

PHOSPHORUS GEOCHEMISTRY IN SEPTIC TANKS, SOIL ABSORPTION SYSTEMS, AND GROUNDWATER

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APRIL 7, 2006

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This work was supported in part by Lombardo Associates, Inc. and in part by the National Decentralized Water Resources Capacity Development Project (NDWRCDP) with funding provided by the U.S. Environmental Protection Agency through a Cooperative Agreement (EPA No. CR827881-01-0) with Washington University in St. Louis. This report has been reviewed by a panel of experts selected by the NDWRCDP. The contents of this report do not necessarily reflect the views and policies of the NDWRCDP, Washington University, or the U.S. Environmental Protection Agency, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

Citations

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and should be referenced as

Lombardo P. 2006. Phosphorus Geochemistry in Septic Tanks, Soil Absorption Systems, and Groundwater. Prepared by Lombardo Associates, Inc., Newton, MA.

ACKNOWLEDGEMENTS

Appreciation is extended to the following individuals for assistance in the preparation of this report:

Section I, Phosphorus Geochemistry, was prepared with major contributions by Dr. Anna Mehrotra and Professors William Robertson, David Blowes, and Carol Ptacek.

Section II, Research Priorities, was prepared with major contributions by Professor Robertson with the project team's review and assistance.

Appreciation is also expressed to the NDWRCDP for their support of this work:

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ABSTRACT

Although phosphorus is an essential nutrient for plant growth, excess phosphorus in aquatic ecosystems may result in water quality degradation due to excessive algae growth. Whereas there exists a substantial body of knowledge with respect to phosphorus removal in subsurface wastewater soil absorption systems, there are gaps in understanding and applying this knowledge to actual situations. The objective of this handbook is to document the current understanding of phosphorus geochemistry. Specifically, the handbook details phosphorus chemistry and removal in septic tanks and soil absorption systems (SAS). In addition, the fate of phosphorus in the groundwater below soil absorption systems is addressed. The information in this handbook is designed to provide guidance on phosphorus removal processes in the subsurface to professionals involved in planning, design, construction, management, and regulation of decentralized wastewater management systems.

Wastewater phosphorus is present in various forms, each of which behaves differently in septic tanks, the biomat portion of soil absorption systems, the vadose zone, and the groundwater zone. In order to understand phosphorus removal in these systems and in the subsurface environment, basic phosphorus geochemistry must be understood. Phosphorus chemistry in wastewater treatment systems is governed by physical, chemical and/or biological processes. Mineral precipitation and adsorption mechanisms dominate phosphorus removal in septic tanks, soil adsorption zones, and the subsurface environment.

Phosphorus removal in septic tanks is largely due to particle settling, although some chemical precipitation also occurs. Approximately 20 to 30 % of wastewater phosphorus is removed in septic tanks. Phosphorus removal in SAS is primarily achieved by mineral precipitation. Research suggests that the dominant phosphorus minerals in SAS are iron and aluminum precipitates, the stability of which is influenced by pH, redox conditions, and the chemistry of aluminum and iron. The vadose zone in soil absorption systems retains a variable amount of phosphorus (23 to 99%). The characteristics of the soil, wastewater, and site influence the degree to which phosphate is retained in the vadose zone. The phosphate concentrations that occur in groundwater appear to be strongly affected by attenuation reactions that are focused in the "rapid transformation zone" immediately underlying the SAS infiltration pipes. Further, adsorption processes are important for determining the rate at which phosphorus migrates through groundwater.

Research priorities to further the understanding of phosphorus geochemical processes are presented and consist of:

- Further microscale plume assessment
- Development of standardized methodologies for assessing transport at the microscale
- Behavior at the groundwater-surface water interface and other 'hotspots'
- Site indexing for vulnerability

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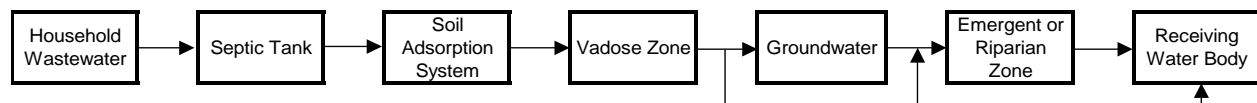
SECTION I: PHOSPHORUS GEOCHEMISTRY

I. OVERVIEW

A. Handbook objectives

There exists a substantial body of knowledge with respect to phosphorus removal in subsurface wastewater soil absorption systems. There are gaps, however, in understanding and applying this knowledge. The objective of this handbook is to document the current understanding of phosphorus geochemical processes. Specifically, the handbook details phosphorus chemistry and removal in septic tanks and soil absorption systems. In addition, the fate of phosphorus in the groundwater below soil absorption systems will be covered. To a more limited extent, the handbook also addresses the sources of phosphorus in wastewater and the ultimate fate, and effects, of phosphorus in receiving water bodies. Thus, the handbook addresses phosphorus removal in the typical on-site wastewater treatment systems composed of a septic tank, drainfield or leachfield, and soil absorption system, and underlain by groundwater (Figure I-1), as well as the receiving water body.

Figure I-1: Components of typical onsite wastewater treatment system



The handbook is designed to provide guidance on phosphorus removal to professionals involved in planning, design, construction, management, and regulation of decentralized wastewater management systems. A companion study is examining phosphorus removal technologies for small flow systems.

B. Handbook outline

The handbook presents information on phosphorus concentrations and forms in wastewater, general phosphorus geochemistry principles, and phosphorus removal and fate in septic tanks, soil absorption systems, vadose zone, groundwater, the riparian zone, and receiving water body. Major conclusions in each section are as follows:

- Phosphorus in Water Bodies (Chapter II)
 - Excess phosphorus in aquatic ecosystems leads to decreased water clarity, low dissolved oxygen, dispersal of toxic compounds, and a shift from macrophyte-dominated ecology characterized by diverse biota to an algae-dominated system with low biodiversity
 - A US EPA survey estimates that 14 to 22% of US water bodies are impaired by nutrients, including phosphorus (Table VII-1)

- Typical phosphorus concentrations in lakes and estuaries vary by trophic status (Table VII-2)
- Phosphorus is typically the controlling nutrient for water quality degradation (algae growth) in fresh waters.
- Phosphorus in Wastewater (Chapter II)
 - Phosphorus in wastewater is estimated to impair 17% of the nation's estuaries and accounts for 5% of total anthropogenic (caused by humans) phosphorus loadings to the environment (Figure II-1)
 - In some watersheds, phosphorus loadings from septic systems specifically can account for 25% or more of total phosphorus loadings (Table II-1).
 - Although ambient water quality standards for phosphorus do exist, septic tanks and soil absorption systems are usually not subject to phosphorus removal requirements unless subject to a groundwater discharge permit
 - Phosphorus in wastewater is present in many physical and chemical forms
 - Although the majority of phosphate in raw wastewater and septic tank effluent is dissolved orthophosphate, regulations are generally based on total phosphorus concentrations
 - Typical total phosphorus concentrations in raw wastewater range from 4 ~ 15 mg-P/l
- Phosphorus Geochemistry (Chapter III)
 - Mineral precipitation and adsorption are the two dominant processes governing phosphorus fate in the environment
 - Mineral precipitation is a three-dimensional process involving the formation of a phosphate mineral
 - Phosphate minerals commonly contain aluminum, iron, and calcium as the co-precipitating cations
 - The stability of phosphate minerals depends on the concentrations of the cations with which phosphate precipitates which, in turn, depend on pH, redox potential and other factors, and dissolved phosphate concentrations can be estimated using solubility products (Table III-2)
 - Adsorption is a two-dimensional process involving the association of phosphate with the surface of a particle
 - Phosphate most commonly adsorbs to the surfaces of aluminum and iron (oxy)hydroxide minerals, as well as some clay minerals
 - Phosphate adsorption to mineral surfaces is very complex and a variety of techniques have been used to describe it. In many instances this can be described by the Freundlich isotherm (Equation 1)
 - pH and redox potential both influence the nature of phosphate mineral precipitation and adsorption in septic tanks, soils, and groundwater
- Phosphorus Removal in Septic Tanks (Chapter IV)
 - Approximately 20 to 30% of total phosphorus in raw wastewater is removed in septic tanks

- Phosphorus removal in septic tanks involves settling of phosphorus-containing particles, as well as some precipitation of the iron mineral vivianite
- Typical concentrations of total phosphorus in the effluent of septic tanks range from 1.2 ~ 16 mg-P/l (Table IV-1)
- Phosphorus Removal in Soil Absorption Systems (Chapter V)
 - The dominant phosphorus removal mechanism in soil absorption systems appears to be mineral precipitation
 - Soils have been observed to be enriched in phosphorus by a factor of 2 to 4 within 1 m of dispersal systems (Figure V-1)
 - Phosphorus minerals in soil absorption systems appear to be both Fe-P and Al-P precipitates
 - Knowing which mineral phase controls phosphate solubility under different environmental conditions should allow prediction of equilibrium phosphate concentrations in the soil porewater and, therefore, phosphorus removal
 - Under oxidizing conditions, the controlling phases can be amorphous hydroxyapatite, beta tricalcium phosphate, strengite or variscite, depending on pH
 - Under reducing conditions, vivianite probably controls phosphate solubility
 - The vadose zone in soil absorption systems retains a variable amount of phosphorus (23 to 99%)
 - The factors that influence phosphorus removal in the vadose zone are:
 - Soil characteristics: fine-grained, noncalcareous soils remove the most phosphorus, while coarse-grained, calcareous soils remove the least amount of phosphorus (Table V-1)
 - Wastewater characteristics: high NH_4^+ concentrations and low alkalinity can enhance removal in noncalcareous soils with gibbsite
 - Site characteristics: high hydraulic loading rates and other conditions that may give rise to rapid lateral movement of water will decrease retention in soil absorption systems and thereby increase transport to surface waters

II. PHOSPHORUS IN WASTEWATER

Introduction

A. Ecological implications of excess phosphorus

Although phosphorus is an essential nutrient for plant growth, excess phosphorus in aquatic ecosystems results in water quality degradation. Of particular concern are the side effects of the algae growth associated with phosphorus enrichment. These include (Vollenweider 1968; Horne and Goldman 1994):

- Decreased water clarity;
- Low dissolved oxygen, which, in turn, can lead to fish kills and poor drinking water quality (due to the presence of reduced substances such as sulfides, Mn(II) and Fe(II));
- Dispersal of toxic compounds (hepatotoxins and neurotoxins) associated with certain types of algae blooms; and
- A shift from a macrophyte-dominated ecology characterized by diverse biota to an algae-dominated system with low biodiversity.

An inventory by the US EPA estimated that 14 to 22% of US water bodies are impaired by nutrients (Table II-1; US EPA 1997). An impaired water body is one that is either partially supporting or not supporting beneficial uses including, but not limited to, drinking water, recreation, and fishing. As much as two-thirds of this nutrient impairment is due to excess phosphorus (Litke 1999).

Table II-1: Summary of nutrient status of streams, lakes, and estuaries in the US

Water Body Type	% Assessed	% Nutrient Impaired	% Impaired by Agricultural Sources	% Impaired by Municipal WWTP⁽¹⁾ Discharge
Streams & Rivers	19	14	25	5
Lakes & Ponds	20	20	19	7
Estuaries	72	22	10	17

Note: (1) WWTP = wastewater treatment plant
Source: US EPA 1997

The process of nutrient enrichment is called eutrophication, and the degree of eutrophication in a given water body can be described by its trophic state. Each trophic state is characterized by a typical range of total phosphorus concentrations (Table II-2). For reference, phosphorus concentrations in streams not impacted by human activities are approximately 0.016 to 0.018 mg/l (Litke 1999), while total phosphorus

concentrations between 0.02 and 0.03 mg-P/l are known to stimulate algae growth (Dillon and Rigler 1974; Schindler 1977).

Table II-2: Typical total phosphorus concentrations (mg/l) by trophic state

Aquatic System	Trophic State			
	Oligotrophic	Mesotrophic	Eutrophic	Hypertrophic
Lake	< 0.01	0.01 – 0.03	0.03 - 0.1	> 0.1
River	--	< 0.01	0.01 – 0.05	> 0.05

Source: Newton and Jarrell 1999

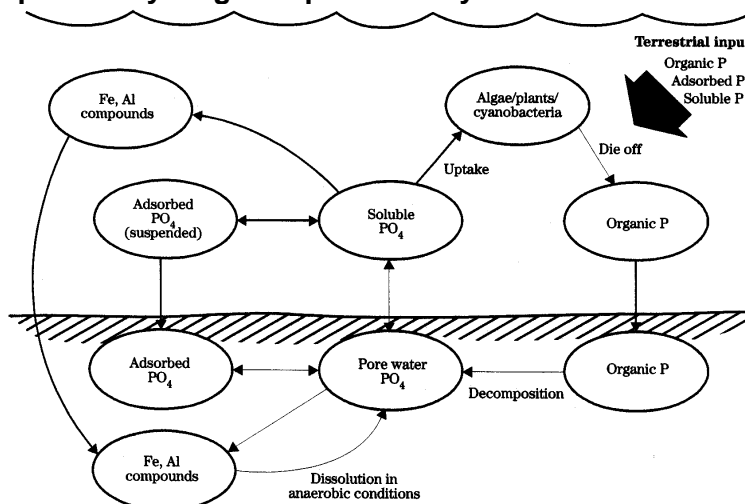
Some aquatic systems are more sensitive to inputs of phosphorus than others. The most sensitive systems are (Newton and Jarrell 1999):

- phytoplankton-dominated small streams
- periphyton-dominated small and large streams and lakes
- mesotrophic lakes
- stratified, deep lakes
- mesotrophic or oligotrophic polymictic lakes
- shallow lakes with high macrophyte coverage

It should be noted that these system types are not mutually exclusive.

The phosphorus in aquatic ecosystems is part of a dynamic cycle that involves numerous environmental compartments (soil, water, and biota) and phosphorus forms (adsorbed, soluble, and organic), as shown in Figure II-1. Thus, the phosphorus concentrations listed in Table II-2 are a small fraction of total phosphorus in a lake or estuary. Moreover, it may sometimes be difficult to relate phosphorus concentrations in water to a given trophic state, because of rapid uptake of phosphorus by algae.

Figure II-1: Phosphorus Cycling in Aquatic Ecosystems

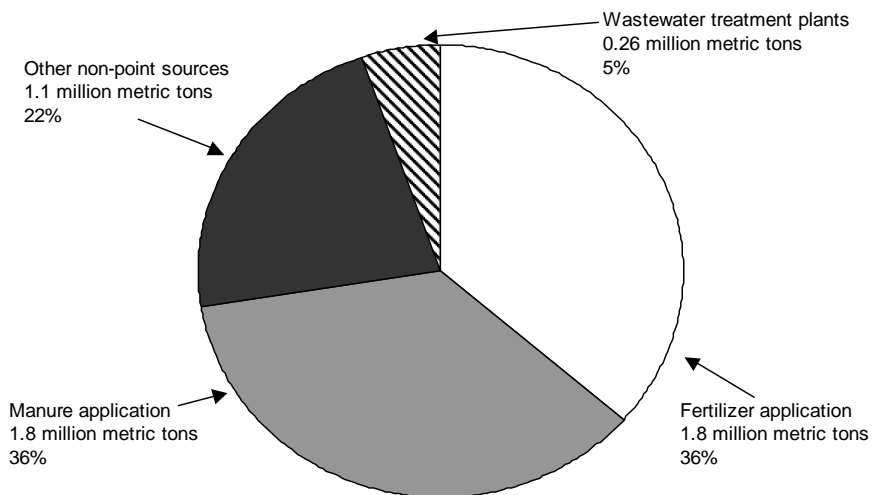


Wastewater phosphorus is present in various forms, each of which behaves differently in septic tanks, soil absorption systems, the vadose zone, groundwater, and the riparian zone. The phosphorus forms are identified in this section, along with the standard analytical methods used to quantify each one. In addition, typical phosphorus concentrations in raw municipal wastewater and regulatory standards applicable to on-site wastewater systems are discussed.

B. Wastewater as an important source of phosphorus

Wastewater treatment plants impair 17, 7, and 5% of estuaries, lakes and ponds, and streams and rivers, respectively. As shown in Figure II-2, the most recent nationwide loading estimates indicate that wastewater treatment plant discharges account for 5% of anthropogenic (caused by humans) phosphorus loadings (Figure II-2; Gianessi and Peskin 1984).

Figure II-2: Anthropogenic sources of phosphorus to the environment



Source: Gianessi and Peskin 1984

There are no national data available for phosphorus contributions from on-site wastewater treatment systems to the environment. However, studies performed as part of total maximum daily load (TMDL) development and lake water quality suggest that septic systems can contribute 4 to 55% of total phosphorus to lakes.

Table II-3: Contributions of septic tanks to phosphorus loads determined during TMDL development

Water Body	Water Body Type	% Total Phosphorus Load from Septic Tanks	Reference
Cottonwood Lake, SD	Freshwater lake	4	SD DENR 2003
Lake Carlton, FL	Freshwater lake	14	FL DEP 2003
Pineview Reservoir, UT	Reservoir	20	UT DEQ 2003
Pend Oreille Lake, ID	Freshwater lake	25	ID WQC 2003
Ontario Lakes	Freshwater lake	55	Dillon <i>et al.</i> 1986
Otsego Lake	Freshwater lake	20	Albright, 1996

C. Chemical forms

Phosphorus forms can be categorized on the basis of physical or chemical characteristics. Physically, phosphorus is divided into two fractions (Jenkins and Hermanowicz 1991):

1. Dissolved phosphorus that passes through a filter, usually 0.2 or 0.45 μm average pore size, and
2. Particulate phosphorus that is associated with particles retained on the filter membrane during filtration.

For many years, the filtration standard was the Millipore filter with a 0.45 μm average pore size. However, some laboratories now use 0.2 μm pore size, in filtration with significant differences in phosphorus loading noted with respect to filtration through a 0.45 μm pore size.

Dissolved phosphorus is sometimes referred to as soluble phosphorus, while particulate phosphorus is sometimes called suspended phosphorus. The sum of dissolved and particulate is equal to total phosphorus. Note that the definition of dissolved phosphorus is an operational one because it is simply equal to the phosphorus that passes through a filter of a given pore size (*i.e.*, 0.2 or 0.45 μm in most cases). This operationally defined dissolved phosphorus may include very small phosphorus-bearing particles and thus this phosphorus is not truly dissolved (*i.e.*, not surrounded solely by

water molecules). Particulate phosphorus is comprised of organic phosphorus, phosphates adsorbed to the surfaces of iron oxide and other minerals, as well as a number of discrete phosphate minerals. A larger portion of particulate phosphorus will pass through a 0.45 µm filter than a 0.2 µm filter and thereby be assigned to the dissolved phosphorus burden. These differences can be large, requiring consideration when interpreting analytical data.

Chemically, phosphorus in wastewater can be categorized as orthophosphate, condensed phosphates, or organic phosphorus:

1. Orthophosphate (o-phosphate) includes H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} . In waters with a pH close to 7, $H_2PO_4^-$ and HPO_4^{2-} are the predominant orthophosphate forms (Figure II-3 and Table II-4; Stumm and Morgan 1981). These forms are also sometimes referred to as inorganic phosphorus, reactive phosphorus or simply phosphate. Table II-4 and Figure II-3 merely represent the distribution of the , the aforementioned orthophosphate species and do not consider other soluble phosphorus species such as the many soluble metal-phosphate complexes are present in wastewater and natural water.
2. Condensed phosphates include various polyphosphate forms such as pyrophosphate ($P_2O_7^{4-}$) and $P_3O_{10}^{5-}$ (Crites and Tchobanoglous 1998). Derived primarily from laundry detergents and other cleansers, condensed phosphates convert slowly to orthophosphate.
3. Organic phosphorus includes phosphorus incorporated with organic compounds, such as sugars, phospholipids, and nucleotides (Jenkins and Hermanowicz 1991).
4. The phosphorus-bearing species listed above can complex or associate with dissolved cations and organic species present in wastewater, soil solutions or groundwater. The formation of these complexes will further enhance the solubility of o-phosphate or limit adsorption reactions.

Table II-4: Equilibrium constants describing acid dissociation chemistry of orthophosphate species

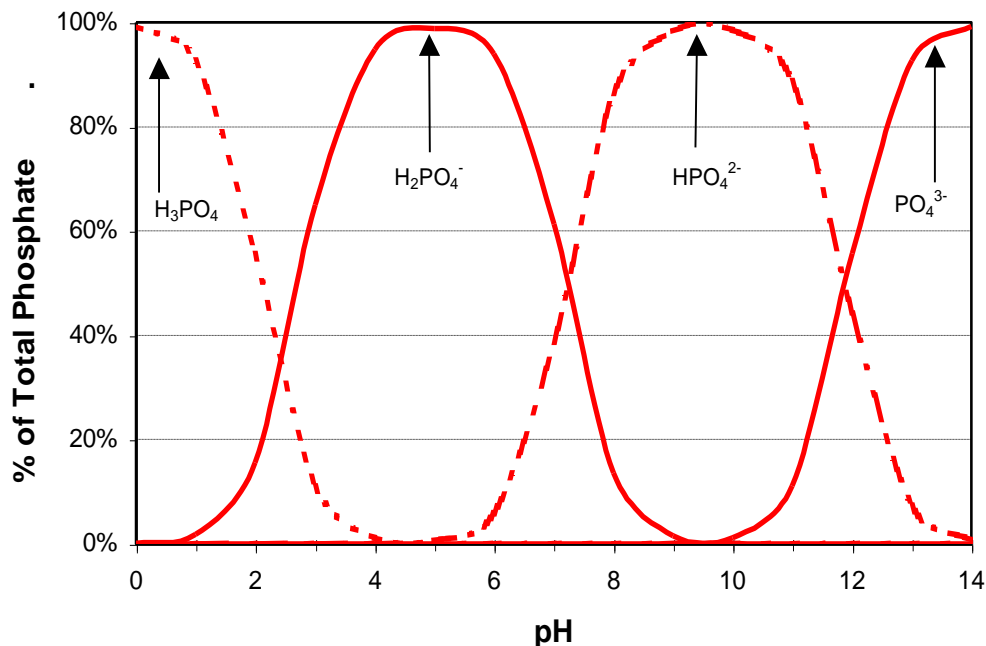
Reaction	pKa ¹
$H_3PO_4 = H_2PO_4^- + H^+$	2.1 to 2.2
$H_2PO_4^- = HPO_4^{2-} + H^+$	7.2
$HPO_4^{2-} = PO_4^{3-} + H^+$	11.9 to 12.4

Note: (1) The pKa is equal to $-\log(K)$ for the reaction.

Source: Smith and Martell 1976; Stumm and Morgan 1981

The chemical and physical classifications overlap. That is, orthophosphate can be dissolved or can be particulate. Similarly, organic phosphorus can be dissolved or particulate.

Figure II-3: Equilibrium species distribution as a function of pH for the orthophosphate system.



Note: (1) The pKa is equal to $-\log(K)$ for the reaction, where K is the equilibrium constant. Calculated using equilibrium constants (pKa = 2.1, 7.2, and 11.9) in Table II-4.

Orthophosphate and, to a lesser degree, polyphosphates are available to algae for growth. Particulate phosphorus may also be available for growth because algae release alkaline phosphatase, an enzyme capable of cleaving orthophosphate from the organic particles (Horne and Goldman 1994). Regulatory standards imposed on wastewater effluent, or water quality criteria set for surface water bodies, are usually based on total phosphorus concentrations as described in Section II.E.

D. Analytical techniques

Phosphorus analysis typically involves colorimetric determination of orthophosphate. If chemical forms of phosphorus other than orthophosphate are desired, they are first converted to orthophosphate and then determined colorimetrically (APHA, 1999).

Colorimetric analysis is most commonly conducted by the ascorbic acid method (Standard Method 4300; APHA 1999) that is suitable for phosphorus concentrations in the range of 0.01 to 6 mg/l. Conversion of condensed phosphates and organic phosphorus to orthophosphate is performed by hydrolysis and oxidation, respectively. Using these analytical techniques phosphorus can be divided into reactive, acid-hydrolyzable, and total fractions as illustrated in Table II-5. These fractions approximately correspond to the chemical forms of phosphorus. There are other procedures targeted at providing additional information, such as the bioavailability of

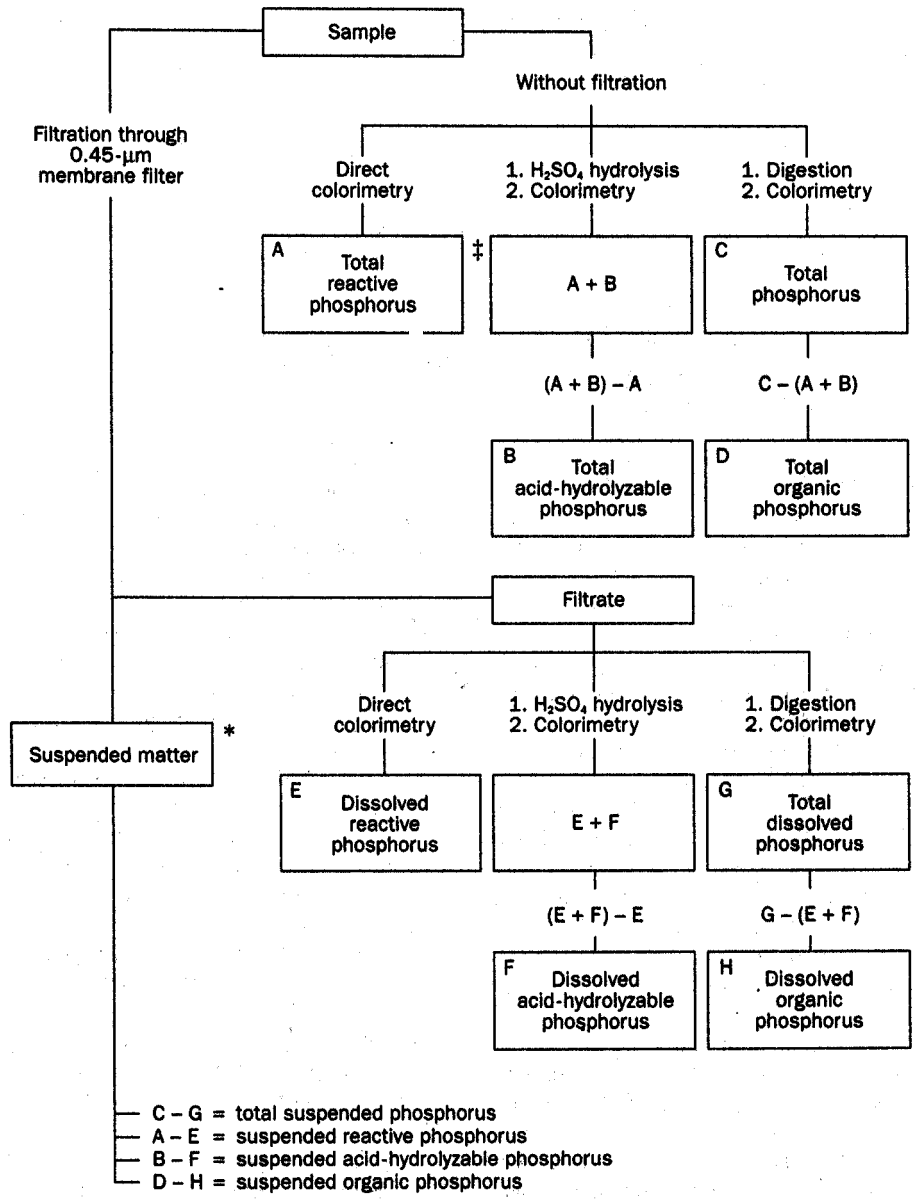
organophosphorus species (e.g. Pant *et al.* 2002). These latter methods are not routinely available in commercial laboratories.

Table II-5: Summary of analytical techniques for phosphorus measurement

Analytical Phosphorus Fraction	Summary of Method	Actual Chemical Form Measured
Reactive phosphorus	Measure phosphate colorimetrically in unhydrolyzed, unoxidized sample	Mostly orthophosphate, some condensed phosphate
Acid-hydrolyzable phosphorus	Boil sample in weak sulfuric acid (H ₂ SO ₄), measure colorimetrically	Orthophosphate, condensed phosphates, some organic phosphorus
Total phosphorus	Oxidize sample with persulfate or another technique (known as "digestion") and measure colorimetrically	Orthophosphate, condensed phosphates, organic phosphorus

Figure II-4 shows how the condensed phosphate and organic phosphorus fractions can be determined by difference from the analytical fraction of Table II-5. Furthermore, each phosphorus fraction can be measured in filtered (*i.e.*, for dissolved phosphorus fractions) or unfiltered (for total phosphorus fractions) samples. The suspended phosphorus fractions are determined by difference from the total phosphorus fractions and dissolved phosphorus fractions as shown in Figure II-4.

Figure II-4: Steps for analysis of phosphorus fractions



Source: APHA 1999

E. Concentrations in raw wastewater

Phosphorus concentrations are generally reported as total phosphorus concentrations. For analyses of total phosphorus, the concentrations are reported in units of “mg-P/L”. These analyses would include all forms of phosphorus species present in the water. For analyses of reactive phosphorus (or o-phosphate), the concentrations are reported in units of “mg/l PO₄-P”, which would correspond to the mg of the element phosphorus present as an orthophosphate species (*i.e.* H₃PO₄⁰, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻ and any other o-PO₄ complexes) in each liter of solution. Thus, the concentration of 1 mg/l PO₄-P corresponds to: 1 mg-P/L (present as orthophosphate), 0.032 mM P as phosphate or simply 0.032 mM PO₄ (phosphorus has a molecular weight of 31 mg/mmol), and 3.1 mg PO₄ (PO₄ has a molecular weight of 95 mg/mmol).

The concentration of total phosphorus in raw municipal wastewater ranges from 4 to 15 mg-P/l in areas where phosphorus-containing detergents are regulated (Table II-6). Total phosphorus in wastewater can be as high as 50 mg-P/l where detergent phosphate is not regulated (Veenstra *et al* 1997). Before the use of phosphorus detergents, the concentration of phosphorus in raw wastewater was approximately 3 mg-P/l (Hetling and Carcich 1972). By 1970, the average phosphorus concentration in raw wastewater increased to 11 mg-P/l, approximately 6 mg/l of which was derived from phosphorus detergents. As of 1999, 27 states had partial or full bans on phosphorus in detergents (Table II-7; Litke 1999). Phosphorus bans typically involve setting a phosphorus limit for detergents, usually 0.5 to 8.7% phosphorus by weight (Litke 1999). In 1994, the detergent industry voluntarily ended the manufacture of phosphate detergent for household laundry (Litke 1999). However, phosphorus remains a significant component of automatic dishwashing detergent.

Table II-6: Phosphorus concentrations in raw wastewater

Reported Total Phosphorus (mg-P/l)	Reported Dissolved Phosphorus (mg-P/l)	Reference
4 to 15 (7 is typical)	--	Crites and Tchobanoglous 1998
6 to 8	5 to 7	Jenkins and Hermanowicz 1991
6 to 12	--	US EPA 2002
7	5	WEF 1992

Approximately 50% of phosphorus in raw wastewater is orthophosphate, 40% polyphosphates, and 10% organic phosphorus (Tchobanoglous and Schroeder 1987). Organic phosphorus, especially particulate organic phosphorus, is more predominant in industrial wastes and wastewater sludges (Crites and Tchobanoglous 1998).

Estimated phosphorus loads from household sources average 1.0 to 1.3 kg/capita/year (Jenkins and Hermanowicz 1991; Crites and Tchobanoglous 1998), broken down as follows:

- Human waste: 0.6 kg/capita/year
- Laundry detergents (with no phosphorus limitation): 0.3 kg/capita/year
- Other household detergents and cleaners: 0.1 kg/capita/year

Industrial and commercial sources of phosphorus are highly variable.

Table II-7: States with phosphorus detergent bans

Years	Detergent Ban	Partial Ban
1970-79	Connecticut Florida Indiana Maine Michigan Minnesota New York Vermont Wisconsin	Illinois
1980-89	Maryland North Carolina Virginia	Idaho Montana Ohio
1990-98	Arkansas Georgia Massachusetts New Hampshire Oregon Pennsylvania Rhode Island South Carolina Washington	Missouri Texas

Source: Litke 1999

F. Regulatory standards

The goal of regulating phosphorus in wastewater is to protect the water quality of the ambient waters that receive wastewater flows. Protection of ambient water quality from excessive phosphorus is accomplished with a two-pronged approach.

First, ambient water quality standards (WQS) are established for surface waters. These WQS are set by states, tribes, or territories as mandated by the 1977 Clean Water Act and may be narrative or numeric. New Jersey's Water Quality Standard provides an example of a narrative nutrient standard (EPA 2003):

“Except as due to natural conditions, nutrients shall not be allowed in concentrations that cause objectionable algal densities, nuisance aquatic vegetation, abnormal diurnal fluctuations in dissolved oxygen or pH, changes to the composition of aquatic ecosystems, or otherwise render the waters unsuitable for the designated uses.” (January 22, 2002)

If numeric criteria are used instead, such criteria are established for a given designated use, water body type or, in some cases, statewide for a specific parameter. A recent US EPA survey of state, tribe, and territory nutrient criteria (EPA 2003) showed that all states have established narrative (i.e. qualitative) nutrient criteria, while two-thirds have adopted numeric criteria as well. Most numeric criteria have been adopted for freshwater lakes, with fewer adopted for estuarine and marine waters, or for rivers and streams. Existing state numeric phosphorus criteria range from 0.001 mg-P/l (for marine and estuarine waters in Alaska) to 0.1 mg-P/l (e.g., for upland streams in Vermont). All numeric criteria are based on total phosphorus concentrations.

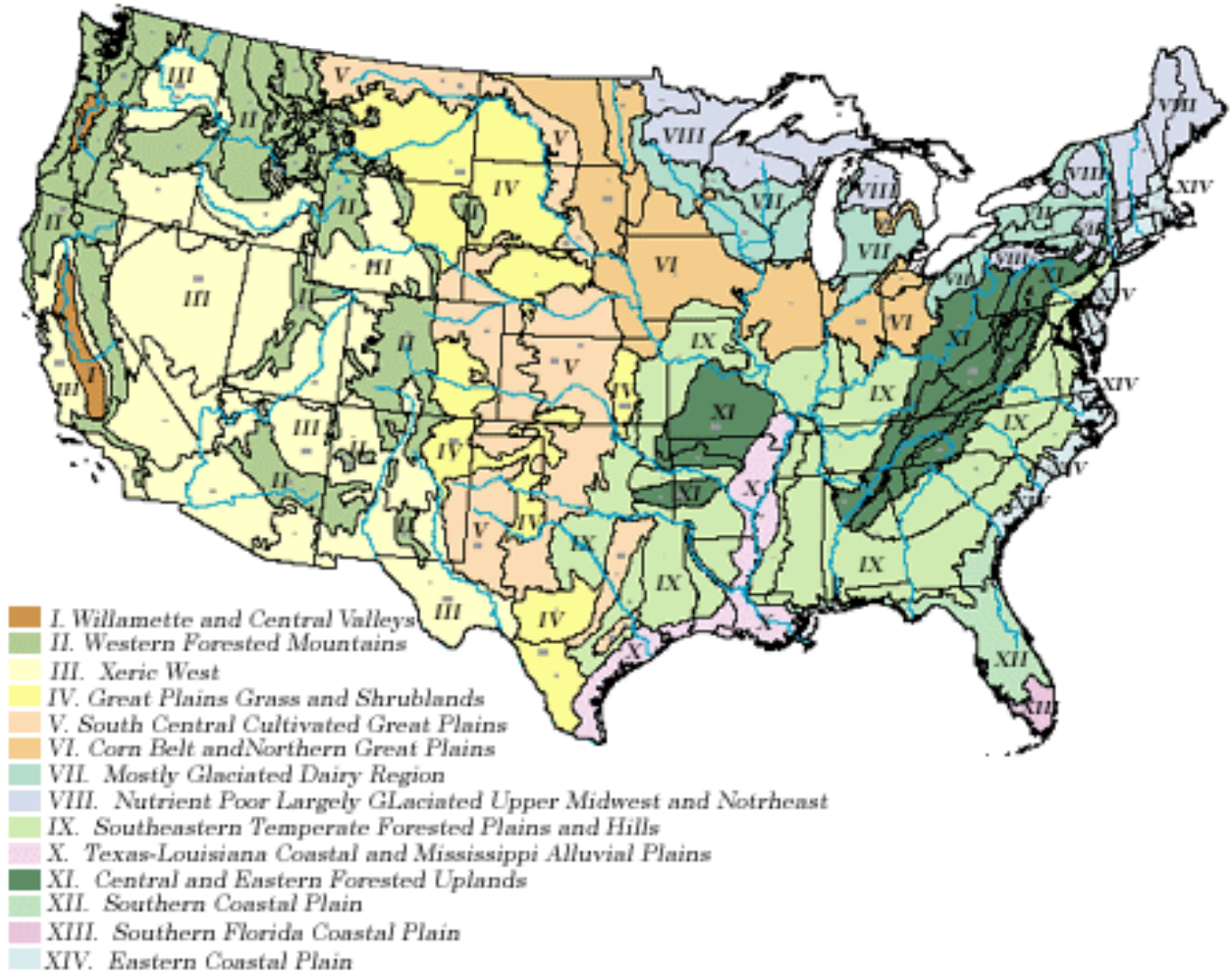
The US EPA is publishing recommended water quality criteria to provide guidance for states and tribes in adoption of regional-specific and locally appropriate water quality criteria for nutrients in lakes, reservoirs, rivers, streams, and wetlands. The current phosphorus criteria established by EPA are summarized in Table II-8. States and tribes are expected to adopt or revise the EPA nutrient criteria into water quality standards by 2004.

Table II-8: US EPA phosphorus criteria by ecoregion

Ecoregion	Total Phosphorus Criteria (µg/l)		
	Lakes & Reservoirs	Rivers & Streams	Wetlands ¹
I	55	47	--
II	8.8	10	--
III	20	22	--
IV	20	23	--
V	33	67	--
VI	38	76	--
VII	15	33	--
VIII	8.0	10	--
IX	20	37	--
X	60	128	--
XI	8.0	10	--
XII	10	40	--
XIII	18	15	10
XIV	8.0	31	

Note: (1) Wetland criteria were developed only for Ecoregion XIII (i.e., the southern Florida coastal plain). Source: EPA 2003

Figure II-5: Ecoregions used for EPA phosphorus criteria development



Source: EPA 2003

The second part of the two-pronged approach for protecting water bodies from excessive phosphorus enrichment is to set phosphorus concentration limits on effluent discharge. Most commonly, these permits are issued under the National Pollutant Discharge Elimination System (NPDES). Phosphorus concentration limits are usually determined by estimating the concentration required to meet the WQS of the receiving water body and are set by the state, tribe, or territory. Prior to 1973, there were few centralized municipal wastewater treatment facilities with phosphorus concentration limits (Litke 1999). By 1997, there were over 1,100 facilities with phosphorus concentration limits, representing 7% of all municipal treatment facilities and 17% of total wastewater flows (Litke 1999). Phosphorus limits on wastewater are typically set between 1 and 1.5 mg-P/l, with some as low as 0.01 mg-P/l.

Septic tank effluent is not subject to NPDES permit requirements because it is discharged in the subsurface environment and enters the groundwater system. Subsurface discharge systems are regulated in two ways. First, small flows below a state-defined cutoff design flow, are regulated by the onsite codes of state Departments of Health or other agencies involved in permitting septic system construction and repair. No onsite codes dictate phosphorus requirements for septic systems yet, most likely because the technologies needed to achieve low phosphorus concentrations in septic tank effluent are not available or it has been assumed that the site soils are capable of removing phosphorus. Second, subsurface discharge systems with high design flows require groundwater discharge permits. The design flow at which groundwater permits become required varies by state, as illustrated Table II-9, which contains a few states for illustration.

Table II-9: Design flow at which groundwater permits are required

State	Design Flow (liters per day)
Arizona	11,350 lpd (3,000 gallons per day)
Connecticut	18,925 lpd (5,000 gpd)
Florida	37,850 lpd (10,000 gpd) for domestic septic system
Massachusetts	37,850 lpd (10,000 gpd)
New Jersey	11,350 lpd (3,000 gpd)
Washington	13,250 lpd (3,500 gpd)

Phosphorus effluent limits may be part of a groundwater discharge permit for cluster systems.

Phosphorus loadings from septic tanks also may be regulated as a non-point source during development of a total maximum daily load (TMDL) for a given water body. A TMDL, as established under section 303 of the Clean Water Act, is a calculation of the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards, and an allocation of that amount to the pollutant's sources. For example, a TMDL developed for Lake Carlton, Florida, requires 41% reduction in non-point phosphorus sources, of which septic systems accounted for 14% (FL DEP 2003).

III. PHOSPHORUS GEOCHEMISTRY

In order to understand phosphorus removal in septic tanks, soil absorption systems, and the subsurface environment (consisting of the vadose zone, groundwater, and riparian zones), basic phosphorus geochemistry must be understood. Phosphorus chemistry in wastewater treatment systems is governed predominantly by physical, chemical and/or biological processes (US EPA 2002). Centralized wastewater treatments facilities, rather than onsite systems, often exploit the biological processes for phosphorus removal (e.g., as part of Sequencing Batch Reactor, A/O – Anaerobic/Oxic (containing oxygen) – and Modified Bardenpho processes; US EPA 1987) and chemical precipitation techniques by addition of iron or aluminum salts. Biological processes are less relevant to a discussion of removal in septic systems. Rather, mineral precipitation and soil adsorption mechanisms dominate phosphorus removal in septic tanks, soil infiltration zones, and the subsurface environment. Both of these mechanisms, the former a chemical process and the latter a combination of physical and chemical processes, will be discussed here. Note that it is common practice to lump the terms precipitation and adsorption together as “sorption”, particularly if it is unclear whether precipitation or adsorption is taking place (Harris 2002). However, each will be discussed separately. An emphasis will be placed on *phosphate* precipitation and adsorption because this form usually accounts for the majority of phosphorus in raw municipal wastewater (Tchobanoglous and Schroeder 1985).

A. Precipitation

Precipitation involves “the formation of a three-dimensional solid phase arrangement of molecules from the solution phase” (Doner and Grossl 2002). This is distinct from adsorption, which involves the formation of a two-dimensional structure (i.e., PO_4^{3-} on the surface of a mineral rather than within the mineral itself). The distinction between these two processes is important because surface adsorption is usually limited by a fixed availability of sorption sites in a particular soil that eventually will be used up if sewage loading occurs over long periods. Precipitation reactions, on the other hand, are potentially sustainable provided that the supply of cations necessary to complete the reaction is also sustainable.

The phosphate minerals potentially formed in septic tanks and soil absorption systems generally contain aluminum, iron and/or calcium (Ptacek *et al.* 1994; Harris 2002). Table III-1 presents typical septic tank effluent concentrations for these species which may participate in forming phosphate minerals.

Table III-1: Typical Concentrations of Aluminum, Iron, and Calcium in Septic Tank Effluent

Element	Typical Concentration (mg/l)
Aluminum	< 0.1
Iron	0.5
Calcium	75

The phosphate minerals include:

- Beta tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$
- Hydroxyapatite $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$
- Fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$
- Strengite $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$
- Struvite $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$
- Variscite $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$
- Vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
- Wavellite $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

Under reducing conditions vivianite solubility probably controls the soluble phosphate concentration (Nriagu *et al.* 1984; Robertson 1998). Under oxidizing conditions the controlling phase can be amorphous hydroxyapatite (Jenkins *et al.* 1971), beta tricalcium phosphate (Moore and Reddy 1994), strengite or variscite (Robertson 1998) depending on the pH (Figure III-1). Nriagu and Reddy (1994) suggest that several other PO_4 minerals are also stable in the vadose zone and groundwater environments.

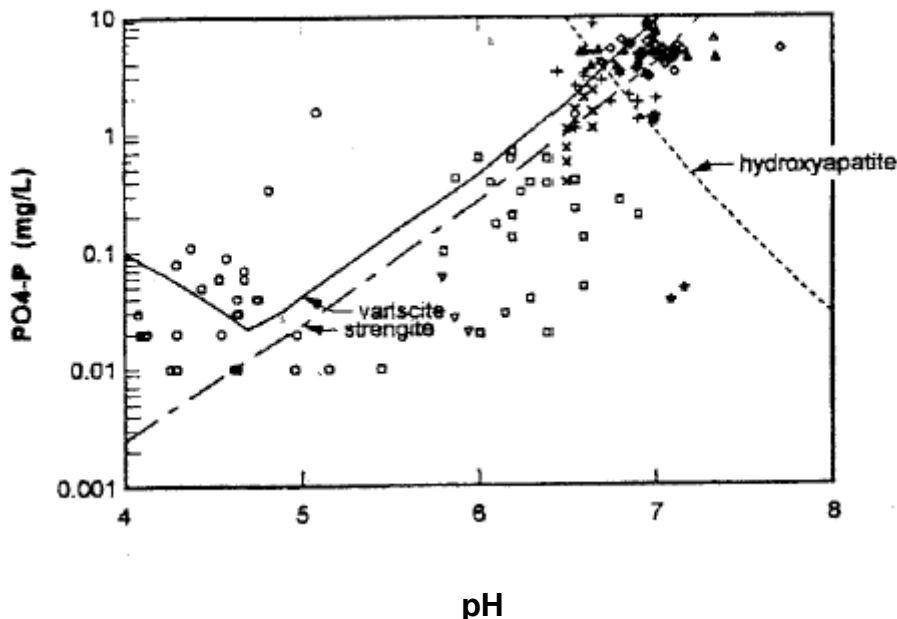
The formation of these mineral phases is described by a solubility product. Solubility products (shortened to K_{sp}) for the important phosphate minerals are shown in Table III-2. Note that phosphate forms minerals with both oxidized iron (Fe^{3+}) and reduced iron (Fe^{2+}), and thus iron-phosphate minerals will behave differently under different redox conditions. Robertson *et al.* (1998) presented the soluble phosphate concentrations that would be expected to be in equilibrium with these mineral forms under oxidizing conditions along with field data as shown in Figure III-1.

Table III-2: Range of solubility products reported for common phosphate minerals

Mineral Name	Dissolution Equation	Solubility Product (25 °C)	Reference(s)
Beta tricalcium phosphate	$\beta\text{-Ca}_3(\text{PO}_4)_2 = 3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-}$	10^{-29}	Schweingruber 1984
Hydroxyapatite	$\text{Ca}_5(\text{OH})(\text{PO}_4)_3 = 5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{OH}^-$	10^{-40} to 10^{-57}	Baker <i>et al.</i> 1998; as cited in Stumm and Morgan 1981
Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F} = 5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{F}^-$	10^{-59}	as cited in Stumm and Morgan 1981
Strengite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O} = \text{Fe}^{3+} + \text{PO}_4^{3-} + 2 \text{H}_2\text{O}$	10^{-26}	as cited in Stumm and Morgan 1981
Struvite	$\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O} = \text{NH}_4^+ + \text{Mg}^{2+} + \text{PO}_4^{3-} + 6 \text{H}_2\text{O}$	$10^{-13.1}$ to $10^{-13.3}$	Taylor <i>et al.</i> 1963; Burns and Finlayson 1982
Variscite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O} = \text{Al}^{3+} + \text{PO}_4^{3-} + 2 \text{H}_2\text{O}$	10^{-21}	as cited in Stumm and Morgan 1981
Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} = 3 \text{Fe}^{2+} + 2 \text{PO}_4^{3-} + 8 \text{H}_2\text{O}$	10^{-36}	Parkhurst <i>et al.</i> 1980

Figure III-1: Phosphate concentrations in proximal plume core zones compared to solubility curves for hydroxyapatite, strengite, variscite and vivianite for oxidizing plumes

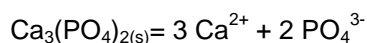
Hydroxyapatite curve calculated using Cambridge plume water composition ($\text{Ca}^{2+} = 74 \text{ mg/L}$); vivianite curve calculated using Delawana reducing plume water composition ($\text{Fe} = 10 \text{ mg/L}$); strengite curve calculated using Cambridge plume water composition assuming equilibrium with amorphous $\text{Fe}(\text{OH})_3$; variscite curve calculated using Muskoka plume water composition assuming equilibrium with gibbsite at $\text{pH} > 4.9$ and jurbanite at $\text{pH} < 4.9$.



Source: Robertston *et al.* (1998)

SOLUBILITY PRODUCTS

The solubility product is the product of the dissolved components that comprise a mineral - each raised to their respective stoichiometric coefficient - assuming the mineral is at equilibrium with the aqueous solution. For example, the precipitation and dissolution of tricalcium phosphate can be described by:



At chemical equilibrium for an ideal solution, the solubility product for tricalcium phosphate formation is:

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 10^{-29} \text{ M}^5$$

The value of the solubility product can generally be obtained from chemical textbooks (e.g., Stumm and Morgan 1981; Appello and Postma 1993) or from compilations of chemical equilibrium constants (e.g., Martell and Smith 1975) and will depend on the temperature, pressure, and ionic strength of the solution. It should be noted that while PO_4^{3-} is the chemical species often used in the solubility product equation, most of the phosphate in the environment will actually be H_2PO_4^- or HPO_4^{2-} . The solution pH must be known so that the concentration of PO_4^{3-} can be calculated from measured total soluble phosphate concentrations (see Figure II-3).

The ion activity product (IAP) is useful for determining whether phosphate is over- or under-saturated with respect to a given mineral. For example, to determine whether wastewater from a septic tank was under-saturated or over-saturated with respect to tricalcium phosphate, the IAP would be calculated as follows:

$$\text{IAP} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

If the calculated IAP is less than the known K_{sp} , then the wastewater effluent is under-saturated with respect to tricalcium phosphate. This suggests that more tricalcium phosphate could dissolve and/or that there is another less soluble mineral phase controlling calcium and/or phosphate concentrations in solution. Conversely, if the IAP is greater than the known K_{sp} , then more tricalcium phosphate should precipitate out because the solution is oversaturated. The saturation index = $\log(\text{IAP}/K_{\text{sp}})$ is another way to assess whether a solution is over or under-saturated with respect to a particular mineral. A negative value for the saturation index indicates undersaturation and a positive value indicates oversaturation. Given the imprecision of IAP calculations, $\log(\text{IAP}/K_{\text{sp}})$ values that lie in the range -0.5 to + 0.5 are indicative of equilibrium conditions.

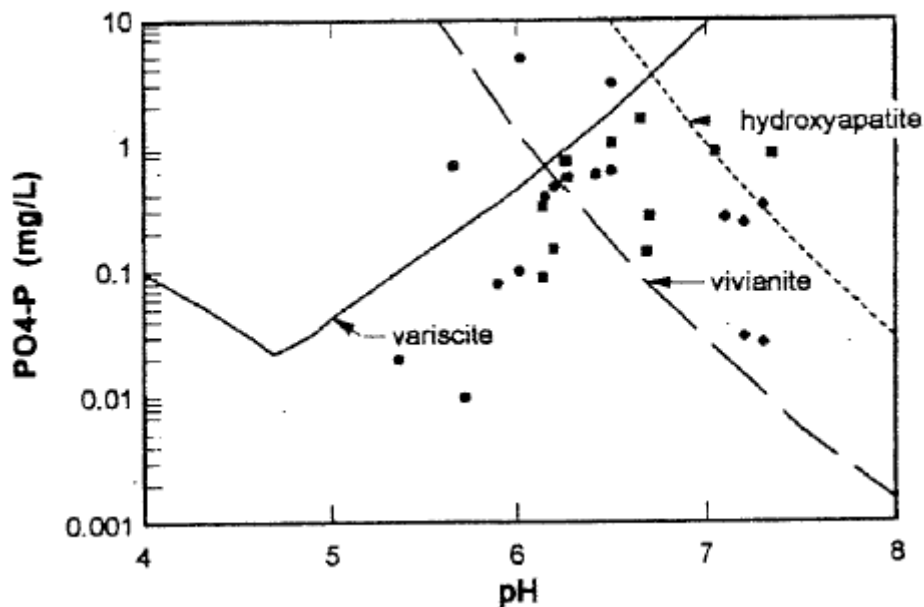
For more information refer to Snoeyink and Jenkins (1980), Stumm and Morgan (1981), Tchobanoglous and Schroeder (1987).

Solubility products are useful for determining the mineral phase that potentially controls the soluble phosphate concentration in septic tanks, soils, and groundwater. The controlling mineral phase is generally the least soluble mineral phase present, that is, the one that will determine the concentration of phosphate in solution. The controlling phase can be assessed by calculating the equilibrium phosphate concentration given the K_{sp} of the mineral, or by inspection of a solubility diagram. The theoretical determination of the controlling phase for phosphate is sensitive to the K_{sp} used, as well as the concentration of important cations, specifically aluminum, calcium, and iron. K_{sp} calculations assume equilibrium conditions exist between the aqueous species and all of the mineral phases considered. However, there are known kinetic limitations to the formation of well-crystalline hydroxyapatite. Freshly precipitated calcium phosphate can

undergo transformation through several metastable precursor phases, from octacalcium phosphate to amorphous calcium phosphate, to calcium-deficient hydroxyapatite and finally to stoichiometric hydroxyapatite (Johnsson and Nancollas, 1992; Liu *et al.* 2001). The precursor phases may be more soluble, but often they precipitate first because of their faster rates of formation. The latter phase is the thermodynamically stable phase and least soluble. The actual pathways will vary depending on inhibitory effects, the presence of organic matter, biological activity, and pH and solution composition. A number of septic system plumes exhibit hydroxyapatite supersaturation (Robertson *et al.* 1998), presumably as a result of the slow rate of mineral formation.

Figure III-2: Phosphate concentrations in proximal plume core zones compared to solubility curves for hydroxyapatite, strengite, variscite and vivianite for reducing plumes

Hydroxyapatite curve calculated using Cambridge plume water composition ($\text{Ca}^{2+} = 74 \text{ mg/L}$); vivianite curve calculated using Delawana reducing plume water composition ($\text{Fe} = 10 \text{ mg/L}$); strengite curve calculated using Cambridge plume water composition assuming equilibrium with amorphous $\text{Fe}(\text{OH})_3$; variscite curve calculated using Muskoka plume water composition assuming equilibrium with gibbsite at $\text{pH} > 4.9$ and jurbanite at $\text{pH} < 4.9$.



Source: Robertson *et al.* (1998)

Iron in the environment exists predominantly in either the reduced ferrous $[\text{Fe}(\text{II})]$ or oxidized ferric $[\text{Fe}(\text{III})]$ form. Ferrous iron is relatively soluble in water and is therefore quite mobile. Ferric iron, on the other hand, tends to form insoluble $\text{Fe}(\text{III})$ oxyhydroxides and is therefore relatively immobile. The iron cycle in most environments involves alternate reduction (mobilization) of ferric iron followed by oxidation (immobilization) of ferrous iron. Most of these reactions are microbially catalyzed under natural conditions.

In addition to depending on the pH and the concentration of the elements with which phosphate forms minerals, the mineral phase controlling phosphate concentrations in septic tanks and soil absorption systems will vary with the redox status of the soil. Iron is a redox active element, existing as Fe(III) at high redox potentials but Fe(II) at low redox potentials. The former precipitates in the form of the phosphate mineral strengite, while the latter forms vivianite. Whereas iron-phosphate minerals are sensitive to changes in redox conditions, aluminum-phosphate and calcium-phosphate minerals are more stable under a wider range of redox conditions (Smith *et al.* 2001). Robertston *et al.* (1998) presented the soluble phosphate concentrations that would be expected to be in equilibrium with these mineral forms under reducing conditions along with field data as shown in Figure III-2.

TERMINOLOGY

pe - pe is the negative logarithm of electron activity, which is a theoretical representation of oxidation/reduction potential. A positive pe represents oxidizing conditions, and a negative pe represents reducing conditions.

Redox - a reversible chemical reaction in which one reaction is an oxidation and the reverse is a reduction

In general, because aluminum and iron are common constituents of phosphate minerals, the concentrations of Al^{3+} , Ca^{2+} , Fe^{3+} (or Fe^{2+}) specifically, not just total aluminum, calcium or iron, must be known if the concentration of phosphate is to be predicted. In Figures III-3 and III-4, these concentrations were predicted with the equilibrium speciation modeling program MINEQL⁺. Many other equilibrium speciation modeling programs, such as the public domain models PHREEQC and Visual MINTEQ and the commercial JESS, can also accomplish this task. Information on these chemical equilibrium speciation programs can be found on the web as follows:

- JESS: http://jess.murdoch.edu.au/jess/jess_home.htm
- MINEQL⁺: <http://www.mineql.com/mineql.html>
- PHREEQC: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/
- Visual MINTEQ: <http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm>

These modeling programs use information on the solubility products of the aluminum-, calcium-, and iron-containing minerals to estimate the Al^{3+} , Ca^{2+} , and Fe^{3+} (or Fe^{2+}) activity in soil solutions. Whether Fe^{3+} or Fe^{2+} will be present will depend on the redox status of the water, with Fe^{2+} predominant at $\text{pe} < 0$ (Stumm and Morgan 1981; see definition of pe in "Redox Concepts").

The most common phases that control Al^{3+} in the shallow subsurface environment are aluminum hydroxides (*e.g.*, gibbsite) and aluminum hydroxysulfate solids (potentially jurbanite) (Table III-3). Thus, knowing the pH and, in the case of jurbanite, the concentration of SO_4^{2-} , would allow prediction of the concentration of Al^{3+} in solution. This is demonstrated in Figure III-3, which shows that, assuming the concentration of SO_4^{2-} is 30 mg/l, gibbsite controls the concentration of Al^{3+} for pH > 5 to 6. Note that

Al³⁺ concentrations would increase from as high as ~3 x 10⁻⁶ mg/l at pH 7 (when gibbsite is controlling Al solubility) to as much as ~90 mg/l at pH 4 (when jurbanite is controlling Al solubility). It should be noted that at pH 7, the total dissolved concentration of Al will be higher than the concentration of Al³⁺, whereas at pH 4 most dissolved Al will be present as Al³⁺. The predicted equilibrium concentration of Al³⁺ in the soil solution is strongly dependent on the Al solids assumed to be controlling the aqueous concentrations and the values of the respective solubility products.

A similar exercise can be performed for calcium and iron. In the case of calcium, calcite usually controls Ca²⁺ concentrations in solution. For some soils, in particular, those found in evaporative settings, gypsum also may control the concentration of Ca²⁺ in solution. In the case of iron, ferrihydrite and goethite control the concentration of Fe³⁺ under oxic conditions (Figure III-4a), while siderite controls the concentration of Fe²⁺ under reducing conditions (Figure III-4b) (Zanini *et al.* 1998, Ptacek, 1998).

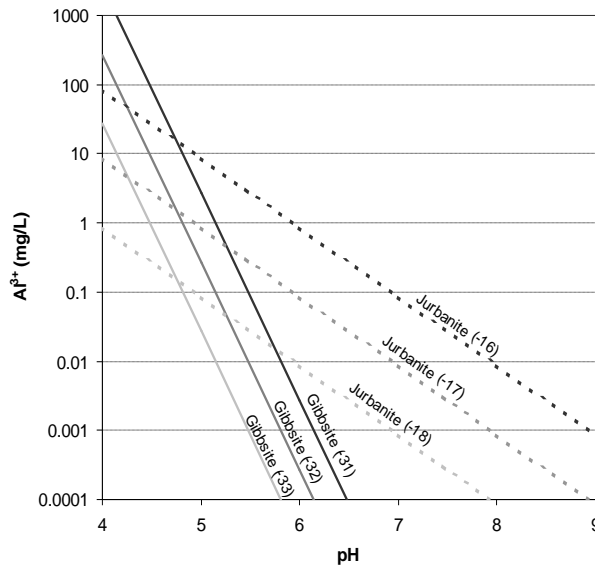
Table III-3: Common aluminum, calcium, and iron mineral phases

Mineral Name	Equation	Reported Range of K _{SP}
Aluminum Minerals		
Gibbsite	Al(OH) ₃ = Al ³⁺ + 3 OH ⁻	10 ⁻³¹ to 10 ⁻³³
Jurbanite	AlOHSO ₄ * 5H ₂ O = Al ³⁺ + OH ⁻ + SO ₄ ²⁻	10 ⁻¹⁷
Calcium Minerals		
Calcite	CaCO ₃ = Ca ²⁺ + CO ₃ ²⁻	10 ⁻¹⁰
Iron (Fe³⁺) Minerals		
Amorphous Ferric Hydroxide	Fe(OH) ₃ = Fe ³⁺ + 3OH ⁻	10 ⁻³⁷ to 10 ⁻³⁹
Goethite	α-FeOOH + H ₂ O = Fe ³⁺ + 3OH ⁻ + H ₂ O	10 ⁻⁴¹ to 10 ⁻⁴²
Hematite	Fe ₂ O ₃ + 3 H ⁺ = 2 Fe ³⁺ + 3 OH ⁻	10 ⁻⁴³
Iron (Fe²⁺) Minerals		
Siderite	FeCO ₃ = Fe ²⁺ + CO ₃ ²⁻	10 ^{-8.4}

Source: as cited in Stumm and Morgan 1981

Figure III-3: Equilibrium concentration of Al^{3+} (not total soluble Al) as a function of pH in the presence of gibbsite and jurbanite and with $[SO_4^{2-}] = 30 \text{ mg/l}$.

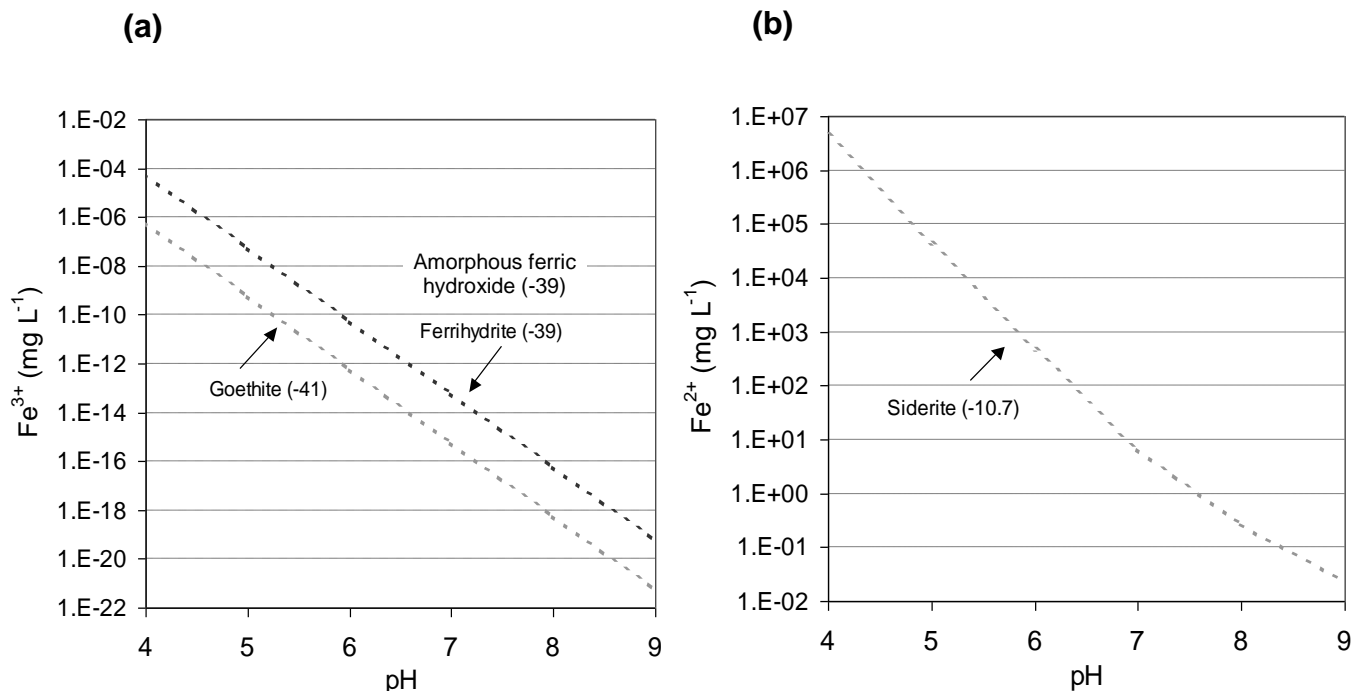
Numbers in parentheses are the log of the K_{sp} for gibbsite or jurbanite dissolution.



The clay minerals kaolinite and montmorillonite may also control Al^{3+} solubility, although this is less common.

Figure III-4: Predicted concentration of Fe^{3+} (not total soluble Fe) as a function of pH in the presence of: (a) amorphous ferric hydroxide and goethite; and (b) siderite.

Numbers in parentheses are the log of the K_{sp} for the dissolution of the iron mineral phases. Note the different y-axes for the graphs.



B. Adsorption

Adsorption is the association of phosphate with the surfaces of a particle. There are a number of different types of adsorption, including (Stumm 1998):

- *Hydrophobic adsorption* due the repulsion of sparingly soluble components by water
- *Electrostatic adsorption* due to forces of attraction arising from the difference in charge of the solute species and the adsorbing solid phase
- *Specific adsorption* includes chemical interactions between a solute and a solid surface that are stronger than simple electrostatic attractions. For example, the formation of chemical bonds between the solute species and a specific surface site on the adsorbing phase

Studies show that phosphate adsorption takes place via specific adsorption, that is the formation of a bond between phosphate and a specific site on the adsorbing solid phase (Figure III-5; Sposito 1989). Specific adsorption binds ions much more strongly than does hydrophobic or electrostatic adsorption.

Because both of the major forms of phosphate present in wastewaters (H_2PO_4^- and HPO_4^{2-}) are anions, they will generally be attracted to positively-charged mineral surfaces. The surface charges of many oxide and hydroxide minerals vary as the pH changes due to protonation/deprotonation of surface hydroxyl groups. As a result, the surface varies from being net positively charged at low pH to net negatively charged at high pH. The pH at which the negative surface charges balance the positive surface charges is referred to as the point of zero charge or pH_{pzc} . The pH_{pzc} is a characteristic which is intrinsic to the mineral. Minerals with high pH_{pzc} values remain positively charged at higher pH values than minerals with lower pH_{pzc} values. Minerals that are positively charged under near-neutral pH conditions in the subsurface include aluminum (hydr)oxides, iron (hydr)oxides, and manganese oxides, and some clay minerals (Ptacek *et al.* 1994; Foussard *et al.* 1995):

- Corundum: $\alpha\text{-Al}_2\text{O}_3$
- Gibbsite: $\text{Al}(\text{OH})_3$
- Boehmite: $\gamma\text{-AlOOH}$
- Goethite $\alpha\text{-FeOOH}$
- Ferrihydrite: $\text{Fe}(\text{OH})_3$
- Hematite: Fe_3O_4
- Pyrolusite: $\beta\text{-MnO}_2$
- Allophane: $\text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_{1.3-2} \cdot 2.5-3 \text{H}_2\text{O}$

These (hydr)oxides and clay minerals are positively charged because of the addition of H^+ atoms to (*i.e.*, protonation of) the surface functional groups.

Note that once the phosphate adsorbs to the surface of these (hydr)oxide or clay minerals, it actually forms a bond with the Al (in the case of corundum, gibbsite, boehmite, allophane), Fe (in the case of goethite, ferrihydrite, or hematite), or Mn (in the case of pyrolusite) atoms.

In one study, the quantity of phosphate adsorbed on goethite was $2.5 \mu\text{mol P m}^{-2}$ compared with $0.97 \mu\text{mol m}^{-2}$ on hematite (Barrón *et al.* 1988), because goethite is characterized by more accessible surface OH groups ($1 \mu\text{mol} = 10^{-6}$ moles). In another study, phosphate adsorption was highest on allophane, followed by ferrihydrite, goethite, gibbsite, hematite, and the clay minerals kaolinite and montmorillonite (Figure III-7). Allophane materials are thought to have a high affinity for phosphate because of their high surface area (Parfitt 1980). Clay minerals adsorb less phosphate because of the lower specific surface area suitable for phosphate adsorption (Parfitt 1978).

Quantifying mineral surface charge

Charge on mineral surfaces can be caused by various processes. With respect to phosphate adsorption, the ionization of surface functional groups is the most important charge-generating process. Surface group ionization refers to hydroxyl groups at the surface of the mineral gaining or losing H^+ atoms, depending on the pH of the surrounding solution.

Whether a mineral surface tends to be positively charged or not can be assessed by measuring the point of zero charge, pH_{pzc} , or the pH at which the clean mineral surface has an equivalent amount of negative and positive charge (i.e. zero net charge). Above the pH_{pzc} , the surface will have a net negative charge, while below the pH_{pzc} the surface will have a net positive charge.

The mineral surfaces that will have a net positive charge at circumneutral pH are those that have a pH_{pzc} greater than 6 to 8. These include the following metal (aluminum, iron, and manganese) oxide and (oxy)hydroxide minerals:

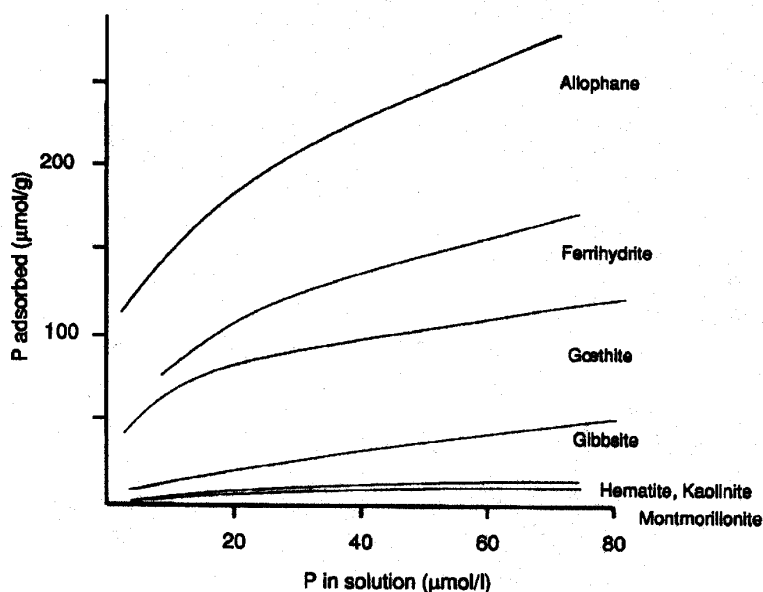
Mineral	pH_{pzc}
○ $\beta\text{-MnO}_2$	7.2
○ $\alpha\text{-FeOOH}$	7.8
○ $\gamma\text{-AlOOH}$	8.2
○ $\text{Fe}(\text{OH})_3$	8.5
○ $\text{Al}(\text{OH})_3$	8.9
○ $\alpha\text{-Al}_2\text{O}_3$	9.1

Therefore, these minerals are the ones that are most likely to adsorb phosphate.

For more information, refer to Sposito 1989 and Stumm 1992.

Phosphate can also adsorb on calcite (CaCO_3) surfaces (Borrero *et al.* 1988), despite calcite having a negative charge under slightly-basic to basic pH conditions (White 1982). Phosphate adsorption apparently occurs on only 5% of the pure calcite surface, but these adsorption sites act as nuclei for the precipitation of calcium phosphate minerals (Cole *et al.* 1953). Nevertheless, it is likely that Al and Fe oxides are the most important components determining phosphate adsorption capacity in soils, including calcareous soils (Holford and Mattingly 1975; Parfitt 1978; Hamad *et al.* 1992).

Figure III-5: Phosphate sorption on various minerals



Source: Sollins *et al.* 1991

The presence of organic matter affects the adsorption of phosphate to minerals. Organic acids (e.g., oxalic, citric, malic acids) can compete with orthophosphate for sites on mineral and soil surfaces, thereby decreasing phosphate adsorption (Fontes *et al.* 1992; Hue 1991). On the other hand, soils that are rich in organic carbon may have an enhanced capacity for immobilization of P as organic-bound material (humic-P, Borie and Zunino, 1983), which could have the effect of counteracting the diminished sorptive capacity of such soils.

Studies have shown that phosphate adsorption to surfaces is characterized by a fast, initial adsorption reaction during which an OH⁻ or H₂O molecule is released from the surface and a phosphate surface complex is formed (Parfitt *et al.* 1976, Goldbery and Sposito 1985, Torrent *et al.* 1992). This initial fast reaction may, in some cases, be followed by a slow process, perhaps involving phosphorus diffusion to adsorption sites within the solid matrix (Olila and Reddy 1997, Torrent *et al.* 1992).

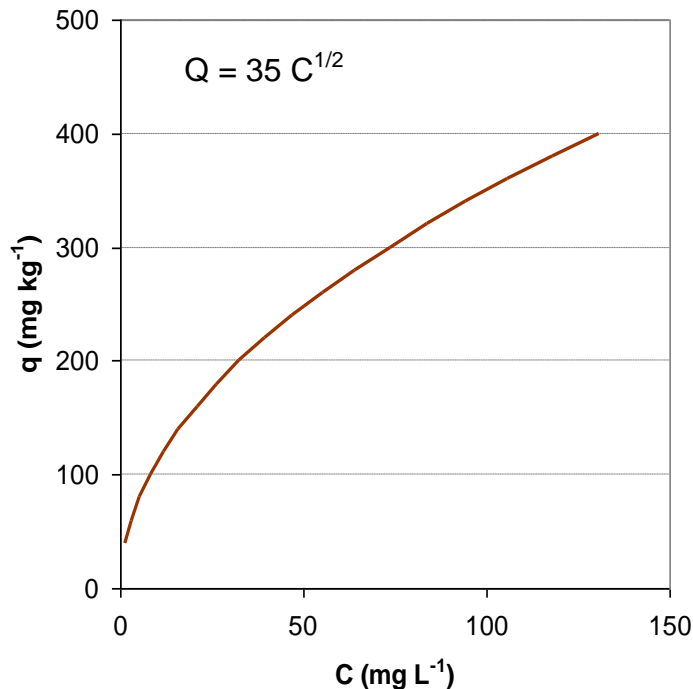
There are many techniques used to explain phosphate adsorption to mineral surfaces. In many instances, equilibrium data describing phosphate adsorption to specific oxide surfaces or to soils in general can be approximated by the Freundlich equation:

$$q = K_f C^{1/n} \quad (1)$$

where q is the mass of phosphate adsorbed to the soil [mg/kg], K_f is a constant, C is the concentration of phosphate in solution at equilibrium [mg/l], and n is a unitless constant (usually close to 2 for phosphate). In its simplest form, considering only the linear portion of the adsorption curve, n is assigned a value of 1 and the ratio of adsorbed phosphate to phosphate in solution is referred to as the distribution coefficient (K_d). This is the commonly used parameter in the well-known retardation equation describing

solute migration velocity in groundwater. There are two main limitations of using a K_f or K_d model to describe adsorption of a hydrolysable species on a variably-charged mineral surface. First, this model does not account for the pH dependent speciation of phosphate, and therefore does not represent changes in the speciation and charge of the phosphate species under varying pH conditions. Second, this model does not account for the change in surface charge of the mineral adsorbent as a function of pH. Many common adsorbents vary from net negative to net positive under the range in pH values that commonly occur at wastewater disposal sites. Note that if the Freundlich isotherm is used to describe phosphate adsorption to soils, it may incorporate both true adsorption processes and mineral precipitation. A theoretical Freundlich isotherm for phosphate adsorption is shown in Figure III-6. Note that the shape is similar to the shape of the curves in Figure III-5.

Figure III-6: Theoretical phosphate adsorption described by a Freundlich isotherm with $K_f = 35$ and $n = 2$



Both the original and modified Freundlich equations demonstrate that the concentration of phosphate in solution is the factor that controls the extent of adsorption (Froussard *et al.* 1995).

The Freundlich isotherm often fails to accurately predict P breakthrough behavior in laboratory column experiments and at field sites. The primary usefulness of Freundlich isotherms is to compare the adsorption affinities for different soils and aquifer materials under a specific set of geochemical conditions.

C. pH and Eh effects

As demonstrated in Figures II-2, III-2, III-3 III-4, pH influences the solubility of phosphate minerals, the adsorption of phosphate onto mineral surfaces, as well as the speciation of the aluminum, calcium, and iron commonly contained in phosphate minerals. Moreover, pH interacts with the redox potential of the septic tank, soil solution, or groundwater to influence the adsorption and precipitation reactions governing phosphate chemistry. The redox potential of a solution, often expressed as pe , is a measure of how oxidizing or reducing that solution is and is explained in more detail in the following section on “Redox Concepts”. The dominant pH and redox effects that influence phosphate chemistry are as follows:

A decrease in pH causes:

- An increase from PO_4^{3-} to HPO_4^{2-} to $H_2PO_4^-$ to H_3PO_4 as the dominant phosphate species (Figure II-3)
- A decrease in the fraction of phosphate species bound as complexed species as the result in changes in the dominant phosphate species and changes in the stability of the complexes
- An increase in the positive surface charge of iron and aluminum (hydr)oxides, and therefore an increase in the affinity that these surfaces have for phosphate adsorption (Goldberg and Sposito 1984)
- An increase in Al^{3+} concentrations in solution (Figure III-3)
- An increase in Fe^{3+} and Fe^{2+} concentrations (Figure III-4)
- An increase in Ca^{2+} concentrations due to the increase in calcite solubility at lower values of pH

An increase in pH, of course, produces the opposite effects.

A decrease in the redox potential (pe) causes:

- An increase in the concentration of Fe(II) relative to Fe(III) and therefore a decrease in the stability of iron(III) (hydr)oxide minerals

These effects interact to determine the nature of adsorption and precipitation phenomena. The most important interactions and their consequences for precipitation and adsorption are described below.

Precipitation

The effects of pH and pe on precipitation can be summarized as follows:

- The higher Al^{3+} and Fe^{3+} (or Fe^{2+}) concentrations at lower pH result in lower phosphate concentrations in solution because of equilibrium with aluminum-phosphate and iron-phosphate minerals, assuming dissolved Al^{3+} and Fe^{3+} (or

Fe²⁺) can be replenished from the soil and aquifer solids and are not limiting (refer to Table III-3 and Figure II-3; Robertson *et al.* 1998; Gold and Sims 2000).

- At higher pH levels, lower soluble phosphate concentrations can also occur if phosphate concentrations are limited by the equilibrium with respect to hydroxyapatite (note that the OH⁻ term in the solubility product equation for hydroxyapatite increases as pH increases; Table III-3).
- Low pe, and the concomitant reduction of Fe³⁺ to Fe²⁺, results in the instability of strengite (a Fe(III) mineral) and the stability of vivianite (a Fe(II) mineral)). At similar total dissolved iron concentrations, phosphate concentrations in equilibrium with respect to vivianite are lower than they are in equilibrium with respect to strengite.

Thus, the mineral phases controlling phosphate precipitation and dissolution depend heavily on pH and pe. In oxidized soils, the solubility of phosphate is controlled by hydroxyapatite, notably the amorphous form rather than the crystalline form (Jenkins *et al.* 1971), possibly beta tricalcium phosphate (Moore and Reddy 1994), strengite or variscite (Robertson *et al.* 1998). Phosphate solubility in the presence of these minerals varies widely as a function of pH. For example, the predicted phosphate concentration at equilibrium with variscite, strengite, and hydroxyapatite is two orders of magnitude higher at pH 7 than at pH 5 (Figure III-1; Robertson *et al.* 1998). Under reducing (low pe) conditions, phosphate solubility varies less widely as a function of pH (Gold and Simms 2000) and is generally lower than it is under oxidizing conditions. This reduction in solubility may be largely due to the precipitation of vivianite (a Fe(II) mineral), which is less soluble than hydroxyapatite or beta tricalcium phosphate (Figure III-2; Nriagu *et al.* 1984; Robertson *et al.* 1998) and because of the relatively high concentration of Fe(II) that often develops under reducing conditions.

Adsorption

The effects of pH and pe on adsorption can be summarized as follows:

- The increase in the positive surface charge of the iron and aluminum oxides that occurs with decreasing pH will increase the extent of phosphate adsorption. However, adsorption will cease below pH 2, despite the fact that the positive surface charge will be very high, because most phosphate is converted to the uncharged species H₃PO₄.
- The reduction of iron that occurs at lower redox potentials leads to dissolution of Fe(III) (hydr)oxides. This reductive iron dissolution decreases the surface area of iron (hydr)oxides available for adsorption, and thus decreases phosphate adsorption to these surfaces. Aluminum hydroxides, however, are less affected by changes in redox potential. Under low pe conditions, reduced iron minerals, including siderite, are stable and may adsorb phosphate.

REDOX CONCEPTS

The transfer of electrons from one chemical species to another is called a reduction or oxidation reaction.

Reduction refers to a gain of electrons (and therefore a decrease in positive charge), whereas **oxidation** refers to a loss of electrons (and therefore an increase in positive charge). Microbes mediate most redox reactions in septic tanks, soils, and groundwater. Adsorbed Fe(II) and zero-valent iron are as effective as microbes at reducing compounds in pore waters.

The **redox potential** of a solution suggests whether certain species should be present in their oxidized or reduced forms. Redox potential is typically described by electrode potential (referenced to a standard hydrogen electrode), **Eh**, according to the Nernst equation:

$$Eh = E^\circ - RT/nF \ln(Q)$$

where E° is the potential for the given reaction at standard temperature and pressure (mV), R is the universal gas constant (8.314 J/mol/K), T is the temperature (K), n is the number of electrons transferred, F is Faraday's constant (96485 coulombs/mol), and Q is the reaction quotient (ratio of product concentrations to the reactant concentrations, all raised to their respective stoichiometric coefficients).

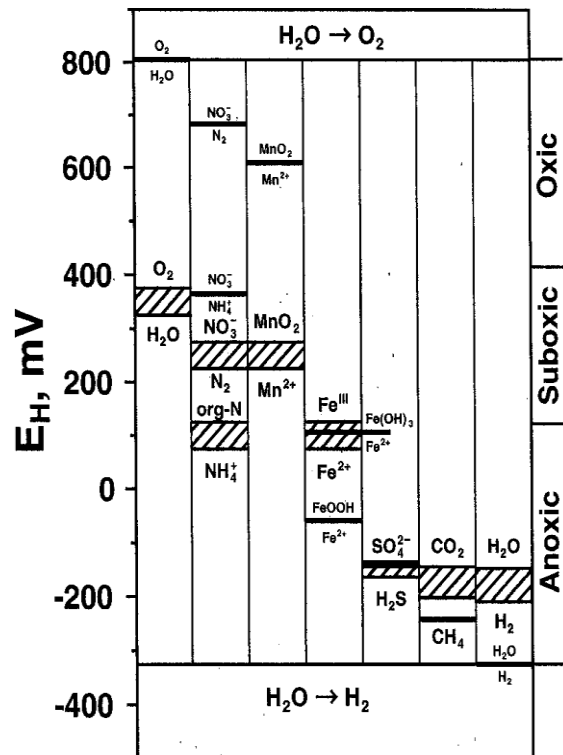
Redox potential can also be described by **pe**, which is the electron activity in p-notation (i.e. $-\log_{10}(e^-)$). At 25°C, the pe is related to Eh as follows:

$$Eh(\text{mV}) = 59.2 \text{ pe}$$

Redox Status	pe	Eh (mV)
Oxic	> 7	> 400
Suboxic	2 to 7	100 to 400
Anoxic	< 2	< 100

Most soils maintain a pe of -6 to +12, or an Eh of -355 to 710 mV. This spans the range of oxic, suboxic, and anoxic redox conditions, as listed below. Note that iron and manganese reduction occurs under suboxic conditions, while sulfate reduction occurs under anoxic conditions.

The redox ladder below shows the Eh at which major redox reactions occur. The observed transformation from oxidized to reduced species occurs in the Eh range indicated by the



Source: Essington 2004.

The concept of highly-reduced areas at the drainfield is typical of subsurface organic plumes in which organic materials are introduced to induce anaerobic conditions and enable reductive biogeochemical activities to occur (Lovley 2001)

D. Kinetic issues

Precipitation of phosphorus minerals can occur over time scales on the order of minutes to hours, although the initial minerals that precipitate are often amorphous forms that may evolve into more crystalline forms over time. Adsorption can be characterized by both rapid and slow reactions, with the initial, rapid adsorption also occurring on the order of hours.

When phosphate is initially exposed to soil, there is rapid uptake of the phosphate through adsorption processes (Ptacek *et al.* 1994) followed by slower development of crystalline phosphate minerals within the adsorbent. For example, initial adsorption of phosphate by Fe-oxide surfaces can be followed by recrystallization to form FePO₄·nH₂O (Stumm and Morgan 1981; Ptacek *et al.* 1994). Phosphate minerals will also form independent of the adsorbent. The initial rapid adsorption may slow down over time as sorption sites are depleted. Furthermore, adsorption on metal oxides may be very slowly reversible (Harris 2002). Reversibility of adsorption reactions, as well as

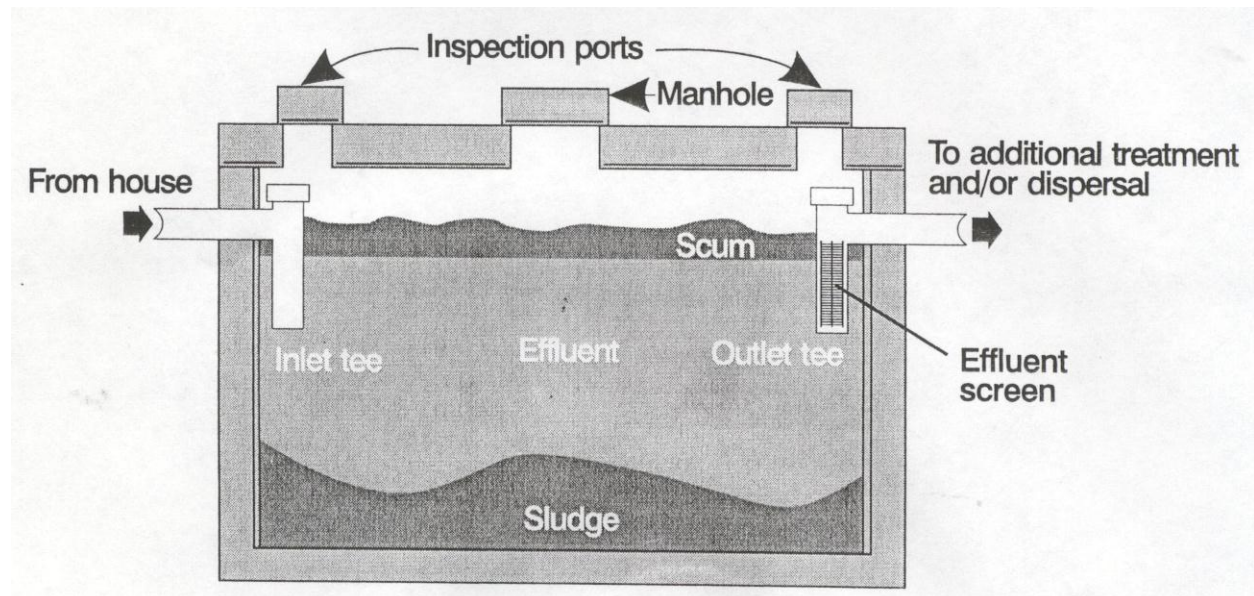
the kinetics of adsorption and precipitation (*i.e.*, of sorption, generally) will greatly influence the ultimate fate of phosphorus from on-site wastewater treatment systems (Robertson *et al.* 1998).

IV. PHOSPHORUS REMOVAL IN SEPTIC TANKS

A. Characteristics of Septic Tanks

Septic tanks receive wastewater from individual residences, as well as other non-sewered facilities (Crites and Tchobanoglous 1998). They are buried, watertight tanks that partially treat raw wastewater by equalizing hydraulic flows and retaining floatable and settleable solids. Grease and oils float to the surface of the tank and form a scum layer, while solids settle to the bottom of the tank and form a sludge layer (Figure IV-1; EPA 2002). The solids in the sludge layer are partially broken via anaerobic digestion, although the sludge must be regularly pumped out of the tank to prevent septic tank failure.

Figure IV-1: Conventional single-compartment septic tank



Source: EPA 2002

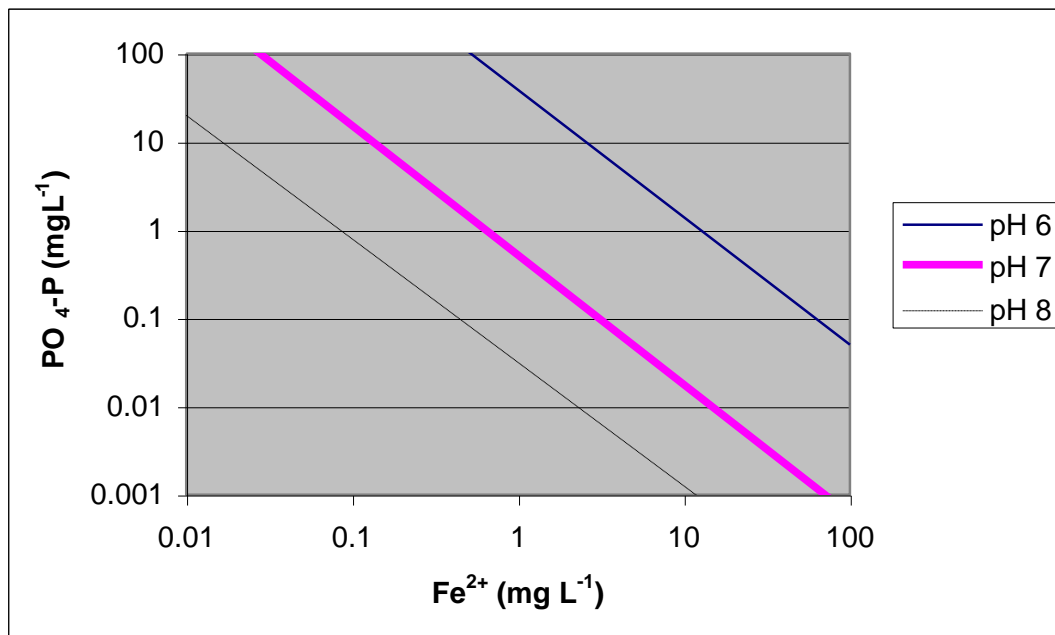
B. Phosphorus Removal Mechanisms

Phosphorus removal in septic tanks is largely a physical process, with some chemical precipitation occurring as well. Between 20 and 30% of total phosphorus in raw wastewater is separated out in the form of sludge in a septic tank (Wood 1993). Most of this phosphorus is particulate phosphorus. Particulate phosphorus in raw wastewater can be in the range of 1 to 3 mg-P/l, or approximately 20% of total phosphorus (assuming total phosphorus is 5 to 15 mg-P/l; Table II-6).

Orthophosphate may also be removed in septic tanks through mineral precipitation reactions particularly vivianite precipitation (Zanini *et al.* 1998). If vivianite precipitation does affect the concentration of orthophosphate in the effluent of a given septic tank, then the equilibrium concentration of orthophosphate in solution is a function of the concentration of Fe^{2+} which is controlled by biological factors. Robertson *et al.* (1998) measured 0.12 to 25 mg/l total Fe in the effluent of 10 septic tanks, most of which was presumed to be Fe(II) generally, and Fe^{2+} specifically, due to the reducing conditions in the tank. In the septic tank, the wastewater approaches or exceeds saturation with respect to vivianite (Robertson *et al.* 1998). Thus it is possible that vivianite precipitation begins initially in the septic tank, thereby limiting phosphorus concentrations occurring in the wastewater (Zanini *et al.* 1998). Orthophosphate concentrations in equilibrium with these iron concentrations would range from $\ll 0.01$ mg/l to 1,000 mg/l, depending on the pH of the septic tank effluent (Figure IV-2).

Figure IV-2: Predicted orthophosphate concentrations in the presence of vivianite as a function of Fe^{2+} concentrations.

This figure assumes equilibrium in pure water, and in the absence of strong complexes. Orthophosphate concentrations observed in the presence of organic complexes are expected to be higher.



C. Effluent loadings and concentrations

Studies of phosphorus concentrations in septic tank effluent have measured total phosphorus in the range of 1.2 to 22 mg-P/l (Table IV-1). Note that these data may reflect wastewater concentrations before bans were placed on phosphorus in

detergents, and thus may be higher than current values. Approximately 85% of phosphorus in septic tank effluent is expected to be dissolved (Gold 2000).

Table IV-1: Concentrations of total phosphorus in septic tank effluent

Location	Type of System	Average Total Phosphorus (mg-P/l)	Reference
Virginia	On-site, single home	16	Reneau <i>et al.</i> 1989
Wisconsin	On-site, single home	13	UW 1978
Wisconsin	On-site, single home	22	Harkin <i>et al.</i> 1979
Florida	On-site, single home	11	Ayres Associates 1993
Florida	On-site, single home	17	Ayres Associates 1996
Wisconsin	SDGS, 90 connections	8.1	Otis 1978
Texas	Nine homes	8.2	Brown <i>et al.</i> 1977
Ontario	10 on-site systems, single homes, campground, school, or resort	1.2-12*	Robertson <i>et al.</i> 1998

* Values represent PO₄-P only at several sites

Total phosphorus loadings from septic tank effluents have been estimated to be 15 to 17 kg/ha/yr (Lombardo Associates 1980; Gold and Sims 2000). The lower number assumes 170 l/capita/day, three people per household, five households per hectare and a wastewater effluent containing 15 mg-P/l. The higher number is based on 3.4 kg-P/household/yr and five households per hectare. These numbers are what might be seen in regions where bans on detergent phosphorus have not been implemented. In regions with phosphorus bans, septic tank effluent would contain approximately 7 to 8 mg-P/l, while household phosphorus production would be closer to 1.3 kg-P/household/yr. This would yield phosphorus loadings from septic tanks closer to 5 to 11 kg/ha/yr. Nevertheless, with the exception of fertilizer in agricultural systems, phosphorus loading from septic tanks effluent remains high relative to other loadings (Table IV-2)

Table IV-2: Annual phosphorus loadings from various sources

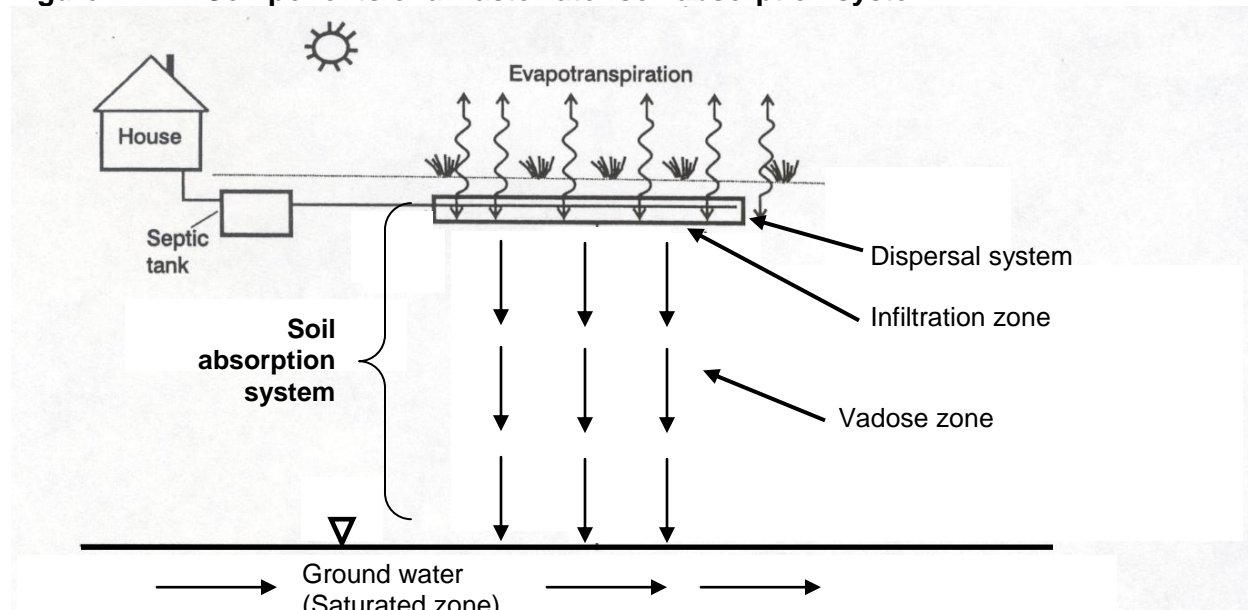
Phosphorus Source	Annual Loading [kg/ha/yr]	Predominant Phosphorus Form	Reference
Septic tank effluent (5 mg-P/l or 1.3 kg-P/household/yr)	5 – 11	Dissolved orthophosphate and polyphosphates	Calculated using data from Table IV-1; see text for assumptions
Septic tank effluent (15-18 mg-P/l or 2.8-3.4 kg-P/household/yr)	15 – 17		Lombardo Associates 1980; Gold and Sims 2000
Atmospheric deposition	<1	Dissolved orthophosphate	Howarth <i>et al.</i> 1996
Maintenance of fertilized lawns	5	Particulate phosphorus	Sharpley <i>et al.</i> 1998; Pierzynski <i>et al.</i> 2000
Fertilizer manure from agricultural production systems	10-150		

V. PHOSPHORUS IN SOIL ABSORPTION SYSTEMS AND GROUNDWATER

A. Soil absorption systems basics

A soil absorption system encompasses the second and third components of a conventional on-site (septic) wastewater system, namely, the treatment and dispersal system. In a soil absorption system, septic tank effluent is discharged via a dispersal system to the infiltration zone, the vadose zone, and, ultimately, to ground water (Figure V-1). The infiltration zone may be only a few centimeters thick, but is the most biologically active zone in the subsurface and is often referred to as the “biomat”. The infiltration zone acts as a fixed-film bioreactor in which BOD is oxidized and ammonia is nitrified. The vadose zone, also called the unsaturated zone is generally required to be at least 1 m or more in depth. This zone allows oxygen transport to the infiltration zone, and also allows geochemical reactions to occur as a result of soil-water interaction. Most of the phosphorus and pathogen removal occurs in the vadose zone (EPA 2002).

Figure V-1: Components of a wastewater soil absorption system



Source: US EPA 1997

Soil absorption systems are usually located in relatively permeable, unsaturated natural soils or imported fill material. Both the type of soil and the soil thickness (*i.e.*, distance between the infiltration zone and groundwater) will influence pollutant removal generally, and phosphorus removal specifically. The depth from the infiltration system to ground water (*i.e.*, thickness of the vadose zone) affects hydraulic function and pollutant removal by influencing soil water content, aeration status, media surface area, and hydraulic retention time (Cuyk *et al.* 2001). Thicker soil absorption systems generally yield better contaminant removal, although there are diminishing benefits beyond a vadose zone depth of 30 to 60 cm for many constituents (Cuyk *et al.* 2001). However, note that if the depth to the water table is only 30 cm below the infiltration

zone, the thickness of the vadose (unsaturated) zone will be essentially zero in all soils finer than medium sand because of the presence of the saturated capillary fringe occurring above the water table. This tension-saturated zone is thicker in fine-grained soils (Lambe and Whittman 1969) and effectively limits the diffusive influx of atmospheric O₂.

Processes controlling phosphorus movement in the vadose zone are generally fundamentally different from those in the groundwater zone. The vadose zone below a septic system infiltration bed is a geochemically dynamic environment where a host of oxidation and biodegradation reactions occur, many of which directly or indirectly effect P. Most of these reactions are largely completed by the time the effluent reaches the water table, with the result that the geochemistry of groundwater zone plume then evolves more slowly and less dramatically. Consequently, understanding vadose zone processes is the key to determining the ultimate fate of phosphorus from septic systems. The following section highlights several of these important processes.

TERMINOLOGY

Drain field: Also called leachfield, tile bed, infiltration bed, dispersal field, or disposal field, the drain field is a series of covered trenches or beds used for subsurface septic tank effluent dispersal. Trenches are usually shallow, level excavations, containing a perforated distribution pipe usually under- and overlain by media, typically rock. Bed systems consist of an excavated area with perforated distribution pipes 1 to 2 m apart. Wastewater effluent is discharged through the trench or bed surfaces, from which it infiltrates into the underlying soil.

Ground water: Also called the saturated zone, ground water is defined by the presence of soil pores that are saturated with water. The water table does not mark the upper limit of the saturated zone, however, as it is always overlain by a tension-saturated capillary fringe of variable thickness. The water table is the point of total water saturation at atmospheric pressure.

Infiltration zone: This is the zone directly below, or adjacent to, the dispersal system. For example, in leachfield trenches, the infiltrative surfaces are the bottom and the sidewalls of the trench. The infiltration zone is usually associated with a biomat that is a very biologically active zone in which BOD oxidization and nitrification occur.

Phosphorus rapid attenuation zone: Zone, immediately underlying the infiltration zone, in which phosphorus accumulates as secondary minerals.

Vadose zone: Also called the unsaturated zone, the vadose zone is the zone immediately below the land surface (and wastewater dispersal system) and above the water table where the pores contain both water and air, but are not totally saturated with water. In the context of soil absorption systems, the vadose zone is also known as the percolation zone. The vadose zone includes the capillary fringe and allows oxygen transport to the infiltration zone

Wastewater soil absorption system: Includes the drain field, the infiltrative surfaces of the drain field, and the soil around and beneath (percolation zone) the drain field.

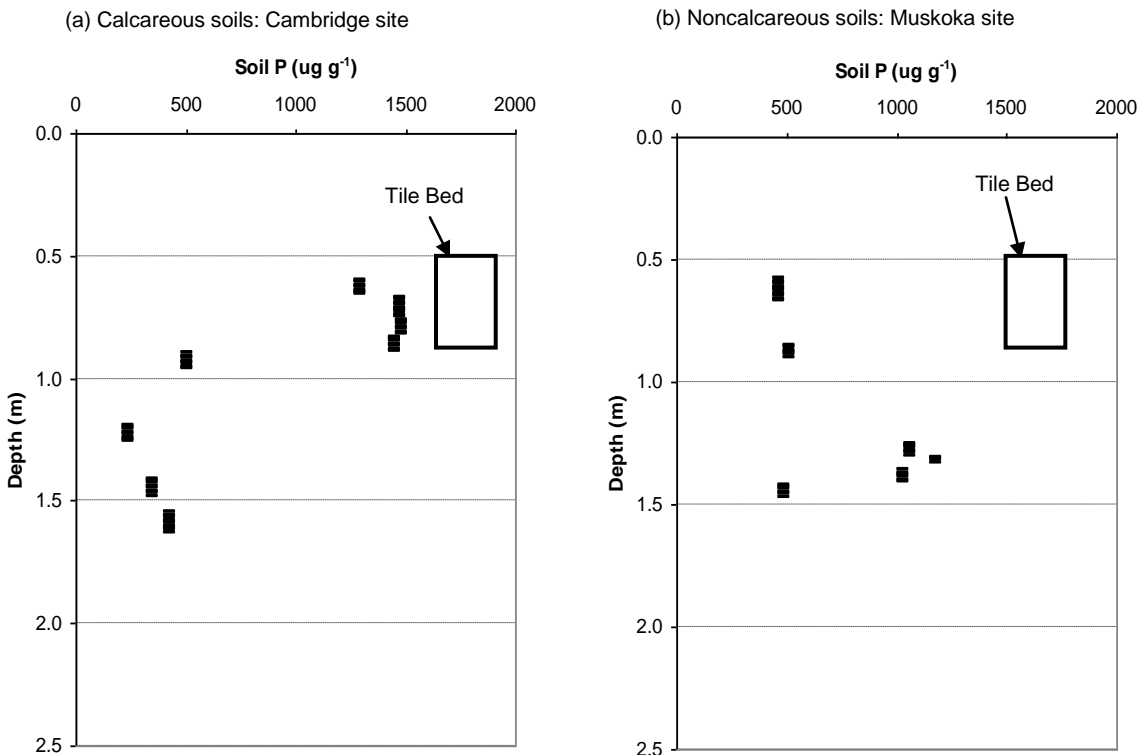
For more information: Crites and Tchobanoglous (1998); EPA (2002).

B. Dominant removal mechanisms

A review of the literature suggests that phosphorus accumulation in the area immediately underlying the infiltration zone appears to be common (Reneau and Petty 1976; Lund *et al.* 1976; Beek *et al.* 1977; Whelan 1988; Wood 1993; Walter *et al.* 1996, Zanini *et al.* 1998). For example, Zanini *et al.* (1998) found the soil at four septic systems was enriched in phosphorus by a factor of 2 to 4 within 1 m of the dispersal system (Figure V-2), while Whelan (1988) measured phosphorus-enriched soil within 20 cm of infiltration pipes at two 10-year old systems.

Figure V-2: Soil phosphorus measured in a calcareous site (a) and a noncalcareous site (b).

Note the zones of enrichment at approximately 0.75 m (a) and 1.4 m (b) below the soil surface.



Source: Zanini *et al.* 1998

The common occurrence of phosphorus attenuation and accumulation in the soils close to the septic system infiltration pipes has led to the description of this environment as the “Phosphorus Rapid Transformation Zone” (Robertson and Harman, 1999) (The transformation is an attenuation of the phosphorus within this zone and is described as such from this point forward). This zone coincides with the biogeochemically active horizon that underlies the infiltration pipes (e.g., the biomat or infiltration zone). Here a variety of reactions occur that can significantly affect phosphate behavior. These reactions are the consequence of organic-rich septic tank effluent oxidizing upon

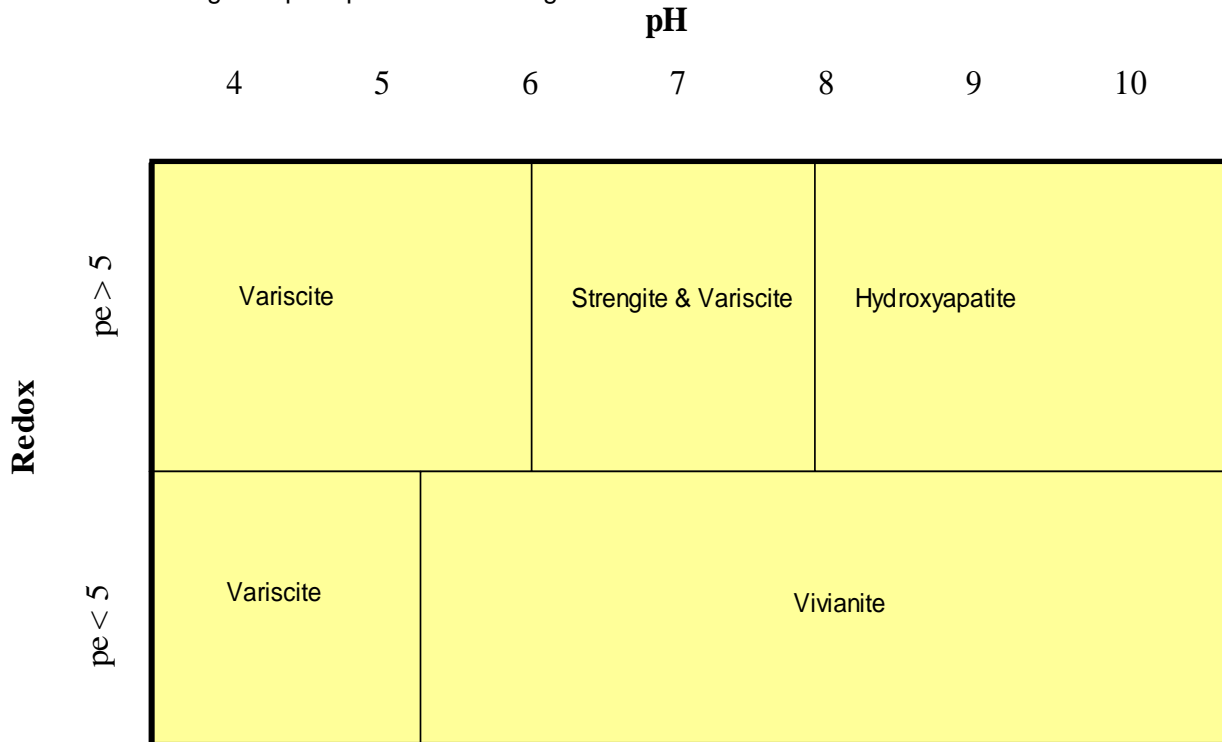
contact with the soil and include reductive dissolution of ferric oxyhydroxide minerals, oxidation of sewage NH_4 , acidity generation, gibbsite dissolution, calcite dissolution, ferrous iron oxidation and others (Wilhelm *et al.* 1994; Zanini *et al.* 1998; Ptacek *et al.* 1994). Carbon oxidation and the associated reduction reactions usually occur within the first few tens of cm of the infiltration zone, although reduced compounds can subsequently travel to the groundwater (Ptacek 1998, Robertson *et al.* 2003). Specifically, if the percolation zone is large, then the wastewater effluent, while it is migrating to the groundwater zone is initially reduced, then will be subsequently oxidized. If the percolation zone is small, reducing conditions can be maintained all the way to the water table (Ptacek *et al.* 1994).

Electron microscope imaging and electron microprobe analyses suggest that the phosphorus that accumulates in the soil near the infiltration pipes often consists of secondary solids with formula consistent with the minerals strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) (Zanini *et al.* 1998). Robertson *et al.* (1998) suggest that precipitation of phosphorus is an important sink in the soil absorption system and in the long term is more important than fast, reversible adsorption reactions. Because the zones of phosphorus enrichment are restricted to the areas close to infiltration pipes (<1m), these reactions must be completed relatively quickly after the effluent enters the subsurface (less than a few days), hence the term “rapid attenuation zone”. Indeed, if adsorption was the dominant attenuation process, one would expect to observe a decrease in phosphorus removal over time in soil absorption systems, as sorption sites are used up. This was not the case during long-term monitoring at two mature septic systems, one in calcareous soil and one in noncalcareous soil, where phosphate concentrations arriving at the water table below the center of the bed remained attenuated by consistent amounts during monitoring that continued for over a decade (Robertson 2003).

Given that precipitation reactions, rather than adsorption reactions, appear to dominate phosphorus removal in the vadose zone, knowing which mineral phase controls phosphate solubility under different environmental conditions should allow prediction of equilibrium phosphate concentrations in the soil porewater, and, therefore, phosphorus removal in the soil. As illustrated in Figures III-1 and III-2, the mineral phases controlling phosphate solubility depend both on pH and p_e . It is quite likely that these also play a role in phosphorus removal in the rapid attenuation zone, although information for these is generally limited. These general trends in mineral phases that could be controlling phosphate concentrations under specific conditions are summarized in Figure V-3. It should be noted that adsorption reactions still play an important, although less dominant, role in phosphorus retention in the vadose zone.

Figure V-3: Examples of mineral phases that may control phosphate solubility for different pH and pe conditions.

pe is the negative logarithm of electron activity, which is a theoretical representation of oxidation / reduction potential. A positive pe represents oxidizing conditions, and a negative pe represents reducing conditions.



C. Typical removal percentages

On mass basis, the vadose zone appears to retain a variable amount of phosphorus from the septic tank effluent. In a review of 10 mature septic system plumes in Ontario, Robertson *et al.* (1998) observed that phosphorus mass removal in the vadose zone was often substantial but variable, ranging from 23-99% depending on site conditions. The site conditions that influence phosphate retention in the vadose zone are discussed in Section V(D) below. Obviously, not all phosphorus is removed, and some does migrate to the groundwater. Predicting how much phosphorus is removed is complicated because soil conditions are heterogeneous and non-equilibrium processes may be present (Harris 2002).

It has been observed that resting a soil absorption system (that is, suspending septic tank effluent loading) for several months can lead to regeneration of some of the phosphate removal capacity in the vadose zone (Gold and Sims 2000). The reason for this is uncertain, but could be related to removal of phosphorus from the surface sorption sites by processes such as intraparticle diffusion or by the generation of fresh sorption sites, for example by the ongoing precipitation of secondary minerals such as ferrihydrite (Fe(OH)₃).

Because precipitation appears to be the dominant removal mechanism in the vadose zone of soil adsorption systems, the possibility of clogging the vadose zone pores with phosphate minerals needs to be considered. However, a simple calculation suggests that this may only be a problem when considering extremely long time frames. Assuming a hydraulic loading of 20.5 l/d/m^2 and 90% removal of the 5 mg/l phosphate in septic tank effluent via variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) precipitation:

- The mass of variscite retained in the vadose zone is $0.137 \text{ g/m}^2/\text{d}$
- The volume of variscite retained in the vadose zone (assuming $\rho = 2.5 \text{ g/cm}^3$) is $3.4 \times 10^{-4} \text{ l/m}^2/\text{d}$
- The total void volume (assuming 25% voids and a depth of 0.5 m) is 12 l/m^2

Thus, it would take 97 years ($= 12 \text{ l/m}^2 / 3.4 \times 10^{-4} \text{ l/m}^2/\text{d}$) for the precipitated variscite to produce enough volume equivalent to clog the pore space of the vadose zone. It is important to note that the effective volume of the pore space can be less due to preferential flow.

D. Factors that influence phosphorus removal

The factors that influence phosphorus removal in soil absorption systems are those that influence the pH and pe of the vadose zone and the availability of Fe and Al. The most important of these are soil characteristics, wastewater characteristics, and site characteristics.

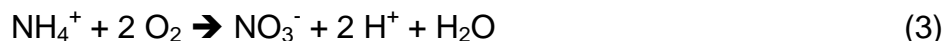
1. Soil characteristics

With respect to phosphorus attenuation in soil absorption systems, the most important soil characteristics to consider are the concentrations of calcium carbonate and ferric (oxy)hydroxide minerals and the grain size characteristics.

Calcareous soils are characterized by the presence of calcium carbonate in the parent material and by a calcic horizon, a layer of secondary accumulation of carbonates (usually Ca or Mg) in excess of 15% calcium carbonate equivalent and at least 5% more carbonate than an underlying layer (EPA 2003). For the purposes of this document however, we have arbitrarily chosen to define calcareous sediments as those which contain sufficient carbonate mineral content to buffer acidic groundwater to near neutral values within a time frame of a few days to a few weeks. Normally sediments with $>1 \text{ wt}\%$ CaCO_3 equivalent content would possess this characteristic and are herein referred to as “calcareous”. Calcareous sediments are normally derived from parent bedrock material containing limestone or dolomite, which includes sediments derived from most of the sedimentary basins in the US (e.g. Michigan Basin). Noncalcareous sediments are normally derived from igneous and metamorphic parent bedrock material and include areas such as much of New England, the Appalachian Mountains, northern Minnesota and Wisconsin, and many local areas in the Western states. Note that sediments that are calcareous may have noncalcareous soil zones, however, due to

carbonate leaching that has occurred due to weathering. Carbonate-leached soil zones can be several meters in thickness (Reardon et al. 1980; Harman et al. 1966), depending on factors such as sediment age, precipitation rates and original carbonate content. The least effective removal of phosphate in the rapid attenuation zone appears to occur in calcareous soils because the acidity generated by the oxidation reactions is rapidly buffered and neutral pH conditions are maintained, which Figure III-1 and Table VI-1 suggest is the least effective environment for precipitating phosphorus minerals. Significant phosphate removal may still occur in calcareous soils however (20-50%), but in this case the process appears to be related to the conversion of Fe^{2+} to Fe^{3+} at the redoxcline, which is the oxic/anoxic transition zone, and the subsequent precipitation of the sparingly soluble Fe-P minerals, such as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$). Scanning electron microscopy shows that Fe is the dominant cation present in association with phosphorus minerals in calcareous soils (Zanini et al. 1998).

Noncalcareous soils are poorly buffered soils that contain less calcium carbonate than their calcareous counterparts and generally are less than 1% by weight CaCO_3 equivalent. Oxidation of septic tank effluent in noncalcareous soils leads to lowering of pH during microbial processes such as oxidation of organic matter and nitrification, described as:



Lower pH, in turn, lead to leaching of Fe^{3+} and Al^{3+} , which become available to precipitate with phosphate as the minerals strengite and variscite, respectively (Zanini et al. 1998). The most complete removal of phosphorus in the rapid attenuation zone (up to 99%) occurs in noncalcareous soils. Low pH enhances PO_4 sorption and can promote the precipitation of the Al-P mineral, variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$). At pH values < 5.5, the precipitation of variscite has the potential to maintain PO_4 concentrations at very low levels (<0.1 mg/l, Robertson 2003). Results of scanning electron microscopy suggest that Al minerals are the dominant phosphate minerals in noncalcareous soils (Robertson 2003). Note, however, that acidity generation in noncalcareous soils depends on both the soil characteristics and the wastewater characteristics. Specifically, lowering of the pH will occur only if complete nitrification of septic tank effluent occurs and the wastewater has low alkalinity and the subsoils are noncalcareous. Lowering of pH does not always occur because septic tank effluent usually has high alkalinity and neutral pH (Robertson 2003).

Fine-grained soils allow more wide-spread development of reducing conditions and have more surface area, leading to increased adsorption and increased reductive dissolution of ferric (oxy)hydroxide solids that leads to increasing Fe(II) concentrations (Zanini et al. 1998). Conversely, coarse-grained soils maintain oxidizing conditions.

The ability of soils to immobilize phosphate, based on observed chemical composition but not on actual mineralogy, is summarized in Table V-1 (Zanini et al. 1998). The lowest phosphate concentrations are generally observed in fine-grained, noncalcareous soils in which the pH is <6 (Robertson 1998).

Table V-1: Hierarchy of soil types and their ability to retain phosphorus

Ability to Retain Phosphate	Soil Type	Dominant Phosphate Minerals
Most ↓ Least	Fine-grained, noncalcareous	Variscite, vivianite
	Coarse-grained, noncalcareous	Variscite
	Fine-grained, calcareous	Strengite
	Coarse-grained, calcareous	Strengite (minor)

2. Wastewater characteristics

The concentration of NH_4^+ and alkalinity are the predominant wastewater characteristics that influence phosphate removal in soil absorption systems. Higher concentrations of NH_4^+ will cause more nitrification in the vadose zone, and therefore a greater possibility for lowering of the vadose zone pH. Whether or not nitrification of the septic tank effluent does, in fact, lead to acidity generation depends on the alkalinity of the wastewater. Lower septic tank effluent alkalinity, combined with high NH_4^+ concentrations, will allow more acidity generation in vadose zone and therefore lead to better phosphorus removal (Robertson 2003). Graywater is an extreme case, with high alkalinity and low NH_4^+ . Graywater thus has a very low potential to generate acidity, and therefore to improve phosphorus removal, in the vadose zone. The typical concentrations of NH_4^+ and alkalinity in septic tank effluent are presented in Table V-2 below.

Table V-2: NH_4^+ and Alkalinity Concentration for Typical Septic Tank Effluent

Compound	Typical Concentration
NH_4^+ -N	30-60 mg/l
Alkalinity*	200 mg/l

* Determined largely by water supply quality

At locations where sewage oxidation reactions are incomplete, neutral pH conditions will normally be maintained and NH_4^+ and reduced iron will persist in the plume. Under these conditions the potential for phosphate removal in the rapid attenuation zone is probably diminished.

3. Site characteristics

A number of characteristics specific to the soil absorption system will influence phosphorus removal in the vadose zone. High hydraulic loading rates, from cluster systems or from high density systems, could lead to more reducing conditions in the vadose zone and thus diminished phosphorus removal.

Some conditions give rise to rapid transport of phosphorus to surface waters without sufficient attenuation in the vadose zone. Due to the slow kinetics of P-mineral

precipitation processes, very rapid flow rates can be particularly problematic. On the one hand, soil absorption systems placed too close to surface waters will not allow sufficient transport time for phosphorus attenuation. On the other hand, the soil absorption system may be sufficiently set back from surface waters, but certain site conditions may give rise to rapid lateral movement of water. For example, saturated flow – from high hydraulic loading rates – can lead to preferential flow paths. Thus, if infiltration of septic tank effluent exceeds its vertical transport across the percolation zone then the pore water content will increase and eventually will start to drain horizontally (Gachter *et al.* 1998). In addition, a high water table can enhance rapid lateral movement of water, as can an impermeable soil horizon. The presence of macropores (*i.e.*, fractures, root channels, animal burrows, etc.) can lead to preferential flow paths for water even under unsaturated flow conditions (Gachter *et al.* 1998).

E. Phosphorus Removal Zones

1. Septic System Phosphorus in the Unsaturated Zone

The common occurrence of phosphorus attenuation in the soils close to septic system infiltration pipes has led to the description of this environment as the “Phosphorus Rapid Transformation Zone” (Robertson and Harman, 1999). This zone coincides with the biogeochemically active horizon that underlies the infiltration pipes. Here a variety of reactions occur that can significantly affect PO_4 behavior including; reductive dissolution of ferric oxyhydroxide minerals, oxidation of sewage organic carbon and NH_4 , acidity generation, gibbsite dissolution, calcite dissolution, ferrous iron oxidation and others (Whilhelm *et al.* 1994; Zanini *et al.* 1998). In a review of 10 mature septic system plumes in Ontario, Robertson *et al.* (1998) observed that phosphorus mass removal in the rapid attenuation zone was often substantial but variable, ranging from 23-99% depending on site conditions. Electron imaging and other evidence suggested that PO_4 was precipitating as secondary phases with stoichiometry consistent with the minerals strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), resulting in localized zones of phosphorus enrichment in the soils. Because the zones of phosphorus enrichment were restricted to the areas close to the infiltration pipes (<1m), these reactions must be completed relatively quickly after the effluent enters the subsurface (less than a few days), hence the term “rapid transformation zone”. The zone underlying the rapid attenuation zone is characterized by porewater and groundwater with distinctly lower PO_4 concentrations (23-99%) compared to the septic tank effluent values (Pounds *et al.* 1978; Enfield *et al.* 1981; Robertson, 1995; Robertson *et al.* 1998) and an absence of further obvious accumulation of phosphorus in the soils. Thus the mineral precipitation reactions that appear to contribute to this process are kinetically fast reactions. Review of the literature suggests that phosphorus accumulation in the localized area immediately underlying the infiltration pipes appears to be widespread (Reneau and Petty, 1976; Lund *et al.* 1976; Beek *et al.* 1977; Whelan, 1988; Wood, 1993; Walter *et al.* 1996).

This evidence suggests that mineral precipitation reactions likely play an important role in attenuating sewage phosphorus concentrations, but these reactions are focused in the soils close to the infiltration pipes and appear to be of lesser importance once the porewater enters the groundwater zone.

2. Septic System Phosphorus in the Groundwater Zone

In most silt and clay rich soils, groundwater velocities are slow enough (<10 m/yr) and phosphate retardation factors are high enough (>30) that phosphate migration (<0.3 m/yr) is not normally of concern. The Killarney site case history, described herein, presents such an example, where PO₄ from a seasonal use cottage septic system has migrated < 1 m in silty fine sand during 17 years of operation. PO₄ migration from septic systems is normally only a concern in permeable sand and gravel soils where relatively high groundwater velocities are present (20-300 m/yr). At these sites, PO₄ migration on the order of 1 m/yr may occur. A number of plume studies have been documented with high concentrations of PO₄ (>1 mg/LP) extending more than 10 m from the tile beds. The Cambridge, Langton and Point Pelee case histories provide such examples. However, not all septic system plumes on permeable sands exhibit significant PO₄ migration. The Muskoka case history provides an example of a septic system on permeable sand where there has been no migration of detectable phosphate away from the tile bed area, during 13 years of operation. Unlike the previous three sites, which are on calcareous sands and have neutral pH plumes, the Muskoka plume is acidic (pH 4.5) because of an absence of buffering capacity in the sand and PO₄ is highly attenuated as a result of mineral precipitation reactions involving Al. Thus, noncalcareous sands (< 1 wt % CaCO₃ equiv.) can be much less vulnerable to phosphorus migration than are similar calcareous sands. Noncalcareous soils are present in a number of regions of the U.S. that are underlain by granitic bedrock, including most of New England, the central Appalachians, Minnesota and various areas in the western states. Noncalcareous terrain is often characterized by headwater streams with low dissolved mineral contents (TDS <100 mg/L, EC <200 uS). The final case history however (Ashumet Valley plume), provides an example of an onsite treatment system located on noncalcareous sand, but where large scale phosphorus plume migration has occurred (600 m). At this site significantly acidic conditions did not develop because of incomplete oxidation of the sewage effluent, thus phosphorus attenuation was incomplete and migration ensued.

Finally, although most soils have a relatively large capacity for natural attenuation of phosphate, the potential for attenuation is probably much less during flow through fractures in bedrock. Thus, septic systems located on thin soils, as often occur in association with lakeside dwellings, are probably most at risk of phosphate contamination. However, we are aware of no field studies that adequately assess the nature of phosphorus migration in thin soil environments, where fracture flow and surface breakout problems are likely to be important transport processes. Certainly septic systems in such environments should be an important focus of future research activity, even though installation of adequate monitoring capability will undoubtedly be an onerous task.

a) Sorption

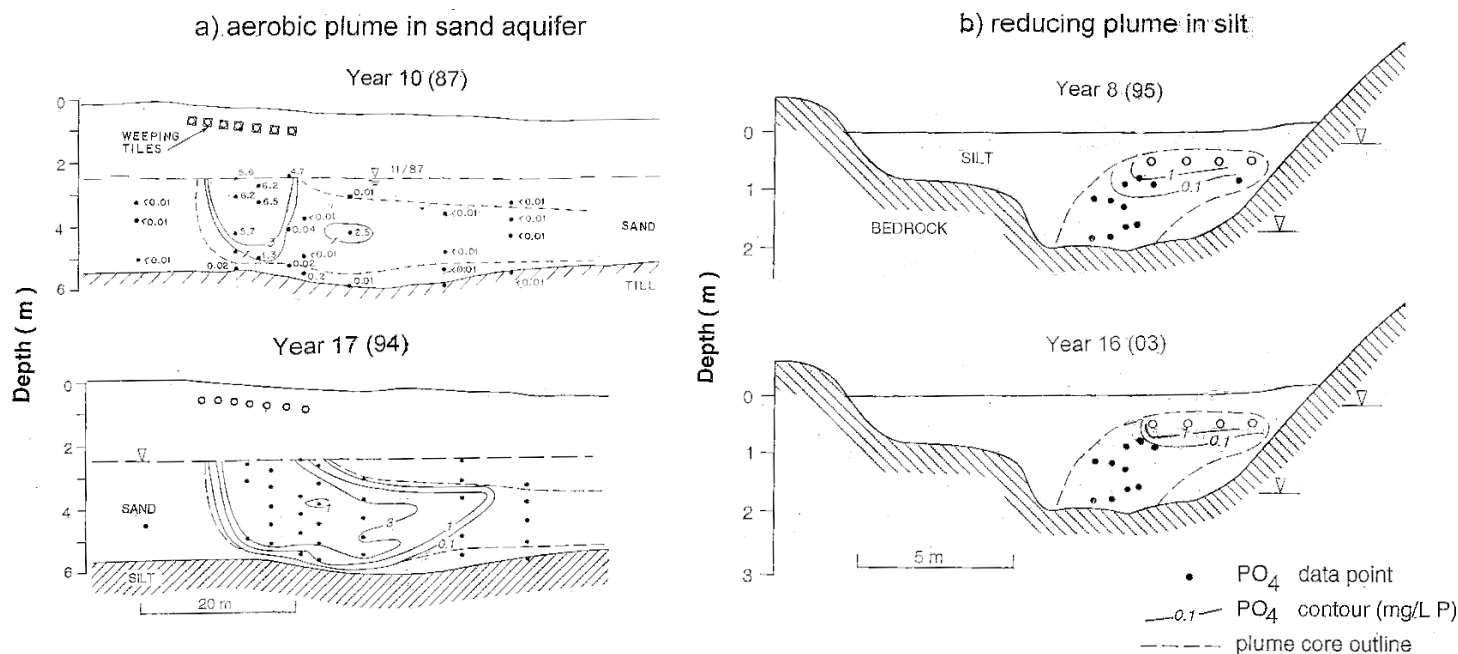
Although phosphorus mineral precipitation reactions appear to be less active once the groundwater zone is encountered, PO_4 often occurs as anionic species (HPO_4^{2-} , H_2PO_4^-) that are highly affected by surface sorption processes. When these processes are fast and reversible they result in retardation of the PO_4 migration velocity, but they do not necessarily diminish concentration levels that are present in the groundwater.

However, most laboratory studies have indicated that phosphate sorption is non-linear (varies with phosphorus concentration and pH) and in some cases is not easily reversible (Goldberg and Sposito, 1985; Barrow, 1991; Torrent *et al.* 1992; Froussard *et al.* 1995). Non-reversible sorption processes have the potential to further attenuate PO_4 concentrations in the groundwater zone, but field evidence in support of this remains uncertain. As a result of sorption processes, PO_4 migration velocity is almost always much slower than that of other mobile plume constituents such as Cl. In their review of 10 mature septic system plumes, Robertson *et al.* 1998 observed PO_4 zones ranging in length from <2m (sites on silts and noncalcareous sands) to 70m (sites on calcareous sands) and inferred from this, PO_4 retardation factors (ratio of groundwater velocity to solute velocity) ranging from 20-100, based on the periods of usage and the measured groundwater velocities. These represented a variety of sand and silt soils and a variety of wastewater sources. The largest reported PO_4 zone in a sewage plume is that of the Ashumet Valley plume originating from the Otis Military Reserve on Cape Cod. Here a P-rich plume zone with $\text{PO}_4\text{-P}$ concentrations of 0.3-3 mg/L, extends 600m downgradient where it subsequently discharges to a small lake (McCobb *et al.* 2003). The groundwater velocity at the site (~130 m/yr) and the period of sewage loading (55 years, 1940-95) implies a retardation factor of ~15 or less for PO_4 migration in the coarse sand aquifer at the site. The precise value cannot be determined because the exact time of arrival of the phosphorus plume at the discharge point is unknown. Laboratory column tests utilizing soil cores from the plume zone suggest a phosphorus retardation factor of about 10 (Walters *et al.* 1995). The magnitude of adsorption is related to the presence of minerals that have a net positive surface charge at normal pH values, including most metal hydroxide species such as ferrihydrite, $\text{Fe}(\text{OH})_3$ and gibbsite $\text{Al}(\text{OH})_3$. Researchers have used the measured content of these hydroxide species, particularly $\text{Fe}(\text{OH})_3$ to predict soil propensity for PO_4 sorption (e.g. Parkhurst *et al.* 2003).

Figure V-4 shows PO_4 plume development during 7-8 years of monitoring at two sites in Ontario, one an aerobic plume on a sand aquifer (Cambridge, R~20) and the second an anaerobic plume on silt (Killarney; Figure V-4; R~100). The higher retardation value for the silt site (R~100) is likely related to higher $\text{Fe}(\text{OH})_3$ content in the finer grained silt soils there, although direct measurements were not made. The Cambridge site shows measurable PO_4 migration, as expected, based on the retardation equation (phosphorus velocity ~ 1 m/yr), however at the Killarney site, the higher retardation

factor (~100) and slower ground water velocity (~1 m/yr) leads to a phosphorus migration velocity (< 0.02 cm/yr) that is too small to measure at that site.

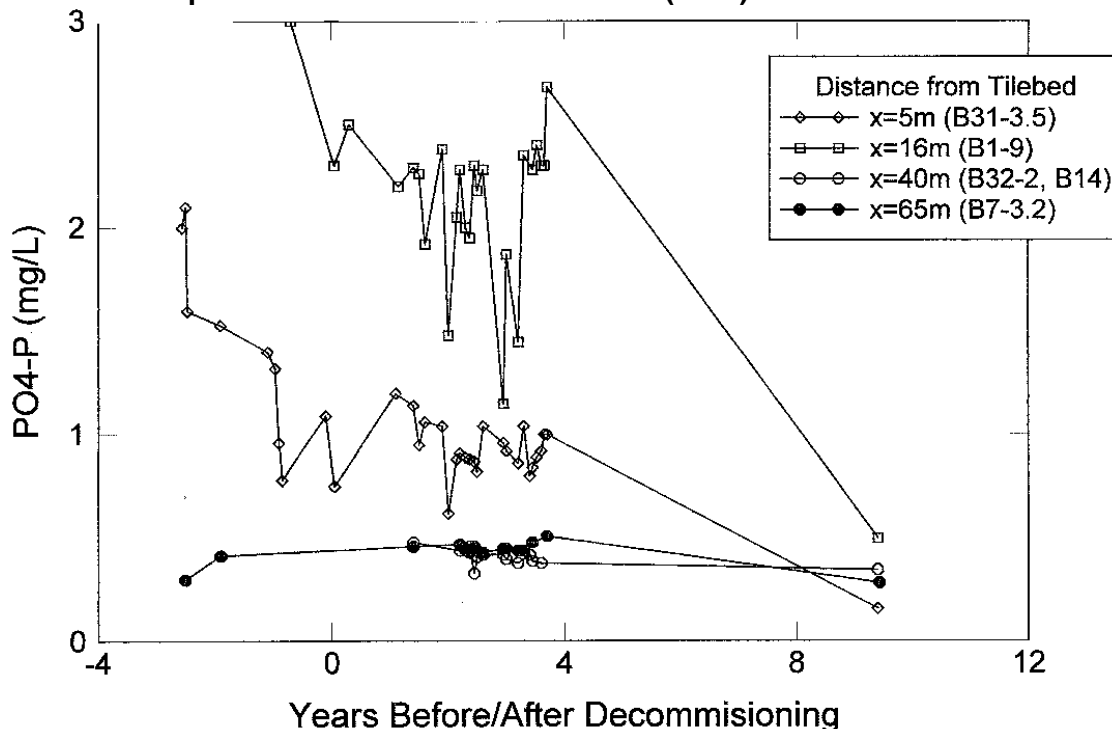
Figure V-4: PO₄ migration in, a) a septic system plume in an aerobic, calcareous sand aquifer (Cambridge site, house, phosphorus retardation factor (R) =20) and b) in a reducing plume on silt-rich soils (Killarney site, seasonal use cottage, R= 100). Adapted from Robertson *et al.* (1998).



Some researchers have noted that PO₄ breakthrough in laboratory column tests often persists at levels lower than that expected based on fast, reversible sorption. To explain the variance, they have inferred the presence of a second irreversible or kinetically slow 'sorption' step to account for this behavior (Chen *et al.* 1973; Martin *et al.* 1988; Davis and Kent, 1990; Isenbeck-Schroter *et al.* 1993). Processes such as intra-particle diffusion, slow surface recrystallization, or rate-limited direct mineral precipitation reactions have been suggested to account for this behavior. Examples of this could be the kinetically slow precipitation of hydroxyapatite. Septic system plume water is often found to be supersaturated with respect to hydroxyapatite in calcareous terrain, or vivianite in Fe-rich reducing plumes (Robertson *et al.* 1998). The importance of these slower secondary processes is that they may be less readily reversible and in some cases may constitute a consumption mechanism that can permanently immobilize P. One way to gain insight into the occurrence of secondary rate-limited attenuation processes is to observe the behavior of phosphorus plumes at sites where septic systems have been decommissioned. If secondary processes are active, phosphorus concentrations should slowly decline after the sewage source has been removed. Robertson and Harman (1999) observed phosphorus behavior for a four year period after decommissioning of a public school septic system on a calcareous sand aquifer in Ontario and observed that phosphorus concentrations in groundwater (0.3-2.0 mg/L)

remained remarkably invariant even though all other plume constituents returned to background values within one year of decommissioning. It was inferred that the 70m long phosphorus plume at the site was migrating at a velocity of 1.6 m/yr, based on the 44 year period of use. This represented a retardation factor of ~60 compared to the groundwater velocity of 100 m/yr. Further sampling of the plume in 2003, nine years after decommissioning (Figure V-5) showed that phosphorus concentrations at the proximal monitoring locations, 5 and 16m respectively from the center of the tiled bed, showed 50-80% declines in phosphorus concentrations, whereas monitoring points located farther downgradient (40 and 62m) showed virtually no change from the in use period. Declining phosphorus concentrations at the upgradient locations were consistent with the previously indicated phosphorus plume migration velocity (1.6 m/yr) which suggests that the upgradient plume boundary should have migrated ~15 m during the 9 years after decommissioning. Overall, this behavior argues against the occurrence of any slow secondary attenuation reactions. This was observed even though the phosphorus plume zone remained supersaturated (SI +0.3 to +1.9) with respect to crystalline hydroxyapatite in the decommissioned period (Robertson and Harman 1998).

Figure V-5: PO₄ persistence after decommissioning of a septic system on a calcareous sand aquifer (Langton public school, groundwater velocity 100 m/yr). Adapted from Robertson and Harman (1999).



b) Anaerobic Plumes

In reducing plumes where significant concentrations of redox sensitive cations such as Fe may be present, PO₄ behavior could be much different upon decommissioning. If the plume zone is subsequently invaded with aerobic groundwater, Fe²⁺ will be oxidized

to Fe^{3+} , promoting the precipitation of Fe hydroxide minerals (e.g., ferrihydrite, $\text{Fe}(\text{OH})_3$) which enhance PO_4 sorption, or PO_4 will precipitate directly as sparingly soluble Fe-P minerals such as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$).

Phosphate behavior in the suboxic, Ashumet Valley plume has been studied extensively by the USGS since decommissioning of the sewage source in 1995 (Walter *et al.* 1996; McCobb *et al.* 2003; Parkhurst *et al.* 2003). The plume has several redox zones, including a proximal core that is devoid of DO, has nitrogen predominantly as NH_4 and has elevated Fe (up to 14 mg/L) resulting from reductive dissolution of ferric hydroxide minerals present in the aquifer promoted by sewage organic carbon load. Farther downgradient, the plume has a suboxic zone in which NH_4 is slowly converted to NO_3 and Fe concentrations decline (<0.1). Walter *et al.* (1996) carried out column tests simulating decommissioning and found that PO_4 concentrations in soils from the proximal anaerobic zone returned to background levels after the passage of five pore volumes of natural groundwater. They concluded that the conversion of Fe^{2+} to Fe^{3+} promoted PO_4 attenuation either by enhanced sorption onto fresh ferric hydroxide mineral surfaces, or by the direct precipitation of Fe-P minerals such as strengite. Parkhurst *et al.* (2003) carried out comprehensive three dimensional reactive transport modeling of the Ashumet Valley phosphorus plume to assist with predicting long term phosphorus loading to the small lake. The model, in addition to surface sorption processes, incorporated equilibrium and rate-limited mineral precipitation/dissolution reactions involving a variety of phosphorus minerals, including variscite, strengite, vivianite, and hydroxyapatite, as well as reactions that affect pH (e.g. organic carbon and NH_4 oxidation) and reactions that affect the concentrations of important cations such as Fe. Sensitivity analyses suggested that reactions involving Fe had the greatest effect on phosphorus concentrations, but that field evidence indicating disequilibrium with important Fe-P minerals such as vivianite and uncertainty in the longevity of ferric hydroxide reductive dissolution reactions, made long term predictions uncertain.

In summary, field evidence suggests that, in aerobic plumes, PO_4 migration in groundwater plumes can be reasonably predicted using the retardation equation, but that in reducing plumes mobility is more difficult to predict because of the strong interaction of PO_4 with redox sensitive cations such as Fe.

3. Septic System Phosphorus in the Riparian Zone

Septic system phosphorus removal in the riparian or hyporheic zone (HZ) is dependent upon groundwater flow paths, as illustrated in Figures V-6 to V-8, to ensure plume contact with the biogeochemically active HZ.

Figure V-6: Riparian Zone – Groundwater Seeps

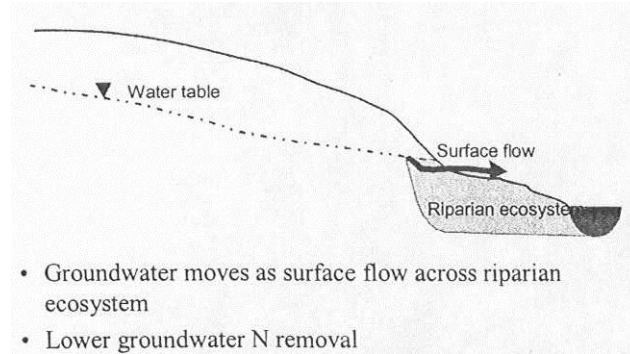


Figure V-7: Riparian Zone – Deep Groundwater Bypass Flow

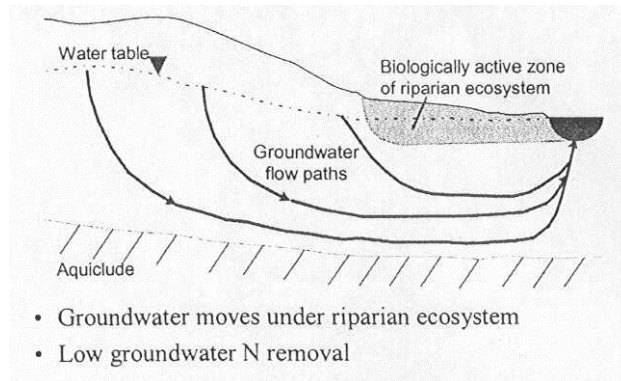
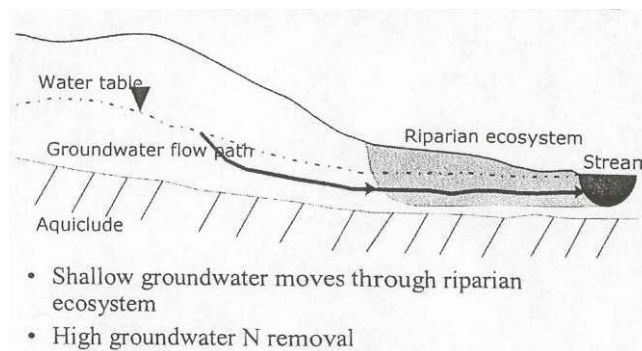


Figure V-8: Riparian Zone – Shallow Subsurface Groundwater Flow



Source: Groffman, P.M. (2003)

Limited research has been performed on septic system phosphorus changes in the riparian zone, in part due to sampling difficulties, (Wood, 1993).

A number of researchers (Moser *et al*, 2003; Correll, 1996) have described the reducing conditions in riparian/hyporheic zones that would entail elevated concentrations of Fe^{2+} as described in the Rapid Attenuation Zone (Section V.E.1.a) and the phosphorus removal mechanisms described therein presumably would occur.

F. Summary

1. Summary of PO₄ Behavior in the Subsurface Environment

- 1) The concentration of PO₄ that occurs in septic system plumes appears to be strongly affected by attenuation reactions that are focused in the “rapid attenuation zone” immediately underlying the tiled infiltration pipes. Migration velocity in the groundwater zone however, appears to be controlled by sorption reactions that are both fast and reversible. In most silt and clay rich soils, because of the relatively slow groundwater velocities present (<10 m/yr) and high PO₄ retardation factors (>30), PO₄ migration, via intergranular flow, will be so slow (<0.3 m/yr) that impact on adjacent water bodies will generally not occur except over extremely long time periods (centuries). In sand aquifers however, where larger groundwater velocities are present, PO₄ migration of up to several meters per year may occur. In these environments impact on nearby surface water bodies can occur over much shorter time frames (decades).
- 2) Phosphorus concentrations in septic tank effluent are remarkably consistent (~8 mg/L average, range 3-20 mg/L) considering the variable nature of wastewater that enters septic tanks. This may indicate that mineral precipitation/dissolution or sorption/desorption reactions actively occur in the septic tank and control phosphorus levels. One possibility is that the ferrous phosphate mineral, vivianite, precipitates in the tank, as it has been noted that septic tank effluent often approaches or exceeds vivianite equilibrium.
- 3) When septic tank effluent is discharged to tilebeds, PO₄ concentrations can be substantially attenuated in the phosphorus “rapid attenuation zone”, the biogeochemically active horizon coinciding with the zone of most intense sewage oxidation. This zone is usually located within several meters of the infiltration pipes and is characterized by accumulation of phosphorus in the soils.
- 4) The most complete removal of phosphorus in the rapid attenuation zone (up to 99%) occurs at locations where the soils are devoid of carbonate minerals such as calcite, in which case low pH conditions, caused by the oxidation of sewage organic carbon and NH₄, can persist in the subsurface environment. Low pH enhances PO₄ sorption and can promote the precipitation of an Al-P phase, potentially variscite (AlPO₄·2H₂O). At pH values < 5.5, the precipitation of variscite has the potential to maintain PO₄ concentrations at very low levels.
- 5) The least effective removal of phosphorus in the rapid attenuation zone appears to occur in soils that are carbonate-rich, in which case the acidity generated by the oxidation reactions is rapidly buffered and neutral pH conditions are maintained. Significant phosphorus removal (20-50%) may

still occur in calcareous soils however, but in this case the process appears to be related to the conversion of Fe^{2+} to Fe^{3+} at the redoxcline and the subsequent precipitation of the sparingly soluble Fe-P mineral strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$).

- 6) At locations where sewage oxidation reactions are incomplete, neutral pH conditions will normally be maintained and ferrous iron will persist in the plume. Under these conditions the potential for phosphorus removal in the rapid attenuation zone is probably lower.
- 7) When a septic system plume reaches the groundwater zone, if aerobic conditions are present, concentrations of PO_4 appear to be consistent; that is, further secondary attenuation reactions do not occur. Migration velocity is strongly retarded, however, likely by sorption reactions that are related to the presence of minerals with positive surface charges (e.g., ferrihydrite) at normal pH ranges. These sorption reactions appear to be both fast and slowly reversible.
- 8) In most sand aquifers PO_4 exhibits a retardation factor in the range of 10-100 whereas retardation in silty soils appears to be higher (>30). Thus, in sand aquifers which generally have groundwater velocities in the range of 10-100 m/yr, PO_4 plume migration velocity will be in the range of 0.1-10 m/yr, whereas in silt soils where groundwater velocities in the range of 1-10 m/yr are common, PO_4 migration velocity will normally range from 0.01-0.3 m/yr. In clay rich soils which normally have groundwater velocities <1 m/yr, PO_4 migration via intergranular flow will normally be <0.03 m/yr.
- 9) In reducing plumes, predicting the mobility and persistence of PO_4 is less certain because of the complexity of reactions involving Fe (e.g. reductive dissolution of ferric hydroxide minerals may cause increasing concentrations of Fe along the flowpath) and the strong interaction of PO_4 and Fe.

G. Impact of Wastewater Pretreatment

With pre-treated wastewater, anaerobic conditions are less likely to occur and therefore iron phosphorus precipitation may be reduced. When pre-treatment includes nitrification, (required for de-nitrification), acidic conditions for aluminum dissolution may be less likely to occur and then mineralization of aluminum-phosphorus compounds (variscite) may be significantly diminished. Thus the potential for further attenuation of PO_4 in the subsurface may be less when secondary treated wastewater is applied, but field studies of pre-treatment are presently lacking and are needed. Also note that pretreated wastewater may have lower initial PO_4 concentration as a result of phosphorus removed by sludge precipitation, filtration, etc.

VI. CASE STUDIES

This section presents case histories of six sites depicting phosphorus behavior in different types of soils and relates this to the geochemistry of the septic tank soil absorption systems presented earlier in this report. Cited references are included. The sites selected represent typical sand and silt characteristics, both calcareous and noncalcareous, acidic and non-acidic conditions. The tables included at the end of this section present a summary of the phosphorus removal process (Table VI-1) and summarize the phosphorus behavior at each case history site.

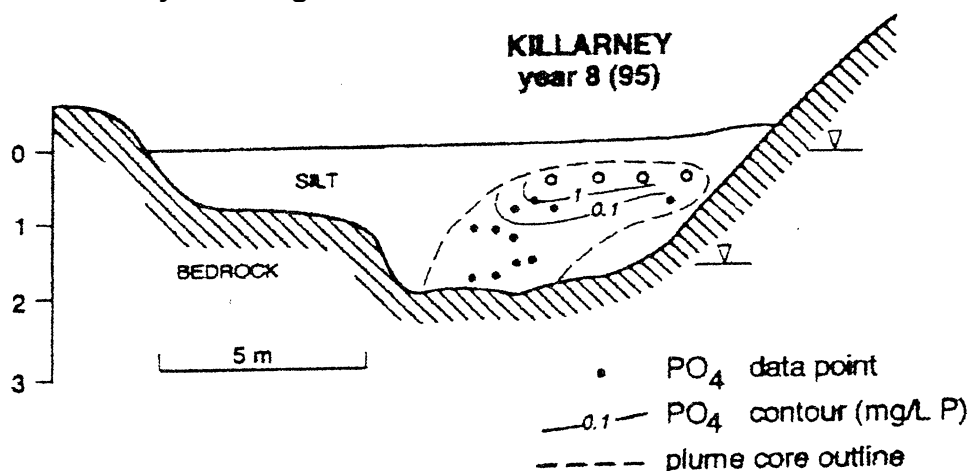
Case History No. 1: Killarney Site (Noncalcareous Silt)

The Killarney site is located 50 km south of Sudbury, Ontario, Canada. The overburden material consists of distinctly varied clayey to sandy lacustrine silt. The septic system is constructed within an isolated 2 meter thick silt pocket that is surrounded by granitic bedrock outcrop and is located 20 meters from a soft-water lake. Acidic conditions dominate at this site. The lake has low CaCO_3 equivalent alkalinity ($< 1 \text{ mg/l}$) and is acid stressed, $\text{pH} = 5.3$. The area is prone to acidification because of the limited buffering capacity of the granitic and quartzitic terrain and the associated thin silty overburden.

The septic system, installed in 1987, serves a seasonal-use family cottage and is used six months of the year. Wastewater is generated from dishwashing, washbasin, and toilet facilities in the cottage, but no showering and clothes laundering is done. Water usage is 180 l/d during peak use in July and August, and about 50 l/d during the remaining four months. The septic system consists of a 3,000 liter septic tank, and a 47 m^2 infiltration bed. The 4" perforated PVC infiltration pipes were placed at a depth of 0.5 to 1.0 m, and are separated from the bedrock by a 1 m thickness of native lacustrine silt.

The soil characteristics are (soil's gradation by weight): Sand ($>0.053 \text{ mm}$): 5 %; Silt ($0.053\text{-}0.002 \text{ mm}$) 94 %; and Clay ($<0.002 \text{ m}$): 1 %; CaCO_3 : 1.6 wt. %; the water table rises to surface in spring, and falls to near the bedrock surface (2 m depth) during summer. The plume $\text{pH} = 5.5$; Phosphorus Retardation factor is >100 ; $\text{EC} >200 \text{ }\mu\text{mhos/cm}$; and $\text{DOC} = 44 \text{ mg/l}$.

Figure VI-1: Killarney Soil Diagram



The acidic soil conditions, and oxidation of the septic tank effluent constituents, such as, organic carbon and ammonia has resulted in lower pH conditions in this poorly buffered lacustrine silt. P removal of > 99% occurs within 0.5 m of the tiles, possibly as a result of precipitation of the Al-P mineral – variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) or the Fe(III) – P mineral strengite, or as a result of sorption reactions. With pH values less than 5.5, the precipitation of variscite has the potential to maintain PO_4 at very low concentration over a long period. The P plume has migrated <1 m in 17 years (1987-2003), and the P concentration at points >0.5 m from the tiled bed is <0.01 mg/l. This indicates that P has a very high retardation factor (>100) and PO_4 migration is limited at this site. Therefore any impact on the adjacent water body would occur only over an extremely long period (centuries).

References:

- Robertson, W.D., and D.W. Blowes. 1995. Major ion and trace metal geochemistry of acidic septic system plume in silt. *Ground Water*, 33:275-283.
- Robertson, W.D., S.L. Schiff, and C.J. Ptacek. 1998. Review of phosphate mobility and persistence in 10 septic system plumes. *Ground Water*, 36:1000-1010.

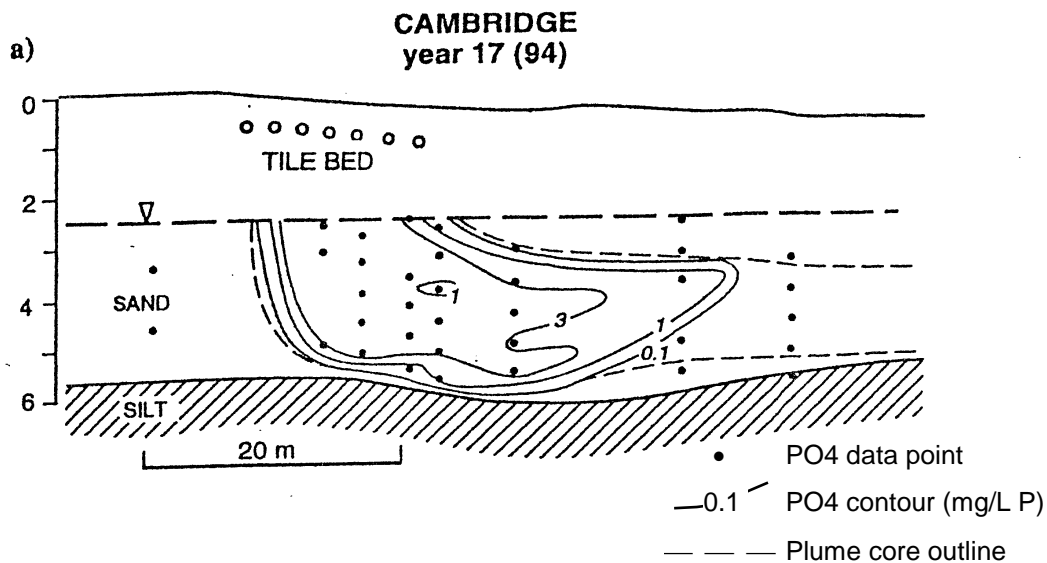
Case History No. 2: Cambridge Site (Calcareous Sand)

The Cambridge Site is located 100 km west of Toronto, Ontario, Canada. The septic system beds have served a four-person household since 1977 and has a gravity fed soil absorption (infiltration) field of 100 m^2 . The flow to the system was metered between March and November of 2000, and averaged $1.3 \text{ m}^3/\text{day}$.

The soil characteristics are (gradation by weight):

Sand (0.06-2mm): 97%; Silt and Clay: 2.8%; Gravel: 0.30%; CaCO_3 : 27%; CEC (Cation Exchange capacity): 5.0 meq/100g; pH: 7.0; Water table at 2.5 m depth.

Figure VI-2: Cambridge Soil Diagram



Septic System Plume: 500 monitoring points were installed to study the plume, enabling a detailed study. 75% of the septic tank $\text{PO}_4\text{-P}$ concentration migrated through the vadose zone and formed a distinct P plume below the tile bed. The aquifer had limited dispersive capacity and dilution for a distance of more than 100 meters downgradient. A bromide tracer was used to determine groundwater velocities within the plume, which indicated that the septic tank effluent resides in the unsaturated zone for about 10 days, and then migrates laterally at a rate of 24 m/yr. In the shallow water table zone, $\text{PO}_4\text{-P}$ advanced much slower, at a rate of 1 m/yr. High concentration of P in the proximal zone plume, 4.8 mg/l (approximately 75 % of the septic tank effluent value) indicates that the calcareous sand with neutral pH (7) has limited capacity to attenuate P in close proximity to the tile bed.

This site is typical of many permeable sands used for on-site sewage disposal. The P retardation factor in the groundwater zone was about 25 at this site, thus migration velocity was modestly slow (4% of plume velocity) plume travel rate. Figure VI-2 shows the P plume zone along the plume core cross-section.

Reference:

Robertson, W.D., S.L. Schiff, and C.J. Ptacek. 1998. "Review of phosphate mobility and persistence in 10 septic system plumes." *Ground Water*, 36:1000-1010.

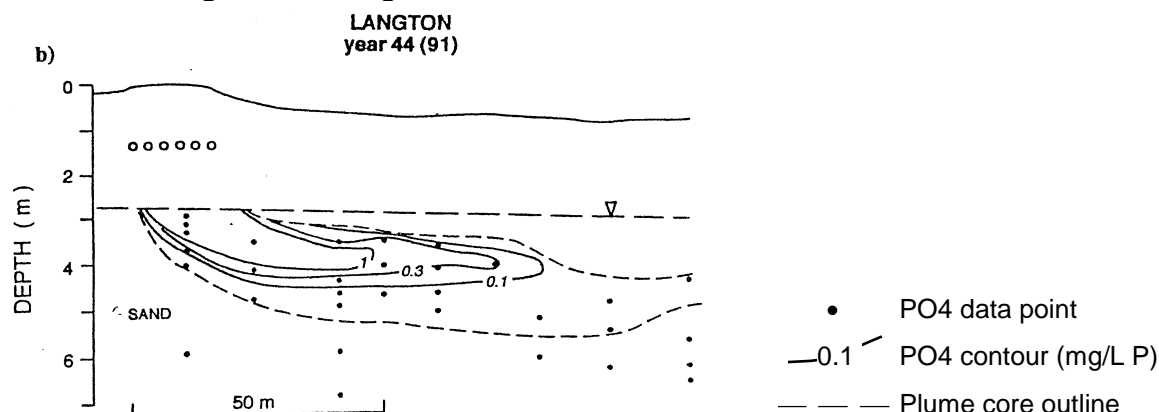
Case History No. 3: Langton Site (Calcareous Sand)

The Langton site is located in the Town of Langton, Ontario, Canada. The site is on a flat-lying deltaic sand deposit that supplies water to the local residents, mostly from shallow wells. The unconfined aquifer consists of homogeneous fine to medium sand to a depth of 8 meters, and is underlain by deposits of sand, silt and clay. The study

highlights the migration of a $\text{PO}_4 - \text{P}$ plume in a calcareous sandy soil, typical of many sites used for disposal of septic tank effluent. The P plume was also studied after the tile bed was decommissioned.

The plume characteristics are: DOC: 0.70; pH: 6.6; Water table: 3.0 m depth.

Figure VI-3: Langton Soil Diagram



The study site is an elementary school with 200 students. The septic system was in operation for 47 years, starting in 1947 and was decommissioned in 1994 when a replacement infiltration bed was constructed. The long-term usage at this site enables one to assess the extent of the long-term capacity of the subsurface to attenuate the sewage derived contaminants. The estimated sewage flow was 30 l/d per student (6,000 l/d total flow). The septic system consists of 325 m² infiltration bed fed by gravity into open joint clay pipes positioned 1.5 m below the surface and 1.6 m above the average water table depth of 3.1 m.

400 monitoring points were installed in the area below the tile bed and for a distance of 110 m, downgradient. Extensive sampling in 1991 mapped the plume in detail. A bromide tracer test indicated that the septic tank effluent resides for one to two weeks in the vadose zone, and then enters the groundwater, traveling at a velocity of about 100 m/yr. The enriched PO_4 zone extends for a distance of 70 m and has $\text{PO}_4\text{-P}$ in the range of 0.3 to 2 mg/l. Beyond 70 m distance, PO_4 levels decline to background values (< 0.05 mg/l P). The P retardation factor (R) is approximately 60 based on the apparent PO_4 migration velocity of 1.5 m/yr compared to a groundwater velocity of 100 m/yr.

The slightly calcareous soil at this site retained 85 % of PO_4 in the 1.6 m thick vadose zone even after 47 years of the infiltration bed use.

In conclusion, the calcium rich sands have moderate sorption capacity, and moderate capacity for precipitating P in the vadose zone. As a result, P migration velocities can be significant (~1 m/yr), which in some cases may lead to a need to protect adjacent surface water bodies.

References:

Harman, J., W.D. Robertson, J.A. Cherry, and L. Zanini. 1996. Impacts on a Sand Aquifer from a Septic System: Nitrate and Phosphate. *Ground Water*. 34:1105-1114.

Robertson, W.D., S.L. Schiff, and C.J. Ptacek. 1998. "Review of phosphate mobility and persistence in 10 septic system plumes." *Ground Water*, 36:1000-1010.

Robertson, W.D. and J. Harman. 1999. Phosphate Plume Persistence at Two Decommissioned Septic System Sites. *Ground Water*, 37: 228-236.

Case History No. 4: Point Pelee – Camp Henry (Calcareous Sand)

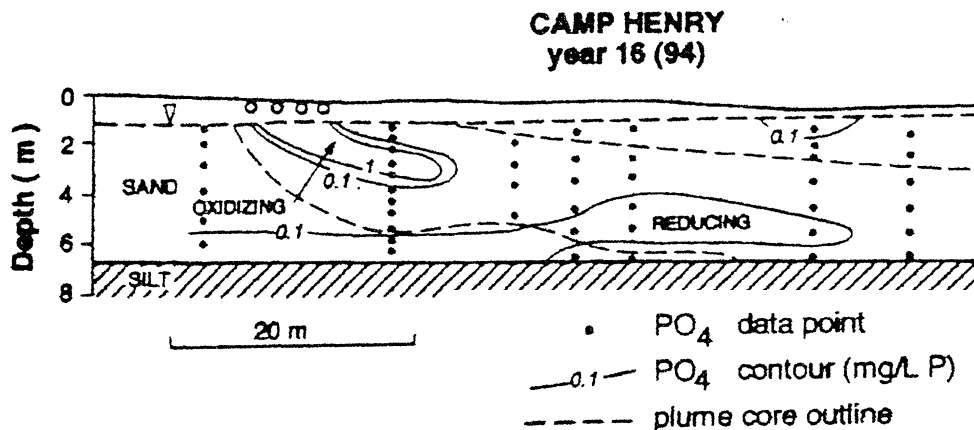
Point Pelee site is located in Point Pelee National Park (PPNP), Ontario, Canada along the north shore of Lake Erie. PPNP encloses the internationally protected Point Pelee marsh. PPNP receives 500,000 visitors and staff annually; wastewater is disposed through 30 separate tile beds. One of these, the Camp Henry site, is presented here.

The soil at the Camp Henry site consists of 7-8 m of poorly sorted sand with occasional pebble layers. The sands consist of 60% quartz, and 25% limestone, including shell fragments, and lesser amounts of microcline, Ca-plagioclase, magnetic, epidote, amphibole, and kyanite. Below the acidified sand aquifer is low permeability clay till.

Wastewater at the site is from seasonal toilets and showers used by a day population of 50 persons, resulting in approximately 2,500 l/d of effluent which is gravity fed to the tile bed. In 1995, after 16 years of use, flow was diverted from the old tile bed to a new raised tile bed.

The aquifer's characteristics are (gradation by weight): 99 % sand with mean grain size of 470 μm and 1% silt + clay. This water table has a seasonal low depth of < 1.5 m; background groundwater pH is neutral (7).

Figure VI-4: Camp Henry Soil Diagram



The observed groundwater plume from the old tile bed was at least 60 m long, 40 m wide, and 7 m thick. Thus, over a 16 year period, the plume has traveled at a velocity of >3.8 m/year. Directly below the tile bed, unsaturated zone, NH₃ and DOC are oxidized and some P is removed. NH₃-N decreased from 90 mg/l to 15 mg/l, and NO₃ increased from 0.05 mg/l to over 80 mg/l. Similarly, DOC decreased from > 30 mg/l in the effluent to a maximum of 13 mg/l in the plume. Concentrations of P in the effluent (12 mg/l) decreased to 1 - 1.5 mg/l at the edge of the tile bed. This attenuation process has increased the solid phase concentration of P from <300 mg/Kg in the background soil to >700 mg/Kg in the attenuation zone. The groundwater chemistry at the site can be divided into discrete redox zones. There is a shallow, 2-3 m thick suboxic zone close to the tile bed with elevated Mn and Fe, and intermediate Eh values (400 mv). At the base of the aquifer, there is 2-3 m thick reducing zone with low Eh values, <200mV.

The P migration conditions that prevail in this permeable sand are of concern because of moderately high groundwater velocities and the proximity of surface water environment. Elevated concentrations of P levels were found in the suboxic zone, close to the tile bed, > 3.0 mg/l, and in the reducing zone P levels were >0.3 mg/l for a distance of 60 m from the tile bed. These P levels are well above levels needed to cause algal blooms when released to surface water bodies. The 30 tile beds at the site are considered sufficient to contribute to the development of local eutrophic conditions in the associated park surface waters.

References:

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- Robertson, W.D., S.L. Schiff, and C.J. Ptacek. 1998. "Review of phosphate mobility and persistence in 10 septic system plumes." *Ground Water*, 36:1000-1010.
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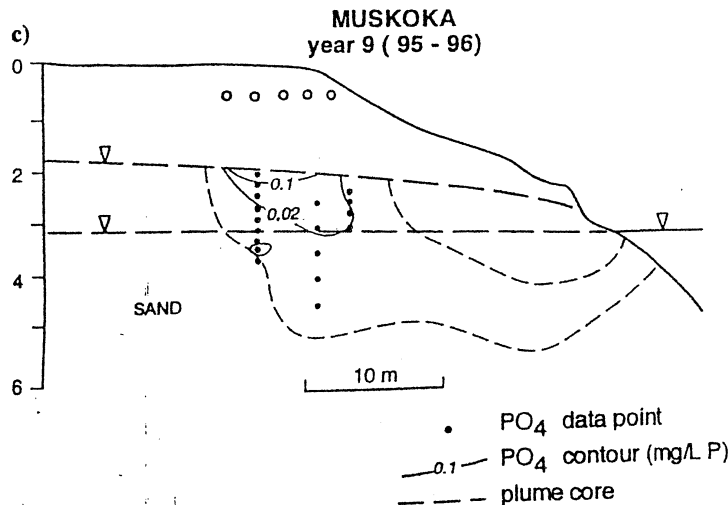
Case History No. 5: Muskoka Site (Noncalcareous sand, acidic)

The Muskoka Site is located on the edge of the Muskoka River near the town of Bracebridge, Ontario, Canada. At this site, fine to medium fluvial sand occurs to a depth of 10 m and overlies granitic bedrock which outcrops within 100 m of the site. The shallow unconfined sand aquifer is noncalcareous sand and background groundwater is acidic (pH ~5.7).

The septic system was installed in 1987 for a two-person household, which generates typical domestic wastewater including laundry and automatic dishwasher effluent. The infiltration bed (80 m²) is gravity fed and is located 20 meters from the edge of the Muskoka River.

The aquifer soil characteristics are (gradation by weight): Sand (0.06-2mm): 87%; Silt: 13 %; Clay (<0.002 mm): 0%; CaCO₃ equivalent content, 0.4 %; CEC: 2.2 meq/100g; the average water table at 3 m; background groundwater has pH: 5.7; DOC: 1.6 mg/l; EC: 75 µmhos/cm.

Figure VI-5: Muskoka Soil Diagram



250 monitoring points were installed. The septic system plume was found to migrate ~20 m to the edge of the river after about one year of operation, thus, the groundwater flow rate is ~20 m/yr. Similar to the Killarney site, DOC and NH₄ are oxidized in the unsaturated zone causing acidic pH values in the plume. pH values of 4.5 to 5.6 occur in the plume core zone. The location of the septic system plume is clearly indicated by the presence of elevated EC values (> 300 µS) but PO₄ levels remained <0.01 mg/l throughout the groundwater plume zone. Phosphate at the site is probably attenuated by precipitation of the sparingly soluble minerals, such as variscite (Al-PO₄•2H₂O) in the vadose zone.

This site presents an example of a permeable sand where P is not present in the plume and there has been no detectable migration of phosphate during 13 years of its operation. With CaCO₃ at a very low level, the soil provided no buffering capacity and, consequently, precipitation of variscite has prevented migration of phosphate.

References:

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- Robertson, W.D., S.L. Schiff, and C.J. Ptacek. 1998. "Review of phosphate mobility and persistence in 10 septic system plumes." *Ground Water*, 36:1000-1010.
- Zanini, L., W.D. Robertson, C.J. Ptacek, S.L. Schiff. 1998. Phosphorus characterization in soils impacted by septic effluent at four sites in central Canada. *Journal of Contaminant Hydrology*. 33: 405-429.

Case History No. 6: Ashumet Valley Plume (Noncalcareous sand , with pH<7)

The Ashumet Valley Plume Pond is on Cape Cod, Massachusetts. The site is on a sand and gravel glacial-outwash plain on western Cape Cod known as the Mashpee Pitted Plain. The soils consist of medium to coarse-grained glaciofluvial sand and gravel underlain by deposits of fine to medium glaciolacustrine sand and silt. The uncontaminated groundwater in the aquifer has: pH: ~5.6; specific conductance < 80 $\mu\text{S}/\text{cm}$; DO concentration > 8 mg/l; P < 0.01 mg/l; Fe & Mn < 0.01 mg/l; and Boron < 0.05 mg/l. This case history presents the longest P plume migration from an on-site sewage disposal system.

The sewage source is from the Massachusetts Military Reservation (MMR), which discharged secondary treated effluent into local infiltration beds beginning in 1936 until termination in 1995 (60 years of operation). Ashumet Pond is ~500 meters from the infiltration beds, and the sewage-contaminated plume has been tracked to local discharge points along the western shore of the pond. The plume has migrated at a groundwater velocity of ~130 m/y, and the length of the P plume (~500 m) indicates a relatively low P retardation factor of <15 over the 60 year migration period.

The phosphate plume discharges have affected Ashumet Pond water quality. The plume has a relatively high concentration of $\text{PO}_4\text{-P}$ (up to 5 mg/l) within 100 m of the shoreline. Along 267 m length of shoreline, P concentration in the pond bottom pore water exceeds the background level of 0.1 mg/l. P values as high as 2-3 mg/l occur within 10 m from the shoreline. Comprehensive data collection has enabled phosphorus flux calculations into the pond, which is estimated at up to 316 Kg/year. This flux is concentrated in a narrow zone near the shore where vigorous upward flow occurs. The pond is currently considered a mesotrophic system, and further increases in P-stimulated algal growth will likely result in the pond deteriorating to a eutrophic state. Mesotrophic lakes have middle fertility that are biologically productive, but not to an extent that their ecology is dominated by algae blooms.

The noncalcareous sand in this case, did not prevent the migration of phosphate from the infiltration beds. Apparently sufficiently acidic condition did not develop to completely attenuate P in this case, possibly as a result of the incomplete oxidation of the sewage constituents in the vadose zone below the infiltration bed.

References:

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Figure VI-6: Migration of Phosphate Plume into Ashumet Pond in Ashumet Valley, Cape Cod, Massachusetts

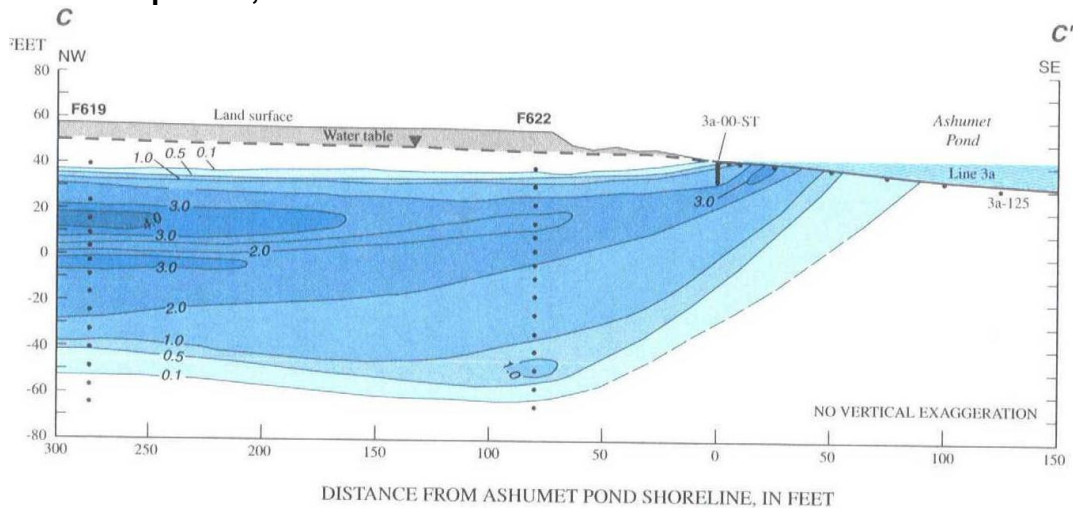


Table VI-1: Septic System Phosphorus Geochemistry

Subsurface Materials	Principal Phosphorus Geochemical Mechanisms	Capacity / Comments	Case Studies	Additional Comments
Silt	Sorption + Ppt.		<ul style="list-style-type: none"> ▪ Killarney 	
Calcareous Sands	Sorption + Fe-P Precipitation	<ul style="list-style-type: none"> ▪ Removal capacity limited ▪ Retardation factor* of ~30 	<ul style="list-style-type: none"> ▪ Cambridge ▪ Langton ▪ Point Pelee 	
Noncalcareous	Precipitation of Al-P mineral variscite due to solubilizing of Al with acidic conditions caused by ammonia nitrification	<ul style="list-style-type: none"> ▪ P concentration <0.1 mg/l Possible ▪ 	<ul style="list-style-type: none"> ▪ Muskoka ▪ Ashumet 	Phosphorus removal may not occur without Al solubilization
Reduced environments	Reductive iron dissolution mineralization to vivianite and strengite	<ul style="list-style-type: none"> ▪ Vivianite produced in reduced environment ▪ Strengite produced when oxidized environment encountered 	<ul style="list-style-type: none"> ▪ Point Pelee 	Phosphorus will be released from strengite if anaerobic conditions redevelop

* Retardation factor is ratio of groundwater velocity to phosphorus plume velocity.

SECTION II: RESEARCH PRIORITIES

VII. RESEARCH NEEDS

In a prior document (Gold and Sims 2000), a number of research priorities relating to P contamination from on-site sewage disposal were outlined. The authors' recommend further work relating to the following topics;

- 1) further microscale assessment of P transport and dynamics in septic system plumes
- 2) development of standardized methodologies for assessing P dynamics and transport at the microscale
- 3) continued rigorous assessment of alternative technologies for improved P removal
- 4) further microscale studies relating to 'sink' or 'hotspot' areas of P attenuation
- 5) development of site indexing to assess vulnerability to nutrient loading from septic systems at the landscape and watershed scales rather than through site specific investigations
- 6) as well as producing a practitioner's manual on determining how sites can be relied upon for P removal, which will also, conversely, identify sites requiring P removal prior to discharge, especially in light of pre-treatment of wastewater, which may change expected subsurface geochemical phosphorus removal.

In the last several years research advances relating to these topics have, in general, been modest, thus the priorities listed above remain valid. However, additional comments are provided below.

1) Further microscale plume assessment

While a number of septic system plume studies have been presented in recent years (*e.g.*, Robertson *et al.* 1998, McCobb *et al.* 1999, Ashumet Valley plume), important information gaps still remain that warrant further site specific investigations.

a. Impact of Pretreatment on Subsurface Phosphorus Removal

With pre-treated wastewater, conditions are less likely to occur for phosphorus removal by iron phosphorus and aluminum phosphorus mineralization. Field studies of phosphorus removal with pre-treated wastewater are presently lacking and are needed.

b. Validity of mineral solubility and adsorption controls;

There is recurring evidence that several P minerals often suggested as important controls on concentrations in groundwater plumes, exhibit persistent supersaturation under field conditions. These include hydroxyapatite [$\text{Ca}_5(\text{OH})(\text{PO}_4)_5$] in several neutral-pH plumes on calcareous sands (Cambridge, Langton, Long Point, Point Pelee plumes; Robertson *et al.* 1998; Ptacek *et al.* 1999) and vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) in several Fe-rich, reducing plumes (Ashumet Valley, Point Pelee plumes, McCobb *et al.* 1999, Ptacek *et al.* 1999). These observations suggest that there are kinetic limitations to the formation of the secondary minerals, and that equilibrium may not be attained under the groundwater flow conditions observed at these sites. Although equilibrium is not observed in field studies, equilibrium may be attained with respect to more soluble and less crystalline precursor phases. Several studies that have been successful in isolating secondary P solids in septic system plumes (Zanini *et al.* 1998, Ptacek and Pratt 1998; Robertson, 2003) have observed chemical compositions which differ somewhat from the common P-minerals for which solubility data is available (*i.e.*, hydroxyapatite, vivianite, strengite and variscite). Thus further work is warranted to more rigorously assess the nature, solubility and kinetics of formation of the solid phases that control P in septic system plumes. This is important because current studies suggest that, in some cases, mineralogical controls are capable of attenuating >99% of the sewage P mass within a few meters of the infiltration pipes (Robertson *et al.* 1998; Robertson, 2003).

Several studies have suggested that adsorption reactions play an important role in attenuating phosphate. Whereas there appears to be compelling evidence that mineral precipitation reactions dominant directly below the tile lines, the relative importance of precipitation versus adsorption is less clear further along groundwater flow paths. More information is needed on the relative importance of adsorption versus precipitation for a variety of site-specific conditions, and for a given site, as pH and oxidation/reduction conditions evolve over the life of a septic system plume.

c. Further confirmation of low pH, low P, septic system plumes in non calcareous terrain;

There are now several examples of acidic to very acidic conditions (pH 5.5-3) developing in septic system plumes on noncalcareous sands (Robertson *et al.* 1998, McCobb *et al.* 1999; Robertson, 2003). These low pH values result from acidity generated by the sewage oxidation reactions, including oxidation of DOC and oxidation of NH_4^+ . The low pH waters normally contain elevated Al concentrations, which in turn have the

potential to limit P to very low concentrations (<0.1 mg/L) as a result of the precipitation of sparingly soluble Al-P minerals with compositions similar to the mineral variscite. In consideration of the potential importance of this attenuation reaction and the rather limited data that is currently available, additional case histories should be developed to further assess the potential for acidic conditions to develop in plumes on these terrains, and to identify the exact phases controlling P concentrations under acidic conditions. Such studies should also investigate other side effects associated with low pH conditions, particularly enhanced mobility of trace metals.

d. P migration via fracture flow, macropores, interflow and overland flow;

There are number of transport pathways that allow 'short circuiting' of septic tank effluent away from the normal porous media flowpaths where the principle natural attenuation processes occur. These include migration via bedrock fractures, overburden macropores (i.e., animal burrows, root channels), and surface 'breakout' with associated overland flow. We are aware of few studies that have been successful in rigorously documenting such transport pathways (Wood, 1993), particularly from a mass flux perspective, thus further work is recommended. This migration pathway has the potential to be of particular importance at many 'cottage country' lakes where onsite sewage disposal often occurs at the minimum setback distances (15-20 m) from the lakeshore, overburden is often thin and slopes may be steep. In these environments, installation of an appropriate monitoring network is often a daunting task, which is the reason few studies have been undertaken. Gachter *et al.* (1998) identified soil macropores and artificial drainage systems as the most important pathways for the vertical and horizontal transport of phosphorous from P enriched soils to water bodies

e. Processes controlling P migration after cessation of wastewater disposal

There is increasing evidence that release and transport of P will continue to be released from some septic systems long after wastewater disposal ceases (Walter *et al.*, 1996; Robertson and Harman, 1999; Ptacek *et al.*, 1999). It appears this release occurs due to long-term dissolution and desorption of P that was attenuated during the active stage of wastewater disposal. After wastewater disposal ceases, production of acid ceases, and an increase in pH is observed, potentially promoting P release. At other sites, if reducing conditions are maintained or become established, release of P can occur through reductive dissolution or desorption of P bound to Fe(III) or Mn(IV) phases. There is concern that this continued release of P from abandoned septic systems may contribute to P loading

to surface water bodies for many years or longer after abandonment. It is unclear which sites will release P and for what duration. Studies are required to identify the geochemical processes controlling P release and to assess the duration of the release after cessation of wastewater disposal.

2) Development of standardized methodologies for assessing P transport at the microscale

There is a need to develop standardized methodologies at the microscale if P transport is to be assessed at the regional scale. These methodologies include standardized site characterization programs, standardized groundwater transport study protocols, and standardized geochemical speciation and groundwater reactive transport models. From this standardized information, assessments of regional-scale fate and transport of P can be developed.

The mobility of P is dependent on a number of site-specific properties, such as grain size, depth to water table, and mineralogy of soil and aquifer solids. Whereas methodologies such as those used to quantify grain size are relatively uniform, other tests that are used to characterize other aquifer properties (e.g. mass of iron and manganese oxide coatings, clay type and content), are less well standardized. Extrapolation of results from individual research sites will only be possible if consistent methods are used at all the research sites, and if these methods are practical for application at the regional scale.

A number of approaches are available for instrumenting septic system sites to evaluate the fate and transport of P. These approaches range from intensive characterization programs that include collection of hundreds of water samples over several years or longer, to relatively simple monitoring programs which rely on a few samples over one season. Given the wealth of information that can be derived from detailed monitoring programs, it is desirable to carry out additional detailed studies under more varied regional conditions, so that detailed information on P transport becomes available for a wider range of geological conditions and soil types. These sampling programs should include installation of large arrays of piezometers. Groundwater should be sampled and analyzed to provide a comprehensive data set to provide the relevant geochemical information for interpreting the mechanisms controlling P transport and attenuation. Samples should be analyzed in a consistent manner for the various P forms (ortho-phosphate, total P, etc), and for parameters which are required to interpret P transport data, including pH, concentrations of major ions, and oxidation-reduction indicator species.

These studies should also include an evaluation of N dynamics, given the close association of redox reactions and P and N transport. Consistent field sampling techniques should be employed. For example, samples are often collected for analysis of total P and o-PO₄ without using preservation. If a groundwater plume contains elevated concentrations of ferrous iron, precipitation of this iron after sample collection may lead to scavenging of PO₄ and reporting of erroneously low concentrations of PO₄. Similarly, if an alternative system is being evaluated to assess the removal of P, information on the broader geochemistry is needed, and suitable sampling methods employed, to provide representative and comprehensive data sets to fully interpret processes controlling P attenuation.

Standardized modeling approaches should be employed to assess the fate and transport of P at the microscale. To date, geochemical speciation calculations to assess solubility and adsorption processes controlling P in septic system plumes have utilized a variety of geochemical computer codes, and different sets of thermodynamic constants for aqueous species, solubility constants, and surface constants for reactions directly affecting P concentrations and overall geochemistry. These differences lead to potentially different interpretations of the processes controlling P fate and transport. Use of a consistent database for P reactions is recommended.

There are a number of comprehensive reactive-solute transport models that incorporate physical, chemical and microbiological processes, including advection, dispersion, mineral precipitation-dissolution reactions, adsorption-desorption reactions, oxidation-reduction reactions, microbiologically mediated reactions and representative kinetic rate equations. There is a need to apply these models in a rigorous manner to existing plume chemistry data at a number of sites in geologically diverse terrain. These models should be applied in a consistent manner and used to assess the sensitivity of P transport to variations in aquifer characteristics. Geochemical data bases, including thermodynamic constants and kinetic rate constants, used in conjunction with reactive solute transport models also vary widely. There is a need to develop a consistent database to facilitate inter-site comparisons.

3) Continued rigorous assessment of alternative technologies for improved P removal

It is recommended that alternative small flows P removal technologies should be categorized by the following scientific mechanisms:

1. Sorption
2. Iron Mineralization

3. Aluminum Mineralization

4. Calcium Mineralization

4) P behavior at the groundwater-surface water interface and other 'hotspots';

The USGS is currently assessing the fate of P from the Ashumet Valley plume as it discharges to a small kettle lake (Ashumet Pond). The groundwater plume is moderately acidic (pH ~5.7) and has P concentrations of ~1-4 mg/L (McCobb, et. al. 1999). Present indications are that P migrates through the lakeshore riparian zone in a relatively conservative manner. Studies of septic system P migration into a wetland also indicated migration into the wetland in a relatively conservative manner (Ptacek *et al.* 1999). Few other studies however, have been successful in documenting P plume discharge to surface water environments. Shorelines with large vegetation, for example, may thrive on the available P in this zone. Further studies should be undertaken to establish if the behavior at Ashumet Pond is typical at other sites. In particular, studies should also include sites on calcareous sands where previous studies have shown that neutral pH plumes with potentially higher P concentrations could be present.

Once discharged to the surface water environment, there is potential for P to be consumed by aquatic species. After senescence, this bound P accumulates in bottom soils. If reducing conditions are present at soil/water interface, P can be released back to the water column, again becoming available as a nutrient for growth. Under certain conditions (e.g. oxidizing soil/water interface, rapid burial environment), P that has entered the water body is not released, and is effectively removed from the system. Detailed studies on P release from wastewater plumes into a variety of water body types would provide greater insight into the fate of P once released to surface water bodies.

The principal 'hotspot' associated with subsurface P migration appears to be the 'rapid transformation zone' (Zanini *et al.* 1998), the zone coinciding with the horizon of most intense sewage oxidation, usually located within 1 m below the tile bed infiltration pipes. Here P removal can be substantial but it is also highly variable (23-99%, Robertson *et al.* 1998). Although Zanini *et al.* (1998) identified the presence of a variety of authogenic P solids in these zones which were indicative of mineral precipitation reactions, their precise mineralogy and solubility characteristics were not established. Thus further mineralogical assessment of the P solids from this zone is warranted.

5) Site indexing for P vulnerability

As suggested previously (Gold and Sims, 2000), the high cost of site-by-site assessment argues for the use of landscape and watershed scale indexing techniques. Although this has yet to be attempted for P vulnerability from septic systems, the knowledge base may now be sufficient to allow preliminary steps in this direction. Maguire and Sims (2002) assessed soil testing to predict phosphorous leaching. Vulnerability scores might include a variety of factors such as those listed below:

- a. septic system P mass loading compared to mass loading from other sources
- b. sensitivity of surface water bodies to additional P loading
- c. overburden permeability
- d. overburden thickness
- e. depth of water table
- f. cation exchange capacity
- g. carbonate mineral content
- h. oxyhydroxide mineral content

6) Practitioner's Manual for Site Selection

A practitioner's manual should be developed providing guidelines for determining whether sites are capable of providing P removal, or whether P removal must be performed prior to discharge. This is especially true where wastewater pre-treatment is performed, as the pre-treatment methods may change the biochemical activity in the subsurface environment and affect the ability and therefore create a need for P removal.

To address the phosphorus geochemistry research needs will require funding of long-term research efforts as the processes that need to be examined require examination of phosphorus geochemical transformations over time. Also, a thorough understanding of hydrogeologic conditions at sites is essential for meaningful analysis. It is important to note that many of the important insights presented in this report have resulted from research programs over 10 +/- years at the internationally acclaimed Earth Science Department at the University of Waterloo. Short-term efforts are unlikely to produce needed breakthroughs.

Also regarding site indexing for phosphorus vulnerability that could produce meaningful guides for practitioners, recommended techniques will need to be field verified to determine their accuracy and practical utility. Proper long-term funding and having objective feedback by practitioners of these efforts is strongly recommended.

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