model predicted a phosphorus load reduction of about 83% (from 14.20mg/l to 2.38mg/l) after 35cm of travel. A similar reduction of 90% (from 1.98mg/l to 0.20mg.l) after 30cm of travel is predicted at this site. The slight difference in load reductions are most likely attributable to the lower adsorption capacity of soil WAV-1 as compared to PF-1 (Table 6.3), however it appears that similar load reductions, on a percentage basis, can be expected from soils with similar characteristics, regardless of initial concentrations. This conclusion is based, of course, on the assumption that first order precipitation reaction rates are also similar at the two sites.

Comparing the results to the predicted phosphorus loads reaching the water table at the Bridgewater site we see that significantly less phosphorus migrates out of the saturated zone at the latter site. This is to be expected in light of the higher adsorption capacity and the much thicker unsaturated zone at the Bridgewater site.

7.5 School System

The analyses of the data collected from this site (section 6.2.2.4) concluded that phosphorus concentrations seen in groundwater downgradient of the disposal trench at this site were related to the old system which had recently been replaced due to its failure. For this reason the modeling runs for this site assumed the old trench was still operating. The only real difference this created for modeling the unsaturated zone was the thickness of the unsaturated layer since the newer trench was actually installed above the pre-existing ground surface. Also since the old trench was assumed all modeling was based on the data generated for soil RS-1 (Table 7.4)

The hydraulic loading rate was determined based on the design flow of $9.08m^3/d$ (2000 IGPD) and a trench approximately 90m long by 3m wide giving a total area of $270m^2$. Note that this assumes the old trench was similar in design to the actual disposal bed in the new sand filter system. This yields a loading rate of 0.034m/d or 0.14cm/hr over the entire trench.

Once again the precipitation rate term is based on the calibrated value derived for the Waverly site and all other terms in Table 7.4 were determined using the procedures outlined in section 6.1.

The unsaturated zone thickness below the original trench was estimated to be 50cm. This assumes that the average static water level was the same as it is now. The elevation of the bottom of the original disposal bed was determined using plan and cross section drawings for the replacement system which showed the location of the original trench. Surveying carried out at the site for this study was tied into these cross sections to locate the water table data relative to the original trench.

Model runs using the above data predicted an undiluted phosphorus concentration of 0.456mg/l at the water table directly below the trench.

If phosphorus reductions are expressed as a percentage of initial concentrations, attenuation at this site is comparable to that at the Waverly site and the recreational facility. A reduction from 3.15mg/l to 0.456mg/l represents a loss of 86% of the phosphorus load over a distance of 50cm. At Waverly a reduction of 83%, from 14.20mg/l to 2.38mg/l, was predicted over a distance of 35cm. Similarly 90% of the initial phosphorus load is lost at the provincial park over 30cm of travel. In this case concentrations decreased from 1.98mg/l to 0.20mg/l. In all three cases soil adsorption capacities and travel distances are much the same. Once again this agrees with the conclusion reached in the preceding section.

8. SUMMARY AND CONCLUSIONS

8.1 Summary

The objective of this research was to develop a modelling methodology that could be used to more accurately estimate annual phosphorus loads to lakes from on-site sewage disposal systems.

The report begins with a review of approaches that have been used to estimate phosphorus loads to lakes. These approaches begin with estimates of the potential annual per-capita load from dwellings. They then estimate the lake loading as all or some proportion of the potential phosphorus loading from dwellings—in the total watershed, or in the portion of the watershed within a specified distance from the lake or its tributaries.

These approaches do not include explicit consideration of factors and processes that control phosphorus removal in soils. These factors and process, and commonly available computer models that have been used to describe them, are explored in detail, based on a thorough review of the relevant literature.

These reviews led to identification of models—CHEMFLO for the unsaturated zone, and MODFLOW and MT3D for the saturated zone—that offered the capability of representing the factors and processes involved in phosphorus removal. Exploration of the use of these models began with sensitivity analyses, based on a range of typical soil parameters; the results suggest responses, in terms of phosphorus removal, to variations in significant model parameters.

Field and laboratory studies provided evidence about possible phosphorus removal under a variety of site and soil conditions. They also provided data for model calibration and verification.

Modelling results reported here include the application of field data from one site to calibrate the unsaturated zone model for phosphorus removal, and application of the calibrated model to other sites. Also included are results of groundwater flow modelling in the saturated zone. Continuing work to apply project data to modelling phosphorus movement in the saturated zone is described.

This study focused on phosphorus movement at the scale of single properties. Modeling at this scale can identify and quantify significant factors and processes that control phosphorus movement. However, further work is necessary to determine the most effective manner in which this information can be incorporated into watershed scale estimates of phosphorus loads.

This project did not include estimation of phosphorus loadings from malfunctioning on-site systems that contribute to lakes via surface discharge.

Examination of results of phosphorus analyses for experimental and field samples identified inconsistencies, which were resolved in consultation with other laboratory facilities.

It became apparent during this study that the analytical limit for detection of phosphorus used by CWRS was an order of magnitude lower than that reported in other studies. The significance of this difference is discussed.

8.2 Conclusions

1. Reported approaches for the estimation of phosphorus loads to lakes from on-site systems do not explicitly consider many of the factors and processes that control phosphorus removal in the soil, and therefore may not accurately represent phosphorus loads reaching lakes from on-site systems.

2. Available computer models—CHEMFLO for the unsaturated zone, and MODFLOW and MT3D for the saturated zone—can adequately represent these factors and processes at the scale of single properties, and can identify and quantify controlling variables.

3. Results based on comparisons with field data indicate that CHEMFLO satisfactorily represents phosphorus removal in the unsaturated zone, and MODFLOW satisfactorily represents saturated flow conditions. Ongoing work is expected to establish the ability of MT3D to represent phosphorus removal in the saturated zone.

4. Results of modelling at this scale can provide guidance about relative effects of soil and topographic characteristics that may influence planning decisions related to phosphorus loadings from on-site systems, but further work is necessary to determine the most effective manner in which this information can be incorporated into watershed scale estimates of phosphorus loads.

5. Most of the reported studies of phosphorus loadings have used results of phosphorus analyses based on a detection limit of 0.02 mg/L. Results of CWRS studies, based on a detection limit of 0.001 mg/L, indicate that phosphorus loads may be underestimated if loads contributed by concentrations lower than 0.02 mg/L are ignored.

6. The stannous chloride method for phosphorus analysis provides a detection limit of 0.001 mg/L, and eliminates some inconsistencies in results of groundwater analysis when compared with the ascorbic acid method.

«Estimation des déversements, dans les lacs, de phosphore provenant d'installations sur place d'élimination des eaux d'égouts»

RÉSUMÉ ET CONCLUSIONS

Résumé

Cette recherche avait pour but d'élaborer un modèle pouvant permettre d'estimer avec plus de précision la quantité de phosphore provenant d'installations sur place d'élimination des eaux d'égouts et déversée annuellement dans les lacs.

Le rapport commence par une récapitulation des méthodes qui sont habituellement utilisées pour estimer les déversements de phosphore dans les lacs. Ces méthodes procèdent d'abord à l'évaluation, par habitant, de la quantité de phosphore pouvant provenir annuellement des habitations. Elles évaluent ensuite la quantité déversée dans les lacs selon que le déversement résulte entièrement ou partiellement des effluents de phosphore susceptibles de provenir des habitations - pour tout le bassin hydrographique ou pour une portion de celui-ci à une distance donnée du lac ou de ses affluents.

Or, ces méthodes ne tiennent pas expressément compte des facteurs et des processus qui agissent sur l'élimination du phosphore dans les sols. Ces facteurs et ces processus, de même que les modèles informatiques courants qui servent à les décrire, sont explorés en détail à partir d'une revue complète de la documentation pertinente.

C'est ainsi que l'on a pu trouver des modèles (CHEMFLO pour la zone non saturée, MODFLOW et MT3D pour la zone saturée) qui pouvaient modéliser les facteurs et les processus agissant sur l'élimination du phosphore. L'exploration de l'emploi de ces modèles a commencé par des analyses de sensibilité fondées sur divers paramètres de sols typiques. Les résultats obtenus évoquent des réponses, sur le plan de l'élimination du phosphore, à des variations touchant d'importants paramètres du modèle.

Des études sur le terrain et en laboratoire ont fourni des preuves d'une possible élimination du phosphore dans divers genres de sites et de conditions de sol. Elles ont également produit des données qui permettent d'étalonner et de vérifier les modèles.

Les résultats de la modélisation fournis dans le présent document portent sur l'application des données recueillies sur un site à l'étalonnage du modèle de la zone non saturée concernant l'élimination du phosphore, et sur l'application du modèle étalonné à d'autres sites. Sont aussi fournis les résultats de la modélisation du mouvement de la nappe souterraine dans la zone saturée. On décrit le travail permanent servant à appliquer les données recueillies à la modélisation des déplacements du phosphore dans la zone saturée.

Cette étude est axée sur le déplacement du phosphore à l'échelle de propriétés individuelles. Une modélisation effectuée à cette échelle peut relever et quantifier des facteurs et des processus significatifs agissant sur les déplacements du phosphore. Cependant, de plus amples travaux seront nécessaires afin de déterminer quel est le moyen le plus efficace de transférer l'information ainsi

recueillie à l'échelle des estimations réalisées pour le bassin hydrographique en vue de déterminer la quantité de phosphore qui s'y déverse.

Cette étude n'a pas porté sur les déversements, dans les lacs, de phosphore issu d'effluents de surface produits par des installations sur place en mauvais état.

L'examen des résultats des analyses du phosphore en laboratoire et sur le terrain a fait état d'inconsistances qui ont toutefois été résolues en consultation avec d'autres laboratoires.

Il est apparu évident durant cette étude que la limite analytique de détection du phosphore utilisée par le CWRS était d'un ordre de grandeur plus faible que ce que d'autres études avaient signalé. L'importance de cette différence est commentée.

Conclusions

1. Les méthodes relevées pour l'estimation des déversements, dans les lacs, du phosphore provenant d'installations sur place ne tiennent pas explicitement compte d'un grand nombre de facteurs et de processus qui agissent sur l'élimination du phosphore dans le sol et peuvent, par conséquent, ne pas donner une idée très précise de la quantité de phosphore qui se déverse dans les lacs à partir d'installations sur place.

2. Les modèles informatiques disponibles - CHEMFLO pour la zone non saturée ainsi que MODFLOW et MT3D pour la zone saturée - peuvent modéliser avec une relative précision ces facteurs et processus à l'échelle des propriétés individuelles et sont en mesure de relever et de quantifier les variables d'influence.

3. Les résultats fondés sur des comparaisons avec des données recueillies sur le terrain indiquent que CHEMFLO modélise fidèlement l'élimination du phosphore dans la zone non saturée et que MODFLOW modélise fidèlement l'élimination en sol saturé. Des travaux en cours devraient établir la capacité de MT3D à modéliser l'élimination du phosphore dans une zone saturée.

4. Les résultats d'une modélisation à cette échelle peuvent fournir des indications quant aux effets relatifs des caractéristiques du sol et de la topographie susceptibles d'influer sur les décisions d'urbanisme ayant trait au déversement de phosphore provenant des installations sur place, mais de plus amples études seront nécessaires pour déterminer la façon la plus efficace de faire correspondre cette information aux estimations réalisées au sujet des déversements de phosphore à l'échelle du bassin hydrographique.

5. La plupart des études signalées faisant état de déversements de phosphore reposent sur des résultats d'analyse de phosphore fondés sur une limite de détection de 0,02 mg/L. Les résultats du CWRS, fondés sur une limite de détection de 0,001 mg/L, indiquent que les déversements de phosphore peuvent être sous-estimés si l'on ne tient pas compte des déversements de phosphore à des concentrations inférieures à 0,02 mg/L.

6. La méthode faisant appel au chlorure stanneux pour l'analyse du phosphore permet une limite de détection de 0,001 mg/L et élimine certaines inconstances dans les résultats des analyses de la nappe souterraine comparativement à la méthode utilisant l'acide ascorbique.

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APPENDIX A - TABLES

Column Thickness	Grain Size of Fill Material*	Phosphorus Retention Coefficient
30 in. Sand	D_{10} = 2.5 mm	0.04
	D_{10} = 1.0 mm	0.01
	D_{10} = 0.6 mm	0.22
	D_{10} = 0.30 mm	0.34
	D_{10} = 0.24 mm	0.48
30 in. Silty Sand		0.63
15 in. 50% sand, 50% clay silt	D_{10} = 0.24 mm	0.74

*D_{10} = diameter exceeded by 90 percent of particles by weight

Table 2.1 Phosphorus Retention Coefficents (after Brandes et al, 1974)

Equation	Reference
$\rho\frac{\partial S}{\partial t}+\theta_w\frac{\partial C}{\partial t}=\theta_w D\frac{\partial^2 C}{\partial z^2}-q\frac{\partial C}{\partial z}-Q$	Mansell et al. (1977)
$\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial z^2}-V\frac{\partial C}{\partial z}-\frac{\rho}{\theta_w}\frac{\partial S}{\partial t}$	Enfield and Shew (1975) Enfield et al. (1981) Mansell et al. (1985) Cameron and Klute (1977)
$D\frac{\partial^2 C}{\partial z^2}=V\frac{\partial C}{\partial z}+\frac{\partial C}{\partial t}+\frac{1}{\theta_w}\frac{\partial S}{\partial t}$	Enfield (1974)
$\frac{\partial(\theta_w C)}{\partial t}=\frac{\partial}{\partial x}\left[D_x\frac{\partial(\theta_w C)}{\partial x}\right]+\frac{\partial}{\partial z}\left[D_z\frac{\partial(\theta_w C)}{\partial_z}\right]$ $+q_x\frac{\partial C}{\partial_x}+q_z\frac{\partial C}{\partial_z}-\rho\frac{\partial S}{\partial t}\pm\phi$	Tim and Mostaghimi (1989)

Table 3.1. Equations used to describe phosphorus transport and transformations.

Soil No.	Soil Type	Grain Size Analysis Sand (%)	Silt (%)	Clay (%)	Bulk Density (g/cm^3)	Porosity (cm^3/cm^3)	Ksat (cm/hr)	Loading Rate (cm/hr)
1	Sandy Soil	96	1.5	2.4	1.39	0.34	18.3	0.17[†]
2	Silty Clay	5.1	49.5	45.4	1.50[*]	0.43[**]	0.22[**]	0.04[†]

Soil No.	van Genuchten Parameters[**]		Langmuir Coef. Parameters		KD	kI
	a (α)	b (n)	K	b		
1	4.64×10^{-2}	1.56	n.g.	n.g.	0.43	0.1
2	6.60×10^{-4}	1.28	4.35	216	14.18[††]	0.25[‡]

Terms:

Ksat = Saturated hydraulic conductivity
KD = Partition coefficient
kI = First order rate constant for precipitation from solution
n.g. - data not given (and not required)

Sources of Data:

Soil 1 - all data from Mansell et al. (1977) or Tim and Mostaghimi (1989)
Soil 2 - data from McCallister and Logan (1978) except as follows:

[*] Value from Dethier (1988) for soil with similar grain size distribution
[**] Value estimated using SOILPROP
[†] Value from Nova Scotia Department of Health and Fitness (1988)
[††] Value determined from Langmuir coefficients using KD = (Kb) / (1+KC), where C = 15 mg/l
[‡] Value assumed

Table 4.1 Data for hypothetical soils used in modeling phosphorus movement with CHEMFLO

Run No.	Soil No.	K_D (cm^3/g)	K_I hr^{-1}	Loading Rate (cm/hr)	Time to Reach Steady State (hrs)	Phosphorus Concentration (mg/l)	
						at 30cm	at 90cm
1	1	0.43	0.0	0.17	1100	15	15
2	2	14.18	0.0	0.04	100 000	15	15
3	1	0.43	0.1	0.17	330	0.955	0.009
4*	2	14.18	0.1	0.04	6000	0.000	0.000
5*	2	14.18	0.25	0.04	2000	0.000	0.000
6	2	14.18	0.1	0.10**	2050	0.038	0.000

Defenition of Soils:

Soil 1 - Sandy Soil
Soil 2 - Silty Clay

Defenition of Terms:

K_D - Partition coefficient for phosphorus.
K_I - Precipitation rate term for phosphorus.

* Phosphorus did not migrate below 30cm in Run 4.
Phosphorus did not migrate below 20cm in Run 5.

** Hydraulic loading rate incorporates potential effects of rain.

Table 4.2 Results of CHEMFLO model runs using hypothetical soils.

Soil	Grain Size (millimetres)																			
	4.75	2.00	0.850	0.425	0.250	0.106	0.075	0.0566	0.0421	0.0313	0.0233	0.0174	0.0129	0.0096	0.0072	0.0053	0.004	0.003	0.0022	0.0016	0.0012
PF-1	99.60	98.45	96.33	91.94	81.85	58.04	45.51	42.13	38.75	36.05	33.07	29.59	25.52	20.28	15.38	11.66	6.46	2.98	1.71	1.22	0.78
PF-2	99.00	96.90	93.55	88.28	78.24	59.13	48.74	45.47	42.19	39.74	36.88	33.13	28.61	22.57	17.16	13.20	7.53	3.84	2.33	1.70	1.13
PF-3	99.60	99.42	98.78	93.14	76.61	29.76	18.99	15.54	13.50	12.08	10.44	8.84	7.42	5.71	4.29	3.28	1.86	0.95	0.63	0.49	0.29
PF-4	99.05	97.60	94.97	90.15	82.01	65.11	49.66	44.76	43.08	41.11	38.96	36.51	32.45	26.77	20.85	16.07	9.37	4.65	2.68	1.96	1.31
WAV-1	93.30	89.63	86.02	81.48	77.11	66.71	56.27	51.66	48.59	45.13	40.97	36.23	30.41	23.62	17.73	13.51	7.75	3.84	1.73	1.09	0.51
WAV-2	98.07	95.05	91.11	86.30	80.86	69.53	57.02	51.45	47.05	43.22	39.08	34.02	28.39	22.23	16.59	12.51	7.07	3.37	1.30	0.72	0.20
BH-1	58.88	49.94	42.67	36.41	30.32	20.08	15.44	13.47	11.15	9.42	7.64	5.90	4.53	3.27	2.32	1.71	0.99	0.58	0.41	0.31	0.19
BH-2	80.72	72.17	64.67	58.62	54.07	46.16	42.97	41.70	39.78	37.51	34.15	29.56	24.10	18.38	13.54	10.04	5.63	2.88	1.83	1.40	0.96
RS-1	65.75	59.08	52.07	44.90	38.60	31.96	28.01	26.62	25.17	23.58	21.33	18.49	15.33	11.78	8.77	6.55	3.63	1.74	1.03	0.76	0.53
RS-2	80.49	69.00	60.36	53.00	47.89	40.37	35.63	33.10	30.50	27.97	25.03	21.74	18.06	13.97	10.33	7.61	4.28	2.03	1.18	0.88	0.57

Table 6.1 Grain Size Distribution Data for Study Soils

Soil	d_{10} (mm)	$K_{(sat)}$* (Hazen) (cm/s)	$K_{(sat)}$ (Soilprop) (cm/s)	$K_{(sat)}$ (Average) (cm/s)	$K_{(sat)}$ (Permeameter) (cm/s)
10A	0.0046	0.005	0.008	0.006	0.0006
10B	0.0044	0.004	0.005	0.005	
10C	0.0220	0.022	0.047	0.035	0.001
10D	0.0041	0.004	0.004	0.004	
WAV-1	0.0043	0.004	0.002	0.003	
WAV-2	0.0045	0.005	0.004	0.004	
BH-1	0.0330	0.033	0.074	0.053	0.001
BH-2	0.0051	0.005	0.003	0.004	
RAW-1	0.0080	0.008	0.009	0.009	0.001
RAW-2	0.0070	0.007	0.008	0.008	

* Assumes Hazen Coefficient = 1.0 (Freeze and Cherry, p350)

Table 6.2 Saturated Hydraulic Conductivties of Study Soils

Soil	Langmuir 'K'	Langmuir 'b'
PF-1 (Saturated)	0.0111	1.18
PF-2 (Saturated)	0.0041	1.22
PF-3 (Saturated)	0.0204	0.63
PF-4 (Saturated)	0.0045	1.23
WAV-1 (Saturated)	7.41x10^{-04}	7.38
WAV-2 (Saturated)	0.0037	2.48
BH-1 (Saturated)	0.0028	7.84
BH-2 (Saturated)	7.15x10^{-06}	881.80
RS-1(Saturated)	0.0027	2.88
RS-2 (Saturated)	7.41x10^{-04}	7.38
PF-1 (Unsaturated)	9.92x10^{-06}	664.40
WAV-1 (Unsaturated)	1.26x10^{-05}	490.60
BH-1 (Unsaturated)	0.0103	3.50
RS-1(Unsaturated)	1.22x10^{-05}	503.20
RS-2 (Unsaturated)	6.25x10^{-04}	9.01

Table 6.3 Results of Adsorption Experiments

Date	Total Dissolved Phosphorus (mg/l)		Percent Removal[1]
	Influent Concentration	Effluent Concentration	
1/02/93	50	0.03	99
5/03/93	14	0.01	99
19/04/93	12.3	0.02	98
3/06/93	14.3	0.01	99
16/08/93	14.7	0.02	99
7/12/93	12.2	0.01	99
25/01/95	14	0.1	93
1/02/95	14.9	0.1	94

[1] Percent removal allows for effect of dilution by groundwater, based on measurements of chloride and TDP in water and sewage entering the model, and mixed water and sewage in effluent.

TABLE 6.4 Phosphorus Removal in Contour Trench Model

Sand Fill Characteristics		(Total Dissolved Phosphorus, mg/l)			Percent Removal (End of Trench)
Uniformity Coefficent	d10	Model Influent (Effluent)	Model Effluent		
			Mid-Point	End	
7.3	0.29	12.2	10.0	5.9	40
5.3	0.15	12.2	0.5	<0.1	99
1.7	0.23	12.2	4.8	0.3	98

TABLE 6.5 Phosphorus Removal in Lateral Sand Filter Model

Well Number	Depth to Water Table (m)	Sample Depth	Total Dissolved Phosphorus (mg/l)		Chloride (mg/l)
	Nov 1993		June 1992	Nov 1993	Nov 1993
14	1.73	Shallow	--	0.006	42.0
		Intermediate	--	0.032	4.0
		Deep	--	0.025	43.5
10	1.75	Shallow	--	0.032	59.0
		Intermediate	0.006	0.061	46.5
		Deep	0.010	0.064	26.0
10A	1.84	Shallow	--	--	--
		Intermediate	0.005	--	--
		Deep	0.002	--	--
15	1.60	Shallow	--	--	--
		Intermediate	0.004	--	--
		Deep	0.004	--	--
9	1.65	Shallow	--	0.161	57.0
		Intermediate	0.021	0.058	63.5
		Deep	--	0.015	24.0
8	1.53	Shallow	--	0.134	82.0
		Intermediate	0.003	0.068	90.5
		Deep	--	0.010	14.0
5	1.33	Shallow	--	0.060	130.0
		Intermediate	0.009	0.124	123.0
		Deep	0.003	0.004	11.5
4	1.42	Shallow	--	0.089	10.5
		Intermediate	0.004	0.021	11.0
		Deep	0.004	0.033	12.0

Table 6.6 Results of Port Maitland Piezometer Sampling

- Water levels measured on November 9, 1993 -

Piez. 1	Piez. 3	Piez. 4	Piez. 5	TW1	TW2	TW3	TW4
0.34	0.48	0.65	0.24	--	--	--	--

All units are meters below ground level (i.e. height of casing above ground has been subtracted from measurement)

- Water levels measured after November 12, 1993 -

Date	Piez . 1	Piez . 2	Piez . 3	Piez . 4	Piez . 5	Piez . 6	Piez . 7	Piez . 8	Piez . 9	Piez . 10	Piez . 11
Jan 16/95	0.21	0.31	0.31	0.51	0.20	0.54	0.22	0.41	0.64	0.42	0.13
Jan 30/95	0.43	0.55	0.48	0.74	0.36	0.53	0.31	0.62	0.62	0.48	0.24
Feb 22/95	0.53	0.61	0.48	0.71	0.40	0.84	**	0.62	1.00	0.73	0.37
Mar 17/95	0.45	0.54	0.49	0.58	**	0.81	**	0.59	0.89	0.50	**
June 16/95	0.24	0.33	0.38	0.55	0.25	0.45	0.25	0.45	0.60	0.43	0.22
June 23/95	0.72	0.78	0.72	0.80	0.58	0.83	0.61	0.91	0.99	0.82	0.60
Sept 8/95	dry	2.14	1.01	dry	dry	2.24	1.91	dry	2.31	2.12	dry

All units are meters below ground level (i.e. height of casing above ground has been subtracted from measurement)

** Water in casing was frozen, therefore no measurement was recorded.

Table 6.7 Water Level Measurements at Waverly Site

- Total Phosphorus Results (all results reported as mg/l) -

Date	Piez. 1	Piez. 3	Piez. 4	Piez. 5	Piez. TW1	Piez. TW2	Piez. TW3	Piez. TW4
Nov 9/93	0.007	10.00	0.075	0.022	--	0.026	0.013	0.011

Date	Raw Effl.	Piez. 1	Piez. 2	Piez. 3	Piez. 4	Piez. 5	Piez. 6	Piez. 7	Piez. 8	Piez. 9	Piez. 10	Piez. 11
Jan 16/95	14.70	0.005	0.020	7.80	0.94	0.015	0.010	0.005	0.061	0.042	0.043	0.059
June 23/95	19.10	0.004	0.011	0.071	n.s.	0.023	0.009	0.004	n.s.	0.026	0.037	0.031

- Chloride Results (all results reported as mg/l) -

Date	Piez. 1	Piez. 3	Piez. 4	Piez. 5	Piez. TW1	Piez. TW2	Piez. TW3	Piez. TW4
Nov 9/93	8.6	35.5	17.5	15.5	--	6.7	7.0	6.8

Date	Raw Effl.	Piez. 1	Piez. 2	Piez. 3	Piez. 4	Piez. 5	Piez. 6	Piez. 7	Piez. 8	Piez. 9	Piez. 10	Piez. 11
Jan 16/95	42.0	8.1	8.1	36.5	24.0	15.0	16.5	24.5	8.3	10.0	9.4	8.2
June 23/95	60.0	8.2	8.9	46.5	n.s.	18.0	17.0	16.0	n.s.	8.7	10.5	7.5

Table 6.8 Concentrations of Phosphorus and Chloride in Raw Effluent and Groundwater at Waverly Site

Date	Piez. 1	Piez. 2	Piez. 3
Sept 19/94	3.58	2.87	2.82
Oct 30/94	3.20	2.41	2.38
Feb 17/95	2.21	1.54	1.59
Apr 27/95	2.03	1.46	1.46
Jun 1/95	2.55	1.87	1.89
June 29/95	2.40	1.74	1.79
July 27/95	2.90	2.19	2.18
Aug??/95	3.43	2.71	2.68

All units are depth of the static water level below the well collar in meters.

Table 6.9 Water Level Measurements at Bridgewater Site

- Total Phosphorus Results (all results reported as mg/l) -

Date	Raw Effl.	Piez. 1	Piez. 2	Piez. 3
Sept 19/94*	n.s.	0.062	0.780**	0.060
Nov 2/94	4.500	0.016	0.018	0.020
Feb 17/95	19.600	0.014	0.044	0.022
Apr 27/95	17.400	0.013	0.026	0.025
June 29/95	26.000	0.017	0.024	0.074

* Piezometers were not purged before sample collection, tubing raised ~20cm off of piezometer bottom during sample collection.

** Likely contaminated sample.

- Chloride Results (all results reported as mg/l) -

Date	Raw Effl.	Piez. 1	Piez. 2	Piez. 3
Sept 19/94*	n.s.	119.5**	68.0	23.0
Nov 2/94	42.0	40.5	49.5	31.0
Feb 17/95	94.0	12.5	16.0	15.5
Apr 27/95	138.0	24.0	20.5	21.0
June 24/95	182.0	35.5	25.5	33.0

* Piezometers were not purged before sample collection, tubing raised ~20cm off of piezometer bottom during sample collection.

** Likely contaminated sample.

Table 6.10 Concentrations of Phosphorus and Chloride in Raw Effluent and Groundwater at Bridgewater Site

Date	Piez. 1	Piez. 2	Piez. 3	Piez. 4	Piez. 5	Piez. 6	Piez. 7
Jul 15/94	1.22	0.63	1.61	1.55	2.41	0.94	0.49
Jul 19/94	1.35	0.69	1.64	1.60	2.49	1.00	0.46
Sept 8/94	1.42	0.77	1.80	1.76	2.96	1.17	0.65
Oct 30/94	1.79	0.96	1.94	1.62	3.14	1.23	0.81
Nov 25/94	0.60	0.45	1.39	1.19	2.75	0.41	0.48

All values refer to the depth of the static water level below the well collar in meters.

Table 6.11 Water Level Measurements at Provincial Recreational Facility

- Chloride Results (all concentrations are expressed as mg/l) -

Date	Piez. 1	Piez. 2	Piez. 3	Piez. 4	Piez. 5	Piez. 6	Piez. 7	Raw Effluent
Jul 19/94	4.3	34.5	5	2.4	4.3	1.8	4.1	82.0
Sept 8/94	4.7	53.0	4.4	2.3	3.2	1.7	7.2	170.0
Oct 30/94	4.4	55.5	4.3	4.6	3.8	2.5	19.0	100.0
Nov 25/94	5.5	50.0	4.3	2.1	3.3	n.s.	16.3	150.0

- Phosphorus Results (all concentrations are expressed as mg/l) -

Date	Piez. 1	Piez. 2	Piez. 3	Piez. 4	Piez. 5	Piez. 6	Piez. 7	Raw Effluent
Jul 19/94	0.030	0.016	0.026	0.006	0.043	0.016	0.011	1.963
Sept 8/94	0.015	0.012	0.032	0.010	0.093	0.025	0.007	1.880
Oct 30/94	0.007	0.002	0.017	0.003	0.052	0.017	0.003	1.780
Nov 25/94	0.042	0.006	0.038	0.009	0.074	n.s.	0.010	2.300

Table 6.12 Concentrations of Phosphorus and Chloride in Raw Effluent and Groundwater at Provincial Recreational Facility

Date	Piez. 1	Piez. 2	Piez. 3	Piez. 4
Dec 18/94	--	1.92	2.13	1.02
Jan 2/95	1.98	dry	1.98	0.90
Jan 28/95	1.92	1.61	1.91	0.70
May 14/95	1.84	dry	2.00	0.94
June 24/95	2.03	dry	2.25	1.15

All values refer to the depth of the static water level below the well collar in meters.

Table 6.13 Water Level Measurements at Elementary School Site

- Total Phosphorus Results (all results reported as mg/l) -

Date	Raw Effl.	Piez. 1	Piez. 2	Piez. 3	Piez. 4
Jan 28/95	n.s.	0.018	n.s.	0.023	0.030
May 14/95	2.500	0.005	n.s.	0.018	0.029
June 24/95	3.800	0.007	n.s.	0.011	0.050

- Chloride Results (all results reported as mg/l) -

Date	Raw Effl.	Piez. 1	Piez. 2	Piez. 3	Piez. 4
Jan 28/95	n.s.	6.3	n.s.	13.0	28.5
May 14/95	915.0	5.3	n.s.	24.0	21.5
June 24/95	945.0	5.7	n.s.	23.5	16.5

Table 6.14 Concentrations of Phosphorus and Chloride in Raw Effluent and Groundwater at Elementary School Site

Soil Parameters	Value
van Genuchten α (cm^{-1})	9.60x10^{-3}
van Genuchten n (unitless)	1.29
Saturated Hyd. Cond. (cm/hr)	1.08
Soil Bulk Density (g/cm^{3})	1.70
Apparent Dispersivity (cm)	5
Partition Coefficient (cm^{3}/g)	0.0062
System Parameters	
Hydraulic Loading Rate (cm/hr)	0.10
Effluent Phosphorus Conc (mg/l)	14.2

Table 7.1 Soil WAV-1 input for Chemflo.

Soil Parameters	Value
van Genuchten α (cm^{-1})	7.07x10^{-2}
van Genuchten n (unitless)	1.38
Saturated Hyd. Cond. (cm/hr)	3.60
Soil Bulk Density (g/cm^{3})	1.66
Apparent Dispersivity (cm)	5
Partition Coefficient (cm^{3}/g)	0.0297
System Parameters	
Hydraulic Loading Rate (cm/hr)	0.08
Effluent Phosphorus Conc (mg/l)	21.0

Table 7.2 Soil BH-1 inputs for Chemflo.

Soil Parameters	Value
van Genuchten α (cm^{-1})	2x10-2
van Genuchten n (unitless)	1.32
Saturated Hyd. Cond. (cm/hr)	2.16
Soil Bulk Density (g/cm^3)	1.53
Apparent Dispersivity (cm)	5
Partition Coefficient (cm^3/g)	0.0066
System Parameters	
Hydraulic Loading Rate (cm/hr)	0.07
Effluent Phosphorus Conc (mg/l)	1.98

Table 7.3 Soil PF-1 inputs for Chemflo.

Soil Parameters	Value
van Genuchten α (cm^{-1})	8.30x10^{-2}
van Genuchten n (unitless)	1.21
Saturated Hyd. Cond. (cm/hr)	3.60
Soil Bulk Density (g/cm^3)	1.68
Apparent Dispersivity (cm)	5
Partition Coefficient (cm^3/g)	0.0062
System Parameters	
Hydraulic Loading Rate (cm/hr)	0.14
Effluent Phosphorus Conc (mg/l)	3.15

Table 7.4 Soil RS-1 inputs for Chemflo.

APPENDIX B - FIGURES

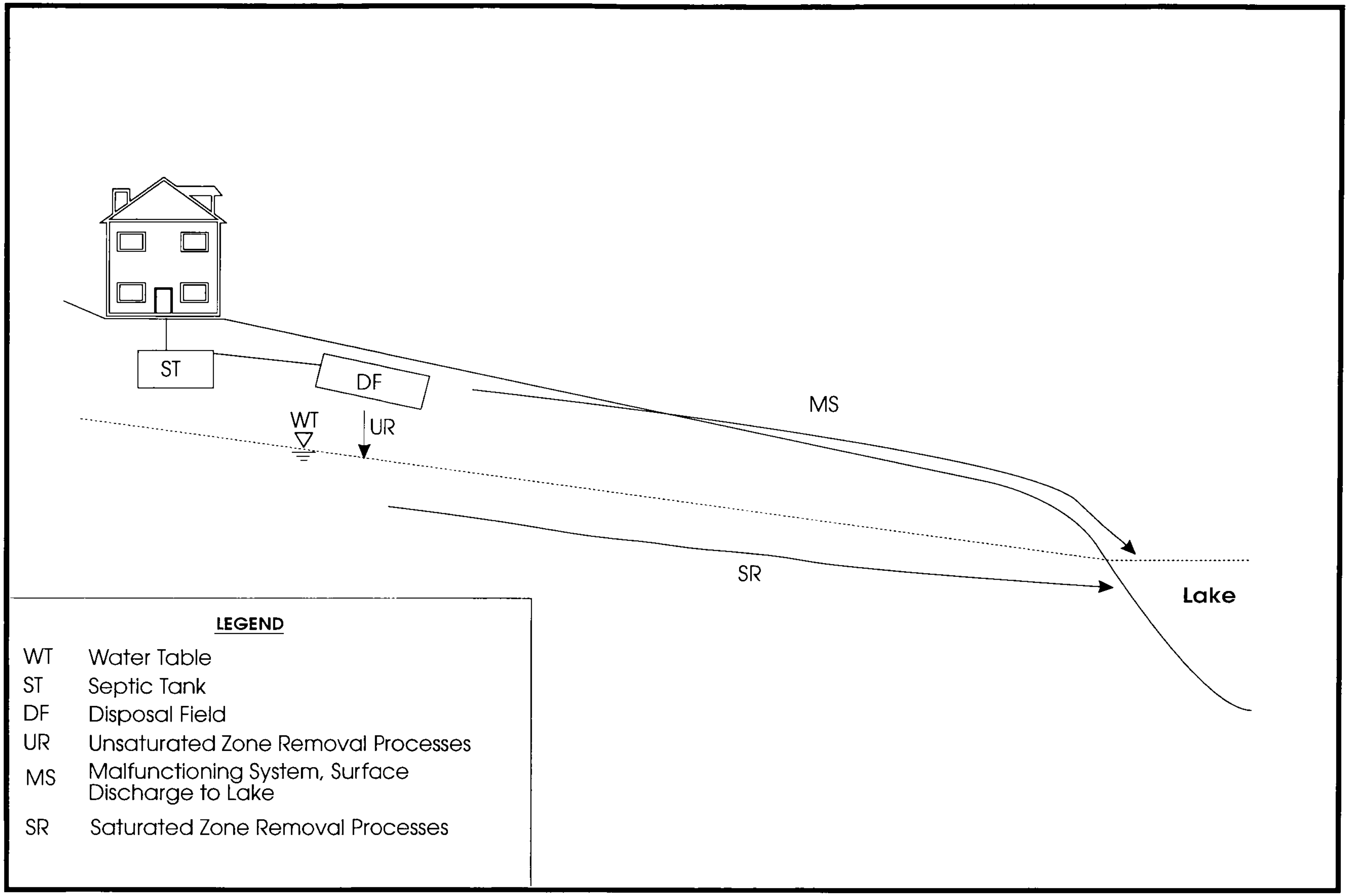

Figure 2.1 Potential Pathways of Phosphorus Migration to Lakes

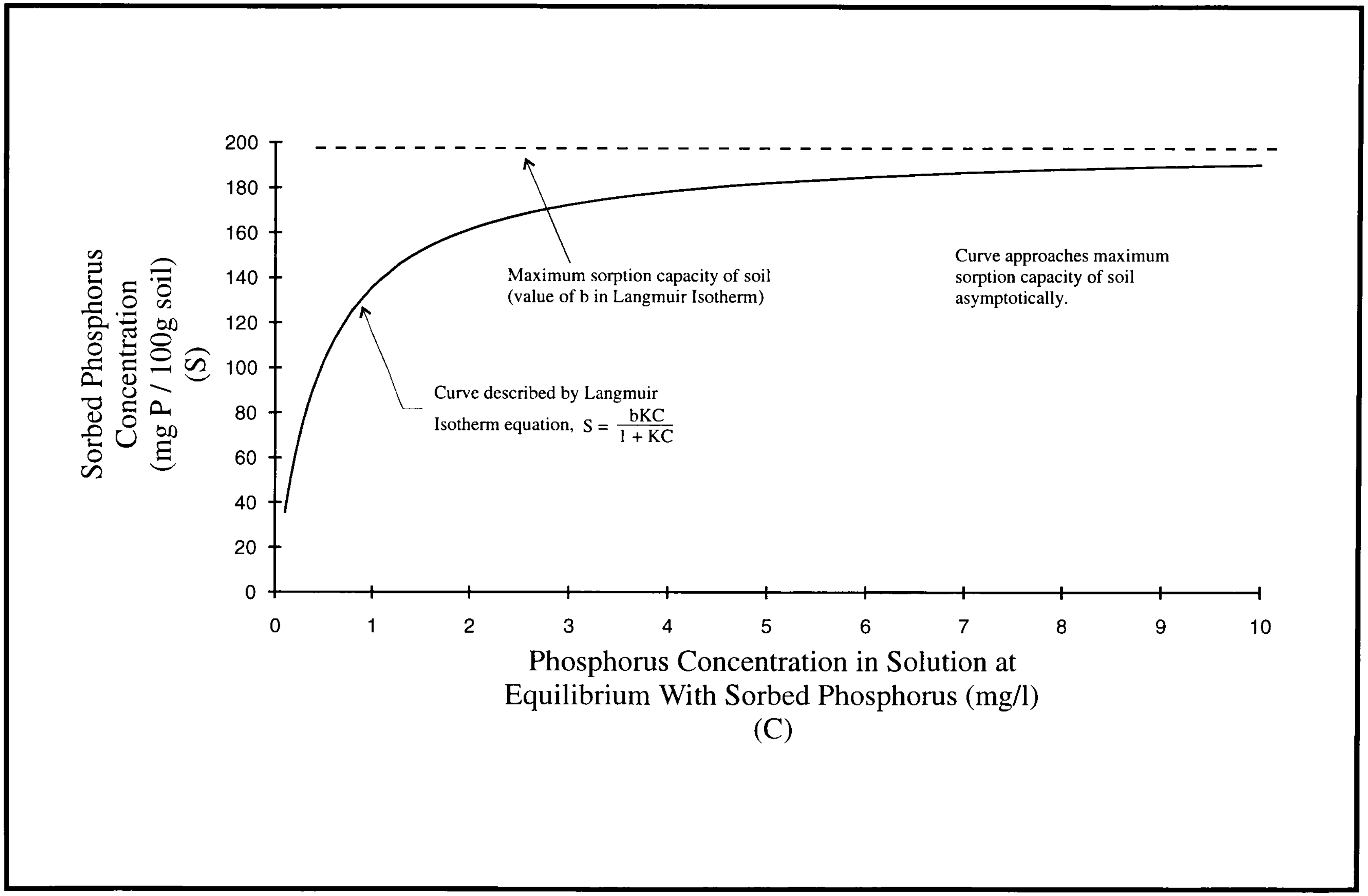

Figure 3.1 Typical Langmuir Isotherm

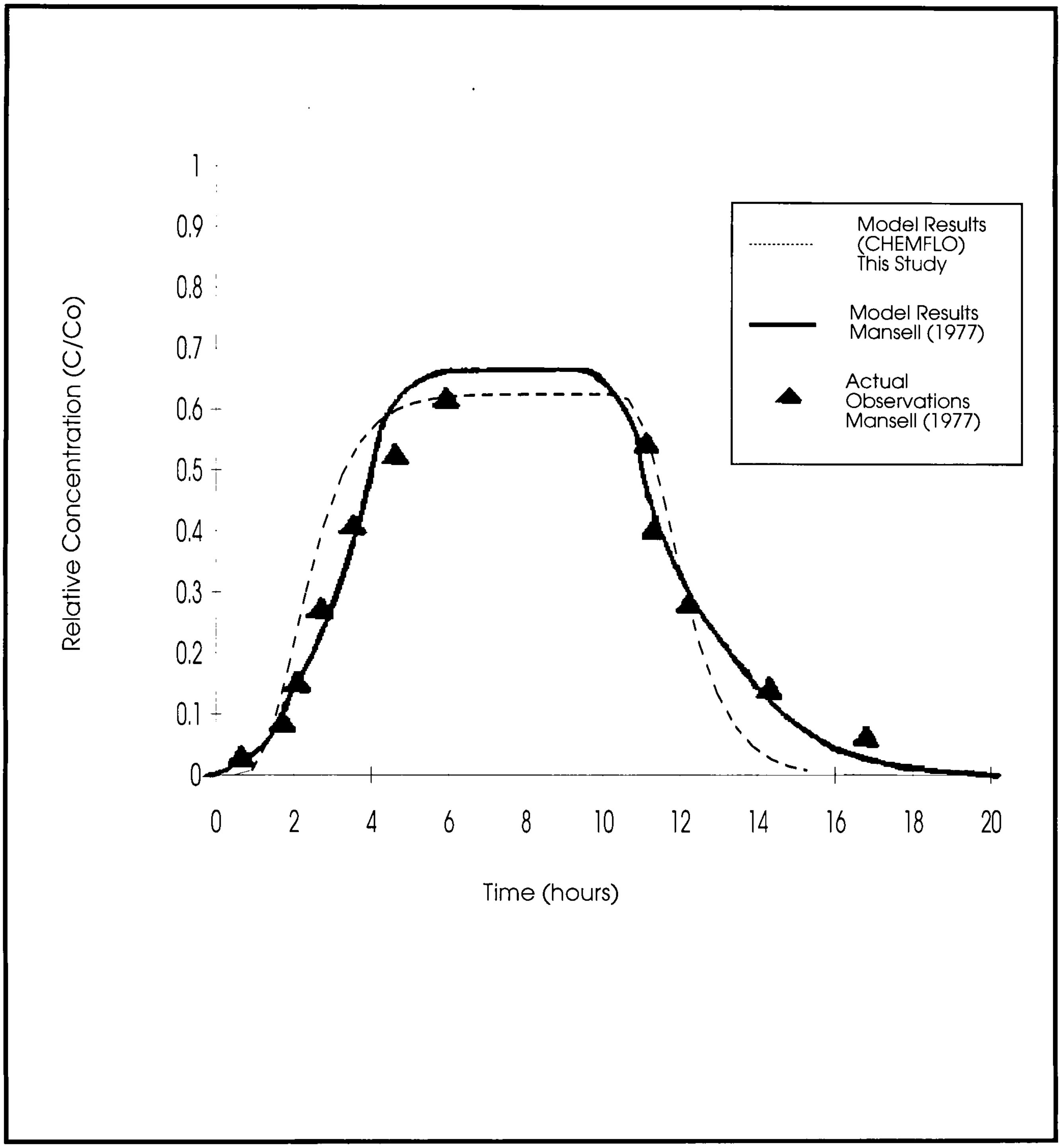

Figure 4.1 Comparison of CHEMFLO results with observations of Mansell (1977).

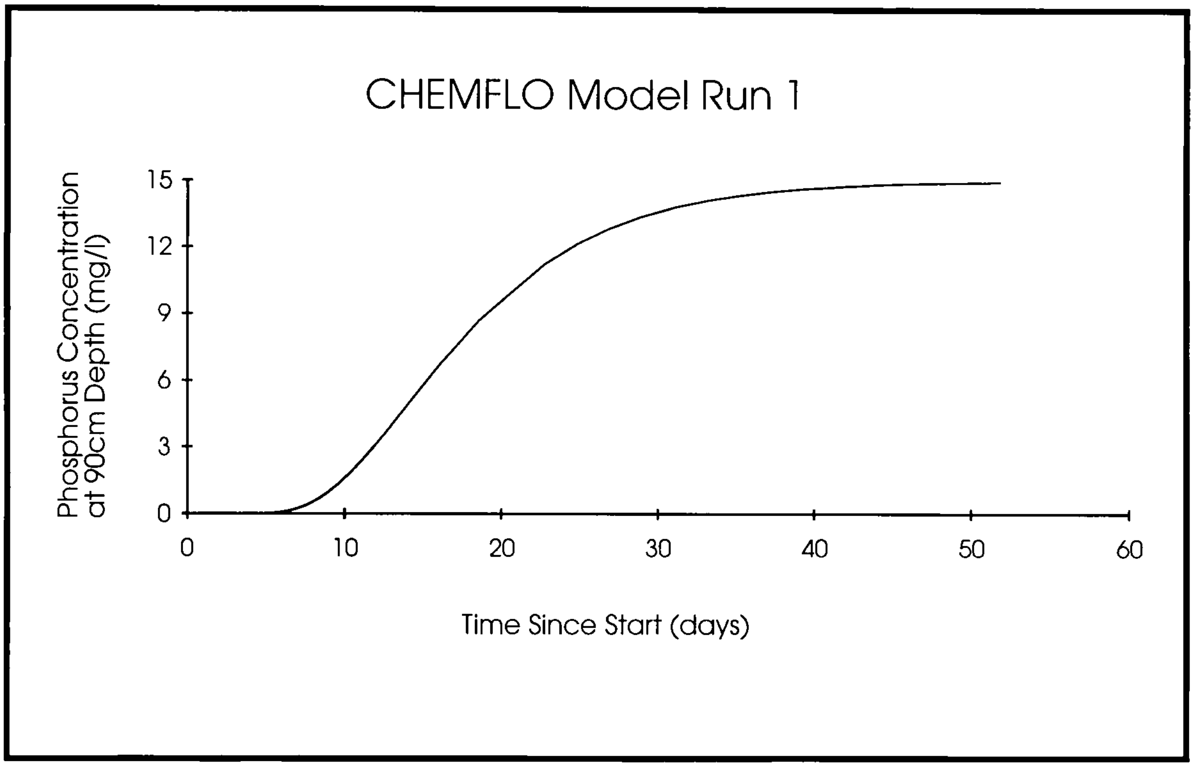

Figure 5.1 Sandy soil phosphorus breakthrough curve at 90cm. First order precipitation rate constant equals 0.0 hr $^{-1}$.

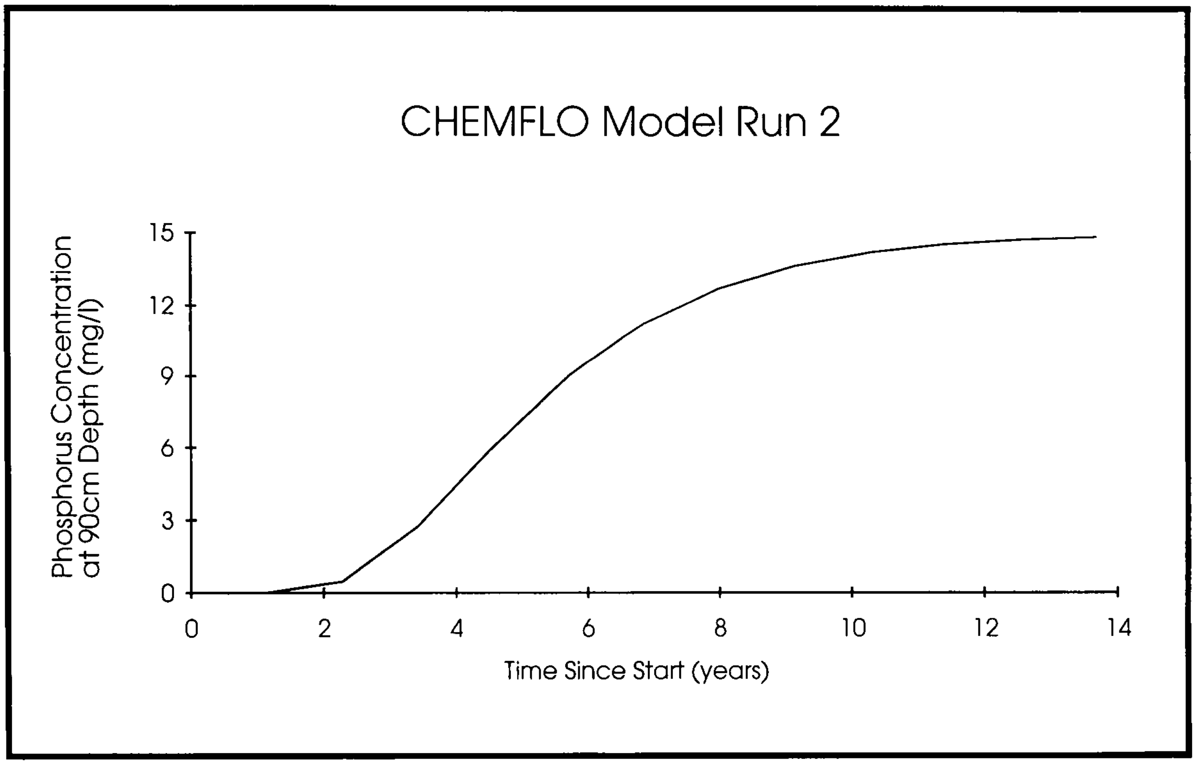

Figure 5.2 Silty clay phosphorus breakthrough curve at 90cm. First order precipitation rate constant equals 0.0 hr $^{-1}$.

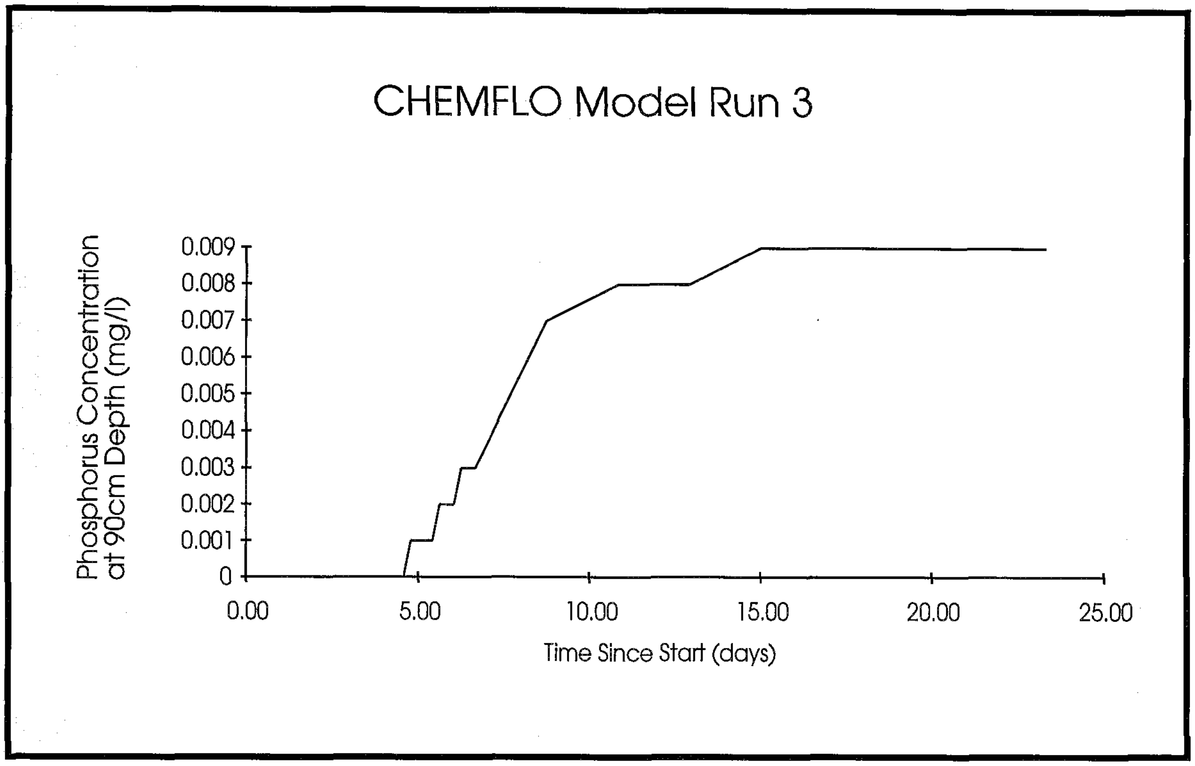

Figure 5.3 Sandy soil phosphorus breakthrough curve at 90cm. First order precipitation rate constant equals 0.1 hr $^{-1}$.

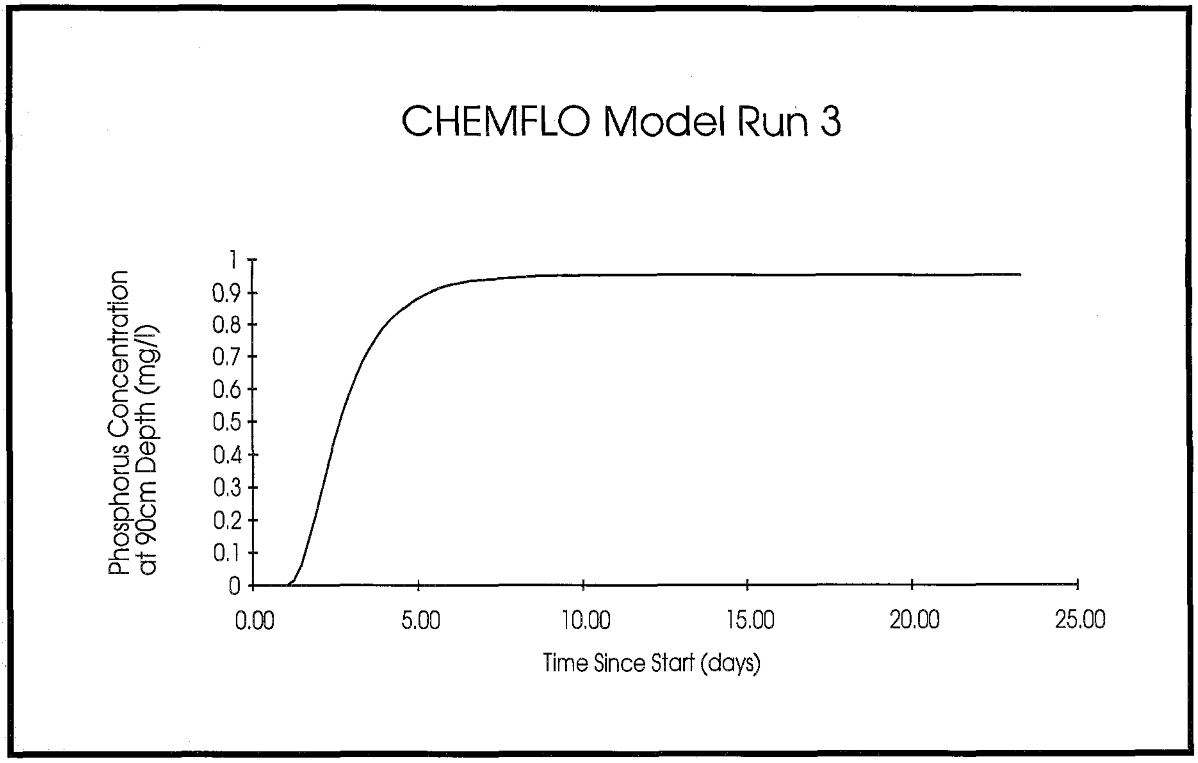

Figure 5.4 Sandy soil phosphorus breakthrough curve at 30cm. First order precipitation rate constant equals 0.1 hr $^{-1}$.

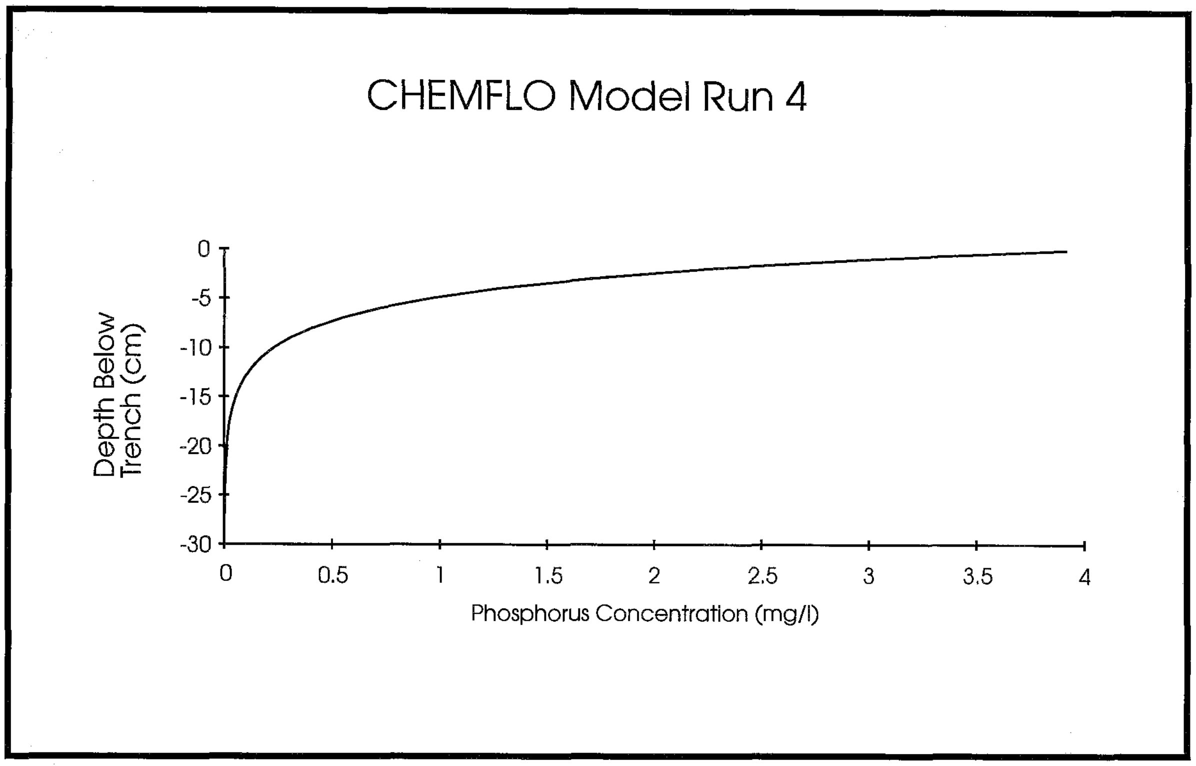

Figure 5.5 Silty clay phosphorus concentration profile.
First order precipitation rate constant equals 0.1 hr $^{-1}$.

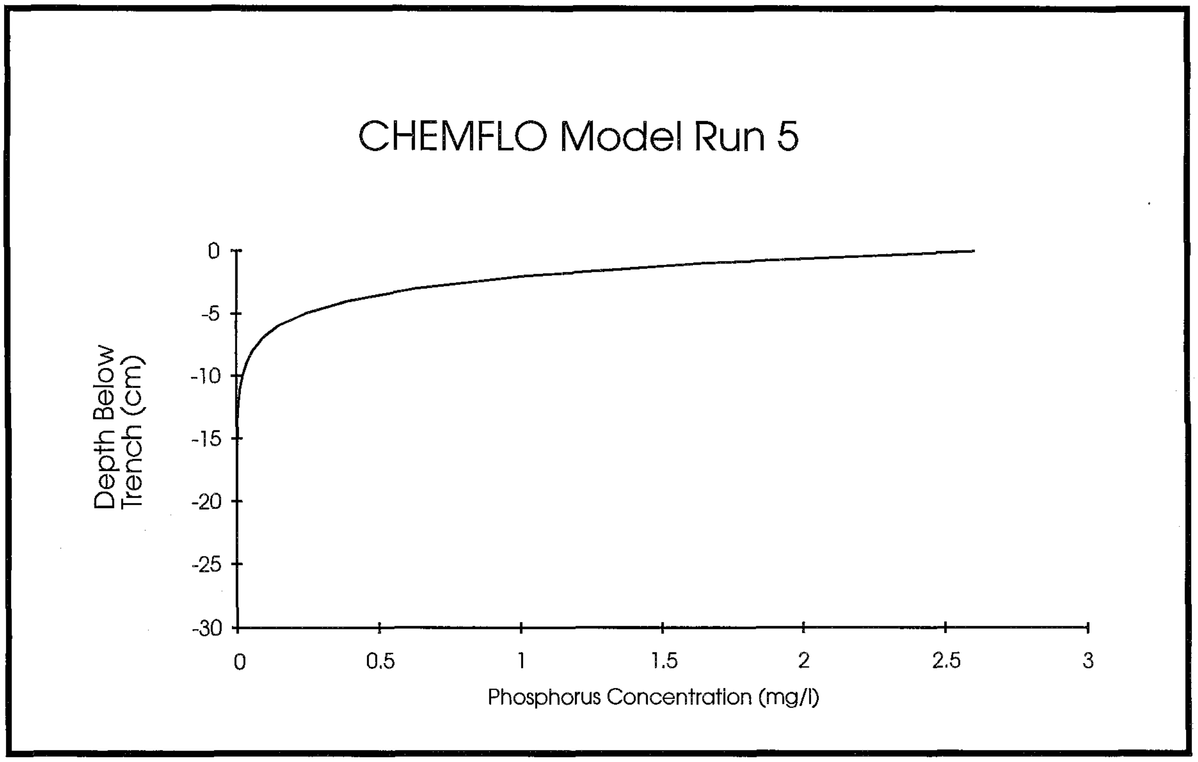

Figure 5.6 Silty clay phosphorus concentration profile.
First order precipitation rate constant equals 0.25 hr $^{-1}$.

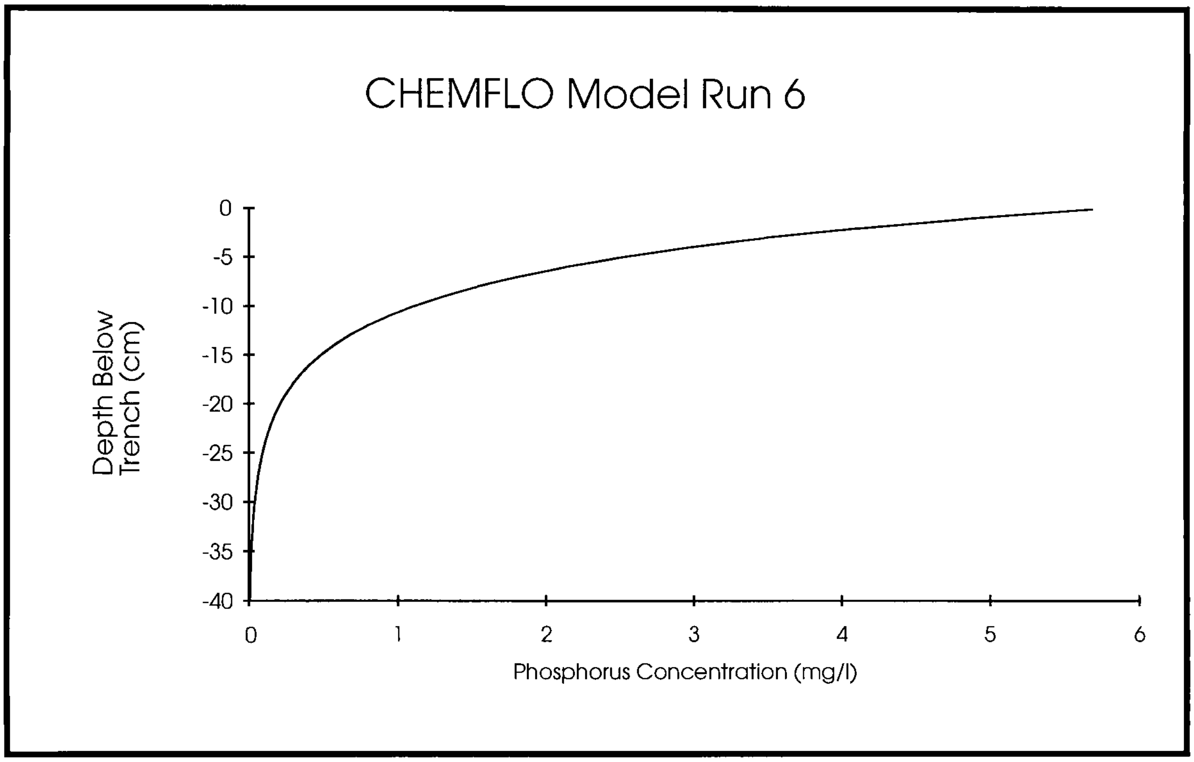

Figure 5.7 Silty clay phosphorus concentration profile. First order precipitation rate constant equals 0.1 hr^{-1}. Hydraulic loading includes rainfall.

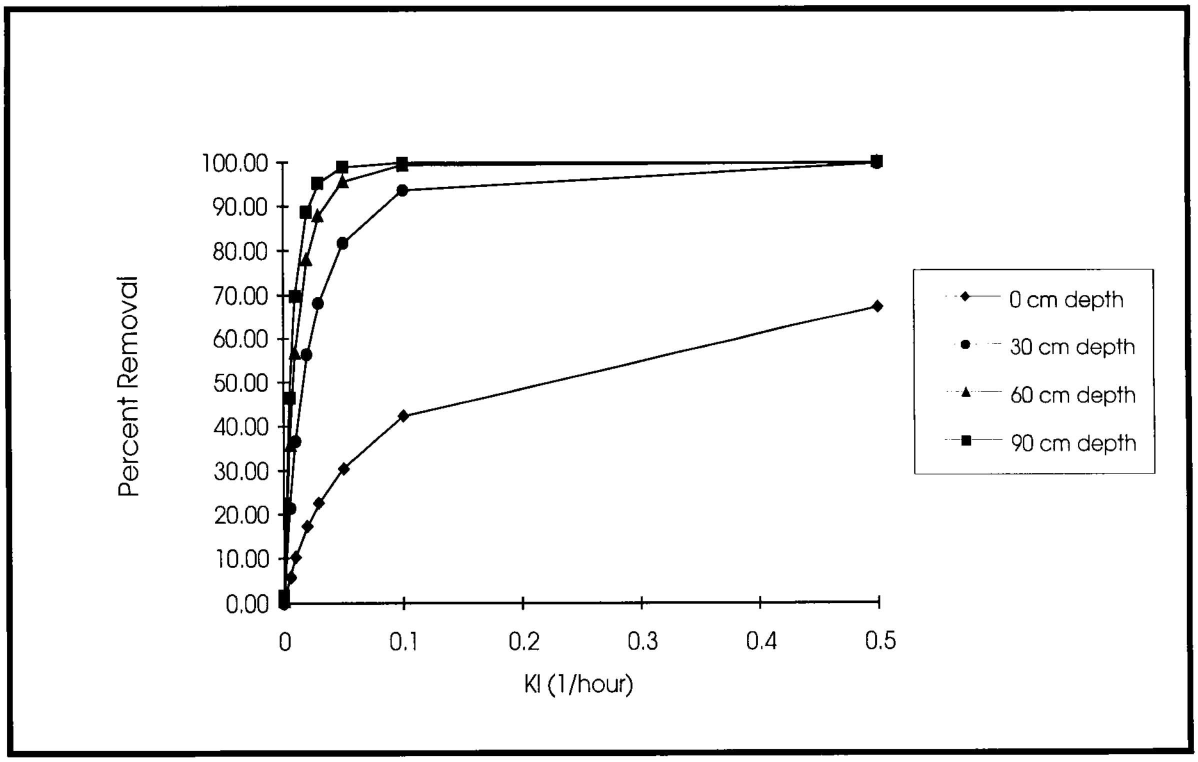

Figure 5.8 Effects of variation in precipitation rate term (Kl) on phosphorus removal efficiency of sandy soil. Partition coefficient equals 0.43 cc/g.

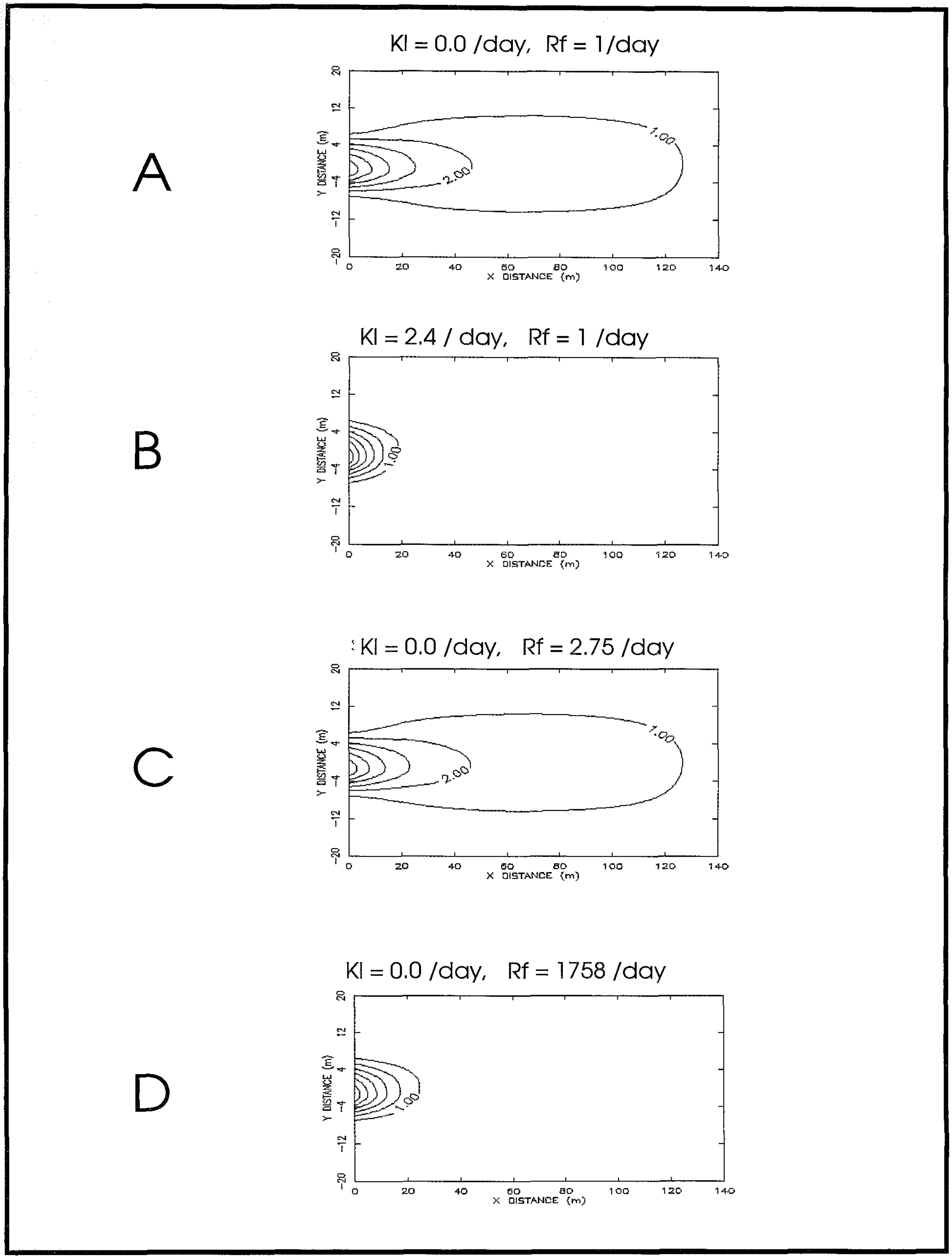

Figure 5.9 Results of saturated zone modeling for sandy soil using Two-D. Plots show phosphorus plume migration after 20 years. Steady state conditions exist in every case.

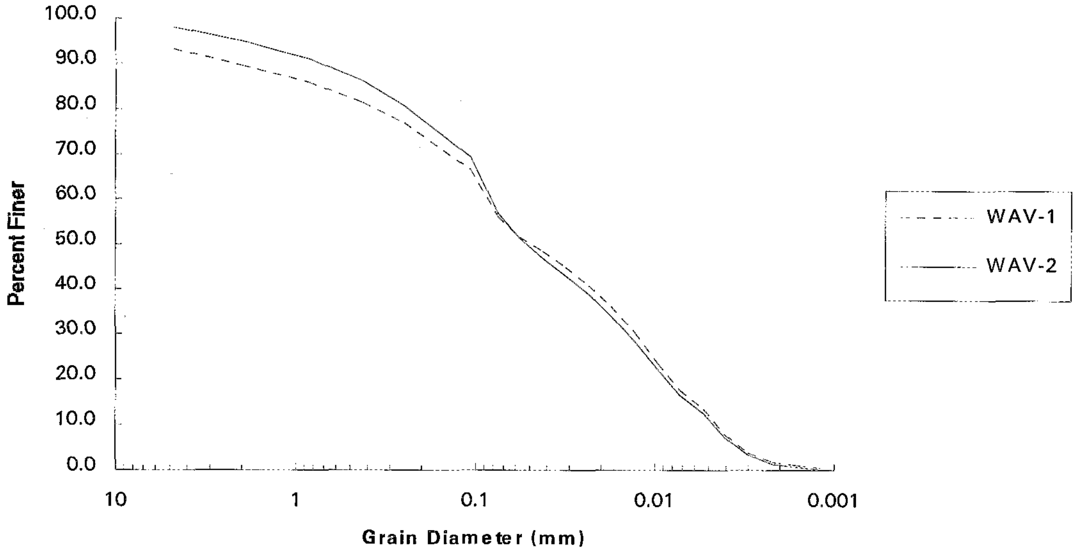

Figure 6.1 Grain Size Distribution Data for Waverly Soils

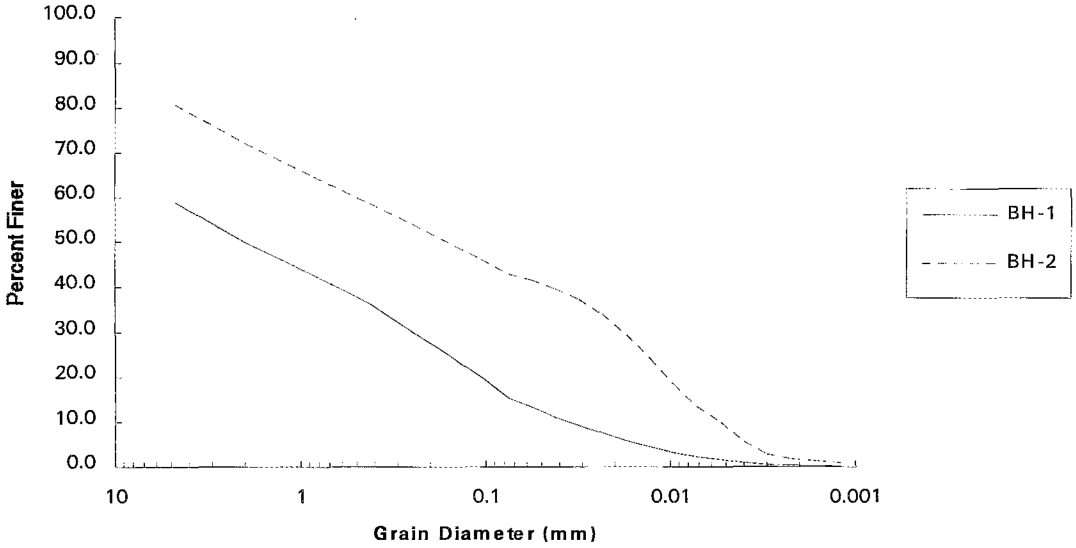

Figure 6.2 Grain Size Distribution Data for Bridgewater Soils

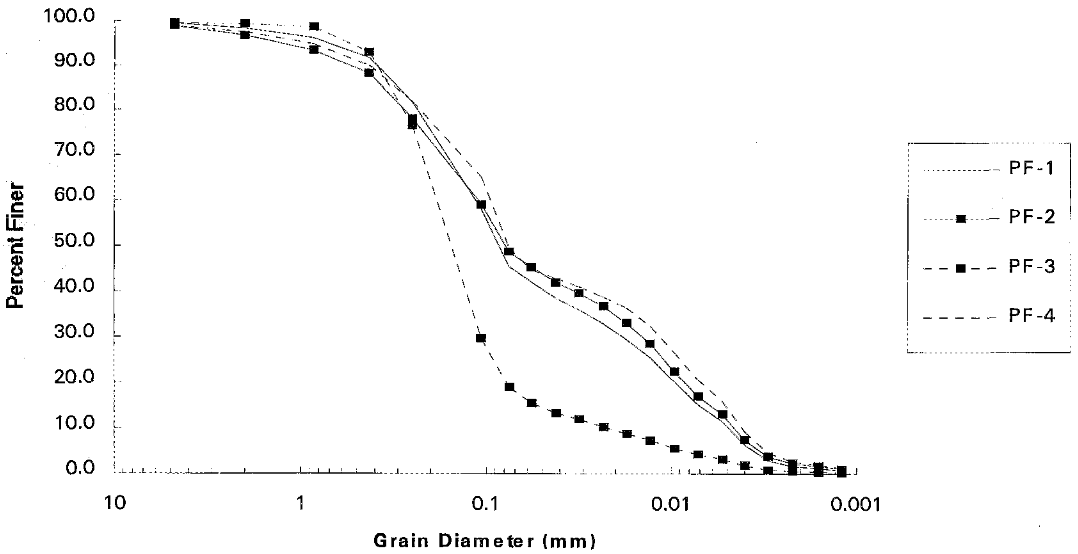

Figure 6.3 Grain Size Distribution Data for Provincial Recreational Facility Soils

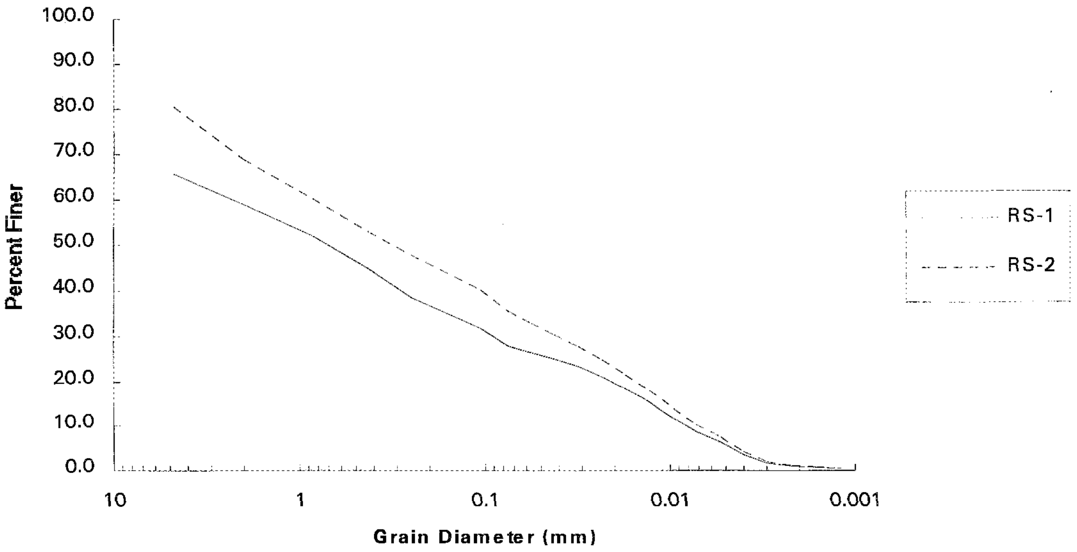

Figure 6.4 Grain Size Distribution Data for Elementary School Soils

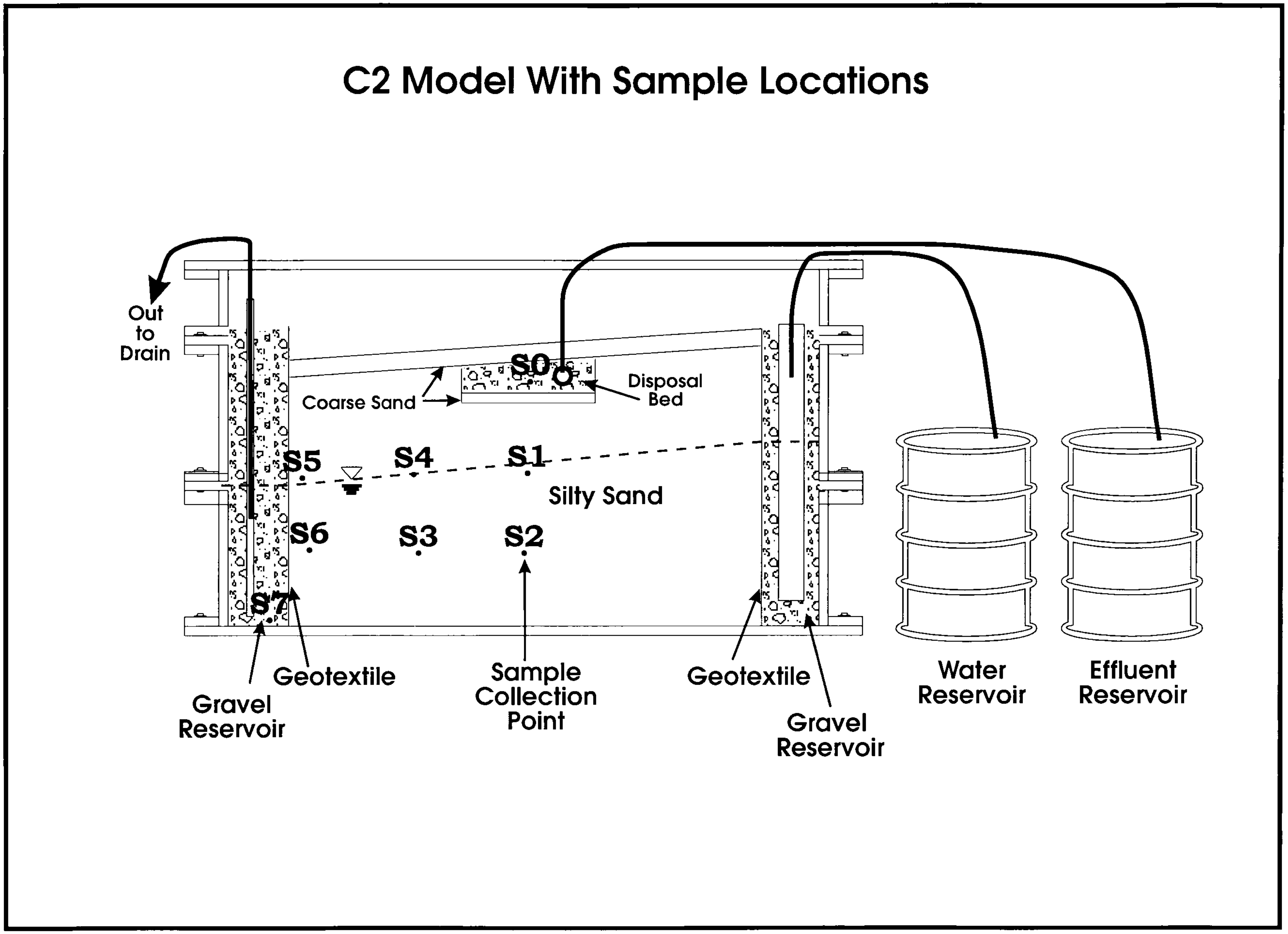

Figure 6.5 C2 model with sample locations.

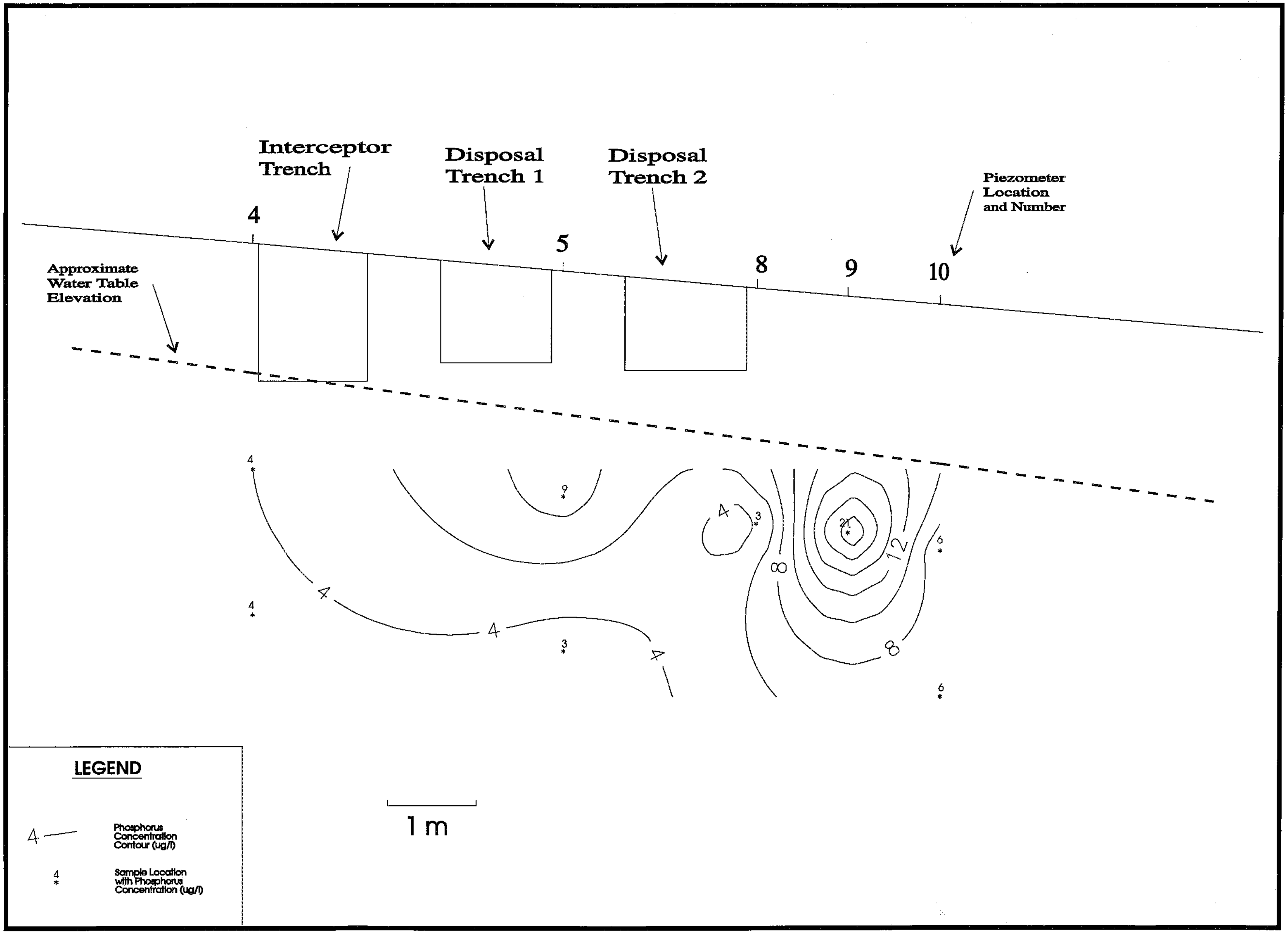

Figure 6.6 Phosphorus distribution below Port Maitland disposal trenches, June 1992.

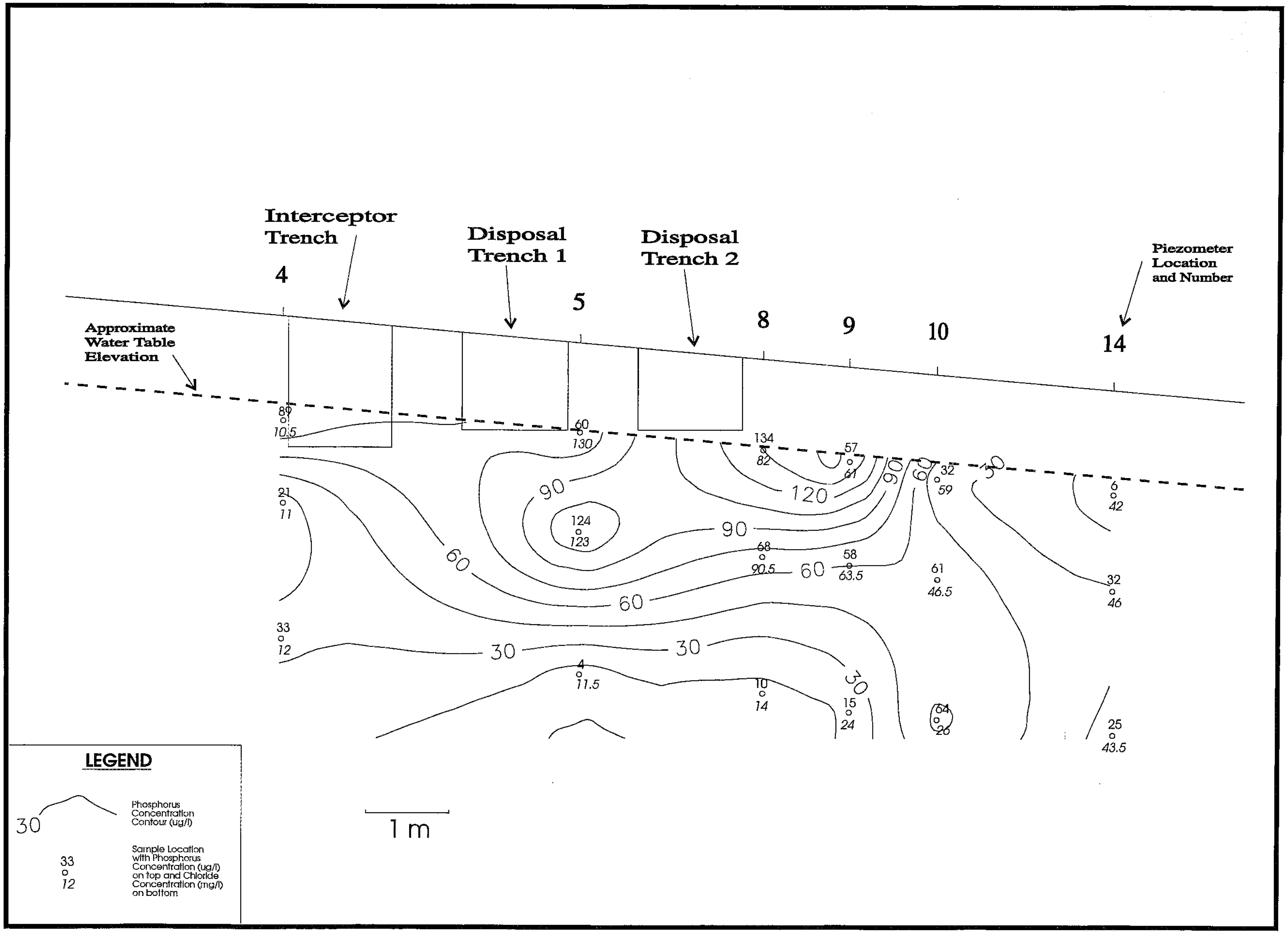

Figure 6.7 Phosphorus distribution below Port Maitland disposal trenches, November 1993.

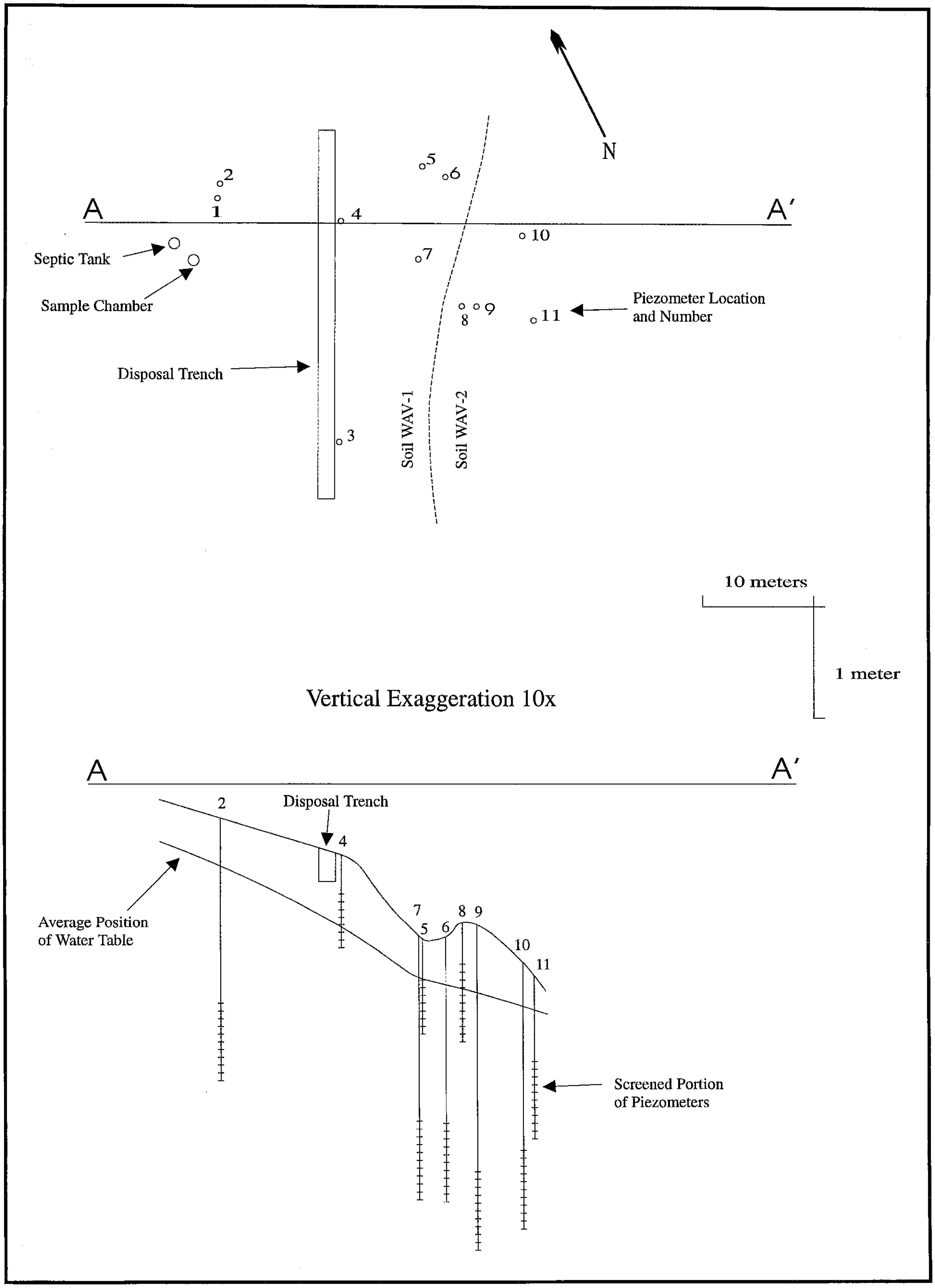

Figure 6.8 Waverly Site Plan and Cross-Section

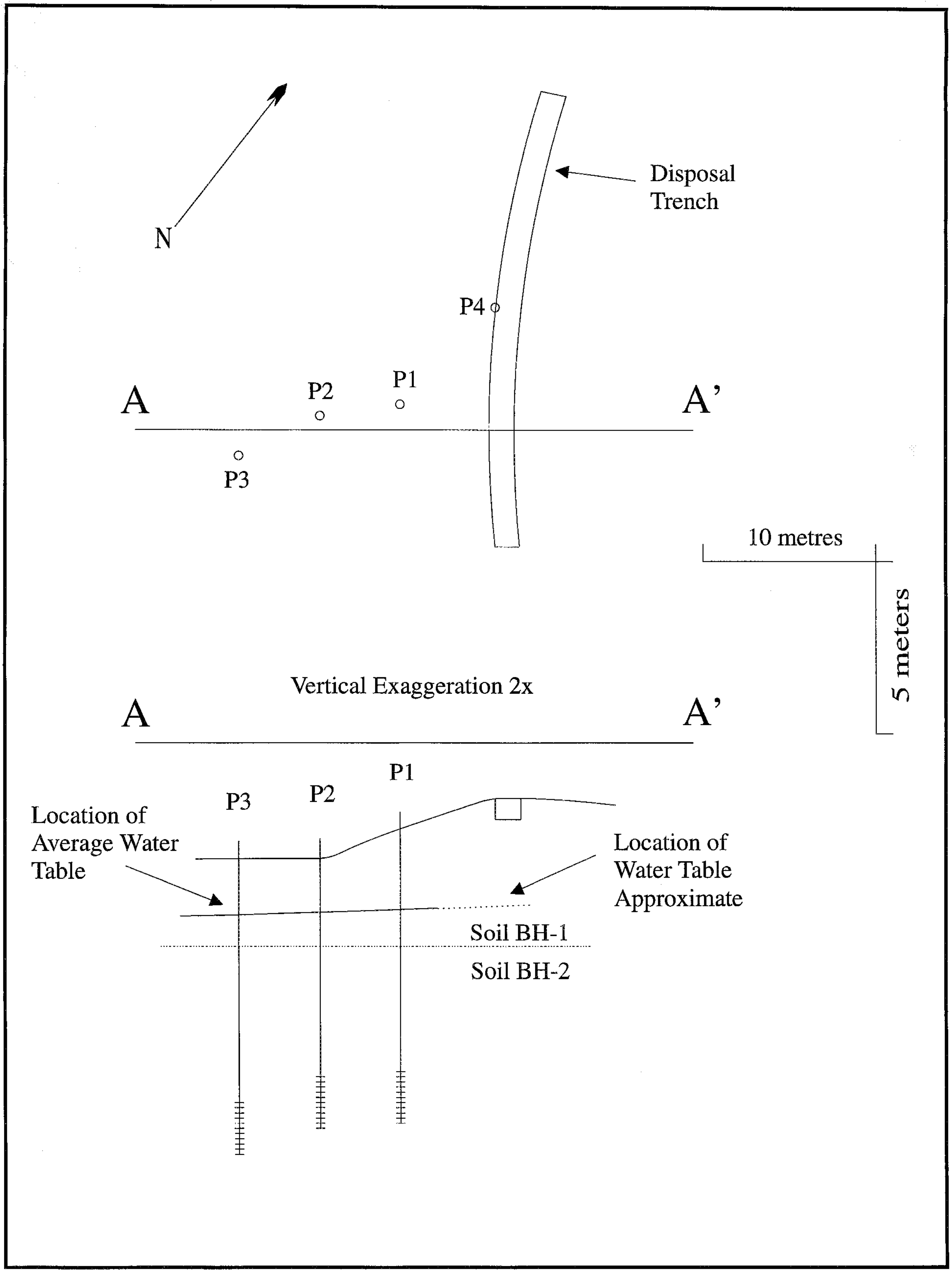

Figure 6.9 Bridgewater Site Plan and Cross-Section

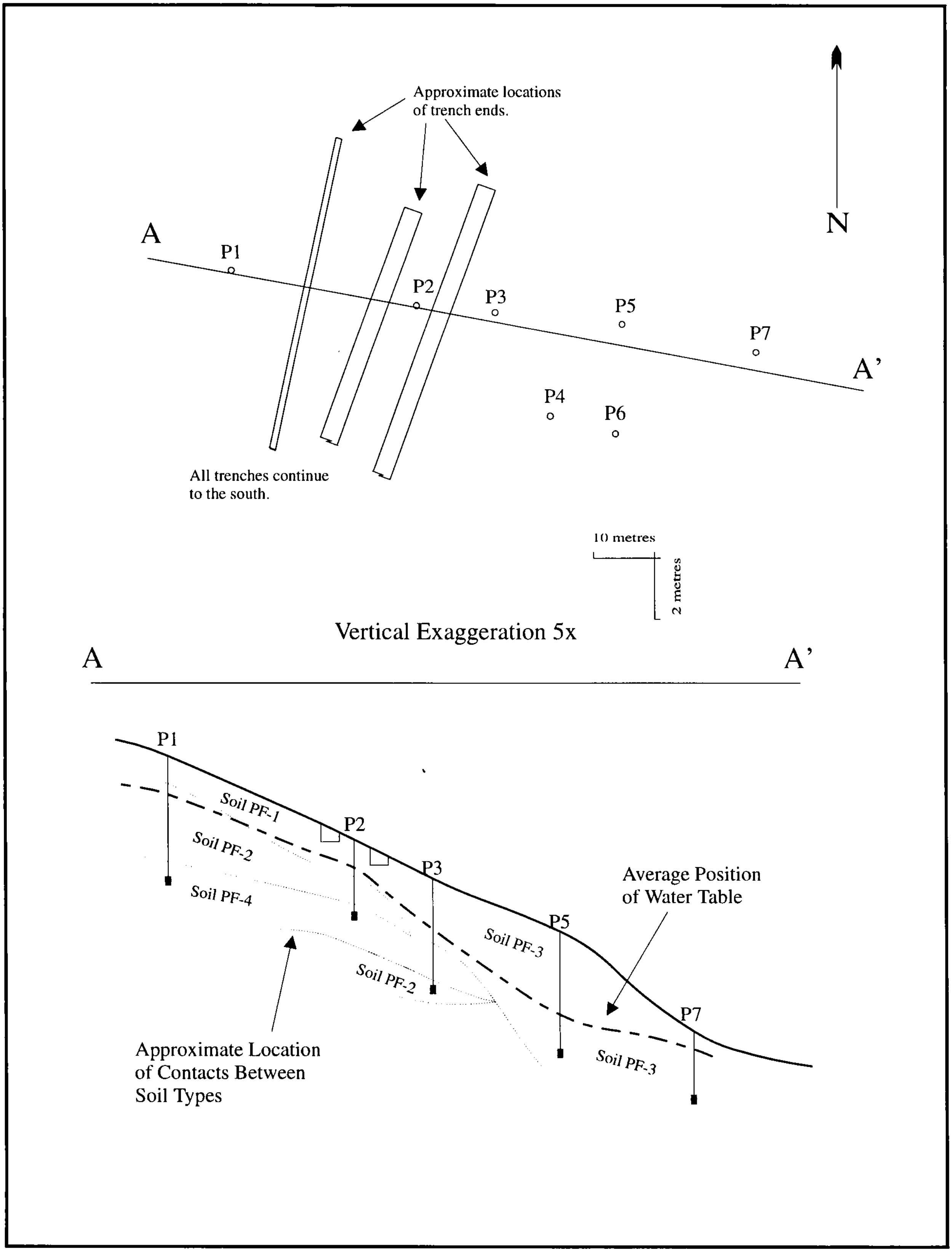

Figure 6.10 Provincial Recreational Facility Site Plan and Cross-Section

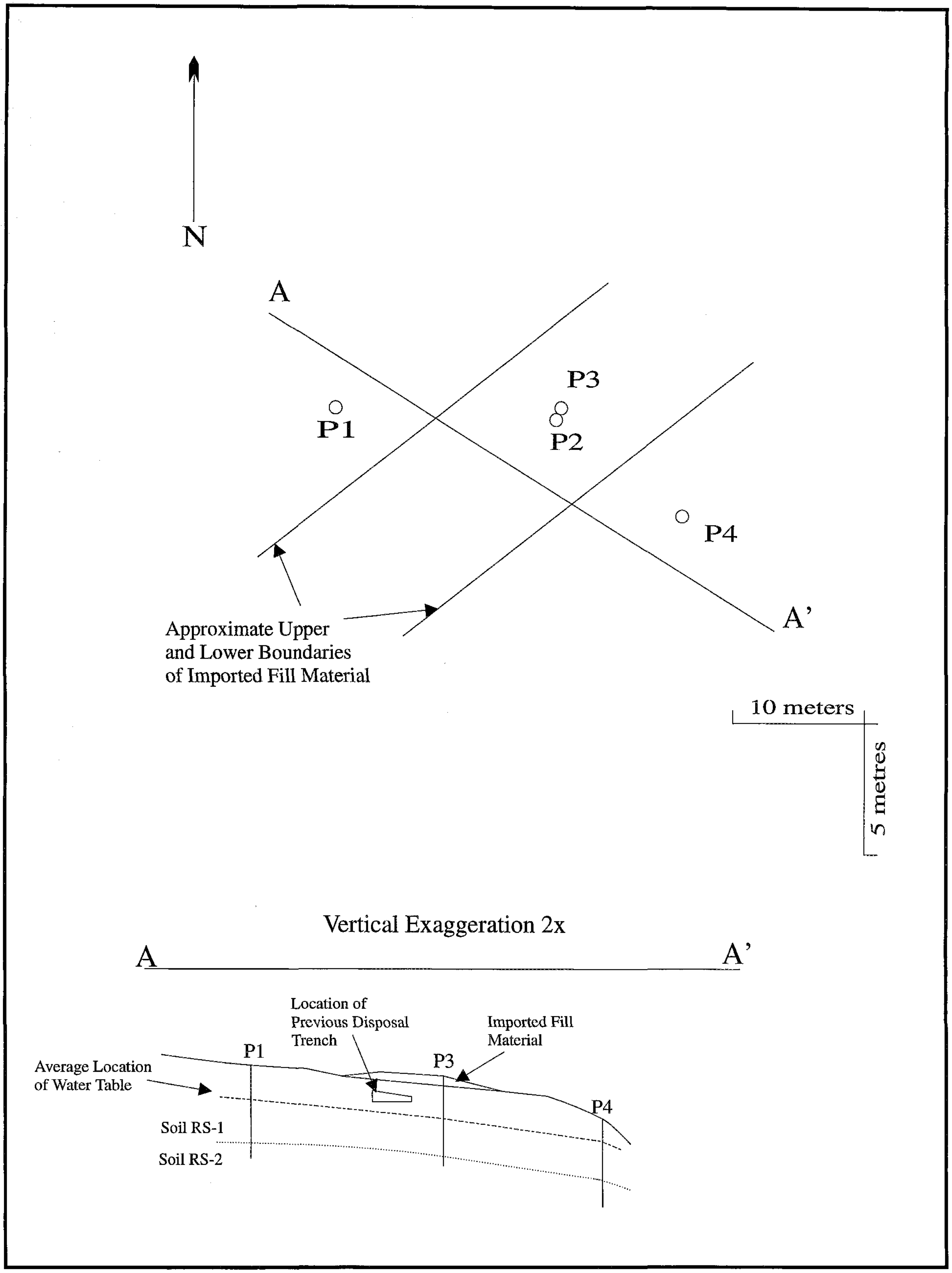

Figure 6.11 Elementary School Site Plan and Cross-Section

APPENDIX C - GLOSSARY OF TERMS

A - angle between flow direction and the vertical (downward) direction

a - soil dependent adjustment parameter

b - maximum phosphorus sorption capacity of soil (mg P / 100g soil)

b' - soil dependent adjustment parameter

$B_{(h)}$ - specific water capacity $= \partial\theta/\partial h$ (θ = volumetric water content)

C - concentration of contaminant (phosphorus) in solution

$\overline{C}$ - sorbed phosphorus concentration

$\overline{C}_s$ - concentration of sources or sinks

D_a - apparent dispersivity

D - dispersion coefficient; hydrodynamic dispersion

D_x - dispersion coefficient in x direction

D_z - dispersion coefficient in z direction

d - soil dependent adjustment parameter

h - matric potential at a particular time and place

K - coefficient indicative of bonding energy of contaminant (phosphorus) on soil

$K_{(h)}$ - hydraulic conductivity as a function of matric potential

k_1 - adsorption rate constant

k_2 - desorption rate constant

k_3 - equilibrium constant (partition coefficient)

k_4 - rate coefficient for immobilization of phosphorus (change of solution phosphorus to organic phosphorus)

k_5 - rate coefficient for precipitation of phosphorus

k_6 - rate constant for chemisorption (precipitation)

k_7 - rate constant for dissolution

k_b - backward rate coefficient

k_c - rate coefficient for immobilization of solution phosphorus

K_D - partition coefficient

k_f - forward rate coefficient

k_s - rate coefficient for immobilization of adsorbed phosphorus

q - flux of water

q_s - volumetric flux of water per unit area of aquifer representing sources or sinks of phosphorus

Q - irreversible phosphorus removal

R - chemical reaction term

R_d - retardation coefficient

R_b - rate of backward (desorption) reaction

R_f - rate of forward (adsorption) reaction

S - sorbed contaminant (phosphorus) concentration

S_1 - solute adsorbed by kinetic reactions

S_2 - solute at equilibrium between adsorbed and dissolved
S_i - physically adsorbed phosphorus (mass P / mass of soil)
S_{ii} - chemisorbed phosphorus (mass P / mass of soil)
t - time
V - flow velocity
v - seepage or linear pore water velocity
x, z - distance along flow path (typically z = vertical direction, x = horizontal direction)
α - first order degradation rate constant for liquid phase chemical
β - first order degradation rate constant for solid phase chemical
λ - first order reaction rate constant
ρ - bulk density of porous medium (soil)
α - soil dependent adjustment parameter
κ - soil dependent adjustment parameter
ϕ - term to describe addition or loss of phosphorus per unit volume of soil
θ - porosity of porous medium
θ_w - volumetric water content of soil
γ - zero order rate constant for liquid phase