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THE EFFECT OF PARTICLE SIZE ON PHOSPHATE ADSORPTION BY FLUVIAL SEDIMENT

BY

Micheal F.A. Stone

B.Sc., University of Waterloo, 1979

THESIS

Submitted to the Department of Geography

in partial fulfilment of the requirements

for the Masters of Arts degree

Wilfrid Laurier University

1987

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ISBN 0-315-37955-3

ABSTRACT

The quantitative phosphate adsorption behaviour of ten grain size fractions of an experimental sediment (silica sand) and fluvial sediment from two Southwesten Ontario rivers, were evaluated and compared to determine the effect of particle size on phosphate adsorption. In addition, the elemental composition of grain size fractions of fluvial sediment were determined by X-Ray fluoresence spectrometry to study the combined effect of particle size and sediment geochemical composition on phosphate adsorption.

Results of the adsorption studies indicate that phosphate adsorption per unit mass increases in a non-linear fashion with decreasing grain size. The capacity of grain size fractions of silica sand and river sediment to adsorb phosphate can be categorized into three phosphate adsorption groups according to particle size. From the poorest to the most efficient phosphate adsorption group, these groups are 1) medium sand to coarse silt, 2) medium to fine silt and 3) clay size particles.

In addition to grain size, sediment geochemical composition and grain mineralogy are important parameters which influence phosphate adsorption. Increased phosphate adsorption activity in the smaller particle sizes was apparently due to the presence of metal oxides (Al, Fe, Mn and Ti) associated with clay minerals and organic material.

Although small grain sizes (<23μm) adsorbed more phosphate than larger grain size fractions, the smaller fractions are also capable of desorbing large amounts of phosphate into solution. Therefore the smaller fractions may act as a phosphate source during times when the phosphate concentration of a river is below the sediment equilibrium phosphate concentration.

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank my supervisor Dr. G. Subins and committee members Dr. M. English, Dr. D. Peirson, Dr. R. Elliott, Dr. S. Schiff (outside reader) and Prof. E. Wickham (Chairman) for their valuable input and constructive criticism of this work. Additional thanks to Dr. H. Saunderson for his perceptive comments and for initially encouraging me to work towards a masters degree.

My appreciation and gratitude are extended to Alena Mudroch for several valuable discussions and for granting permission to use the Warman Cyclosizer at CCIW. In addition, a very special thanks to Barry Smith at the Water Survey of Canada in Guelph for several helpful suggestions and for supplying sediment and discharge data. Thanks to Pam Carnochan for doing such an excellent job with the maps and figures, Svein Vik and Dr. R. Gebotys (W.L.U) for assistance with computing, Otto Mudroch (McMaster) who performed the elemental analyses and Dr. D. Lawson (U of W) and Ken Varley for their helpful comments.

To my wife Janis and daughter Meghan, thank you for your continual support and encouragement throughout this project.

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CHAPTER 1

INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

In recent years, phosphorus (P) has been identified as a major factor in the deleterious fertilization of natural waters. In addition, its role in accelerating the process of eutrophication has been well documented (Vollenweider, 1968; Frink, 1969; Allen and Kramer, 1972; Armstrong et al, 1974). Increased amounts of this nutrient in lakes has substantially reduced water quality for municipal water supplies, recreation and fish habitat (PLUARG, 1978).

Sediments significantly influence the nutrient flux in lake (Harter, 1968; Syers et al, 1973 ; Bostrom et al, 1982) and river systems (Edzwald et al, 1976; Green et al, 1978; Hill, 1982). Whereas numerous studies have emphasized the importance of sediment-P dynamics in lakes (Stumm and Morgan, 1981; Williams et al, 1971; PLUARG, 1978), little information is presently available concerning the effect of sediments on P transport, retention and transformation processes in tributaries draining into downstream waterbodies (Brown, 1983; Ontario Ministry of the Environment, 1986).

The adsorption of phosphate onto solid particles has been cited as a process which alters the mobility of this nutrient in the aquatic environment (Olsen, 1964; Williams et al, 1971). It has been suggested that particle size, which is an important physical characteristic of sediment (Folk and Ward, 1956), plays a role in both the adsorption process (Hwang et al, 1976; De Pinto, 1981; Mudroch, 1986) and the subsequent transport and deposition of

sediment-bound P (Mayer and Gloss, 1980; Miller et al, 1982) thus influencing the availability of this nutrient for biotic uptake (Williams et al, 1980). While some researchers have studied the effect of river sediment on P dynamics in fluvial systems (Taylor and Kunishi, 1971; McCallister and Logan, 1978; Hill, 1982), the importance of sediment grain size fractions in this process was acknowledged but not fully investigated.

The exchange of phosphorus between sediment and water is an important aspect of phosphorus dynamics in natural waters. Sediment particles, serving as carriers of P, provide a prime transport medium of this nutrient from the land to the lakes (Miller and Spires, 1978; Allan, 1979; Ongley et al, 1982). The extent to which specific grain size fractions of river sediment participate in this process is not well documented. To evaluate the potential transport of sediment-bound P through river systems into lakes, knowledge of the phosphate adsorption characteristics of specific grain sizes of river sediment is required. The following section of this chapter is a review of much of the recent literature related to the role of sediment in phosphorus dynamics of natural waters and will include discussion of the following; the bioavailability of P, the forms of P found in water and sediment, the adsorption of P by sediment and the role of particle size in P dynamics.

1.2 REVIEW OF LITERATURE

The ecological significance of phosphorus in primary productivity and biological metabolism of aquatic plants in lakes has been well researched (Kramer et al, 1972). Phosphorus is a major limiting nutrient, controlling primary productivity in many aquatic systems. Inputs of P into such systems have caused algal blooms and associated water quality problems (Cook et al, 1986). However, it is not so much the quantity of P entering a body of water, but rather the fraction of P that is biologically available that causes eutrophication. Lee et al, (1979) have defined biologically available P as that fraction which is available for use by living cells during a growing season.

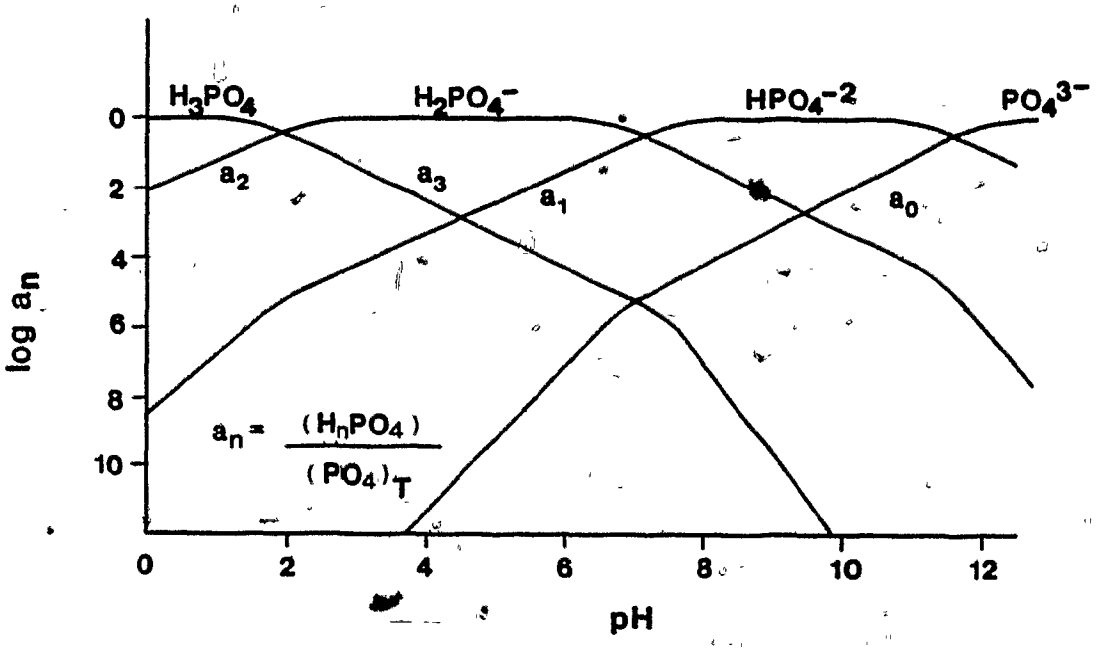
Reviews of P forms and their bioavailability indicate that the P form which is directly available is dissolved inorganic phosphate (Logan et al, 1979; De Pinto et al, 1981; Hegemann et al, 1983). The predominant species of dissolved inorganic phosphate at pH ranges in natural waters are HPO_4^{2-} and $H_2PO_4^-$ (Figure 1). Other forms become available through conversion to dissolved inorganic phosphate (Dorich et al, 1985; Sagler et al, 1975).

Sediments play an important role in the spatial and temporal distribution of P in aquatic ecosystems. Phosphorus associated with suspended sediment (particulate P), contributes approximately 75% of the tributary total P load to the lower Great Lakes (Sonzogni et al, 1979). The biological availability of particulate P is determined by the rate at which particulate P is converted to inorganic phosphate. The relationships between particulate P, dissolved inorganic P and algal P are illustrated in Figure 2. Factors controlling the availability of particulate P on suspended sediments include:

1) the forms and amounts of P in the particulate fraction (Section 1.2.2);

Figure 1

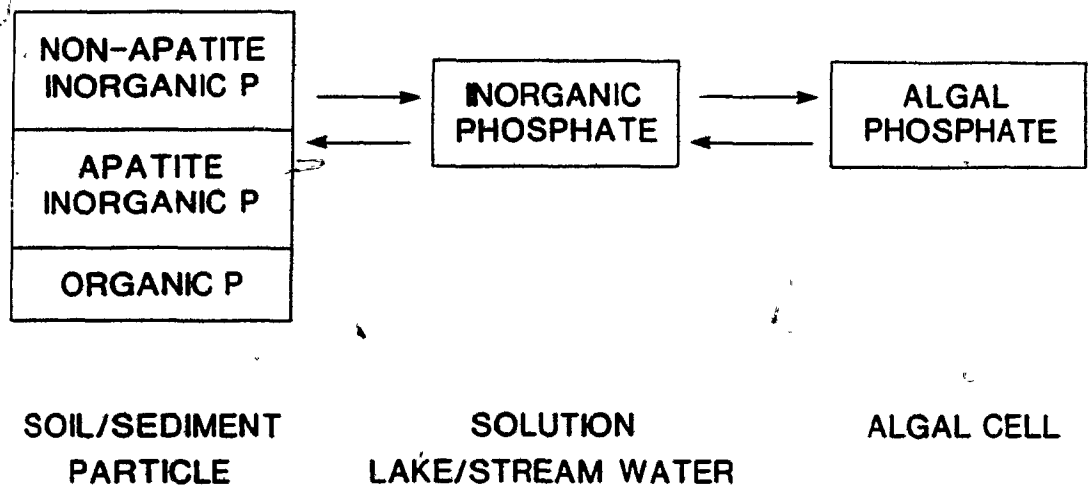
Speciation of phosphate as a function of pH



Source: Beekheiser et al. (1980)

Figure 2

Diagram of the relationships between particulate- and Algal-P.



Source: Armstrong et al (1979)

2) the residence time of the particle in the water;

3) the P status of the algal population;

4) the solution concentration maintained by the algal and other sites where P is adsorbed and desorbed;

5) and other factors controlling the solubility of particulate P such as pH and Eh (Armstrong et al, 1979).

1.2.1 Forms of Phosphorus in the Water Column

Two forms of P are generally considered to be present in natural waters; dissolved P and particulate P (Wetzel, 1975). A summary of these forms is found in Table 1.

Although dissolved inorganic P constitutes a small percentage of total P (Miller et al, 1982), it is the directly bioavailable form in most natural waters (Logan et al, 1979; Hegemann et al, 1983). Other forms of P in solution may include dissolved condensed phosphates, and dissolved organic-P compounds which may become bioavailable through conversion to inorganic phosphate (Sonzogni et al, 1982).

Particulate P which consists of both detrital and sediment-bound P, often comprises a high proportion of the total P input to lakes and reservoirs (PLUARG, 1978). This fraction can consist of inorganic, organic and condensed forms (Table 1). Of these, the inorganic fraction is most significant as a source of bioavailable P in most natural waters (Sonzogni et al, 1982).

The forms and amounts of P in aquatic ecosystems are a function of the input, output and interchange between sediment and water compartments (Syers et al, 1973). Figure 3 represents in schematic form, potential

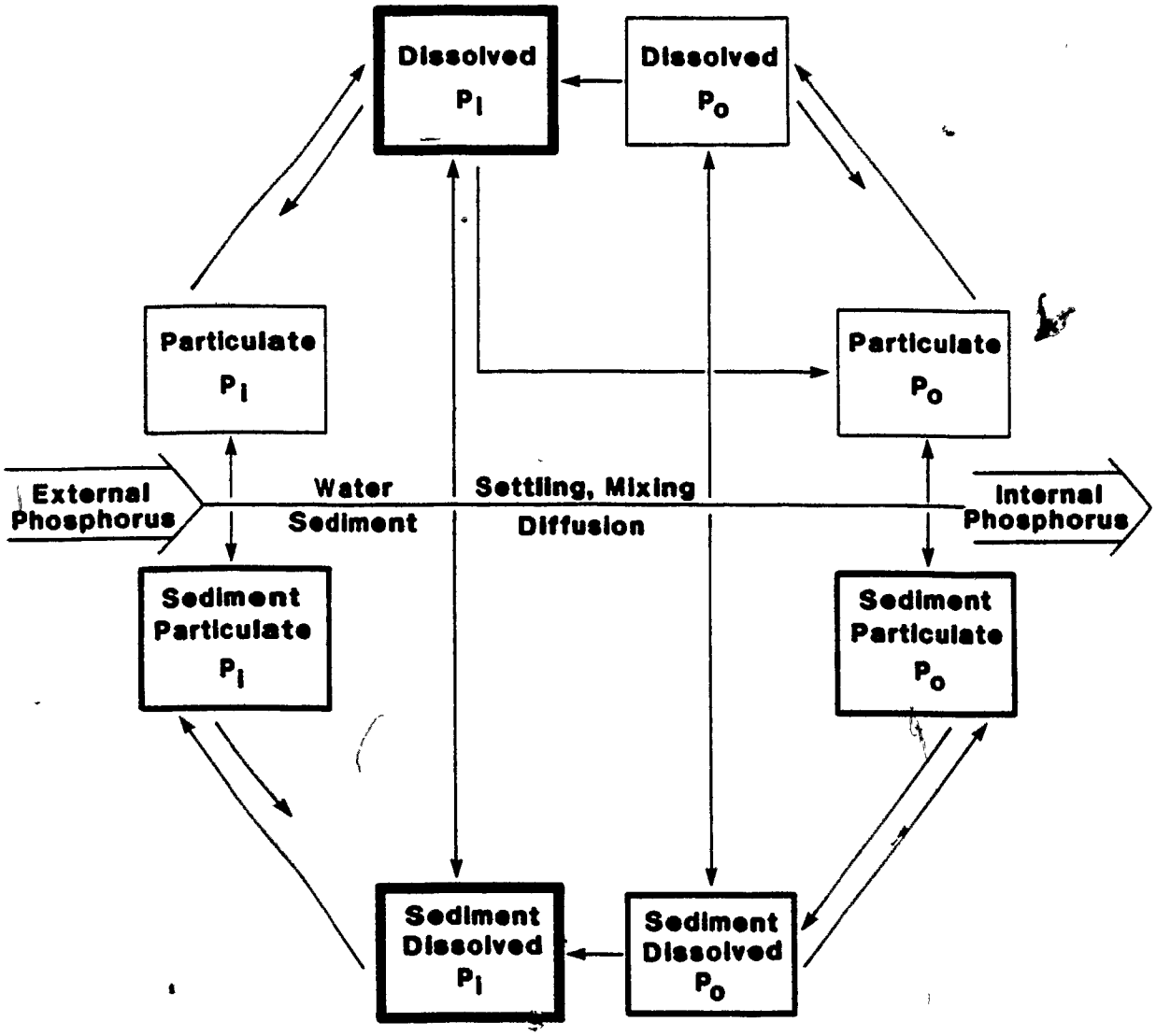
Table 1 Forms of phosphorus in water column.

Dissolved Forms of P	Dissolved Species	Suspended Particulate Forms of P	Solid Representative
Dissolved inorganic P "Dissolved P_i"	Orthophosphates ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $FeHPO_4^+$)	Particulate inorganic	Mineral phases of rock and soil (hydroxyapatite)
	Hydrolyzable polyphosphates ($H_2P_2O_7^{2-}$, $CaP_2O_7^{2-}$, $P_3O_{10}^{5-}$, $P_3O_9^{3-}$)		Phosphorus adsorbed on clays and other inorganic complexes
Soluble organic P "Dissolved P_o"	Low molecular organic compounds (glucose 1-phosphate, inositol hexaphosphate)	Particular organic P "Particulate P_o"	Phosphorus in organisms
	Macromolecular colloidal phosphorus		Phosphorus adsorbed on dead particulate matter
			P in macro-organic aggregations

Source: (Mayer, 1984)

Figure 3

Interchange between water and sediment compartments



Source: Syers et al 1973.

interchanges which may occur between the major P compartments. The mobility of P in these systems is dependent upon the rates of various chemical and biological reactions (De Pinto et al, 1981). Processes influencing these reactions are physical-chemical (adsorption/desorption, precipitation/dissolution), biological (microbial induced dissolution of particulate P) and mechanical (mixing dynamics). Thus P is in a continuous state of flux between dissolved and particulate P compartments in which sediments play a major role (Mortimer, 1941; Keup, 1968; Kramer et al, 1972).

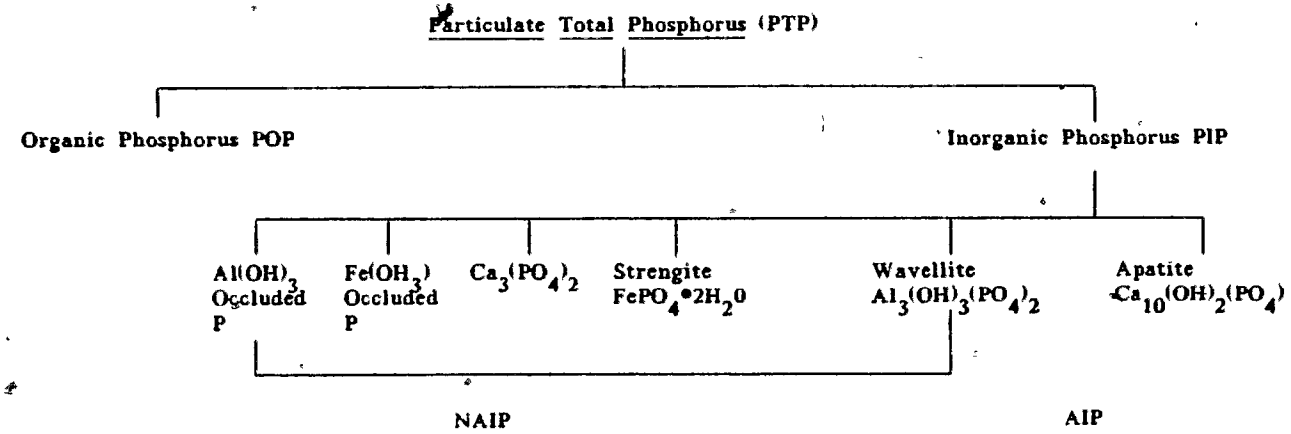
1.2.2 Forms of Phosphorus in Sediments

Our present knowledge of the forms and amounts of P in sediments has resulted from sequential chemical extraction schemes, based initially on that of Chang and Jackson (1957) for soils. Subsequent modifications of their scheme (Williams et al, 1967, 1971, 1976) have resulted in the use of operational definitions which categorize various P forms found in sediments based on current extraction methodology (Figure 4). These categories can be conveniently discussed as inorganic and organic P.

Inorganic P, frequently constituting a major portion of the total P in lake sediments, (Syers et al, 1973), is dependent upon drainage basin geology (Keup, 1968; Logan, 1978, 1979), land use activities (Omernik, 1976; Hill, 1981) and agricultural practices (Logan, 1977). Two fractions of inorganic P usually present in sediments are nonapatite inorganic P (NAIP) and apatite inorganic P (AIP) (Sonzogni et al, 1982).

The NAIP fraction of sediments mainly include discrete mineral phases of Fe (stregnite, vivianite), Al (variscite), Ca (anapatite) and inorganic P

Figure 4 Possible Components of Particulate Phosphorus and Their Susceptibility to various chemical extraction methods



Chemical Extraction Method					
(i) NTA			$Ca_3(PO_4)_2$	$FePO_4 \cdot 2H_2O$	
(ii)Anion Exchange	all exchangeable P in equilibrium with soluble ortho-PO_4				
(iii) NaOH	$Al(OH)_3$ occluded P	$Fe(OH_3$ occluded P		$FePO_4 \cdot 2H_2O$	$Al_3(OH)_3(PO_4)_2$
(iv) Citrate	$Al(OH)_3$ occluded P	$Fe(OH)_3$ occluded P		$FePO_4 \cdot 2H_2O$	$Al_3(OH)_3(PO_4)_2$
(v) HCL					$Ca_{10}(OH)_2(PO_4)_6$

Source: Armstrong et al, 1979

adsorbed on Fe- and Al-hydrous oxides. This fraction is considered partially bioavailable through dissolution or desorption of phosphate when dissolved inorganic P concentrations are low, either due to dilution, biological uptake or chemical immobilization (Dorich et al, 1985).

The AIP fraction consists of inorganic P in the mineral form apatite. Due to the slow dissolution of apatites in natural waters, AIP is considered essentially unavailable (Stumm and Morgan, 1981).

The organic P status of sediment is a function of the rate of input of organic P in the form of plant and animal residues and of the balance between organic P mineralization and immobilization processes. Organic P levels ranging from 10 to 70 per cent of the total P in lake sediments have been reported (Frink, 1969; Sommers et al, 1972). In a study by Mayer (1984), organic-P values in samples from acid lakes varied between 40-70% of the total P and were considerably higher than those observed in samples from neutral lakes (14-25% of total P). Hence this fraction may constitute a major reservoir of P in lake systems.

Few workers have investigated the nature and association between organic P and other soil components. The relatively high correlations found between organic P and organic carbon (C), indicate that much of the sediment organic P is associated with organic matter complexes (Sommers et al, 1972). Williams et al (1971) have reported oxalate-extractable aluminum (Al) to be significantly related to the total organic P of lake sediments in Wisconsin. However they found no relationship between organic P and oxalate iron (Fe), which is a sediment parameter considered important in determining the inorganic P levels of lake sediment. This lack of relationship suggests that factors which control total inorganic and organic P levels in sediment are

relatively independent.

Although the influence of organic matter on phosphate adsorption has been debated, organic matter appears to affect phosphate adsorption in an indirect manner. Organically complexed Fe^{3+} and Al^{3+} are the most likely sites for adsorption on organic matter surfaces (Weir and Soper, 1962; Syers et al, 1971).

Specific organic P compounds that have been identified include adenosine triphosphate (ATP) and phosphate esters (Syers et al, 1973). Rodel et al, (1977) found that hydrolysis of sediment-bound organic P occurred at a much reduced rate compared to soluble organic P.

1.2.3 Phosphate Adsorption on Sediment

Adsorption onto solid partieles has been cited as a mechanism which affects the mobility of P in aquatic systems (Olsen, 1958; Williams et al, 1971; Syers et al, 1973). The extent to which this occurs is a function of temperature (Mack and Barber, 1960), pH (Muljadi et al, 1966; Parks, 1975; Holford and Patrick, 1978), competitor ions (Hingston, 1968), sediment type (van Olphen, 1963, Hsu, 1964; Chen et al, 1973; Parfitt and Atkinson, 1976), oxidation reduction status (Mortimer, 1940; 1971; Patrick and Khalid, 1974; Nurnberg, 1984) and particle size (Williams and Saunders, 1956; Hwang et al, 1976; Williams et al, 1980; De Pinto et al, 1981).

Mechanisms by which P is adsorbed and retained by sediment have been studied in lakes (Hwang et al, 1976; Nriagu and Dell, 1974; Shulka et al, 1971; Syers et al, 1973). Most investigators believe that hydrated surfaces of aluminium and iron oxides and clays are responsible for the adsorption process.

Laboratory studies have shown that inorganic P when added in concentrations considerably greater than those present in the interstitial waters of sediments, is retained by oxides and hydrous oxides of iron (Fe) and aluminium (Al) (Gastuche et al, 1963; Muljadi et al, 1966) and by calcium carbonate ($CaCO_3$) (Cole et al, 1953) by an adsorption rather than a precipitation mechanism.

The mechanism of adsorption is due to the pH-dependent charge of metal oxides found in aquatic environments (Stumm and Morgan, 1981). Metal oxides result from proton transfers at the amphoteric surface by:

a) amphoteric dissociation

$$\equiv MeOH_2 \rightleftharpoons \equiv MeOH + H^+ \qquad (1)$$

b) hydrolysis

$$\equiv MeOH \rightleftharpoons \equiv Me^- + H^+ \qquad (2)$$

The P sorbing species is bound directly to the metal coordinating ion by the ligand exchange between OH_2^+ or OH groups. For protonated anions, such as HPO_4^{2-}, the ligand exchange may be accompanied by a deprotonation of the ligand at the metal oxide surface;

$$\equiv MeOH + HPO_4^{2-} \rightleftharpoons \equiv MeHPO_4^- + OH^-$$
$$\rightleftharpoons \equiv MePO_4^{2-} + H_2O \qquad (3)$$

An important characteristic of the adsorption of phosphate is that adsorption increases the negative surface charge on the surface of the sediment (Hingston et al, 1972). Hence, the affinity of the surface to adsorb P decreases as adsorption increases.

Although considerable progress has been made towards understanding the adsorption of phosphate to solid surfaces this process is not yet fully understood. The combination of chemical heterogeneity of the surfaces involved and their sensitivity to experimental technique, complicates adsorption studies

of natural sediment. Furthermore, grain size, nature of mineral surface and degree of crystallinity as well as mineralogy have been cited as factors that profoundly affect P adsorption by solids (Kramer et al, 1972).

The adsorption of a solute on a solid is generally quantified by an adsorption density parameter Γ (mol g^{-1}) representing the number of moles of solute adsorbed per unit mass of solid. Adsorption is described mathematically as a function of the solute concentration (C) at constant temperature (T); that is

$$\Gamma = f(C,T) \tag{4}$$

Hence an adsorption isotherm

$$\Gamma = f_T(C) \tag{5}$$

can be determined for a set of given experimental conditions. The following is a discussion of equations most commonly used in the study of phosphate adsorption.

A nonlinear dependance of adsorbed concentration C_s in solution is often represented by the Freundlich adsorption equation

$$C_s = KC^n \tag{6}$$

where K and n are constants that have to be determined experimentally. Over limited ranges of concentrations this equation often describes adsorption well (Barrow and Shaw, 1975).

The Langmuir equation, originally developed for gas-solid systems, has been adopted for use in modeling the adsorption of phosphate ions on charged surfaces. This equation relates the amount of species adsorbed Γ_a to its concentration in solution C

$$\Gamma_a = (\Gamma_m C) / (K + C) \tag{7}$$

where K is a constant and Γ_m is the adsorption density at full monolayer

coverage of the adsorbing substrate. K is related to the free energy of adsorption (ΔG) (Stumm and Morgan, 1981) through the equation

$$K = \exp [-\Delta G/RT] \quad (8)$$

where R is the gas constant (8.314 $Jmol^{-1}K^{-1}$) and T is the absolute temperature.

The Langmuir model assumes that the surface consists of adsorption sites, that all adsorbed species interact only with a site and not with each other and that adsorption is limited to a monolayer. Although these assumptions are violated in aquatic systems (Stumm and Morgan, 1981), reviews by Harter and Baker (1977) and Barrow (1978) indicate that the widely used Langmuir model does provide a reasonable mathematical description of experimental data and is consistent with a possible mechanism of phosphate binding in water (Section 1.2.3). Therefore the Langmuir equation was preferred over the Freundlich equation in the present study. This equation is also useful in summarizing a mass of adsorption data into one maximum value (Γ_m) which may be correlated with chemical, mineralogical and physical properties of sediment, such as particle size (Berkheiser et al, 1980).

Adsorption functions have been used to predict pesticide movement in runoff on sediment (Leonard and Wauchope, 1980). Wendt and Alberts (1984) used a similar approach to estimate concentrations of soil-adsorbed and dissolved P in surface runoff from results of soil adsorption analyses and knowledge of the amount and size distribution of eroded soil particles. Similarly, this approach may provide a suitable method to evaluate the P transport capacity of sediment grain size fractions in rivers. If adsorption maxima were experimentally determined for individual grain size fractions of riverine sediment, then information of this nature, when used in combination with existing instantaneous discharge and sediment particle size data

(Environment Canada data), may provide suitable methodology to evaluate and predict the rate and amount of sediment-P export to lakes.

1.2.4 Particle Size and Phosphorus Dynamics

Particle size is a sediment parameter which influences the nutrient flux in fluvial systems by virtue of its role in adsorption processes (Ongley et al, 1982). Although several researchers have indicated the significance of particle size in P sediment dynamics (Kuo and Lotse, 1973; Hwang et al, 1976; Mayer and Gloss, 1980; De Pinto et al, 1981; Mudroch, 1986) little information is available on the adsorption of inorganic P by various size fractions of river sediment.

Variation in particle size can influence the chemical behavior of sediment in fluvial systems. The surface area of a constant mass of sediment increases with decreasing particle size and the adsorption rate is directly proportional to the surface area (Adamson, 1967). Thus based on surface area, it can be expected that compared with the coarser fractions, finer grain fractions will have a higher adsorption potential.

Preliminary investigations of particle size and P adsorption characteristics have been conducted on lake and river sediment. Hwang et al (1976) investigated the adsorption characteristics of lake sediment fractionated into five particle size ranges (all < 50μm) and concluded the best adsorption efficiency was at the size fractions of 2 to 5μm. Mudroch and Duncan (1986) studied the major and trace element concentrations in different particle size fractions of sediment from the Niagara River. They reported an increase in P with decreasing particle size particularly in the < 13μm size fractions. In a

study of offshore and nearshore sediment of Lake Erie, Mudroch (1984) reported significant correlations between Fe and P with respect to grain size. In addition, she found that the distribution of P was correlated to the metals according to grain size. This finding is consistent with other studies which show that Fe and Mn oxide coatings on sediment particles act as a substrate for P (Jenne, 1968; Forstner, 1982).

The P availability for algae in suspended sediments of varying particle size was studied by Dorich et al, (1984). They reported that P available for algae is not necessarily concentrated in the smaller size aggregates. Larger aggregates were also found to contain available forms of inorganic P due to their silt and clay composition. In a similar study, Wall et al, (1978) found that a significant proportion of the bed load fraction of unconsolidated bottom sediments of the Maumee River, Ohio, actively adsorb and transport P. In addition, Armstrong et al, 1979 investigated the relationship of available P to suspended sediment particle size in five Ohio rivers. They reported that available P concentrations were similar for each of the different particle size fractions studied. Therefore, contrary to the belief that smaller size fractions transport more P, this research demonstrates that larger grain fractions are also significant carriers of P in rivers.

Particle size and density influence the hydraulic behavior of sediment. The relative rate of removal of particles from the water column depends largely on particle size, shape, density and particle concentration. Due to differential settling rates, silt and clay particles which are often higher in P content, settle more slowly than coarser material allowing more time for P to be utilized by algae (Armstrong et al, 1979; Sharpley, 1980). Hence, particle size and P fractionation by particle size class will also influence the rate of

available P release (De Pinto et al, 1980; Williams et al; 1980).

Numerous studies have investigated the relationship between the transport of total P and river discharge regime (Baker and Kramer, 1973; Johnson et al, 1976; Muir et al, 1973; Verhoff et al, 1979, 1980, 1982, 1983; Yaksich et al, 1980). Results from this research show that the transport of total P is governed by discharge because most of the P transported is particulate P and is associated with sediments. Hence P export is strongly correlated with both sediment load and discharge.

Phosphorus introduced to streams from point or nonpoint sources can be adsorbed to stream-bed or suspended sediments or assimilated by the phytoplankton. With increased flow or decreased viscosity, stream turbulence can scour and resuspend the bottom sediments thereby potentially increasing the P concentration in the water (Keup, 1968). Harms et al, (1978) studied the role of stream bed sediments with respect to increased P concentrations during periods of high discharge. The authors attributed increased total P levels during high flow events due to the suspension of particulate P from scour. In this research inorganic P concentrations were also found to increase as a result of the release of interstitial P from bottom sediments. Studies by Connell (1965) and Verhoff (1982, 1983) also suggest P transport results from the resuspension and deposition of sediment.

In conclusion, P in aquatic ecosystems is in a constant state of flux due to physical-chemical, biological and mechanical processes. Although sediments alter the mobility of P in aquatic systems (Harter, 1968; Syers et al, 1973; Bostrom et al, 1982), the role and the extent to which particle size distributions in fluvial systems influence the rate and form of P export to lakes is not fully understood.

1.5 OBJECTIVES OF THE STUDY

Phosphorus is one of the main nutrients which accelerates the process of eutrophication. Sediments in aquatic ecosystems alter both the amount and temporal pattern of P exports to lakes. Many of the physical and chemical relationships between P and sediment have been studied for soils and lake sediment. However, the extent to which fluvial sediment will adsorb P as a function of particle size is not well documented. Information of this nature is required to further understand the influence of P-sediment interactions on available P concentrations that exist in streams, rivers and lakes and to address the role of particle size in the fluvial transport of sediment-associated nutrients. Therefore, the present work examines the effect of particle size on phosphate adsorption by fluvial sediment.

Specific goals of this research are:

1) to examine the effect of grain size on the adsorption of inorganic P by silica sand;

2) to investigate P adsorption properties of specific grain size fractions of river sediment;

3) to evaluate the combined effect of sediment geochemical composition and grain size on P adsorption.

CHAPTER 2

METHODOLOGY

2.1 INTRODUCTION

River sediment can exert a strong influence on the partitioning of phosphorus (P) between solid and aqueous phases through adsorption/desorption reactions (Edzwald et al, 1976) and thereby can affect the nutrient flux in a river system. Although particle size is considered important in this process, few studies have directly examined P adsorption behavior of specific grain size classes of natural river sediment. To more fully understand the relationship between particle size and P adsorption, the following experiments were undertaken:

1) The first series of experiments examine the effect of grain size on the P adsorption behavior of pure silica sand. This approach allowed the effect of particle size to be studied, while eliminating other physical and chemical sediment parameters considered important in P adsorption. These included organic-C, inorganic-C, Ca, Fe and Al.

2) A second series of experiments examine the P adsorption properties of specific grain size classes of natural river sediment to evaluate the combined effect of grain size and sediment geochemical composition on P adsorption.

Adsorption experiments with discrete particle size fractions of an experimental sediment (silica sand) and natural river sediment (Big Creek and Big Otter Creek) were carried out to meet the above objectives. The effect of

particle size was investigated by mixing varying P concentrations with ten separate grain size fractions for each of three sediment types.

2.2 LOCATION AND GEOLOGY OF STUDY AREA

The two study sites of this thesis are located in the adjoining drainage basins of Big Creek and Big Otter Creek. These basins, which drain into Lake Erie, are located in Southwestern Ontario (Figure 5).

The Big Creek basin is located between longitudes 80° 23' and 80° 41' W, and latitudes 42° 35' and 43° 05' N. This basin has an area of 725 km², a length of about 90 km in a north south direction and a width which varies between 21 and 36 km in an east west direction (Yakutchick and Lammers, 1970). The actual study site is located at Environment Canada gauging station No. 02GC007, near Walsingham (Figure 6).

The Big Otter Creek basin is located between longitudes 80° 29' and 80° 57' W and latitudes 42° 38' and 43° 03' N and drains an area of 712 km² (Sibul, 1969). The study site in this basin is located at Environment Canada gauging station No. 02GC006 near Calton (Figure 7).

The surficial geology of Big Creek and Big Otter Creek basins are shown separately in Figures 8 and 9, respectively. Two main physiographic forms which predominate in this area are the morainic ridges in the north and northwest, known as the Mount Elgin Ridges and the sand plain in the south and southeast, known as the Norfolk Sand Plain (Chapman and Putnam, 1973). The surficial deposits of the Norfolk Sand Plain consist of lacustrine sand and silt deposited in glacial lakes Whittlesey and Warren (Sibul, 1969). Unstratified or morainic deposits consist mainly of till whereas stratified

Figure 5
Location Map of Big Creek and Big Otter Creek Drainage Basins

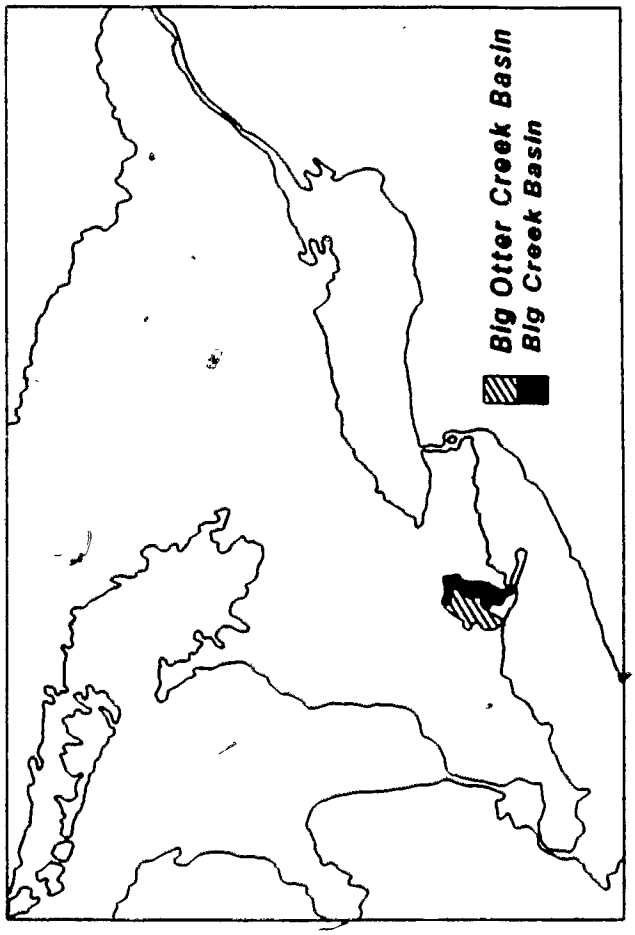


Figure 6

Big Creek Watershed

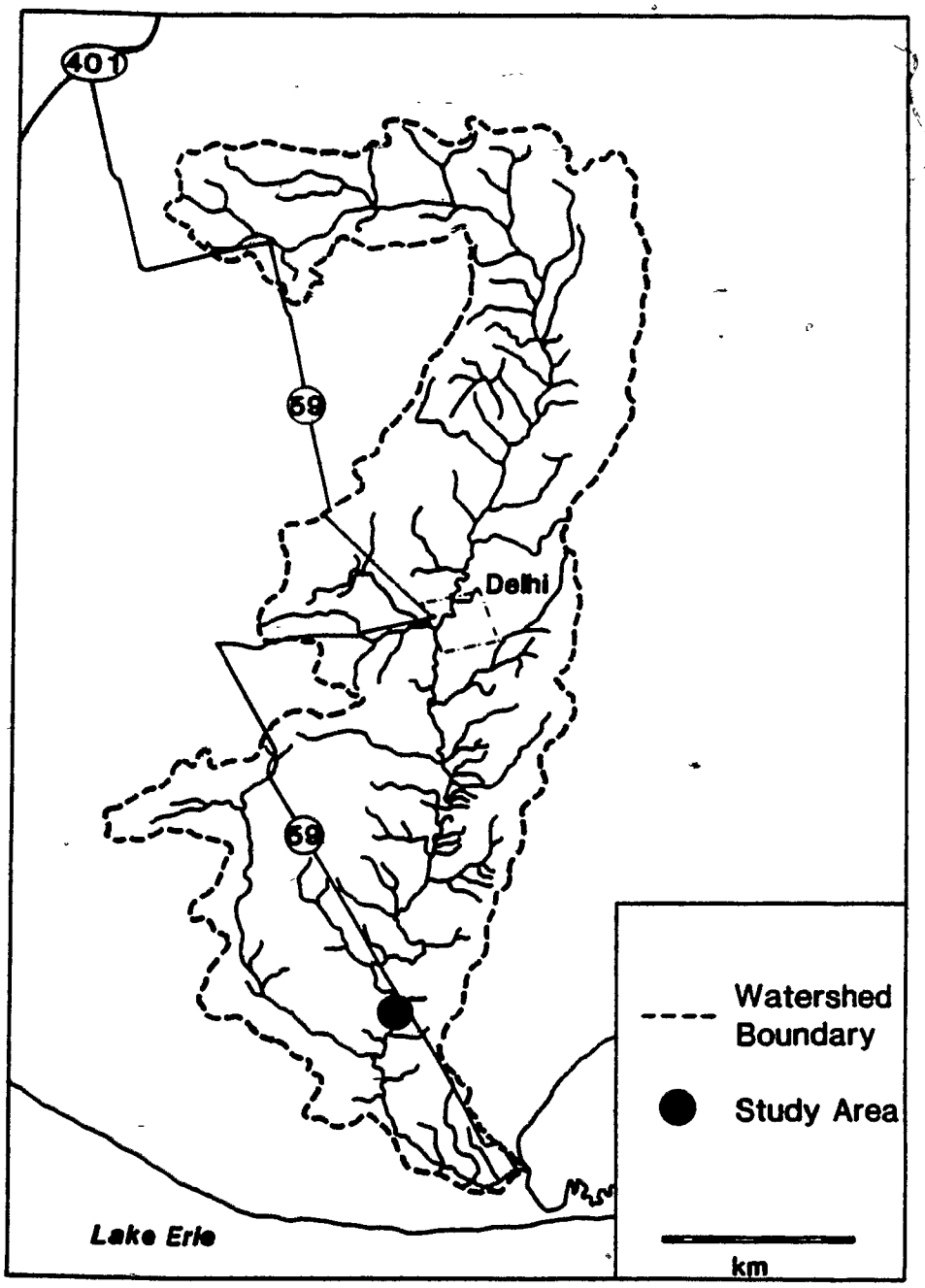
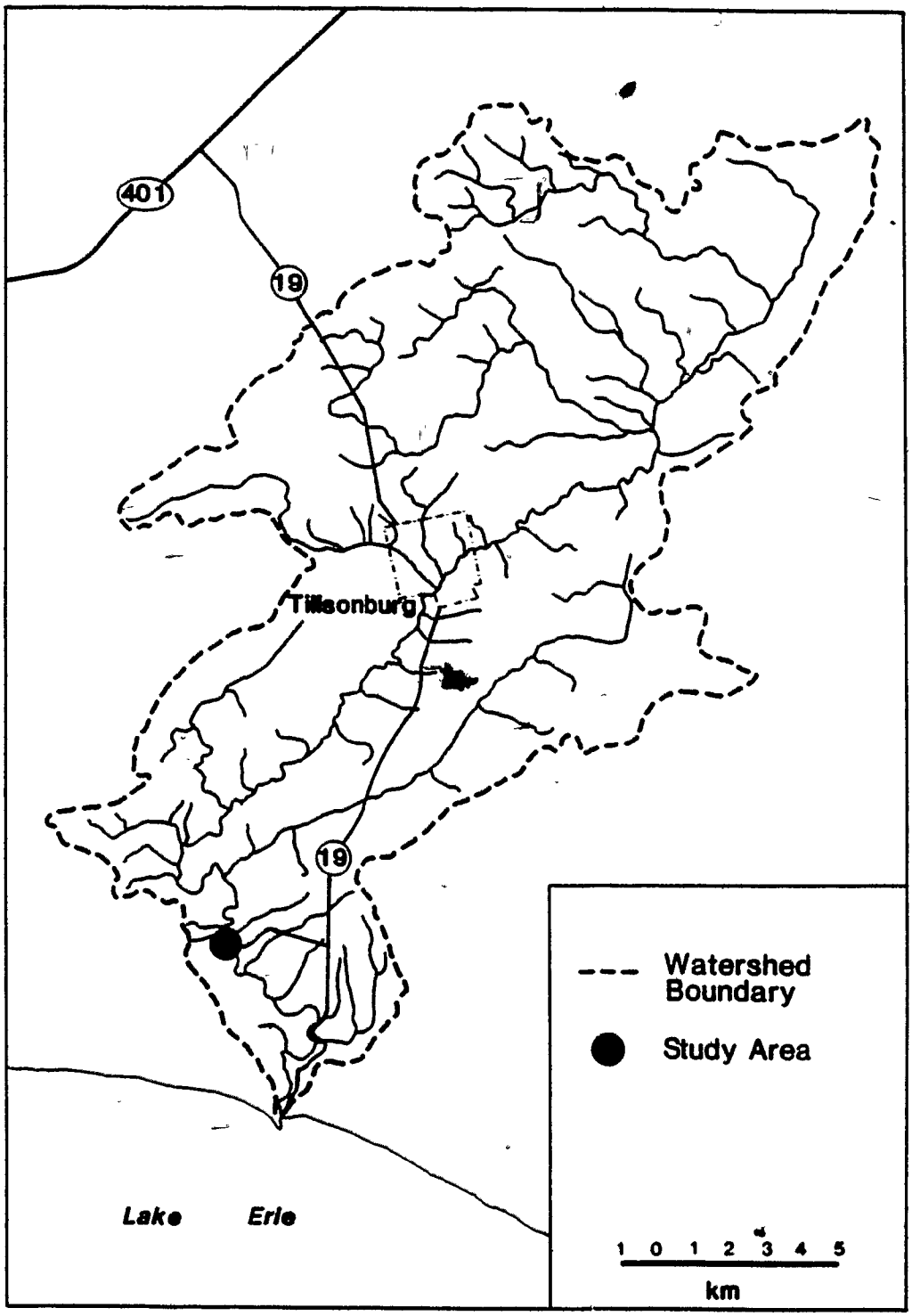


Figure 7

Big Otter Creek Watershed



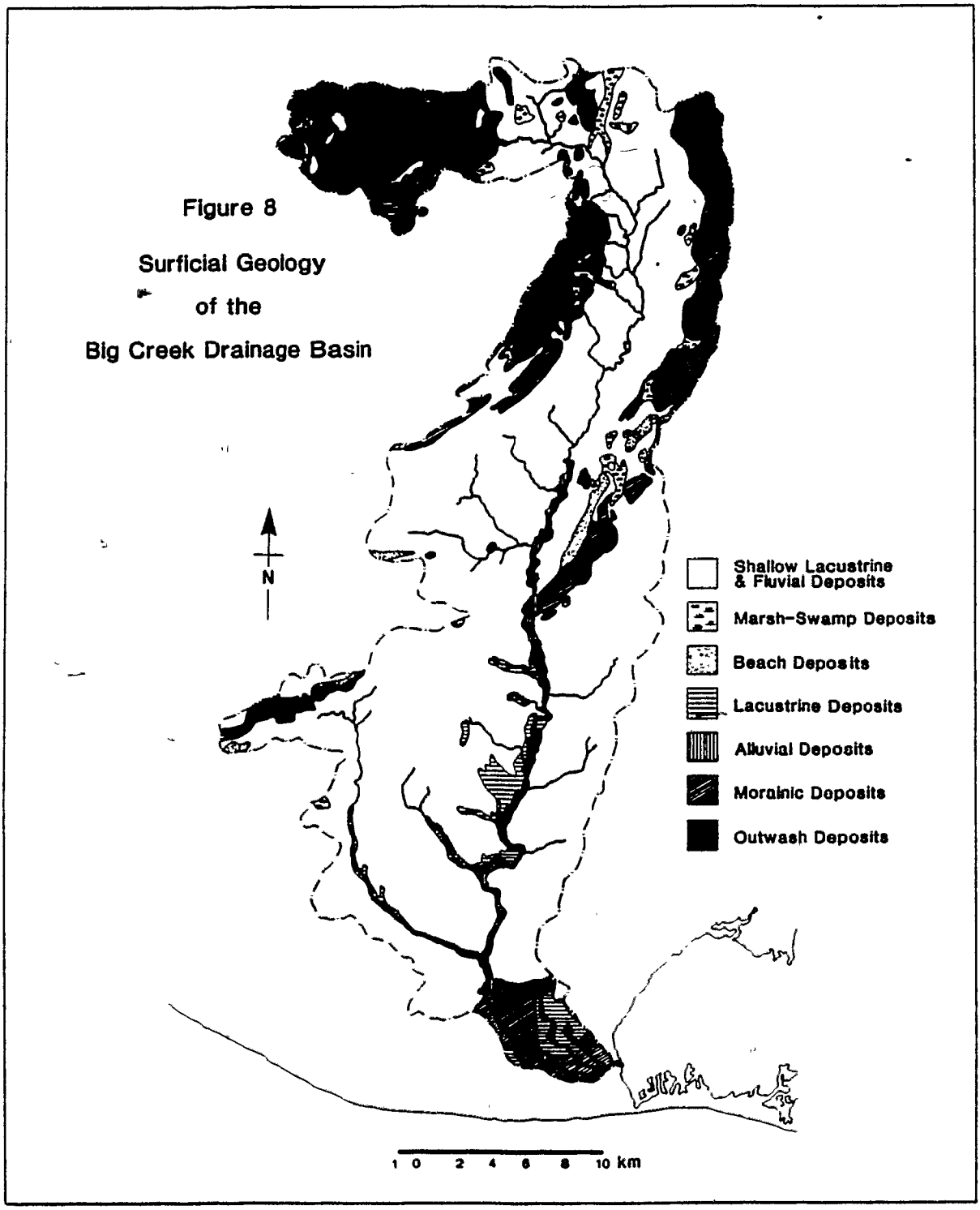
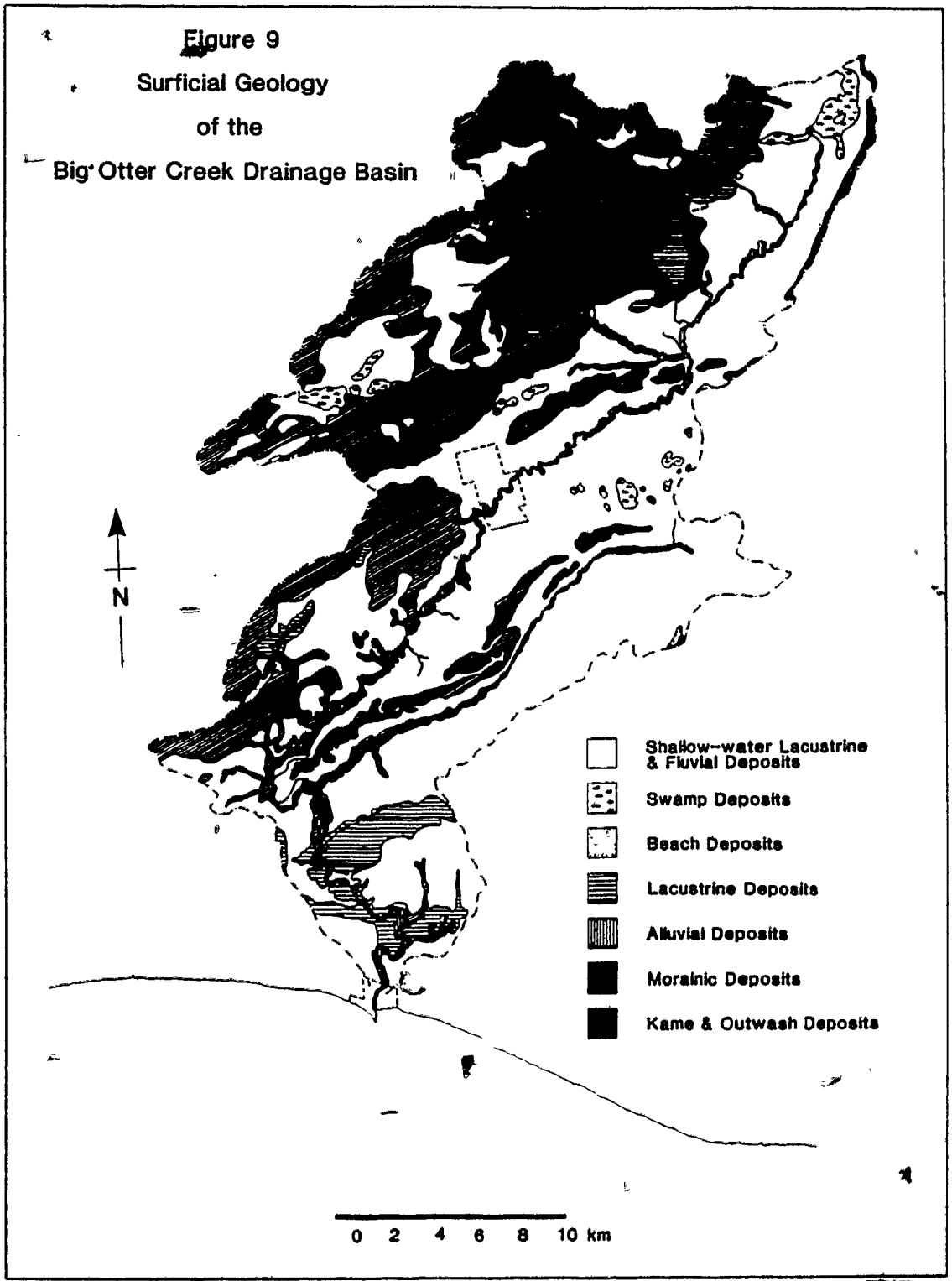


Figure 8
Surficial Geology
of the
Big Creek Drainage Basin
N
Shallow Lacustrine & Fluvial Deposits
Marsh-Swamp Deposits
Beach Deposits
Lacustrine Deposits
Alluvial Deposits
Morainic Deposits
Outwash Deposits
1 0 2 4 6 8 10 km

Figure 9
Surficial Geology
of the
Big Otter Creek Drainage Basin



deposits include glacial outwash or kame sand and gravel, lacustrine clay, silt and fine sand (Yakutchik and Lammers, 1970).

A schematic vertical section showing the general sequence and distribution of stratigraphic units in the Big Creek and Big Otter drainage basins (Novakovic and Farvolden, 1974), is presented in Figure 10.

2.3 SAMPLE COLLECTION

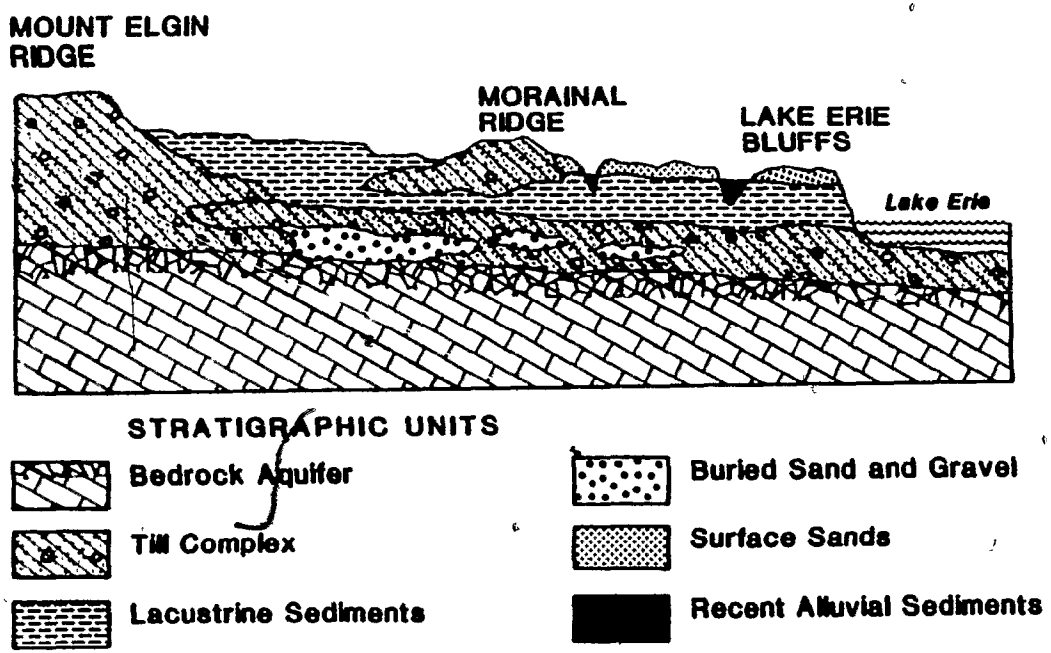
The silica sands used for P adsorption experiments in this study were purchased in various grades (Bond, F17, F75, F125, 270, 290, 295) from Wilkinson Foundry Supplies, Toronto. Typical chemical composition obtained from Product Data Sheets indicated this material consisted of 98.815% SiO_2, 0.015% Fe_2O_3, 0.047% Al_2O_3, 0.013% TiO_2, <0.01% CaO and <0.01% MgO.

River bed and bank sediments were collected from Big Creek and Big Otter Creek September 7, 1986. On this date, the discharge was recorded at 2.88 and 3.06 m^3/s for Big Otter Creek and Big Creek, respectively (Barry Smith, pers. comm.).

The location and cross-channel geometry of the transects for Big Creek (BC1, BC2) and Big Otter Creek (BOC1, BOC2) are presented in Figures 11 and 12, respectively. Samples were collected from the top 10 to 15 cm of river bed at each location, placed in plastic bags and later air dried in the lab. Composite samples to be used in P adsorption experiments were obtained by mixing 500 g of sample from each of the eight locations indicated above for both rivers.

Figure 10

General stratigraphic sequence in the basins of Big Creek and Big Otter Creek



Source: Novakovic and Farvolden, 1974

Figure 11

Location and cross channel geometry of Big Creek transects

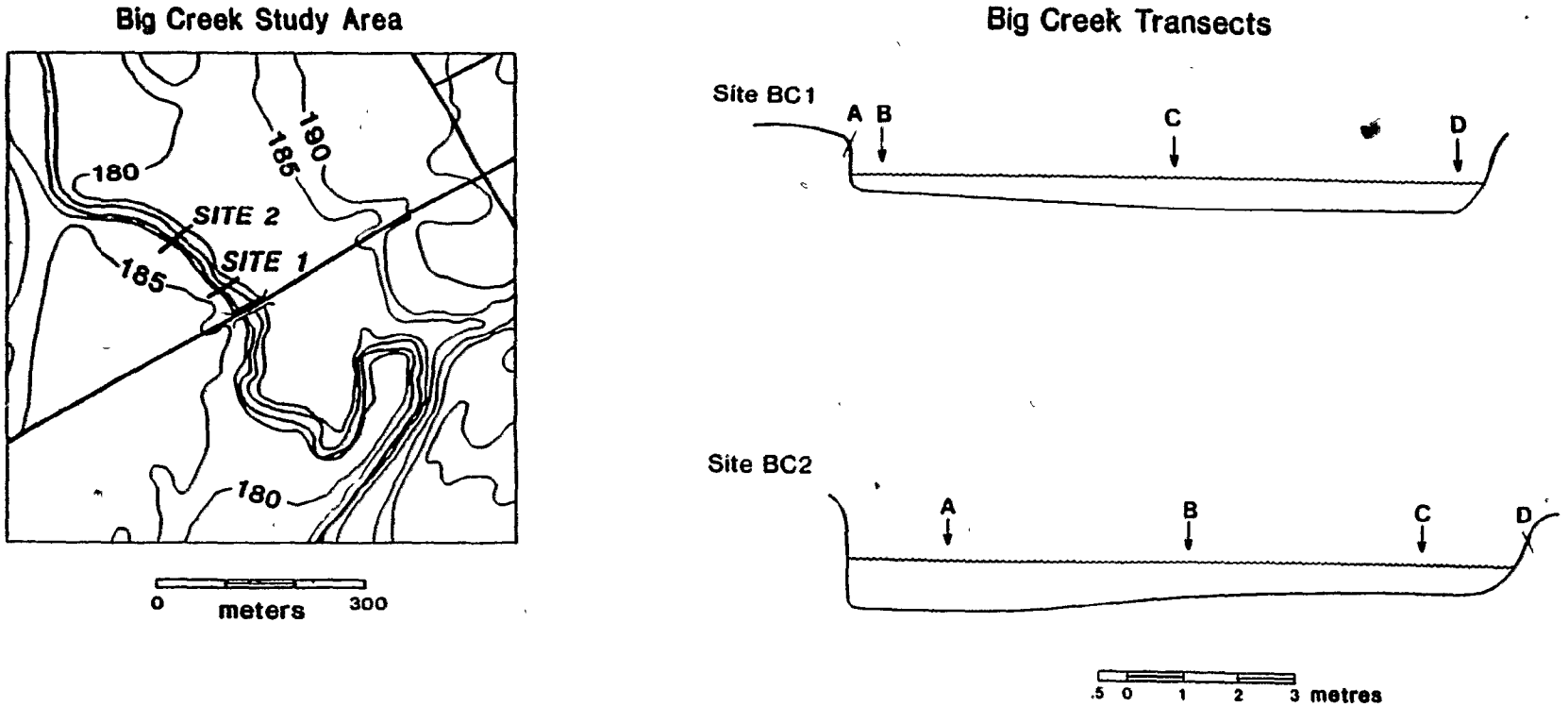
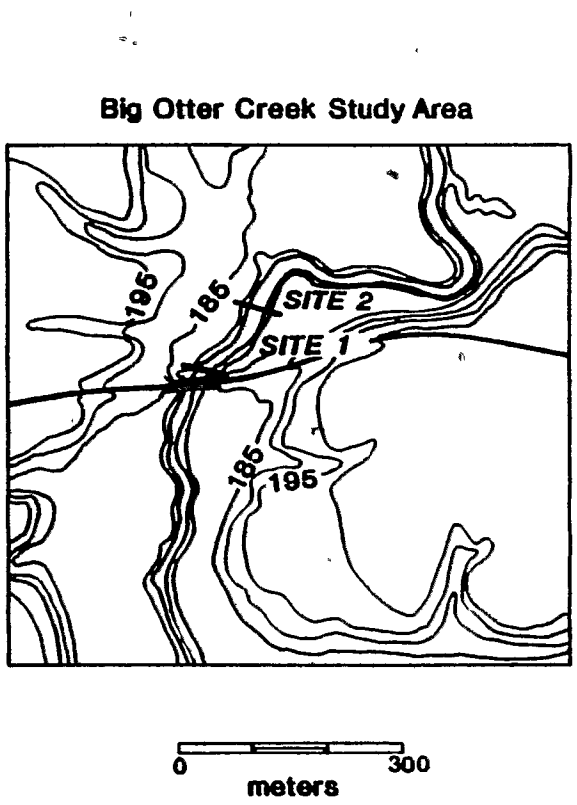
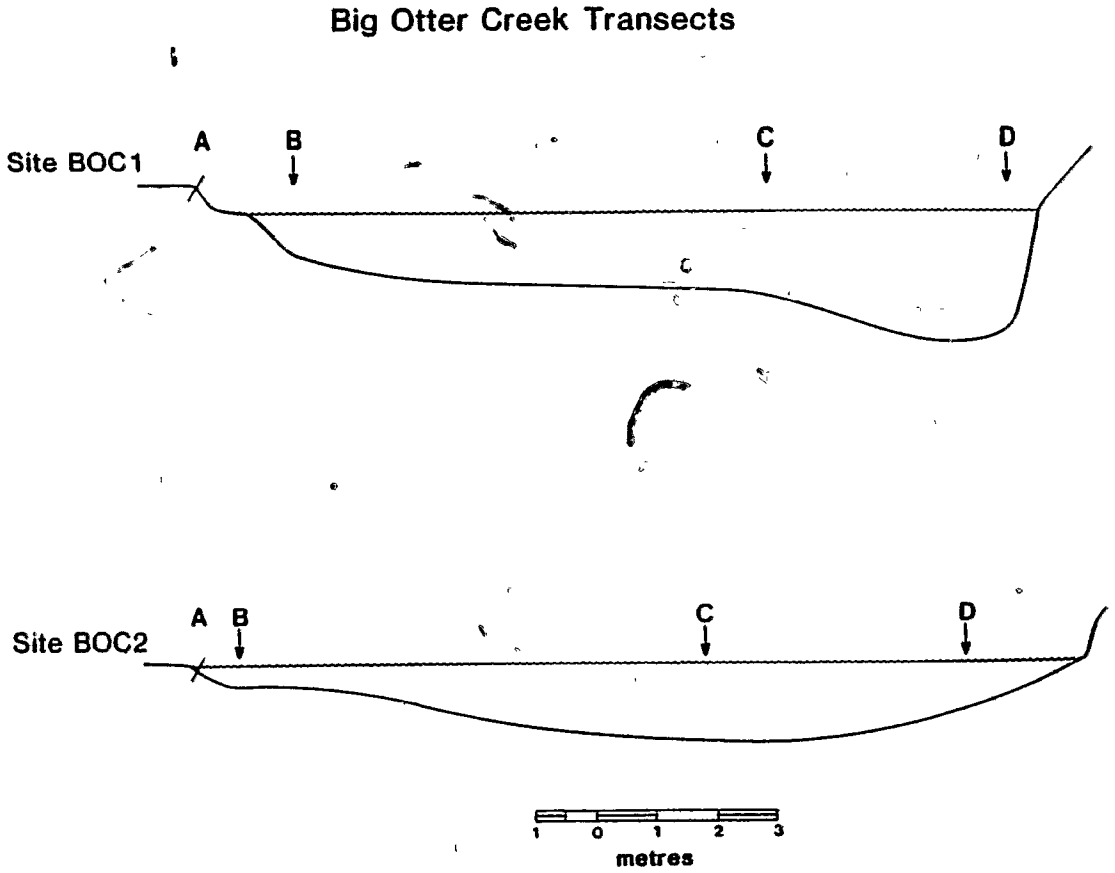


Figure 12

Location and cross channel geometry of Big Otter Creek transects





2.4 PARTICLE FRACTIONATION

The following section outlines procedures used to fractionate composite samples of silica sand and river sediment into discrete grain size fractions. Particle fractionation consisted of a two step process using Tyler (Canadian Standard) sieves and a Warman Cyclosizer.

All composite samples were mechanically sieved at 0.25 phi intervals (from -2.0 to 4.0 phi) for 15 minutes with a Ro-Tap Testing Sieve Shaker (BS1377, 1967). The portion of sediment remaining in the bottom pan was saved for subsequent fractionation by Cyclosizer. The 1.0, 2.0, 3.0 and 4.0 phi fractions were wet sieved with one litre of distilled water, allowed to air dry then stored for P adsorption experiments.

The sub-sieve fractions of each composite sample were further separated by the Warman Cyclosizer into the following size fractions: 54-62.5μm, 40-54μm, 27-40μm, 19-27μm, 13-19μm, and <13μm. The effective particle separation was calculated after the weight percentages retained in the five cyclones had been determined. Correction factors for water temperature, particle specific gravity, actual flow rate and time of elutriation were calculated according to the Cyclosizer instruction manual (Warman International Ltd, 1981). The smallest size fraction (<13μm) was recovered from the separation by settling, decanting and centrifugation.

Information regarding the size characteristics of the grain size fractions used in this study is presented in Table 2. Although each grain size fraction will have an associated size distribution, for convenience with the graphical and tabular presentation of data, the mean particle diameter will be used to describe the various grain sizes throughout this study.

TABLE 2 SIZE CHARACTERISTICS OF GRAIN SIZE RANGES

Number	Mean Particle Size (μm)	Size Range (μm)	Wentworth Size Class
1	500*		medium sand
2	250*		
3	125*		fine sand
4	63*		very fine sand
5	58	54–62	coarse silt
6	47	40–54	
7	34	27–40	
8	23	19–27	
9	16	13–19	fine silt
10	6	<13	clay

* refers to the least size rather than the mean size

2.5 ELEMENTAL AND MINERALOGICAL ANALYSES

The concentration of major elements (Si, Al, Fe, Mn, Ca, Mg, Ti, P, K, Na) of individual grain size fractions of river sediment was determined by X-ray fluorescence spectrometry. Samples were prepared by fusion with lithium metaborate ($LiBO_2$) and results reported as a percentage of total weight. Loss on ignition resulted from heating dry sediments to 475 °C for 12 hours. The accuracy of the analyses was determined by running Canadian Reference Standards (SO-1, SO-4) and comparing the analytical results with the reference values for major elements (Gladney et al, 1985). Elemental analyses were performed in the Geology Dept at McMaster University by Otto Mudroch.

The mineralogical composition of river sediment samples was investigated by powder X-ray diffraction using a Cu-target with a Ni-filter. The concentration of organic and inorganic C in river sediment was determined with a Leco Carbon Analyzer.

2.6 ADSORPTION EXPERIMENTS

The adsorption of inorganic P was investigated by equilibrating sediment suspensions of individual grain size fractions with various concentrations of phosphorus. All adsorption experiments were performed in triplicate.

A series of P concentrations (0, 50, 100, 200, 400, and 800 ug P/L) in 25 ml aliquots, was added separately to 0.5 g of sediment for ten grain size fractions of three sediment types. In addition, 0.5 ml of 0.5 M $CaCl_2$ and 3 drops of toluene were added to each 50 ml erlenmeyer flask to reduce the

effect of unequal ionic concentrations and potential bacterial uptake of P, respectively. The flasks were sealed with parafilm and shaken for 18 hours at low speed on an Eberbach Shaker. Temperature varied between 19.5 and 21 degrees C. After equilibration, samples were centrifuged for 5 minutes at 2500 RPM then filtered through a 0.45 μm filter. The filtrate was analyzed for phosphate with a Technicon Autoanalyzer using the stannous chloride procedure NAQUADAT No. 15254 (Environment Canada, 1979). Adsorption values greater than zero were interpreted as inorganic-P adsorbed from solution onto sediment, while adsorption values less than zero indicated inorganic-P desorbed from sediment into solution. The amount of inorganic-P adsorbed od desorbed was determined by measuring the difference in P concentration after equilibration for eighteen hours, using the following equation:

$$P_{ads} = [(P_{initial} - P_{final}) * 0.025l\ ] * wt_{sed}^{-1} \quad (9)$$

where P_{ads} = μg P adsorbed gram^{-1} sediment

$P_{initial}$ = initial phosphate concentration (μg P L^{-1})

P_{final} = final phosphate concentration (μg P L^{-1})

wt_{sed} = weight of sediment (g)

The widely used Langmuir equation was chosen over other equations to evaluate the phosphate adsorption behavior of grain size fractions of silica sand, Big Creek and Big Otter Creek for two reasons. First, the Langmuir equation is consistent with a possible mechanism of phosphate binding in water and secondly is useful to summarize a mass of adsorption data into one

maximum value (Γ_m) which may provide a method to compare individual grain size fractions of different sediment types.

The standard non-linear form of the Langmuir equation (equation 7) is constrained to pass through the origin; which, in the present context, appropriately describes the adsorption behavior of phosphate free sediment such as pure silica sand. However, in nature, phosphate is found adsorbed onto sediment from fluvial systems. When this sediment is placed in a phosphate free solution, phosphate may desorb from the sediment into solution. Therefore, the Y-intercept in this case would be negative. To accomodate this behavior, a non-zero, presumably negative, intercept was added to the model and the algebraically equivalent expression $Y = (\beta_0 + \beta_2 X)/(1 + \beta_1 X)$ was fit to the phosphate adsorption data using the P3R program of the UCLA Biomedical Data Package (Dixon et el, 1981). In the above modified version of the Langmuir equation, β_0 is the Y-intercept, $\beta_1^{-1}\beta_2$ is analogous to the adsorption maxima Γ_m and $\beta_1^{-1} - 2\beta_0\beta_2^{-1}$ is analogous to K.

2.7 WATER ANALYSES

In addition to sampling both Big Creek and Big Otter Creek for river sediment, water samples were simultaneously taken to determine total P (TP) and dissolved reactive P (DRP) concentrations. By definition, DRP is the phosphate not retained by a 0.45μm filter (Sonzogni et al, 1982). The pH at each site was recorded with a Hellige Digital pH meter. A DH-48 depth integrated suspended sediment sampler was used to collect water samples at three equidistant locations along each transect indicated in Figures 11 and 12.

Water samples for total P analysis were placed in 125 ml glass bottles containing 1.0 ml of 20% H_2SO_4. Samples for dissolved reactive P were filtered through 0.45 μm filters into 25 ml glass bottles, stored on ice and analyzed nine hours after sampling. Results from water analyses are presented in chapter 3.

Water samples were analyzed for total P and dissolved reactive P using the stannous chloride procedure outlined in section 2.6. However, samples for total P determination were digested in 25 ml aliquots with 0.3 ml of saturated potassium persulfate on hot plates until 3-5 ml remained. Samples were diluted to 25 ml with distilled water then filtered (0.45 μm filter). The filtrate was analyzed using the procedure for dissolved reactive P (section 2.6).

CHAPTER 3

RESULTS

3.1 INTRODUCTION

In this chapter, results from experiments designed to investigate the adsorption of phosphorus (P) onto different particle size fractions of silica sand and fluvial sediment from the two study sites are presented.

3.2 GEOCHEMICAL COMPOSITION OF SEDIMENTS

The elemental composition of grain size fractions of both fluvial sediments were determined by X-ray fluorescence (XRF) spectrometry to evaluate the effect of sediment geochemical composition on P adsorption as a function of grain size. This technique is useful when interpreting the relationship between sediment associated phosphorus and other chemical parameters, such as metal oxides, which are important in the adsorption of P onto solids (Stumm and Morgan, 1981).

The results of XRF spectrometry analysis for ten grain size fractions of Big Creek and Big Otter Creek are presented in Tables 3 and 4, respectively. The content in weight percent of the oxides of the ten major elements Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn and P is given for each grain size fraction. In addition, inorganic carbon, organic carbon and loss on ignition (LOI) values are included in these tables.

Correlation coefficients between sediment chemical parameters (Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn, P, LOI), Langmuir adsorption coefficients (Γ_m, K)

TABLE 3 BIG CREEK

Concentration of major elements in separated sediment size fractions (% dry weight).

median particle size (um)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Inorg-C	Org-C	LOI
500	64.40	6.18	1.35	4.52	11 29	2.11	1.71	0.19	0.08	0.12	0.65	2.64	8.05
250	71.68	8.98	1.45	2.13	6.42	2.11	1.84	0.22	0.04	0.08	0.54	0.85	5.03
125	66.27	10.52	3.60	2.68	6.43	2.44	2 13	0.68	0.10	0.16	0.11	1.32	4.97
63	59.17	10.08	4.73	3.45	8.69	2.51	2.02	0.99	0.13	0.23	0.22	2.02	7.99
58	53.06	9.28	6.89	5.68	10.14	2.67	1.76	1.59	0.16	0.21	0.91	1 44	8.56
47	59.86	9.51	2.59	4.06	9.32	2.70	2.05	0.42	0.07	0.17	1.14	1.36	9.25
34	58.46	8.88	2.72	4.15	9.55	2.51	2.04	0.51	0.09	0.17	0.80	2.18	10.91
	58.40	8.93	2.68	4.23	9.52	2.54	2.05	0.50	0.09	0.18	0.44	2.52	10.86
23	54 56	9 13	3.41	3.47	9.91	2.15	2.05	0.55	0.14	0.21	•	•	14.44
	56.64	9.37	4.58	3.47	10.42	2.10	2.17	0.56	0.13	0.26	0.60	3.86	10.30
16	52.37	9.44	4.70	3.27	10.73	1.70	2.18	0.58	0.15	0.28	0.21	5.40	14.60
	50.88	8.91	4 09	3.33	10.20	2.08	2.02	0.59	0.16	0.22	•	•	17.51
<13	47.08	10.81	7.00	2.77	10.11	1.53	2.38	0.72	0.21	0 34	•	•	17.05
Canadian Soil Standards													
SO-1	54.78	17.42	8.63	3.73	2.49	2.60	3.24	0.85	0.11	0.15	•	•	6.00
SO-4	68.55	10.43	3.40	1.00	1.50	1.33	2.11	0.59	0.08	0 21	•	•	10.80

• - no data

TABLE 4 BIG OTTER CREEK

Concentration of major elements in separated sediment size fractions (% dry weight).

median particle size (um)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Inorg-C	Org-C	LOI
500	59.64	6.81	1.29	4.02	13.19	1.80	1.67	0.21	0.06	0.17	2.19	1.84	11.77
250	70.73	8.36	1.27	1.89	7.07	1.91	1.94	0.22	0.03	0.16	0.15	3.90	6.42
125	62.96	9.95	2.96	3.09	8.74	2.30	2.04	0.59	0.08	0.20	0.35	1.89	7.07
63	53.13	9.20	8.00	4.56	10.34	2.20	1.83	1.68	0.16	0.28	1.86	0.54	8.62
58	47.63	8.57	10.25	5.23	12.27	2.05	1.55	2.16	0.19	0.25	1.74	0.94	9.85
	48.27	8.25	10.53	5.45	12.23	2.24	1.48	2.15	0.20	0.24	1.99	0.69	8.95
47	58.30	9.07	2.81	4.30	10.50	2.28	1.98	0.58	0.06	0.24	2.10	0.57	10.14
	58.16	8 92	2.93	4.15	10.49	2.26	1.19	0.59	0.08	0.25	2.27	0.42	10.26
34	59.88	8.34	2.46	4.33	9.69	2.20	1.99	0.48	0.06	0.22	1.97	0.66	10.16
	59.70	8.66	2.38	4.28	9.79	2.24	2.01	0.49	0.05	0.23	1.89	0.70	10.16
23	59.72	8.84	2 72	3.67	9.98	1.99	2.12	0.50	0.07	0.22	2.43	0.52	10.17
	59.71	8.80	2 69	3.95	9 77	1.96	2.10	0.54	0.06	0.23	•	•	10.17
16	57.93	9 43	3.48	3 18	9 81	1.88	2.26	0.58	0.11	0.23	2.25	1.34	11.11
	58.39	9.07	3.24	3.44	9.71	1.90	2.20	0.60	0.09	0.24	•	•	11.11
<13	50.67	11.90	6.53	3.11	9 25	1.37	2.73	0.76	0.20	0.29	•	•	13.20
Canadian Soil Standards													
SO-1	54.78	17.42	8.63	3.73	2.43	2.60	3.24	0.85	0.11	0.15	•	•	6.00
SO-4	68.55	10.43	3.40	1.00	1.50	1.33	2.11	0.59	0.08	0.21	•	•	10.80

• - no data

and mean particle size are presented in Tables 5 and 6 for Big Creek and Big Otter Creek, respectively. Geochemical variation in solids composition between grain size fractions of both fluvial sediment types is evident (Tables 3 and 4). However, there are significant relationships between P and other sediment parameters which are common to both fluvial sediment types (Tables 5 and 6). The sediment P content increased with the concentration of metal oxides (Al, Fe, Ti, Mn) and loss on ignition (LOI) while the concentrations of P and Si exhibit an inverse relationship. There is an inverse relationship between P and particle size which illustrates a trend of increasing P content with decreasing grain size in sediment from Big Creek and Big Otter Creek. A complete discussion and interpretation of these relationships with respect to phosphate adsorption as a function of grain size is found in Chapter 4.

3.3 PHOSPHATE ADSORPTION BY GRAIN SIZE

To evaluate the effect of particle size on P adsorption, experiments were designed to compare the adsorption behavior of grain size fractions of an experimental sediment (pure silica sand) with natural river sediment (Big Creek and Big Otter Creek).

Phosphate adsorption data for grain size fractions of silica sand, Big Creek and Big Otter Creek sediment are given in Tables 7, 8 and 9, respectively. In these tables the mean and standard deviation of triplicate analyses are presented.

Adsorption isotherms for ten grain size fractions of silica sand, Big Creek and Big Otter Creek are presented in Figures 13, 14 and 15, respectively. In these figures, each line represents a least squares fit to the non-constrained

TABLE 5 BIG CREEK Correlation coefficients between sediment properties (n=10)

Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	P	LOI	Langmuir Coefficients Γ_m	Langmuir Coefficients K	Mean Particle Size (μm)	
1.00	n.s.	−.81••	n.s.	−.68•	n.s	− 52	−.49	−.90•••	− 93•••	−.88•••	− 56•	n.s.	.64•	Si
	1.00	.61•	n.s.	−.45	n.s.	.75••	n.s.	.46	.55•	n.s.	n.s.	n.s.	−.80••	Al
		1.00	n.s.	n.s.	n.s.	n.s.	.82••	.92•••	.84••	51	n.s.	n.s.	−.63•	Fe
			1.00	.63•	.53	−.52	n.s.	n.s.	n.s.	n.s.	n.s	n s	n.s.	Mg
				1.00	n.s.	n.s.	n.s.	.47	.45	65•	n s	n.s	n.s.	Ca
					1.00	− 44	n.s.	−.46	−.45	−.63•	− 53	n.s.	n.s.	Na
						1.00	n.s.	.53	.73••	.62•	47	n.s	− 68•	K
							1.00	.60•	.45	n.s.	n.s.	n.s.	−.48	Ti
								1.00	.94•••	.75••	n s	n s	−.54	Mn
									1.00	.84••	55•	n s	−.69•	P
										1.00	.68•	48	−.51	LOI
											1 00	.95•••	n.s.	Γ_m
												1 00	n.s.	K
													1.00	Mean Particle Size (μm)

Values not marked are significant at the 10% level; those marked with a "•" are significant at the 5% level; those marked with a "••" are significant at the 1% level; those marked with a "•••" are significant at the 0.1% level; "n.s." indicates no significant relationship between the factors at the 10% level.

TABLE 6 BIG OTTER CREEK Correlation coefficients between sediment properties (n=10)

Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	P	LOI	Langmuir Coefficients Γ_m	Langmuir Coefficients K	Mean Particle Size (μm)	
1.00	n.s.	-.86***	-.73**	-.58*	n.s.	n.s.	-.77**	-.91***	-.78**	-.56*	n.s.	n.s.	n.s.	Si
	1.00	n.s.	n.s.	-.49	n.s.	.78**	n.s.	.53	.67*	n.s.	.74**	n.s.	-.66*	Al
		1.00	.59*	n.s.	n.s.	n.s.	.96***	.94***	.66*	n.s.	n.s.	n.s.	-.44	Fe
			1.00	.79**	n.s.	-.54	.69*	.45	n.s.	n.s.	n.s.	-.57*	n.s.	Mg
				1.00	n.s.	-.53	n.s.	n.s.	n.s.	.49	n.s.	-.56*	n.s.	Ca
					1.00	-.68*	n.s.	n.s.	n.s.	-.63*	n.s.	n.s.	n.s.	Na
						1.00	n.s.	n.s.	n.s.	n.s.	.75**	n.s.	n.s.	K
							1.00	.80**	.54*	n.s.	n.s.	n.s.	n.s.	Ti
								1.00	.74**	n.s.	.43	n.s.	-.43	Mn
									1.00	.46	.43	n.s.	-.77**	P
										1.00	.51	n.s.	n.s.	LOI
											1.00	.48	n.s.	Γ_m
												1.00	n.s.	K
													1.00	Mean Particle Size (μm)

Values not marked are significant at the 10% level; those marked with a "*" are significant at the 5% level, those marked with a "**" are significant at the 1% level, those marked with a "***" are significant at the 0.1% level; "n.s." indicates no significant relationship between the factors at the 10% level

TABLE 7 SILICA SAND PHOSPHATE SORPTION DATA
(μg P adsorbed/ gram sediment)
mean values

Median Particle Size (μm)	Initial Phosphate Concentration (μg P/l)					
	0	50	100	200	400	800
500	0	2.33 (0.10)	3.78 (0.88)	6.70 (0.27)	8.00 (0.48)	10.66 (1.02)
250	0	1.61 (0.22)	3.43 (0.76)	4.86 (0.57)	8.49 (1.64)	9.21 (0.67)
125	0	1.57 (0.26)	3.98 (0.55)	5.42 (0.17)	9.06 (0.24)	9.85 (0.73)
63	0	1.63 (0.18)	2.97 (0.16)	5.07 (0.79)	8.93 (1.17)	13.43 (2.08)
58	0	1.22 (0.16)	1.80 (0.16)	3.59 (0.40)	7.07 (0.35)	11.23 (0.76)
47	0	0.81 (0.10)	1.60 (0.03)	2.64 (0.19)	5.88 (0.31)	9.71 (0.53)
34	0	0.75 (0.00)	1.35 (0.09)	3.18 (0.22)	5.41 (0.52)	9.10 (0.21)
23	0	1.20 (0.10)	1.76 (0.08)	3.07 (0.14)	5.41 (0.16)	8.56 (0.12)
16	0	2.16 (0.20)	3.19 (0.26)	5.29 (0.31)	10.11 (0.05)	18.17 (2.85)
<13	0	1.11 (0.01)	1.90 (0.08)	3.87 (0.27)	7.81 (0.97)	16.68 (1.33)

Values in brackets represent standard deviation about the mean for n=3.

TABLE 8 BIG CREEK PHOSPHATE SORPTION DATA
(μg P adsorbed/ gram sediment)
mean values

Median Particle Size (μm)	Initial Phosphate Concentration (μg P/l)					
	0	50	100	200	400	800
500	-1.31 (0.06)	0.87 (0.25)	1.80 (0.40)	4.56 (0.18)	9.24 (0.13)	15.64 (0.80)
250	-1.25 (0.96)	0.50 (0.33)	1.23 (0.04)	3.43 (0.39)	6.46 (0.14)	10.31 (0.51)
125	-2.03 (0.42)	-0.55 (0.17)	0.64 (0.07)	3.23 (0.14)	8.19 (0.13)	14.92 (0.77)
63	-2.03 (0.29)	-0.17 (0.21)	1.14 (0.13)	4.10 (0.16)	9.54 (0.36)	18.27 (0 81)
58	-1.54 (0.02)	-0.02 (0.02)	1.47 (0.16)	4.27 (0.19)	8.54 (0.10)	15.24 (0 48)
47	-2.20 (0.19)	0.02 (0.14)	1.31 (0.06)	4.04 (0.02)	8.78 (0.66)	16 23 (0.85)
34	-3.06 (0.35)	0.05 (0.14)	1.95 (0.16)	5.77 (0.15)	13.17 (0.13)	24.61 (1 33)
23	-2.85 (0.13)	-0.65 (0.07)	1.41 (0.13)	5.84 (0.13)	14.49 (0.15)	31.26 (0.44)
16	-2.83 (0.10)	-0.26 (0.14)	1.84 (0.03)	6.47 (0.15)	15.43 (0.21)	32.77 (0.60)
<13	-16.19 (0.91)	-5.70 (0.36)	3.36 (0.01)	23.12 (0.74)	57.80 (0.[illegible])	114.66 (0 76)

Values in brackets represent standard deviation about the mean for n=3.

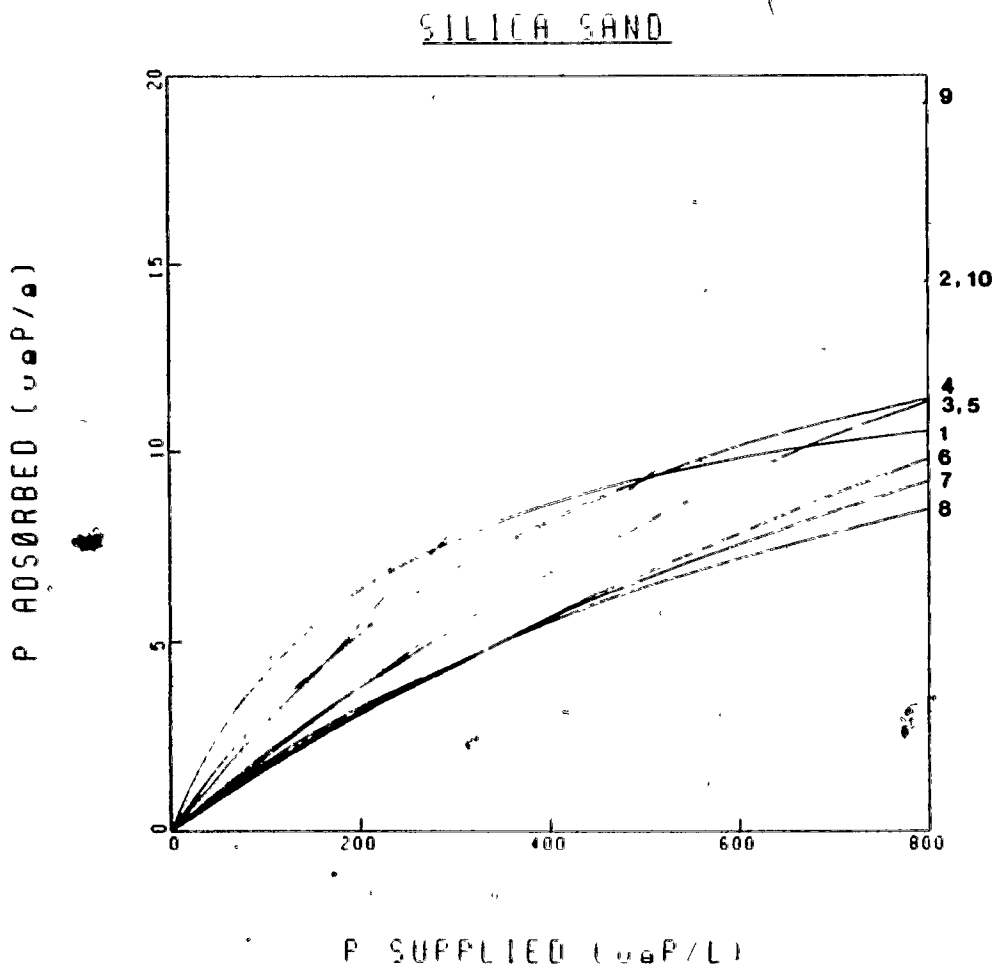
TABLE 9 BIG OTTER CREEK PHOSPHATE SORPTION DATA
(μg P adsorbed/ gram sediment)
mean values

Median Particle Size (μm)	Initial Phosphate Concentration (μg P/l) 0	50	100	200	400	800
500	-0.83 (0.03)	0.43 (0.10)	1.47 (0.13)	3.77 (0.46)	7.88 (0.42)	13.63 (0.92)
250	-0.57 (0.43)	0.51 (0.21)	1.37 (0.10)	3.34 (0.21)	5.49 (0.03)	11.91 (1.64)
125	-0.79 (0.06)	0.55 (0.16)	1.45 (0.20)	2.87 (0.06)	6.14 (0.37)	10.31 (1.48)
63	-0.94 (0.19)	0.72 (0.13)	1.85 (0.16)	4.14 (0.15)	8.12 (0.60)	12.80 (1.02)
58	-0.88 (0.10)	0.43 (0.06)	1.30 (0.32)	3.61 (0.29)	6.98 (0.39)	14.18 (0.20)
47	-0.95 (0.07)	0.58 (0.09)	1.72 (0.14)	2.98 (0.67)	7.98 (0.74)	15.71 (0.03)
34	-1.19 (0.08)	0.46 (0.14)	2.11 (0.15)	4.80 (0.47)	9.61 (0.65)	17.60 (2.87)
23	-1.28 (0.07)	0.79 (0.05)	2.84 (0.05)	6.75 (0.02)	13.79 (0.52)	26.59 (0.87)
16	-1.78 (0.15)	0.87 (0.15)	3.55 (0.12)	8.83 (0.07)	18.69 (0.08)	36.48 (0.73)
<13	-2.83 (0.17)	3.19 (0.09)	7.35 (2.67)	19.51 (0.10)	41.32 (0.23)	82.18 (1.25)

Values in brackets represent standard deviation about the mean for n=3.

Figure 13

Adsorption Isotherms for Silica Sand



Number	Median Particle Size (μm)
1	500
2	250
3	125
4	63
5	58
6	47
7	34
8	23
9	16
10	<13

Figure 14

Adsorption Isotherms for Big Creek Sediment

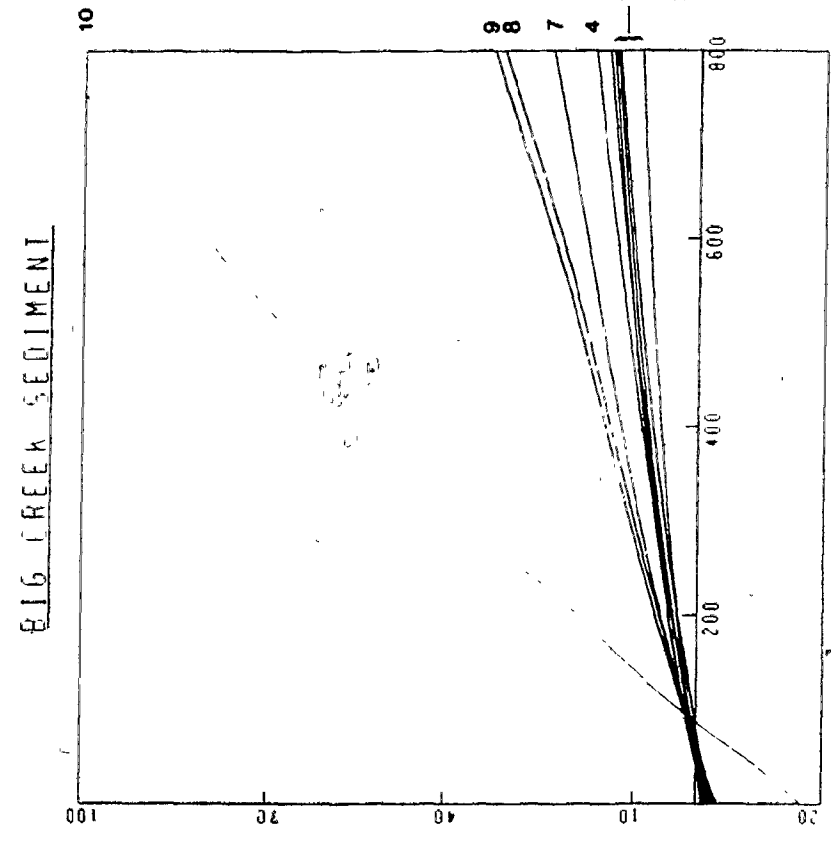
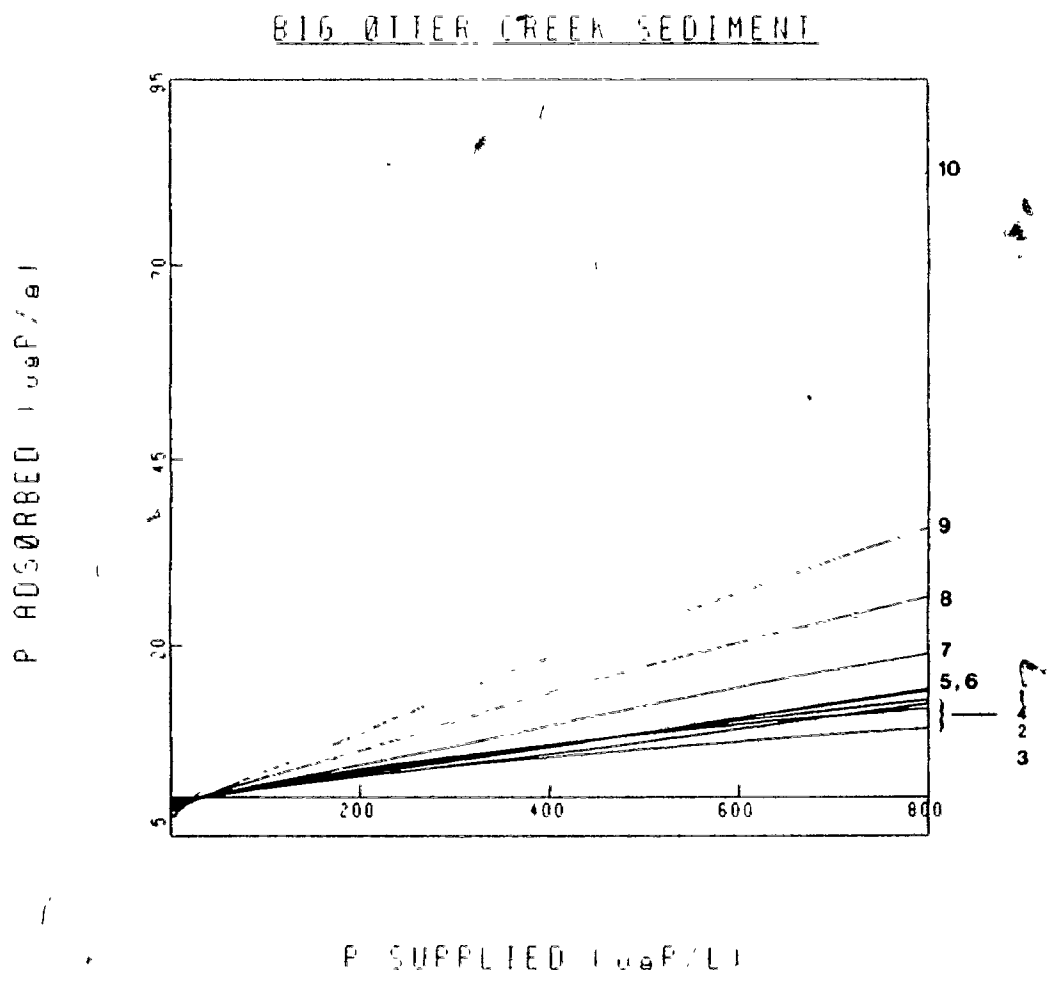


Figure 15

Adsorption Isotherms for Big Otter Creek Sediment



Number	Median Particle Size (μm)
1	500
2	250
3	125
4	63
5	58
6	47
7	34
8	23
9	16
10	<13

form of the Langmuir equation.

Despite differences in phosphate adsorption for each sediment type, the overall shape of the isotherms is similar. The <13μm particle size fraction of both fluvial sediments was the most efficient grain size to adsorb phosphate. In this size fraction, Big Creek sediment adsorbed more phosphate than Big Otter Creek sediment. The 16μm fraction adsorbed the most phosphate of all the silica sand particle size fractions studied. The other particle sizes for all three sediment types adsorbed less phosphate and their adsorption isotherms were grouped more closely together.

Since the adsorption isotherms of silica sand (Figure 13) pass through the origin, phosphate was apparently neither adsorbed nor desorbed from this material when placed in a phosphate free solution. However, Figure 14 and Figure 15 indicate that phosphate was desorbed from Big Creek and Big Otter Creek sediment into solution when placed into phosphate free solution. The environmental significance of phosphate desorbed from sediment into solution will be discussed in the following chapter.

Langmuir parameters (Γ_m and K) were estimated using the P3R program and are presented in Table 10 for comparison according to grain size and sediment type. These parameters will be used to compare the adsorption behavior of various grain size fractions of three sediment types and discuss the relationship between P adsorption and grain size.

TABLE 10 ESTIMATES OF LANGMUIR PARAMETERS

Median Particle Size (μm)	Silica Sand		Big Creek		Big Otter Creek	
	Γ_m	K	Γ_m	K	Γ_m	K
500	14	228	39	1221	45	1835
250	14	340	22	942	441	27079
125	15	308	51	1845	25	1168
63	19	538	101	3337	27	913
58	35	1655	43	1463	145	7160
47	38	2336	55	1843	299	15451
34	26	1490	148	3637	158	5593
23	19	951	1338	30437	234	5907
16	130	4608	806	17360	254	4673
<13	299	15625	560	2877	1589	14132

Units Γ_m ($\mu g\ P\ g^{-1}$)

K ($\mu g\ P\ L^{-1}$)

3.4 WATER ANALYSIS

The chemistry of river water was determined to compare P concentrations in Big Creek and Big Otter Creek and the concentrations that could be predicted from laboratory studies on the equilibrium levels of phosphate in specific grain size fractions of fluvial sediment. Results of this nature may provide information to better understand the role of particle size in the buffering of phosphate by river sediment.

The total P (TP) and dissolved reactive P (DRP) concentrations present in Big Creek and Big Otter Creek, when sediment samples were collected, are presented in Table 11. Although the mean DRP concentrations were similar in both rivers, the TP concentration was higher in Big Otter Creek.

The equilibrium phosphate concentration (EPC), which can be determined experimentally, refers to the phosphate concentration at which no net adsorption or desorption takes place (Taylor and Kunishi, 1971). This empirical reference point, permits a direct estimate of the capacity of sediment to adsorb or release phosphate and gives some indication of the phosphate buffering capacity of sediments. The EPC values of fluvial sediment also indicate approximate phosphate concentrations that might be expected in rivers resulting from the influence of sediment (Taylor and Kunishi, 1971).

The experimentally determined EPC values for grain size fractions of river sediment are presented in Table 12. The EPC values ranged from 24 to 38μgP/L and 39 to 88μgP/L for Big Otter Creek and Big Creek, respectively.

TABLE 11 WATER CHEMISTRY OF BIG CREEK AND BIG OTTER CREEK •

Location		Range	Mean	Standard Deviation	Coefficient of Variation (%)
Big Creek	TP	23–38	28.6	5.7	19.9
	DRP	10–23	15.8	4 3	27.2
	pH	8 3–8.5	8.4		
Big Otter	TP	36–46	39 6	3 5	8.8
Creek	DRP	11–20	15.5	3.2	20.6
	pH	8.3–8.5	8 4		

TP = total phosphorus (ppb)
DRP= dissolved reactive phosphorus (ppb)

• Water samples were taken during the collection of composite sediment samples (September 7, 1986).

TABLE 12 EQUILIBRIUM PHOSPHATE CONCENTRATION of GRAIN SIZE FRACTIONS ($\mu g\ P\ g^{-1}$)

Median Particle Size (um)	Silica Sand EPC	Big Creek EPC	Big Otter Creek EPC
500	0	39	36
250	0	45	36
125	0	81	34
63	0	64	38
58	0	55	34
47	0	60	32
34	0	54	35
23	0	68	24
16	0	60	33
13	0	88	24

Bottom Sediments *

Independence	Composite sample	EPC 24-35
Augalize	"	EPC 24-54
Tiffin	"	EPC 26

*Source: McCallister and Logan, 1978

3.5 SUMMARY

The results of the experimental studies provide information about the effect of particle size and sediment geochemical composition on phosphate adsorption. The results show:

1) Grain size fractions of silica sand, Big Creek and Big Otter Creek sediment (Tables 7, 8, 9) display a trend of increased phosphate adsorption with decreasing grain size and increasing concentration of phosphate supplied.

2) The experimentally derived adsorption maxima (Γ_m) for grain size fractions of silica sand generally increased with decreasing grain size (Table 10), especially in the smaller grain size ranges. Similar results were observed for Big Creek and Big Otter Creek sediment.

3) At higher phosphate concentrations (200-800 μg P/L), the <13μm particle size fraction of fluvial sediment adsorbed the most phosphate of all grain sizes examined. Big Creek and Big Otter Creek sediment had the highest adsorption levels for this grain size which also corresponded to elevated Al, Fe and Mn oxide concentrations (Tables 3 and 4).

4) At low phosphate concentrations (0-100 μg P/L), the larger grain size fractions of silica sand (500, 250, 125, 63 μm) adsorbed more phosphate than similar grain size fractions of fluvial sediment (Tables 7, 8, 9).

5) Increased phosphate desorption occurred with decreasing grain size in both fluvial sediments (Tables 8 and 9) when equilibrated in a phosphate free solution.

6) Significant linear relationships between P and other sediment parameters were observed (Tables 5 and 6). The sediment P content increased with the

concentration of metal oxides (Al, Fe, Ti, Mn) and loss on ignition (LOI) while the concentration of P and Si exhibited an inverse relationship. There is an inverse relationship between the sediment P content and particle size.

7) The experimentally determined equilibrium phosphate concentration for grain size fractions of Big Creek and Big Otter Creek ranged from 39 to 88μgP/L and 24 to 38μgP/L, respectively.

INTERPRETATION AND DISCUSSION

4.1 INTRODUCTION

The purpose of this chapter is to discuss the effect of particle size on phosphate adsorption. Based on the results presented in the previous chapter, adsorption characteristics of ten grain size fractions of an experimental sediment (silica sand) and two fluvial sediments (Big Creek and Big Otter Creek) are compared and interpreted to assess the combined effect of particle size and sediment geochemical composition on phosphate adsorption in fluvial systems.

4.2 PHYSICAL CHARACTERISTICS OF SEDIMENTS

The physical characteristics of in situ sediments from Big Creek and Big Otter Creek varied considerably. While sediment samples were being collected, Big Creek sediment appeared silty and fine grained. Areas of thick black and dark grey ooze were predominant near the river banks and large amounts of organic debris were observed in transport as bedload. In contrast, Big Otter Creek sediment appeared to be sandy, larger grained and generally less organic in nature.

Loss-on-ignition (LOI), which is determined by X-ray fluorescence (XRF) spectrometry, is a measure of the bound water and organic content of sediments. Although the organic C content of grain size fractions of fluvial sediment were determined (Tables 3 and 4), some values are missing. Therefore LOI values were used as a surrogate measure for organic C. Correlation coefficients between LOI and other sediment properties were calculated and

presented in Tables 5 and 6 for Big Creek and Big Otter Creek, respectively. These tables show that LOI is linearly correlated with other sediment parameters which include particle size, Si, P and Γ_m.

The LOI concentrations of Big Creek sediment increased with decreasing particle size ($r=-.51$ $p=0.1$) which implies that larger concentrations of organic matter are associated with the smaller particle size ranges. A similar relationship was observed in bottom sediments of Conception Bay, Newfoundland (Slatt, 1974) and in grain size fractions of Lake Erie sediment (Mudroch and Duncan, 1986) which suggests that in these depositional environments an inverse relationship exists between grain size and organic matter. Slatt (1974) has suggested this may result from the accumulation of light weight organic matter with the finest grained inorganic particles due to the low energy regime in these depositional environments. In contrast to Big Creek sediment, there was no significant relationship between the LOI values and particle size in Big Otter Creek sediment. The poor correlation between these two sediment characteristics may be due, in part, to large magnitude discharges which occur several times a year in this basin (Dickinson et al, 1975). This may produce a flushing effect and therefore reduce the availability of organic matter to sediments within this drainage basin. In addition, the lack of relationship between LOI and particle size in Big Otter Creek sediment may result from the way in which composite sediment samples were fractionated into their constituent grain size fractions (wet sieving and Warman cyclosizer). This procedure may account for a loss of loosely bound organic matter from the sediment.

Although the influence of organic matter on phosphate adsorption has been debated, organic matter appears to affect phosphate adsorption in an

indirect manner. Organically complexed Fe^{3+} and Al^{3+} are the most likely sites for adsorption on organic matter surfaces (Weir et al, 1962; Syers et al, 1971). In the present study, a linear correlation between LOI and Fe (r=.51 p=0.10) was observed in Big Creek sediment. No significant relationship between LOI and Al was found in either of the fluvial sediments. However, in addition to particle size, LOI concentrations of both fluvial sediments were also correlated with P, Si and Γ_m. In Big Creek sediments, LOI was associated with P (r=.84 p=0.01), Si (r=-.88 p=0.001) and Γ_m (r=.68 p=0.05). Similarly, for Big Otter Creek sediments, LOI was associated with P (r=.46 p=0.1), Si (r=-.56 p=0.05) and Γ_m (r=.51 p=0.1). The positive correlations between LOI, Γ_m and P in combination with negative correlations between LOI and particle size suggest that organic matter does influence phosphate adsorption as a function of grain size. The extent to which a specific grain size is coated with organic matter will influence its ability to adsorb P by altering the number of potential adsorption sites available to bioavailable forms of P. As a result a fraction of dissolved inorganic P which might have been preferentially adsorbed onto coated grains or aggregations of sediment may remain in solution and therefore increase the availability of potentially adsorbed P for biotic uptake.

4.3 PHOSPHATE ADSORPTION AND GRAIN SIZE

Adsorption characteristics varied considerably among grain size fractions for each of the sediment types investigated. In tables 7, 8 and 9, it appears that for each sediment type less variation in P adsorption occurred within grain size fractions of each sediment type than between grain size fractions.

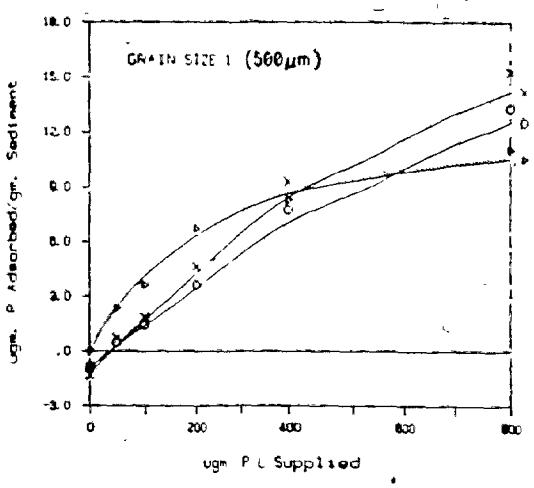
This implies that for a given phosphate concentration, grain size fractions of each sediment type have a relatively consistent adsorption behavior.

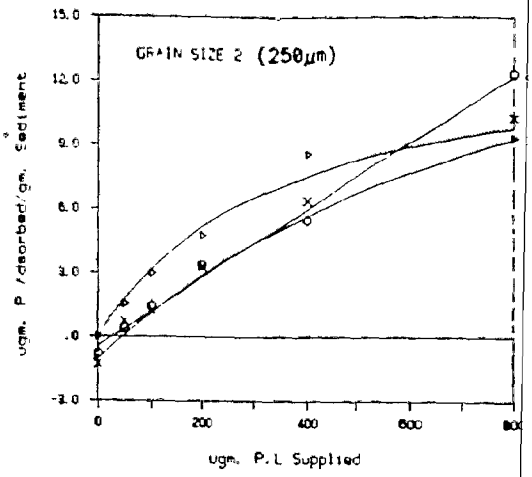
Adsorption isotherms of individual grain size fractions for silica sand, Big Creek and Big Otter Creek are presented in Figure 16. In this figure, each curve represents the least squares fit to the experimental data while the points (designated with a triangle, x and circle) represent the median value of three replicate analyses. Points outside of each graph identify the sediment type for each grain size.

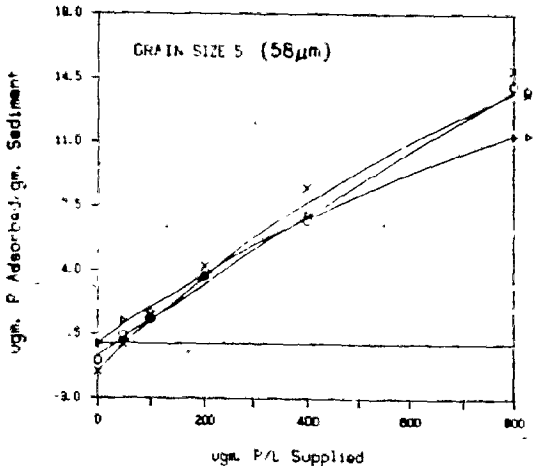
Overall the general shape of adsorption isotherms for each grain size fraction was similar. However, two major differences in the behavior of similar grain size fractions of silica sand and fluvial sediment are apparent in Figure 16; 1) At higher phosphate concentrations (400-800μgP/L), grain size fractions of silica sand generally adsorbed less phosphate than similar grain size fractions of fluvial sediment. Decreased phosphate adsorption in silica sand is especially pronounced in the 34, 23, 16 and <13μm fractions. As previously explained in Section 1.2.3, the presence of oxides of Fe, Al, Mn and organic C on the surface of sediment significantly enhance the adsorption of phosphate. The virtual absence of metal oxides in pure silica sand accounts for the observed adsorption values which are lower than for similar sizes of fluvial sediment. Furthermore, phosphate and silica ions in solution have been shown to compete for the same adsorption sites (Obihara and Russel, 1972; Mayer and Gloss, 1980) which may also account for the lower observed adsorption values of silica sand grain size fractions. At low phosphate concentrations (0-100μgP/L), grain size fractions of silica sand (500, 250, 125, 63μm) adsorbed more phosphate than the two fluvial sediments. This lower range of phosphate concentrations approximates dissolved inorganic phosphate levels found in

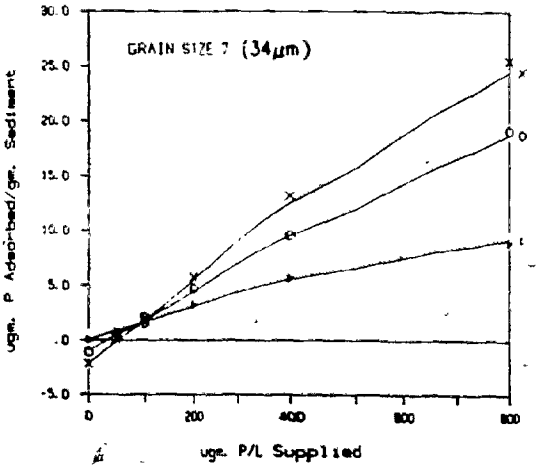
FIGURE 16 COMPARISON OF PHOSPHATE ADSORPTION

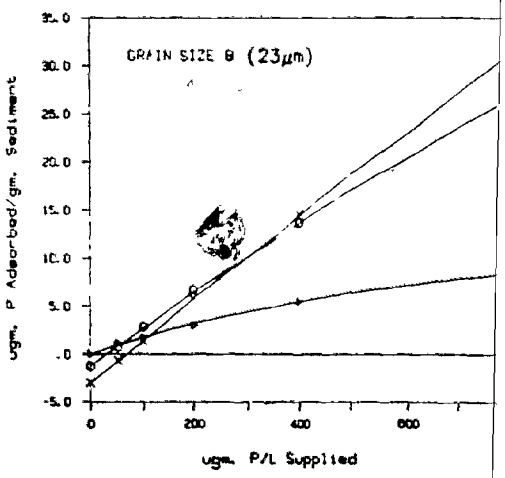
The lines were obtained by least squares fit to the Langmuir equa







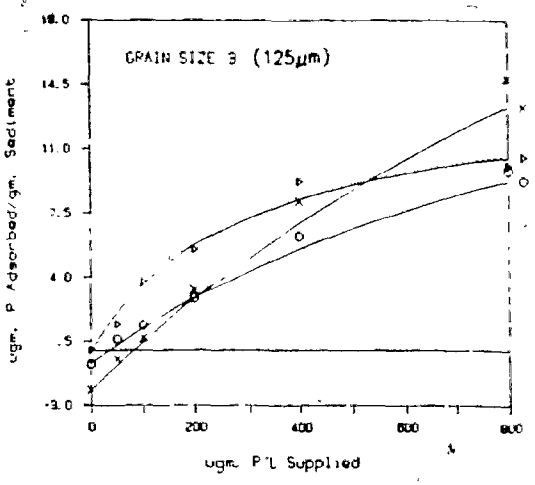


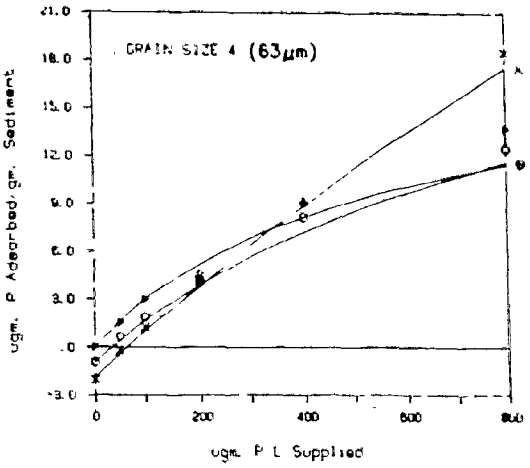


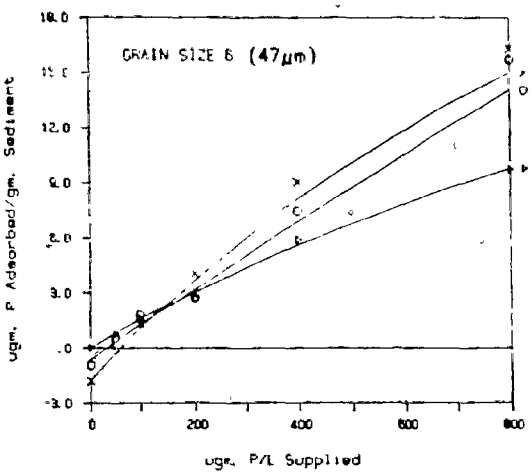
TION BY GRAIN SIZE

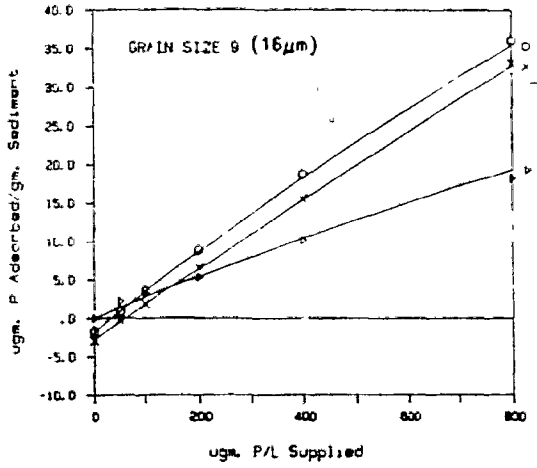
r equation.

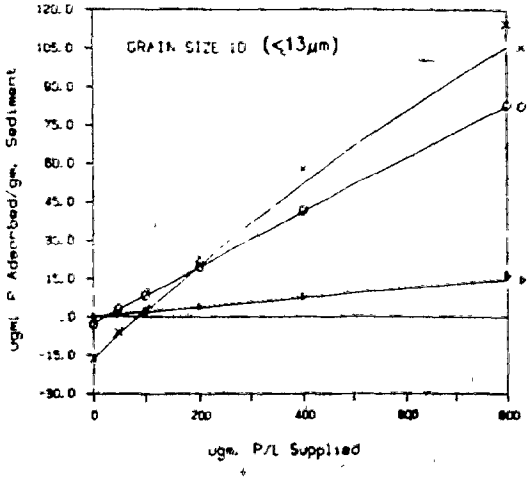
SILICA SAND ▷
BIG CREEK x
BIG OTTER CREEK O











aquatic systems which suggests that medium grain size fractions with a high silica content adsorb more phosphate than smaller grain size fractions of similar composition. 2) In contrast to silica sand, all grain size fractions of both fluvial sediments desorbed phosphate into solution when each fraction was equilibrated in a phosphate free solution. The largest values of desorbed phosphate were generated from the smallest grain size fraction (< 13μm) investigated. Therefore, smaller grain size fractions of fluvial sediment have the capacity to adsorb more phosphate than larger grain size fractions and they also have the potential to desorb more phosphate into solution when dissolved phosphate concentrations in rivers are low.

Phosphate adsorption behavior of grain size fractions generally fall into three groups (Figure 16). The first group, representing medium sand to coarse silt (500, 250, 125, 63, 58, 47μm), exhibits the lowest adsorption, while the second group consisting of medium to fine silt (34, 23, 16μm) adsorbed more than the first group. The third group, which consists of clay minerals (<13μm), adsorbed the most phosphate of all the grain sizes examined.

The relationship between Γ_m and median particle size for each of the three sediment types investigated is presented in Figure 17. In general, there is a tendency for the Langmuir adsorption maxima to increase with decreasing grain size. This becomes increasingly pronounced in smaller fractions of the grain size distribution. Median particle size and estimates of Γ_m were linearly correlated for silica sand (r=-.36 p=0.151), Big Creek (r= -.42 p=0.114) and Big Otter Creek (r=-.27 p=0.222). However, this relationship is complex and appears to be non-linear. Therefore, the use of Pearson correlation coefficients to establish the level of association between these two sediment parameters may be misleading and should be interpreted with caution. Pure silica sand was

used in the adsorption experiments as a control for sediment parameters characteristicly found in fluvial sediment (metal oxides, organic matter) which influence the rate and extent of phosphate adsorption. A comparison of the Γ_m values in Figure 17 for the three sediment types suggests that other sediment parameters, in addition to particle size, are responsible for the adsorption of phosphate to sediment. These parameters will be discussed in Section 4.4.

In Figure 17, a decrease in Γ_m occurred for the 16 and <13μm grain size fractions of Big Creek which may partially result from the procedures used in this study to separate composite samples into grain size ranges. River sediment can consist of aggregates of varying sizes that are composed of finer-textured particles (Ongley et al, 1982; Dorich et al, 1984). Size estimates of bottom sediments can vary depending upon the fractionation technique and the pretreatment methods used (Wall et al, 1978). The particle size ranges fractionated in this study are not absolute because organic matter was not removed from composite samples and no chemical dispersants were used. The reason this methodology was chosen was to keep the chemical characteristics of the fluvial sediment as natural as possible for the adsorption experiments. Because this fractionation procedure does not dissociate soil aggregates into discrete particles without sample pretreatment, the increased chemical activity in the 23μm fraction of Big Creek sediment may result from the aggregation of a large percentage of clay particles. Wall et al (1978) reported that in sediment samples not pretreated before particle size analysis, the percentage of total clay found in the silt and sand sized aggregates ranged from 15 to 60%. This implies that aggregates can be as chemically active as smaller grain sizes although their hydraulic behavior will approximate that of larger grain sizes. Therefore aggregates may play an important role in the transport of

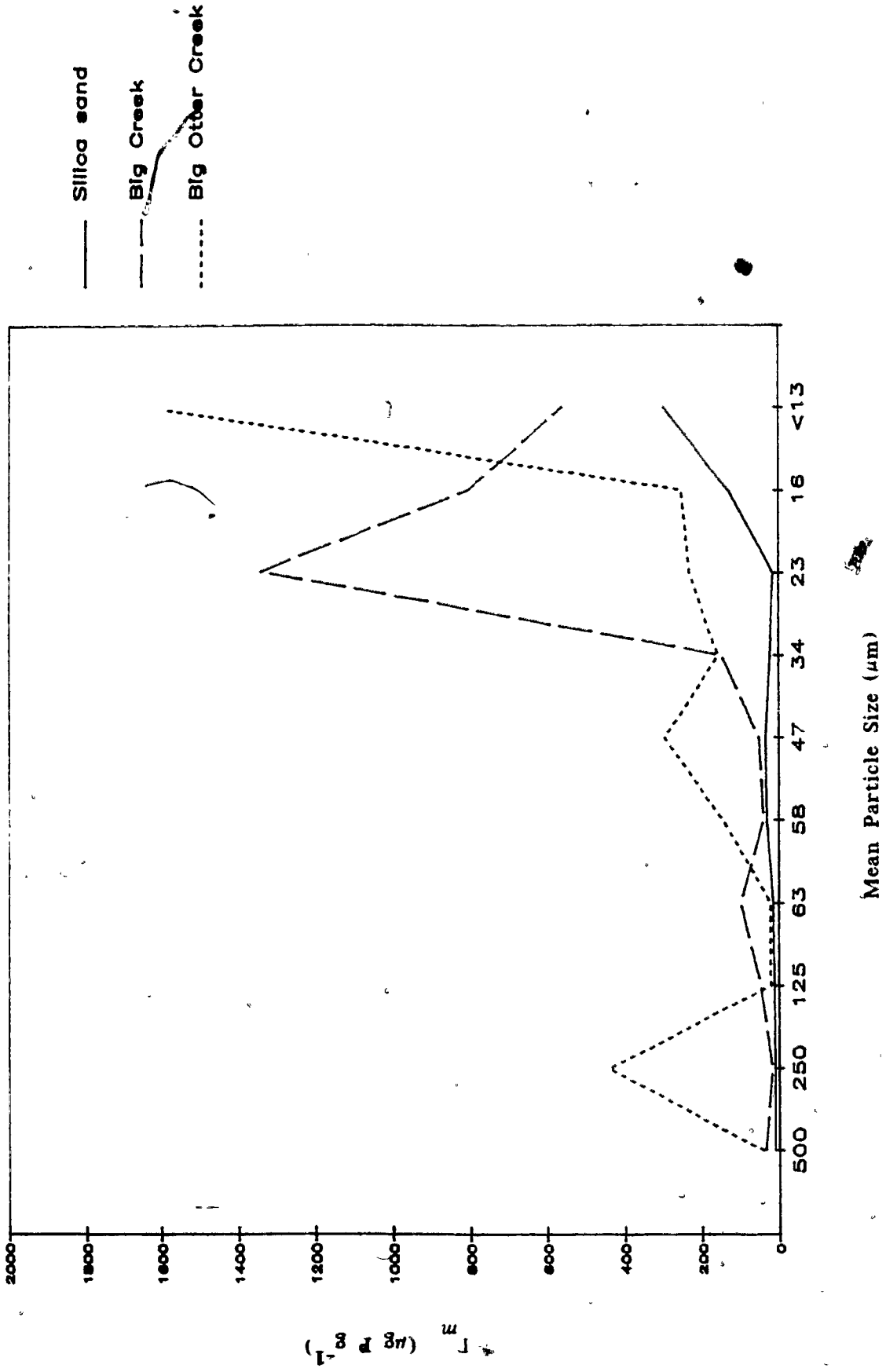


FIGURE 17 Relationship between Γ_m and Grain Size

sediment-associated P through fluvial systems as bed and suspended load.

The relationship between median particle size and estimates of K for each sediment type is presented in Figure 18. Although K appears to increase with decreasing particle size in silica sand, the relationship between these two sediment parameters is less clear for both fluvial sediments.

4.4 SEDIMENT GEOCHEMICAL COMPOSITION AND GRAIN SIZE

The concentration of major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn, P) in separate size fractions of sediment from Big Creek and Big Otter Creek were presented in Tables 3 and 4, respectively. Elemental analyses were performed in duplicate when sample size permitted. The closeness of duplicate elemental analyses of fluvial sediment grain size fractions in these tables suggests that a certain degree of chemical homogeneity exists within each grain size fraction. However, considerable chemical variation is apparent when the chemical composition between grain size fractions are compared.

In sediment from Big Creek, the concentration pattern of SiO_2, abundant as quartz and a constituent of various silicates, ranged from 47.08 to 71.68%, with the lowest concentration of SiO_2 in the <13μm fraction. The concentration of Si increased with mean particle size ($r=.64$ $p=0.05$). Similar concentrations of SiO_2 (47.63 to 70.73%) were found in grain size fractions of Big Otter Creek. No significant relationship ($p=0.10$) was observed between particle size and Si oxide concentration in this sediment type.

In Big Creek sediments, the concentrations of Al, Fe and Mn oxides were distributed in a bimodal fashion over the ten grain size ranges tested. Their high concentrations in the 125 to 58μm ranges is associated with

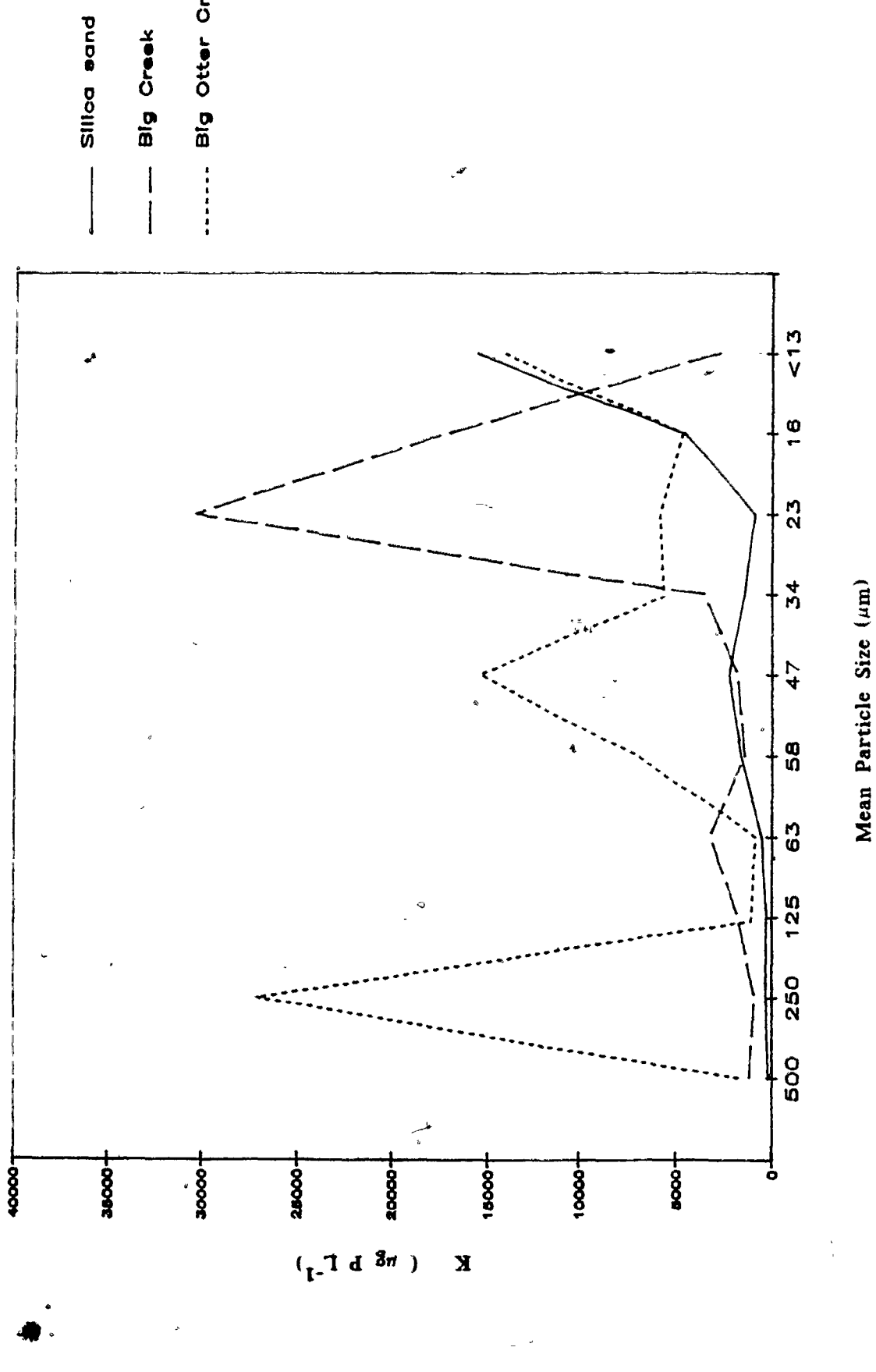


FIGURE 18 Relationship between K and Grain Size

feldspars, whereas the high concentrations of these elements in the <13μm fraction reflect the presence of two clay minerals, illite and chlorite. An inverse relationship was observed between particle size and the oxides of Al (r=-.80 p=0.01), Fe (r=-.63 p=0.05), Ti (r=-.48 p=0.10) and Mn (r=-.54 p=0.10). The sediment P content increased with decreasing grain size (r=-.69 p=0.05). In Big Otter Creek sediment, an inverse relationship was also observed between particle size and the oxides of Al (r=-.66 p=0.05), Fe (r=-.44 p=0.10), and Mn (r=-.43 p=0.10). In addition, the concentration of P increased with decreasing particle size (r=-.77 p=0.01). Therefore, in both sediment types, increased concentrations of P are associated with increased concentrations of metal oxides and organic matter in the smaller grain size fractions.

In both sediment types, a common pattern emerges when the geochemical composition of sediment particle size ranges are examined. Positive correlations were observed between P and the metal oxides in sediment from Big Creek [Al (r=.55 p=0.05), Fe (r=.84 p=0.01), Mn (r=.94 p=0.001), Ti (r=.45 p=0.1)] and Big Otter Creek [Al (r=.67 p=0.05), Fe (r=.66 p=0.05), Mn (r=.74 p=0.01), Ti (r=.54 p=0.1)]. Similar associations between these elements have been previously reported. A relationship between Fe and P in lake sediments has been reported by Frink (1967), Jenne (1968) and Wentz and Lee (1969) while McCallister and Logan (1978) reported a similar association in bottom sediments of the Maumee River in Ohio. Significant correlations between P and Mn in sediments were reported by Delfino et al (1969) and Williams et al (1971). These findings are consistent with the fact that metal oxides on sediment particles act as a substrate for P (Stumm and Morgan, 1980). This accounts for the observed increase of P adsorption in smaller particle size ranges of fluvial sediment compared to the adsorption behavior of similar size

ranges of silica sand thus demonstrating the importance of metal oxides in the retention of P by sediment.

Considerable variation in the chemical composition of fluvial sediment occurs as a function of source rock, grain size, depositional environment, and maturity of the sediment (Pettijohn, 1957). This geochemical variation will in turn influence the nutrient flux in river systems to varying degrees, depending upon sediment type. Previous studies have suggested that P is associated with certain types of sediment in sedimentary environments. Mackereth (1966) and Wentz and Lee (1969) proposed various modes of P association in sediments. These include detrital phosphate minerals (derived from the watershed), phosphate coprecipitated with Fe and Mn, phosphate adsorbed on clays and metaloxyhydroxides, phosphates associated with carbonates and in combination with autochtonous or allochotonous organic matter. In the present study, factor analysis is used to delineate sediment type according to elemental composition and to determine which sediment types are associated with P in Big Creek and Big Otter Creek.

Factor analysis is an extension of correlation analysis and is a technique whereby highly intercorrelated variables can sometimes be separated into disjoint subsets by creating one or more new surrogate variables or factors, each representing a cluster of interrelated variables within the data set (Krumbein and Graybill, 1965). Davies and Wixon (1980) have used factor analysis as a method to investigate the variation in the concentration of elements of surface soil by grouping the elements according to origin. In the present context, factor analysis is used to reduce the geochemical variation in the data sets of Big Creek (Table 3) and Big Otter Creek (Table 4) into new surrogate variables which can be interpreted, geologically as sediment type.

These sediment types will then be examined in terms of their potential association with P in Big Creek and Big Otter Creek.

Factor analysis was performed on the geochemical data sets for grain size fractions from Big Creek (Table 3) and Big Otter Creek (Table 4). Data for inorganic-C and organic-C were not included in the factor analysis because of missing values. The results of this analysis, which include the proportion of the variance explained and the loadings of each variable on the three factors are given in Table 13 and Table 14 for Big Creek and Big Otter Creek, respectively.

Three factors associated with eigen values >1.0 explained 92% of the variance in each of the data sets. In Big Otter Creek, factor 1 is dominated by the elements Si, Al, Fe, K, Ti, Mn and P, factor 2 by Mg, Ca, Na, and Al and factor 3 by Al, Ca, Na and Ti. The factor loadings were slightly different for Big Otter Creek sediment. Factor 1 is dominated by the elements Si, Fe, Mg, Ca, Ti, Mn and P, factor 2 by Al, Mg, Ca, Na, K and P and factor 3 by Ca, and Na.

The chemical composition of a given sediment type is characterized by a specific combination of elements. Factor analysis has divided the geochemical data into three factors, which in the present context, represent sediment types characteristic of these two river basins. The combination of Si, Al, Fe, K, Mn, and Ti in factor 1 is generally associated with clay minerals and metaloxyhydroxides in sedimentary environments (Pettijohn, 1957; Millot, 1970; Blatt et al; 1980). Factor 1 also has a high loading in P and although P is not a component of clay minerals its presence in this factor can be explained as P adsorbed to clay minerals. Factor 2 is comprised of Mg, Ca, Na, and K which in combination with chloride, sulphate and carbonate ions constitute carbonate

TABLE 13 FACTOR ANALYSIS OF BIG CREEK GEOCHEMICAL DATA

Proportion of the data explained by three factors extracted from the variable variances

Factor	Eigen value	% value	Cummulative % variance
1	5.07	50.7	50.7
2	2.59	25.9	76.6
3	1.74	17.4	94 0

The loadings of each variable on each of three factors
Loadings <0 400 [illegible] not quoted

Variable	Factor		
	1	2	3
Si	-0.932	<	<
Al	0.588	-0.554	0 571
Fe	0.929	<	<
Mg	<	0.975	<
Ca	0.411	0.647	-0.617
Na	<	0.454	0 704
K	0.647	-0.631	<
Ti	0 599	0.447	0 621
Mn	0 973	<	<
P	0.977	<	<

TABLE 14 FACTOR ANALYSIS OF BIG OTTER CREEK GEOCHEMICAL DATA

Proportion of the data explained by three factors extracted from the variable variances

Factor	Eigen value	% value	Cummulative % variance
1	4.99	49.9	49 9
2	3 14	31.4	81 3
3	1.07	10 7	92 0

The loadings of each variable on each of three factors
Loadings <0 400 are not quoted

Variable	Factor		
	1	2	3
Si	−0.970	<	<
Al	<	0.873	<
Fe	0.944	<	<
Mg	0.745	0.535	<
Ca	0.496	−0.615	−0 577
Na	<	−0.662	0 703
K	<	0 951	<
Ti	0.893	<	<
Mn	0 924	<	<
P	0.777	0.415	<

and evaporite sediments (Pettijohn, 1957; Krauskopf, 1976). The predominant elements in factor 3 are Ca and Na which in combination with Al and Si comprise feldspar. Feldspar occurs in sandstone, shales and limestone and is predominant in Pleistocene glacial sands (Pettijohn, 1957) The above interpretations are supported by the detection of calcite, dolomite, feldspars, illite and chlorite by X-ray diffraction. However, to further substantiate the proposed geochemical interpretation of these sediments, several qualitative and quantitative mineralogical analyses are required.

Based on the interpretation of these three factors, phosphorus appears to be associated predominantly with clay minerals in Big Creek, whereas in Big Otter Creek, P is associated primarily with clay minerals and to a lesser extent, carbonate sediments.

4.5 EQUILIBRIUM PHOSPHATE CONCENTRATION AND PARTICLE SIZE

The buffering effect of sediment on the nutrient flux in river systems has been demonstrated by research which examined P adsorption characteristics of composite samples of stream bottom sediments (Edzwald et al, 1976; Green et al, 1978). However, these studies did not investigate the role of specific grain size fractions with regards to the exchange of P between sediment and water. The composition and mechanical properties of grains, as well as the mode of transport and deposition all vary with grain size and, in turn will influence the nutrient chemistry of rivers. In this study, the equilibrium phosphate concentration (EPC) of ten grain size fractions of sediment from Big Creek and Big Otter Creek have been determined to provide more information about the effect of grain size on the phosphate chemistry in rivers.

The following calculations demonstrate the reversible nature of the adsorption process and the importance of sediment particles as a potential source of inorganic phosphate in natural waters. In the <13μm fraction of Big Creek sediment, the following values were determined experimentally; EPC=88μg/L, Γ_m=560μg/L. When sediment samples were collected, the mean dissolved reactive phosphate (DRP) concentration of Big Creek was 15.5 μgP/L. Therefore, given the experimentally determined EPC value for a given grain size and the DRP concentration, the amount of phosphate adsorbed or desorbed from a sediment fraction can be determined (DRP - EPC= μgP/L). This shows that for this specific DRP concentration, the 13μm fraction of Big Creek sediment was capable of desorbing 72.5μgP/L from the sediment into solution because the EPC values are higher than the observed DRP concentrations. Therefore, in order for certain grain size fractions to adsorb rather than desorb DRP into these rivers, DRP concentrations of Big Creek and Big Otter Creek would have to range from 39 to 88μgP/L and 24 to 38μgP/L, respectively.

The EPC values of composite fluvial sediment samples from the Maumee river basin, Ohio, ranged from 24 to 54μgP/L (McCallister and Logan, 1978). These values are remarkably similar to the predicted EPC values of Big Creek and Big Otter Creek sediment and are most likely due to the glacial lacustrine origin of the investigated sediments.

4.6 CONCLUSIONS

On the basis of the experimental evidence in this study the following conclusions are presented:

1) Results of the adsorption studies indicate that P adsorption increases in a

non-linear fashion with decreasing grain size. The experimentally derived adsorption maxima (Γ_m) for grain size fractions of silica sand generally increased with decreasing grain size (Table 10). This behavior became more pronounced in smaller grain size ranges (<23μm) of the grain size distribution. Similar results were observed for Big Creek and Big Otter Creek sediment although the Γ_m values of fluvial sediment grain size fractions were generally higher than similar grain size fractions of silica sand.

2) In addition to grain size, sediment geochemical composition and grain mineralogy are important parameters which influence phosphate adsorption. For a given phosphate concentration, each grain size had a characteristic phosphate adsorption behavior which may be due in part, to a degree of chemical homogeneity observed within grain size fractions of fluvial sediment. Significant linear relationships between P and other sediment parameters were observed. The sediment P content increased with the concentration of metal oxides (Al, Fe, Ti, Mn) and loss on ignition (LOI) while the concentration of P and Si exhibited an inverse relationship. There is an inverse relationship between the concentration of P and particle size. Metal oxides associated with clay minerals appeared to be responsible for the increased adsorption of phosphate observed in the small grain sizes of fluvial sediment. Although organic metal oxide coatings may also contribute to increased phosphate adsorption.

3) The phosphate adsorption behavior of grain size fractions of the three sediment types varied with the initial concentration of phosphate supplied. At higher phosphate concentrations (200-800 μg P/L), the <13μm particle size fraction of fluvial sediment adsorbed the most phosphate of all grain

sizes examined. Big Creek sediment had the highest adsorption levels for this grain size which also corresponded to elevated Al, Fe and Mn oxide concentrations (Table 3). At low phosphate concentrations (0-100 μg P/L), the larger grain size fractions of silica sand (500, 250, 125, 63 μm) adsorbed more phosphate than similar grain size fractions of fluvial sediment (Tables 7, 8, 9).

4) With the exception of silica sand grain sizes <34μm, the capacity of grain size fractions of silica sand, Big Creek and Big Otter Creek sediment to adsorb phosphate can be categorized into three phosphate adsorption groups. From the poorest to the most efficient phosphate adsorption group, these groups are; group 1 (medium sand to coarse silt), group 2 (medium to fine silt) and group 3 (clay minerals).

5) When equilibrated in a phosphate free solution, increased phosphate desorption occurred with decreasing grain size in both fluvial sediments (Tables 8 and 9). Therefore, although small grain size fractions adsorb more phosphate than larger grain size fractions, the smaller fractions are also capable of desorbing large amounts of phosphate into solution when the DRP concentration falls below the EPC.

6) The experimentally determined equilibrium phosphate concentration for grain size fractions of Big Creek and Big Otter Creek ranged from 39 to 88μgP/L and 24 to 38μgP/L, respectively. This suggests that sediment from Big Creek can potentially desorb more phosphate into solution than sediment from Big Otter Creek.

4.7 RECOMMENDED FUTURE WORK

The purpose of this section is to make practical recommendations for future studies. These recommendations include consideration of improved experimental technique, sampling strategy and suggested areas for future research.

4.7.1 Experimental Technique

This study has formed the basis of a methodology to asses P adsorption behavior of sediment as a function of particle size. The following recommendations should be considered to improve the experimental technique of future studies;

1) Dissociate soil aggregates into discrete particles before the particle fractionation procedure,

2) Determine the amount of phosphate desorbed from sediment during the process of wet sieving,

3) Investigate the influence of equilibration time, solution pH, temperature and soil-solution ratio on the experimental results,

4) Freeze dry sediment samples.

4.7.2 Sampling Strategy

To account for potential variations in P adsorption behavior resulting from seasonal changes in sediment and to make future studies more holistic in nature, the following sampling strategies are recommended;

1) Sample during various discharge regimes to account for variations

in flow which may influence phosphate sediment dynamics,

2) Sample during various times of the year to account for seasonal variations in temperature, sediment size distribution and sediment coatings which may influence the adsorption behavior of sediment,

3) Compare the sediment adsorption characteristics of river basins with contrasting geology.

4.7.3 Future Research

Recent increased awareness of the role of particulate solids in the transport of pollutants in rivers has focused attention on the need to understand and predict the behavior of suspended solids in natural water systems from the perspective of water quality transformations. Such an understanding would lead to more accurate descriptions of the environmental distribution and accumulation of pollutants adsorbed on particulate solids and in addition, help to determine their impact on aquatic ecosystems and toxicological implications to man.

Sediment particles serve as carriers of P and provide a prime transport medium of this nutrient from the land to the lakes (Miller and Spires, 1978). As discussed in Chapter 1, several researchers have investigated the transport of total P in river systems as a function of discharge. It is generally agreed that the total P load increases with increasing river flow rate and also, is associated with the transport of suspended solids. However the extent to which specific grain size fractions of river sediment participate in this process is not fully understood or well documented. Appropriate methodology is required to determine the phosphate carrying capacity of particle sizes and determine

whether an optimal grain size exists which maximizes the transport of adsorbed P in fluvial systems.

As stated in Chapter 1, the total P transported in river systems consists of a dissolved fraction and a particulate fraction. In this study, fluvial sediment displayed a characteristic adsorption behavior with respect to grain size. Thus a simple model is proposed as an area of future research, to better understand the maximum transport of sediment associated-P (P_{sed}) as a function of discharge (Q), adsorption maxima for a given grain size ($\Gamma_{m_{\phi i}}$) and the weight of a grain size fraction in transport ($wt_{\phi i}$) for a given discharge in fluvial systems. This relationship is stated in the following transport function

$$P_{sed} = f(Q, \Gamma_{m_{\phi i}}, wt_{\phi i}) \tag{10}$$

The conceptual model is developed by assuming that the maximum transport of adsorbed phosphate through river systems is a function of the adsorption maxima for a given grain size fraction, discharge and the weight of each grain size fraction transported for a given discharge. To describe this relationship, the following equation can be written

$$P_{sed} = \Sigma\, Q * \Sigma\, \Gamma_{m_{\phi i}} * wt_{\phi i} * C \tag{11}$$

where P_{sed} = maximum adsorbed phosphate transported (μgP/g sediment)

Q = discharge

$\Gamma_{m_{\phi i}}$ = adsorption maximum for a given grain size fraction

$wt_{\phi i}$ = weight of a grain size fraction for given discharge

C = coefficient (organic matter, metal oxide coatings, DRP concentration in solution)

Such a model, if investigated further, may provide a method to evaluate the P carrying capacity of particle size fractions of sediment in fluvial systems. Such information may eventually lead to the development of sediment-phosphorus rating curves and more accurate estimates of phosphorus loading into lakes and reservoirs.

In addition to a proposed sediment P transport model, the following areas of future research are suggested;

1) Compare the effect of metal oxides associated with sediment surfaces and organic metal oxide coatings on phosphate adsorption,

2) Determine which types of phosphorus are associated with specific grain size fractions,

3) Determine the phosphate adsorption characteristics of sediment grain size fractions in oxic and anoxic conditions,

4) Use the methodology established in this study to examine the adsorption behavior of other nutrients and contaminants associated with and transported by fluvial sediment.

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