DISSERTATION

NUTRIENT DYNAMICS IN AN EFFLUENT DOMINATED RESERVOIR

Submitted by

David Gilbert

Department of Earth Resources

In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Fall 2001

UMI Number: 3038636

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

COLORADO STATE UNIVERSITY

May 25, 2001

WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY DAVID MARK GILBERT ENTITLED "NUTRIENT DYNAMICS IN AN EFFLUENT DOMINATED RESERVOIR" BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

Committee on Graduate Work

Sally J. Sutton

Adviser

Department Head

ABSTRACT OF DISSERTATION

NUTRIENT DYNAMICS IN AN EFFLUENT DOMINATED RESERVOIR

In arid climates, increasing diversion of surface waters for domestic, commercial and industrial use has led to wastewater effluent dominated streams and reservoirs. Downstream use of these waters for irrigation, drinking water supply, wildlife habitat, and recreation, has led to increasing concern regarding water quality. The objective of this research was to quantify hydrochemical loads and nutrient dynamics in an effluent dominated reservoir, Barr Lake, located northeast of Denver, Colorado, USA.

During the three years of study (1997-1999), Barr Lake received annual loads of nitrate-N of 207,000 kg, 164,000 kg and 138,000 kg respectively. Orthophosphate-P loading to Barr Lake during the study was 30,000 kg, 15,000 kg, and 13,000 kg, respectively. Mass budget analysis indicated that nitrogen was removed from the Barr Lake water column in each year of study (139,000 kg, 135,000 kg, and 109,000 kg respectively). Orthophosphate-P retention was indicated by mass budget analysis (18,000 kg, 600 kg, and 3500 kg, respectively), but inclusion of uncertainty in the mass budget calculation indicated that orthophosphate-P was not retained in Barr Lake during 1998 and 1999.

In-lake nutrient dynamics were quantified using depth discrete sampling, sediment analysis, groundwater sampling and laboratory redox manipulation of sediments. Analysis of sediment taken from Barr Lake indicated that only minor amounts of phosphorus are bound to particulates in the sediment, despite the high water column concentration of orthophosphate. Laboratory analysis of sediment phosphorus behavior under controlled redox conditions indicated that the sediment has the capacity to adsorb more phosphorus than in-lake sampling would suggest. The high pH conditions and low CO_2 partial pressures resulting from photosynthetic activity associated with the high nutrient loading to Barr Lake limit sediment removal mechanisms such as orthophosphate adsorption to iron (hydr)oxides and calcite coprecipitation. Competition for adsorption sites by OH^- or SO_4^{2-} is likely the cause of low sediment retention of orthophosphate. Laboratory redox manipulation experiments suggest that organic phase phosphorus is the control on orthophosphate and nitrate is controlled by organic phase removal mechanisms followed by denitrification occurring under moderately reducing conditions in Barr Lake.

David Mark Gilbert
Department of Earth Resources
Colorado State University
Fort Collins, CO 80523
Fall 2001

ACKNOWLEDGEMENTS

The research presented here is the result of several years of collaboration between many individuals and organizations. Particular thanks go to my Graduate Committee: John Stednick, Timothy Steele, Sally Sutton, Grant Cardon, and Willard Lindsay; to those who provided analytical work and data analysis: Louise O'Deen, Steve Brinkman, and Curtis Cooper; and to those who provided funding for this research: The Farmers Reservoir and Irrigation Company, Metropolitan Wastewater Reclamation District, the Colorado State University Agricultural Experiment Station, and the Colorado Water Resources Research Institute.

Thanks also to Tom Sale for patience and Susan Howe for support and understanding during the preparation of this paper.

TABLE OF CONTENTS

List of Figures

List of Figures (continued)

List of Tables

1. Introduction and Problem Statement

Increasing diversion of surface waters for urban use in the western United States has led to the development of "effluent-dominated" aquatic systems. Effluent-dominated systems exist when natural water sources are used in large fraction for domestic, industrial or commercial water supply and are replaced by treated wastewater (Dennehy, et al., 1993). Estimates of treated wastewater in the South Platte River downstream of the Denver, Colorado metropolitan area range from minor fractions during snowmelt periods to over 95% during low flow periods (McMahon, et al. 1995). As a result, reservoirs that are filled using South Platte River water on the eastern plains of Colorado are subject to mass loadings and concentrations of wastewater-related constituents that are atypical compared to lakes and reservoirs usually reported in the limnological literature.

Treated wastewater differs from natural waters in terms of nutrient concentrations (e.g. dissolved nitrogen, phosphorus), concentrations of other constituents (e.g. chloride, sulfate), and ratios between constituents. The addition of wastewater-related constituents to aquatic systems has led to water quality issues such as eutrophication (Dillon and Rigler, 1974; Smith, 1979) and hypolimnetic oxygen deficits (Lasenby, 1975; Cornett and Rigler, 1980). While these conditions are well documented, few studies to date have reported the effluent-dominated hypereutrophic conditions that exist in many reservoirs on the eastern plains of Colorado. The majority of research to date into nutrient loading and dynamics in lakes and reservoirs has been conducted in systems in which treated wastewater inputs are a minor fraction of the overall hydraulic load and mass budgets for nutrients have indicated significant sedimentation of phosphorus and loss of nitrogen in the lake or reservoir (Malueg, et al., 1975; Larsen, et al., 1979; Edmondson and Lehman, 1981). The resulting in-lake nutrient concentrations are typically less than 10% of those observed in effluent-dominated lakes and reservoirs of eastern Colorado.

Anthropogenic sources such as secondary treatment plant effluent have been shown to be responsible for over 70% of the phosphorus entering surface waters in some impacted areas (Larsen, et al., 1979). Although many of the reported systems receive substantial annual loads of phosphorus, dilution flows from unimpacted sources result in in-lake concentrations of phosphorus in the range of 0.01-0.05 mg/L and inorganic N of approximately 0.2 mg/L (e.g. Gale and Reddy, 1994). For this reason, very few systems discussed in the limnological literature can be classified as hypereutrophic (in-lake concentrations of total phosphorus >0.1 mg/L). Other researchers have reported hypereutrophic conditions as the result of wastewater and/or stormwater influxes (Penn et al., 2000), but dilution from groundwater results in low in-lake P concentrations or N:P ratios on the order of 35:1 by weight (Sondergaard, et al., 1990).

Effluent dominated systems in eastern Colorado, by contrast, are characterized by very high concentrations of phosphorus (in the range of 0.10 – 3.50 mg/L orthophosphate as P) and N:P ratios on the order of 10:1 by weight (Stednick and Gilbert, 2000). These very high phosphorus concentrations and relatively low N:P ratios, combined with high loadings and high concentrations of other wastewater related constituents are expected to result in different nutrient dynamics than observed in impacted systems that receive significant dilution flows.

In addition to the limited information regarding the chemical behavior of effluent-dominated systems, few studies to date have rigorously included chemical loading uncertainty into the analysis of nutrient cycling. Previous efforts to evaluate the uncertainty in mass loading estimates have focused on error associated with the hydrologic component (LaBaugh and Winter, 1984; LaBaugh, 1985), or use estimates of error based on a fraction of the calculated load (e.g. Reckhow, 1979; Reckhow and Chapra, 1979). Estimation of the uncertainty is conducted assuming a normal distribution and using Monte Carlo simulation to develop a loading distribution (Winter, 1981). To date, attention to error associated with other components of the mass loading estimate have not been identified in the literature. In addition to error associated with the hydrologic component, error is also introduced into the mass loading estimate through uncertainty associated with the concentration measurement. Since financial constraints limit the number of water quality samples that can be included in any study, uncertainty is introduced to the mass loading estimate by the method used to extrapolate between water - quality sampling dates (Dann et al., 1986). Other sources of uncertainty to the concentration measurement include analytical error, sampling error and natural variability (Gilbert, 1987). These sources of uncertainty have not been explicitly addressed in the existing literature.

Application of existing conceptual models of nutrient cycling to effluent-dominated systems is also limited. The generally accepted model (referred to as the Fe:P model) for the control of aqueous phase orthophosphate in limnic systems is based on adsorption of the PO_4^{3-} ion (and related protonated species) to the surface of amorphous iron (hydr)oxides at the sediment-water interface (e.g. Mortimer, 1942; Lotse, 1973; Lijklema, 1977). This model is based on the assumption that aqueous-phase concentrations of PO_4^{3-} are minor relative to available sorption sites, that pH and Eh conditions are met, and that competing ions are in low concentration. In effluent-dominated systems, the combination of high concentration of nutrients in the water column and high annual external loading of nutrients may limit or preclude the application of this model. Other conditions, such as pH and Eh, may also limit the capacity for formation of iron (hydr)oxides and/or may result in competition for adsorption sites by hydroxide ions. High concentration of other ions frequently present in effluent dominated systems (e.g. SO_4^{2-}) may also compete for sorption sites, and high pH or calcium concentrations may contribute to phosphorus removal mechanisms not addressed by the Fe:P model. Additionally, relatively shallow reservoirs which are not subject to seasonal thermal stratification are not expected to behave as described by the Fe:P model. Alternate models for phosphorus removal have been advanced for calcareous systems in which coprecipitation with calcite and/or precipitation of hydroxyapatite are considered controls on phosphorus. These systems are considered to be supersaturated with respect to calcite at pH values typically observed in eutrophic lakes and reservoirs. Difficulties in application of this type of model to high sulfate hypereutrophic systems, is the control on calcium by gypsum precipitation and decreased partial pressure of CO_2 by phytoplanktonic uptake (Livingstone, 1963, Hem, 1992).

The lack of understanding of nutrient dynamics in effluent-dominated lakes and reservoirs has led to confusion in the management and control of nutrients entering these systems. Differences in behavior of these systems compared to those described in the existing literature has led to misguided reclamation efforts and, in some cases, inaction. With increasing interest in the recreational and wildlife value of these effluent-dominated systems, greater understanding of the nutrient loading and dynamics will provide necessary information to direct water quality management, and decisions regarding wastewater treatment and water-rights exchange policy. To this end, this research intends to provide characterization of loading and nutrient cycling in effluent-dominated systems that are common in eastern Colorado.

2. Objectives

The goal of this study was to assess the loading and fate of orthophosphate and nitrate in effluent-dominated reservoirs using Barr Lake as an example. Historically, Barr Lake has received over 50% of its annual water volume as treated wastewater. To understand the nutrient dynamics of these effluent-dominated systems, the hydrochemical mass (volume multiplied by concentration) entering and exiting the reservoir was quantified to evaluate retention or release of chemical constituents. Once the overall hydrochemical budget for the lake or reservoir was understood, mechanisms of retention or release of specific constituents were examined.

Specific study objectives were to:

1. calculate an annual chemical mass balance for Barr Lake using input and output fluxes for calcium, sodium, nitrate, orthophosphate, and sulfate;
2. evaluate in-lake phosphorus retention mechanisms using field data and laboratory based analysis of sediment taken from Barr Lake.
3. evaluate in-lake nitrogen dynamics in Barr Lake, using field data and laboratory based analysis of sediment taken from Barr Lake.

In a larger context, this work provides a rigorous analysis of the loading and fate of orthophosphate and nitrate in an effluent-dominated reservoir.

3. Background

3.1. Fate of phosphorus and nitrogen in effluent dominated systems

The addition of nitrogen and phosphorous to effluent dominated receiving waters leads to several water quality issues. The primary concern is the intensification of biological productivity which may lead to accelerated hydrochemical processes such as hypolimnetic anoxia (Dillon and Rigler, 1974; Rast and Lee, 1978), decreased oxidation reduction (redox) potential at the sediment water interface (Boström, et al., 1988), photosynthetically controlled fluctuation in pH (Otsuki and Wetzel, 1972) and concurrent changes in solubility of related constituents (Nurnberg, 1988). To better understand how phosphorus and nitrogen behave in effluent dominated lakes and reservoirs, a review of nutrient sources and potential retention mechanisms is provided in the following section.

Phosphorus in natural aquatic systems generally originates from the weathering of phosphate bearing minerals (e.g. phosphate rich volcanics, hydroxyapatite, vivianite, variscite), while anthropogenic sources contribute significantly greater loadings than those observed in unimpacted systems (Pettersson, et al., 1988; Stumm and Morgan, 1996). Phosphorus in the aqueous phase exists primarily as the orthophosphate ion (PO_4^{3-} and associated protonated forms) and has a low solubility relative to other nutrients such as NO_3^- (Lindsay, 1979). Aqueous phase orthophosphate is generally considered a limiting nutrient in aquatic ecosystems, an increase of which often leads to increased primary productivity (e.g. Levine and Schindler, 1989; Haraughty and Burks, 1996; Bulgakov and Levich, 1999). In effluent dominated systems, high external orthophosphate loads are expected to accumulate through one or more of the following mechanisms:

1. accumulation in planktonic biomass and subsequent precipitation as organic phase phosphorus.
2. surface adsorption to amorphous phase minerals or clays; or
3. supersaturation and precipitation of mineral phase phosphate

Nitrogen by contrast, is abundant (in the atmosphere) but is limited in aquatic systems due to high activation energies associated with dissolution of atmospheric nitrogen. Nitrogen in the aqueous phase under oxidizing conditions exists as the nitrate anion (NO_3^-). Reduced forms of aqueous phase nitrogen (e.g. NO_2^-, NH_4^+) can reach high concentrations but are thermodynamically unstable relative to nitrate in the presence of atmospheric oxygen (Lindsay, 1979). Aqueous phase nitrate is expected to cycle through planktonic biomass and:

1. accumulate in organic sediment, or
2. be released back to the aqueous phase upon mineralization of the organic molecule.

Denitrification of inorganic nitrogen (aqueous) is also possible under the reducing conditions commonly observed in effluent-dominated systems (McMahon, et al., 1995) and denitrification is considered to be the dominant loss mechanism for nitrogen in many lakes (Seitzinger, 1988; Lijklema, 1994).

Organic phase phosphorus and nitrogen

Phosphorus in many aquatic systems has been speculated to be the limiting nutrient for phytoplankton growth (Downing and McCauley, 1992; Haraughty and Burks, 1996). Phosphorus rich lithologies are not abundant and atmospheric sources tend to be limited (Pettersson, et al., 1988). Addition of minor amounts of nitrogen and phosphorus to aquatic systems is generally adequate to increase algal growth and may result in nuisance algal blooms (e.g. Knowlton and Jones, 1996; Levine and Schindler, 1989). in general, nutrients in limnic systems are consumed by aquatic organisms and depleted from the water column. Previous studies suggest that planktonic organisms are continually consuming and releasing aqueous phase orthophosphate and nitrogen and that the turnover rate is on the order of minutes during active periods (Rigler, 1964). Phosphorus and nitrogen in the organic phase are bound within the carbon-oxygen molecule of plant, planktonic, bacterial, and detrital material. Algal biomass is reported to have the theoretical chemical ratio C:N:P of 104:16:1 (Stumm and Morgan, 1996) or the commonly used Redfield ratio C:N:P of 106:16:1 (Redfield, et al., 1963). This ratio reflects the relative importance of the macronutrients in aquatic systems. Since carbon is readily available from atmospheric CO_2, and weathering of carbonate minerals, nitrogen: phosphorus ratios (N:P) are more commonly used to compare nutrient availability to nutrient requirement (Hecky, et al., 1993).

The concept of nutrient limitation in aquatic systems has received much attention with respect to deviation from the stoichiometric ratios listed above (Gibson, 1971; Rhee, 1978; Levine and Schindler, 1992). Empirically derived values reported for the N:P ratio (molar) in aquatic biomass range from 44:1 in phosphorus deficient algae to 22:1 for non-phosphorus deficient algae (Downing and McCauley, 1992) and are species specific

(Rhee, 1978). Other researchers have suggested nitrogen limitation in systems where N:P is less than 12:1 (by weight)(Dillon and Rigler, 1974; Levine and Schindler, 1989). Other researchers have suggested other ratios (Downing and McCauley, 1992). Regardless of the ratio that implies nutrient limitation, the N:P ratio is useful for comparison between systems and for identifying general shifts in algal species. The difference between theoretical and empirically derived values of N:P is a function of the water quality and limiting nutrients and/or conditions under which the algae were grown (Smith, 1979; Kopacek, et al., 1995; Guildford and Hecky, 2000). Comparison of water column N:P and biomass N:P is intended to provide information on the potential for removal of nutrients from the water column by the organic phase, but demonstrating direct relationships between N:P and production of chlorophyll has proven difficult (Molot and Dillon, 1991). The removal of phosphorus (and nitrogen) from the water column by this mechanism can provide a control on water column nutrient concentrations (Boers, et al., 1998), but is not considered a long term sink for nutrients in aquatic systems other than wetlands (Danen-Louwerse, et al., 1993).

The phosphorus and nitrogen containing organic molecule is relatively unstable chemically (Danen-Louwerse, et al., 1993) and release of soluble phosphorus and nitrogen from organic molecules is generally considered an important source of nutrients to aquatic ecosystems (Rigler, 1964). Phosphorus and nitrogen containing biomass is accumulated in the sediment and becomes available for dissolution to the hypolimnion following degradation or chemical alteration (Jensen and Andersen, 1992; Berner and Berner, 1996). Oxidation of organic biomass provides not only a release mechanism for organic phosphorus and nitrogen but also provides an electron source for the depletion of dissolved oxygen from the sediment solution and the hypolimnion. Under hypereutrophic conditions, high organic mass loading to the sediment is expected, potentially resulting in significant variation in redox conditions at the sediment water – interface (Theis and McCabe, 1978). Redox conditions at the sediment – water interface will affect the fate of both phosphorus and nitrogen in the aqueous phase. Sediment can act as a source or sink of phosphorus to/from the aqueous phase depending on the hydrochemical conditions at the sediment water interface (Baccini, 1985). Several researchers have investigated phosphorus release under anoxic conditions at the sediment water interface (Nurnberg, 1988; Penn, et al., 2000). Nitrate reduction and/or denitrification can occur under the reducing conditions typically achieved under anoxic hypolimnia (Nurnberg, 1988; Lijklema, 1994).

Release of nutrients from the organic phase under oxidizing conditions is dependent on several limnologic variables including degree of thermal stratification, water temperature, and the degree of mixing. Seasonal thermal stratification is a condition that may develop in surface water impoundments as a result of density differences in water of varying temperatures. This density driven stratification provides an isolation of the hypolimnion from atmospheric oxygen diffusion as well as chemical isolation from epilimnetic waters (Berner and Berner, 1996). This isolation may result in conditions of hypolimnetic oxygen deficit or anoxia with particular geochemical significance at the sediment - water interface and within the interstitial waters of the sediment (Stumm and Morgan, 1996, Boström, et al., 1988). The degree of anoxia may limit the release of organically bound phosphorus and nitrogen while simultaneously causing the release of inorganically bound phosphorus adsorbed to redox sensitive sediment mineral phases (see below). The degree of anoxia at the sediment - water interface depends on the availability of reducing agents (e.g. aquatic biomass) and the stability of the thermal stratification (i.e. the degree of mixing with oxygenated waters) (Lee, et al., 1977; Lind, 1987). Previous studies have found that depth of impoundment, climatic conditions and degree of eutrophication are major factors in the development of anoxic conditions in the hypolimnion (Lasenby, 1975; Welch and Perkins, 1979; Cornett and Rigler, 1980; Lind, 1987). The resultant redox conditions in the hypolimnion will thus dictate the rate and extent of release of phosphorus and nitrogen from the organic phase. Oxidizing conditions are expected to result in high phosphorus and nitrogen turnover rate (Rigler, 1964) and reducing conditions are expected to result in organic accumulation, slow phosphorus turnover rate, ammonification of nitrate, and/or denitrification (McMahon, et al., 1995). The organic phase is therefore expected to influence inorganic phase phosphorus and nitrogen by controlling the redox condition at the sediment water interface, controlling the concentration gradient between the sediment phase and the aqueous phase, or both.

Since aqueous nitrogen species are not typically controlled by adsorption processes or by solid phase precipitation, the following section includes inorganic removal mechanisms for phosphorus only.

Adsorption of orthophosphate to clays and metallo(hydr)oxides

The original conceptual model for the control of phosphate concentrations observed in lakes and reservoirs considered surface adsorption of the orthophosphate ion to amorphous ferric hydroxide under oxidizing to moderately reducing conditions (Mortimer, 1941; Hasler and Einsele, 1948). Adsorption and desorption of the orthophosphate ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) ion to the surface of metallo(hydr)oxide solids and clay minerals has been examined extensively by researchers in the past few decades. In general, adsorption (and desorption) are considered to occur on a much shorter time scale than solid phase precipitation/dissolution reactions. Adsorption of phosphate to the surfaces of sediment in lakes and reservoirs has been the focus of much research due to the application of the research to the reclamation of eutrophic systems.

The affinity of PO_4 related species to the surface charge on amorphous ferric hydroxides and clays has been demonstrated in the laboratory (Spear, 1970). Several studies indicate that adsorption of phosphate to ferric hydroxide surfaces can be described using Langmuir adsorption isotherms and adsorption is therefore correlated to aqueous phase phosphate concentration as well as pH (Lijklema, 1993, Golterman, 1995). These studies indicate that reduction of the iron solid phase ($Fe(OH)_3$ of FeOOH) will therefore result in a release of orthophosphate to the soil solution (Mortimer, 1941; Lijklema, 1993; Caraco, et al., 1993).

In general, chemical factors controlling adsorption/desorption in natural systems are (Davis and Kent, 1990):

1. pH - commonly determines the sign of the surface charge

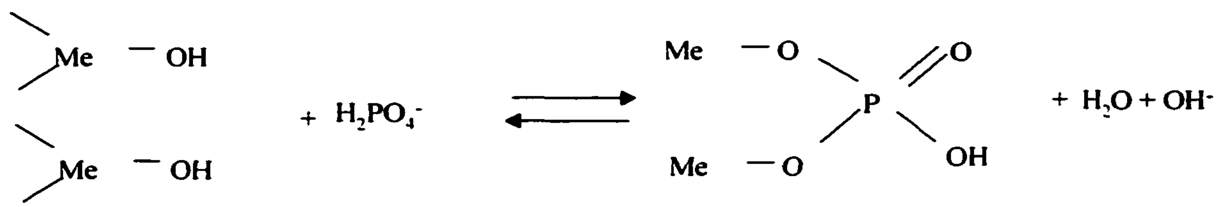
2. ionic strength - affects the influence of the diffuse double layer
3. concentration of adsorbate affects chemical potential between the surface and the solution
4. solid - water ratio - determines abundance of adsorption sites
5. concentration of competing ions - particularly organic anions.

Organic anions have been shown to decrease adsorption of phosphate ions through competition for adsorption sites (de Mesquita Filho and Torrent, 1993; Sibanda and Young, 1986). note: nitrate and chloride have been shown to be largely ineffective in competing with phosphate for anion adsorption sites due to geometrical differences (Grim, 1953).

Clay mineral adsorption has not received much attention, but is considered to be important in some systems (Kuo and Lotse, 1972, Kuo and Lotse, 1974). Existing literature suggests hysteretic behavior of phosphate adsorption-desorption from clay surfaces associated with kinetically differing reactions involved and that desorption tends to be more time and temperature dependent (e.g. Bar-Yosef and Kafkafi, 1978).

This mechanism has its basis in the relatively high surface areas possessed by many of the (hydr)oxides as well as their abundance. Adsorption of ions to the metallo(hydr)oxide surface is considered to be strictly specific (i.e. positive surface charge at low pH values exists on many oxides and hydroxides) and are pH dependent, with the zero point of charge determining adsorptive behavior of an individual solid. In general, sorption to oxide and hydroxide surfaces is considered to consist of two steps, a fast step and slow step, which typically reach equilibrium on the order of days (Portielje and Lijklema, 1993; Barrow and Shaw, 1975). The fast step is diffusion controlled specific adsorption (i.e. binuclear bridging of the phosphate ion to the metallic functional group), and the slow step is thought to consist of either surface precipitation, solid solution formation or micropore diffusion (Davis and Kent, 1990).

In general, adsorption of phosphate to a metallic (hydr)oxide surface is expected to be of the form:



Me is typically the cation Al, Fe or Mn (Lijklema, 1976). Of importance to the general model is the 2:1 Me:P ratio and the apparent dependence of phosphate adsorption on $H_2PO_4^-$. Evaluation of adsorption of HPO_4^{2-} to iron (hydr)oxides suggests a poor relationship (Golterman, 1995). This finding is significant to hypereutrophic systems that frequently exhibit high pH, potentially limiting adsorption as a removal mechanism for orthophosphate.

Research by others have indicated that the ionic composition of the liquid phase may significantly alter the adsorptive characteristics of the metallo(hydr)oxide through sorption of small cations into vacancies in the hexagonal crystalline structure of the general formula Me_2O_3 molecule (Brinkman, 1993). This adsorption would result in a greater positive charge on the surface of the oxide leading to greater adsorptive capacity.

The following section discusses specific metallo(hydr)oxides with regard to phosphate adsorption.

Ferrohydroxides

Ferrohydroxides (includes $Fe_3O_{4(magnetite)}$, $FeOOH_{(goethite)}$, FeOOH, $Fe_2O_{3(hematite)}$, $Fe(OH)_{3(amorph)}$) are traditionally thought to be a major sorbate for phosphate in natural systems under oxidizing conditions (Lijklema, 1977). Several studies have indicated a relationship between ferric iron precipitate (as $Fe(OH)_3$ or FeOOH) and phosphate adsorption (Lijklema, 1980; Ku, et al., 1978). The surface charge on oxides and hydroxides are pH dependent. Zero points of charge are given for several ferro(hydr)oxides (Stumm and Morgan, 1996):

Table 1. Zero point of charge for ferrohydroxide minerals

Solid	**pH_{zpc}**
$Fe_3O_{4(magnetite)}$	6.5
$FeOOH_{(goethite)}$	7.8
$Fe_2O_{3(hematite)}$	6.7
$Fe(OH)_{3(amorph)}$	8.5

Phosphate adsorption to the iron oxides has been shown to be through the formation of a surface complex by the coordination of phosphate ligands (i.e. phosphate ions) to Fe^{3+} ions (Parfitt, et al., 1975; Parfitt, 1977). Specific ferrohydroxides will display differing adsorptive behavior, generally related to availability of surface ferrol (≡FeOH) groups and degree of crystallization, with $Fe(OH)_{3(amorph)}$ having the highest adsorptive capacity (McCallister and Logan, 1978).

Phosphate adsorption to $Fe(OH)_3$ has been shown to increase with decreasing pH and increasing activity of PO_4 in solution (Lijklema, 1980). Phosphate adsorption to goethite has been shown to decrease with increasing pH (consistent with zero point of charge) with distinct changes in adsorptive behavior occurring at the pK values for the deprotonation of orthophosphoric acid (Hingston, et al., 1967). Several studies identified that the effect of speciation of orthophosphoric acid on adsorption onto ferro(hydr)oxides results in decreasing adsorption with increasing pH (Hingston, et al., 1967, Brinkman, 1993). Because adsorption of phosphate is generally considered to be pH dependent, the dominant specie of the orthophosphate ion at a particular pH is expected to affect adsorptive behavior. The hypothesized mechanism for this behavior is the increasing presence of HPO_4^{2-} and PO_4^{3-} with increasing pH occupying two to three adsorptive sites relative to $H_2PO_4^-$ occupying only one (Brinkman, 1993). This is of particular significance in effluent dominated surface impoundments in which pH values typically range from 8.0 – 10.0.

Due to the redox dependency of the formation of the above listed iron (hydr)oxides, their capacity to adsorb phosphate is likewise redox sensitive. This redox sensitive behavior of phosphate adsorption has been hypothesized to be the major controlling factor in the release of phosphate to waters from anoxic lake sediments

(Mortimer, 1942). The hypothesis indicates that when $Fe(OH)_{3(amorph)}$ reduced to $Fe_3O_{4(magnetite)}$ at Eh values in the range of 400 mV, phosphate is desorbed (Lijklema, 1977). This has gained broad acceptance as the dominant mechanism for the frequent observation of phosphorous release from sediments.

Manganohydroxides

The manganese (hydr)oxides are characterized by poorly crystalline structure, high number of structural defects and are prone to solid solution behavior (Sposito, 1990). These attributes lead to potentially significant phosphate adsorptive behavior by the manganese (hydr)oxides. The charge on the surface of the manganese (hydr)oxides is expected to be pH dependent (as discussed above). The zero points of charge for Mn(IV) minerals are given below:

Table 2. Zero point of charge for manganese oxides.

Solid	pH_{zpc}
$MnO_{2(bimessite)}$	2.8
$MnO_{2(pyrolusite)}$	7.2

Few studies have been identified that evaluate the adsorption of phosphate to manganese (hydr)oxides, but the generally low reported zpc would indicate that phosphate adsorption could significantly occur only at very low pH values. Kawishima, et al. (1986) indicated that phosphate adsorption to hydrous manganese oxide (zpc = 2.3) was observed in the presence of alkaline earth cations (e.g. Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}) and that cation exchange with H^+ on the manganol (≡MnOH) functional group, led to a positively charged surface to which phosphate could adsorb. The specific adsorption (or cation exchange) on the surface of the hydrous manganese oxide by divalents were shown to exhibit differing capacities to adsorb phosphate (Ba>Sr>Ca>Mg indicating a geometric dependence on cation adsorption). This type of non-specific adsorption (although not explicitly indicated by the authors) was shown to decrease above pH 7 where it was hypothesized that competition with OH^- led to the decrease (Kawishima, et al., 1986). This behavior is also of significance to effluent dominated surface impoundments in which high pH conditions are common. Other studies have not indicated that non-specific adsorption is significant in the adsorption of phosphate.

Since manganese minerals are highly redox sensitive, the adsorptive capacity with respect to phosphate is also expected to be redox sensitive. Since Mn(IV) is expected to become reduced to Mn(II) under mildly reducing conditions, pyrolusite and birnessite (given above) are expected to be stable in only highly oxidizing conditions (Eh > 600 mV). Although no research has been identified on the adsorptive behavior of Mn(II) mineral phases, it is hypothesized that reduction of Mn(IV) would lead to a similar release of phosphate as observed for iron reduction.

Aluminohydroxides

Aluminum hydroxides are expected to behave as aluminol functional groups with respect to phosphate adsorption. The zpc for several aluminum minerals are given below:

Table 3. Zero point of charge for alumino(hydr)oxide minerals.

Solid	$\mathbf{pH_{zpc}}$
$Al_2O_{3(corundum)}$	9.1
$Al(OH)_{3(bayerite)}$	5.0
$AlOOH_{(boehemite)}$	8.2

As indicated by the zpc for the given minerals, aluminol functional groups will tend to adsorb phosphate at moderate to high pH values and adsorption tends to increase with decreasing pH (Lijklema, 1980).

Calcite

Coprecipitation of aqueous phase phosphorus with calcite has been demonstrated both in field and laboratory studies and is increasingly considered a major control on phosphorus in calcareous systems (Golterman, 1995). Since formation of authigenic calcite is dependent on solution pH, calcium concentration and partial pressure of $CO_{2(aqueous)}$, this removal mechanism is most important in systems exhibiting high pH waters and in systems receiving calcareous wastes (Theis and McCabe, 1978).

Solid phase phosphorus minerals

Agricultural reservoirs are susceptible to significant redox fluctuations at the sediment water interface due to the nature of reservoir operations. Seasonal anoxia is expected to result in increased solubility of redox dependent constituents residing in the sediment (e.g. Fe, Mn) (Lindsay, 1979). The control of solubilities by amorphous phase minerals is expected because crystalline forms are not favored kinetically on the short time frames associated with reservoir operations (filling and draining). Orthophosphate concentrations may change depending on which amorphous phase develops under specific redox conditions.

Few studies to date have addressed the behavior of solid phase phosphorus containing substances at specific redox potentials lower than that commonly achieved in extraction based experimentation. Several experiments have been conducted under which "anoxic" conditions were achieved, but the pe, or Eh, value under which phosphorus activities were evaluated were not reported (Spear, 1970). These experiments indicated that phosphorus release from sediments under anoxic conditions is a kinetically more rapid process than oxic release, and that under oxic conditions, phosphorus release would approach that of release under anoxic conditions given adequate time (Spear, 1970). Equilibrium activity of P under the study conditions was calculated by MINTEQA2 (Allison, et al., 1991) and resulted in a P activity of $10^{-3.15}$ M. Although not specifically discussed, the increase in phosphorus in solution observed under oxic conditions suggests a non-equilibrium state with other solid phase phosphorus minerals such as octacalcium phosphate (i.e. pH = 5.6, P = 0.8 mg/L = $10^{-4.58}$ M). The study was conducted over 1400 hours with increasing phosphate activity over the entire period (under oxic conditions) (Spear, 1970). It is likely that this period was too short for octacalcium phosphate to achieve equilibrium with phosphate activity in solution.

Other experiments evaluated phosphorus solubility in Lake Okeechobee sediments at several Eh and pH values fixed in the laboratory (Moore and Reddy, 1994). This study was based on the premise that "since the reduced forms of Fe and Mn mineral phases are more soluble than their oxidized counterparts, P release from sediments is normally greater under anaerobic conditions than aerobic". This model for phosphorus control at the sediment-water interface is consistent with earlier models and the generally accepted control of phosphorus activity in the hypolimnion of eutrophic reservoirs (e.g. Mortimer, 1941). The study suggested iron solubility controlled the flux of phosphate from the sediment to interstitial waters or across the sediment-water interface and that observed Fe:P ratio can be calculated using stoichiometry assuming that the most stable iron phosphate mineral (i.e. strengite or vivianite) is known (Moore and Reddy, 1994). However, the study did not address the theoretical depression of phosphate solubility under oxidizing conditions by manganese phosphate nor did it attempt to explain the mechanisms responsible for the Fe:P ratios observed in the laboratory.

Studies of the control of phosphate activity in the interstitial waters of sediment have indicated the formation of vivianite and have found that the Fe:P ratio is consistent with vivianite control of soluble phosphate (Emerson and Widmer, 1976; Emerson, 1976). In general, these studies indicate that formation kinetics may prohibit the most thermodynamically favorable control of phosphate activity under oxidizing conditions. The extensive body of literature that exists on phosphorus dynamics in lakes and reservoirs is indicative of the importance of understanding how nutrients behave in aquatic systems such that measures can be taken to improve the water quality of the impacted lake or reservoir. Much attention has been given to nutrient retention and release mechanisms from sediments. The research presented here is intended to add to the existing body of knowledge by providing an extreme case study of nutrient loading and nutrient concentrations. A major goal of this research is to assess aqueous phase phosphorus concentrations under simulated degrees of anoxia without the use of chemical extractants to more accurately simulate the reducing conditions existing at the sediment-water interface and within the interstitial waters of the sediment residing in effluent dominated reservoirs. In addition, pe and pH values will be carefully measured throughout the experiment providing redox potential poises at which soluble phosphorus controls are expected to change.

4. Methods

Barr Lake was selected as a research site due to its proximity to Denver Metropolitan Wastewater Reclamation District (Metro) central facility discharge and because inflows to Barr Lake are often effluent-dominated. The Barr Lake irrigation supply system is owned and operated by the Farmers Reservoir and Irrigation Company (FRICO) of Brighton, Colorado. The system consists of one major diversion canal (the Burlington Canal) that originates at the South Platte River in Denver, Colorado and terminates at Barr Lake. Two outlet structures feed five irrigation canals that extend north from Barr Lake (Figure 1). The water rights associated with the filling of Barr Lake total 33,000 acre-feet (40,705,500 m^3) of water. Water from the South Platte River has been diverted to Barr Lake since establishment of the reservoir in 1885 (Farmers Reservoir and Irrigation Company, 1994). Filling of Barr Lake generally begins in November and continues until the water rights are fulfilled. Excess water, if available from higher than normal precipitation, may also be used to fill Barr Lake, typically occurring during June or July.

Percentages of treated wastewater entering Barr Lake range from 2% to over 90% on a daily basis, calculated using flow records obtained from major dischargers to the South Platte River and the Burlington Canal. The majority of the treated wastewater entering Barr Lake originates at the Littleton-Englewood Wastewater Treatment Plant which discharges to the South Platte River approximately 16 km above the Burlington Canal diversion. Direct discharge of treated wastewater to the Burlington Canal

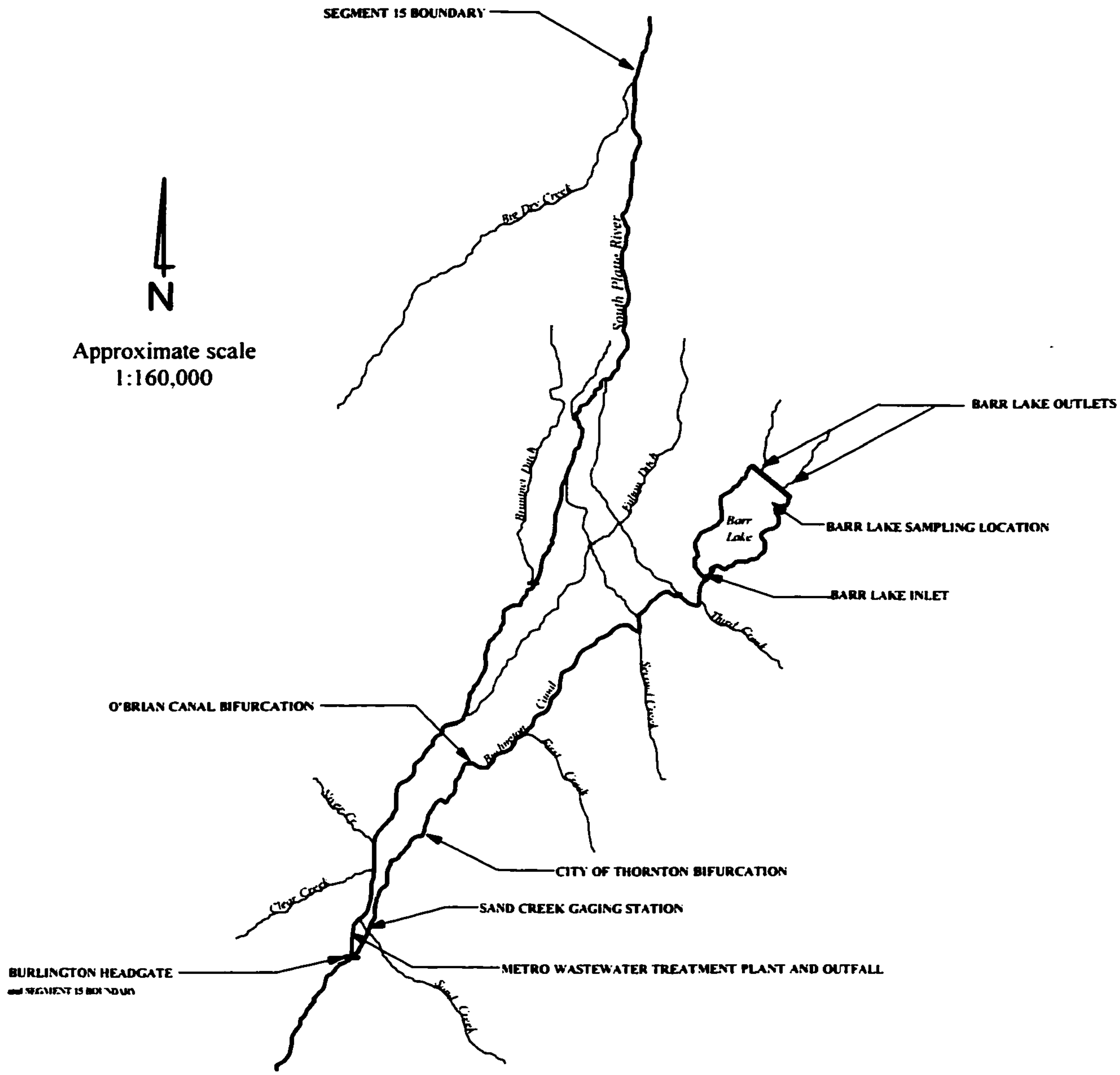


Figure 1. Barr Lake irrigation system.

also occurs from Metro. The direct discharge of treated wastewater to the Burlington Canal varies on an annual basis depending on water availability in the South Platte River.

4.1. Calculation of an annual hydrochemical mass budget for Barr Lake

To understand the fate of nutrients in Barr Lake, annual hydrochemical budgets were conducted on selected constituents from 1997 - 1999. The mass budget for Barr Lake was intended to provide an overall understanding of system behavior with respect to the primary nutrients affecting eutrophication: orthophosphate and nitrate.

In its most basic form, hydrochemical mass loading is simply the product of volume (flow) and concentration. Since the true value of the mass loading is an impractical measurement for most systems (requiring continuous water quality sampling) calculation of mass loading requires some method of extrapolation of concentration between sampling dates. Methods for calculation of solute loading currently in use include periodic mean calculations (e.g. Likens, 1977) or regression based flow-weighted calculations (Dann, et al., 1986; Swistock, et al., 1997), which have been developed in response to data availability (i.e. continuous flow measurement, periodic concentration measurement). Regardless of the method used, the result of the calculation is an estimated chemical mass for a specific time period.

The difference between the input mass loading and output mass loading + Δ storage can be interpreted to be equal to the mass of constituent lost through either a biological or chemical process.

The chemical budget is conceptualized by the equation:

$$R_i = I_i - O_i - GW_i + \Delta S_i \qquad \text{Equation 1}$$

where:

R_i = mass of constituent *i* retained in sediment or biomass

I_i = mass of constituent *i* into Barr Lake (measured at Barr Lake inlet)

O_i = mass of constituent *i* out of Barr Lake in surface water (measured at outlet structures)

GW_i = mass of constituent *i* out of Barr Lake through groundwater seepage

ΔS_i = difference in the mass of constituent *i* in Barr Lake from the beginning of the water year to the end (measured as a difference in volume of Barr Lake on Oct. 1 and Sept. 30)

The initial step in calculation of the chemical budget for Barr Lake was to quantify the amount of water associated with each component Equation 1.

4.1.1. Water budget

Barr Lake is an ideal system for calculation of a water budget, because all surface inflows and outflows have permanent flow - measurement structures (either broad crested weir or flume). To estimate the volume of water through Barr Lake, a daily water budget was calculated for water years 1997 through 1999 (October 1 – September 30). Surface water influent and effluent volumes were measured at stations immediately upstream of

Barr Lake and the outlet works, respectively (Figure 2). To complete the mass budget, an estimate of mass flux to the groundwater was required. In this analysis, the residual method was used to estimate the hydraulic flux to groundwater. The residual method required that precipitation and evaporation volumes be determined for Barr Lake. Daily precipitation values were obtained from a nearby (approximately 5 km) U.S. National Weather Service Station (Denver International Airport, Colorado) and multiplied by the surface area of the reservoir.

Evaporation was calculated using the Penman estimation equation applicable to open water surfaces (Shuttleworth, 1993):

$$E_p = \frac{\Delta}{\Delta+\gamma}(R_n + A_h) + \frac{\gamma}{\Delta+\gamma}\frac{6.43\left(1+0.536\,U_2\right)D}{\lambda}$$ Equation 2

where:

$E_p =$ evaporation in mm/day

$\Delta = \dfrac{4098\,e_s}{(237.3+T)^2}$

$\lambda = 2.501 - 0.002361\,T_s$

$R_n =$ net radiation exchange for the free water surface (mm/day)

$A_h =$ energy advected to the water body (mm/day)

$\gamma = \dfrac{c_p P}{\in\lambda} * 10^{-3}$

$U_2 =$ wind speed measured at 2 m (m/s)

$D =$ vapor pressure deficit (kPa)

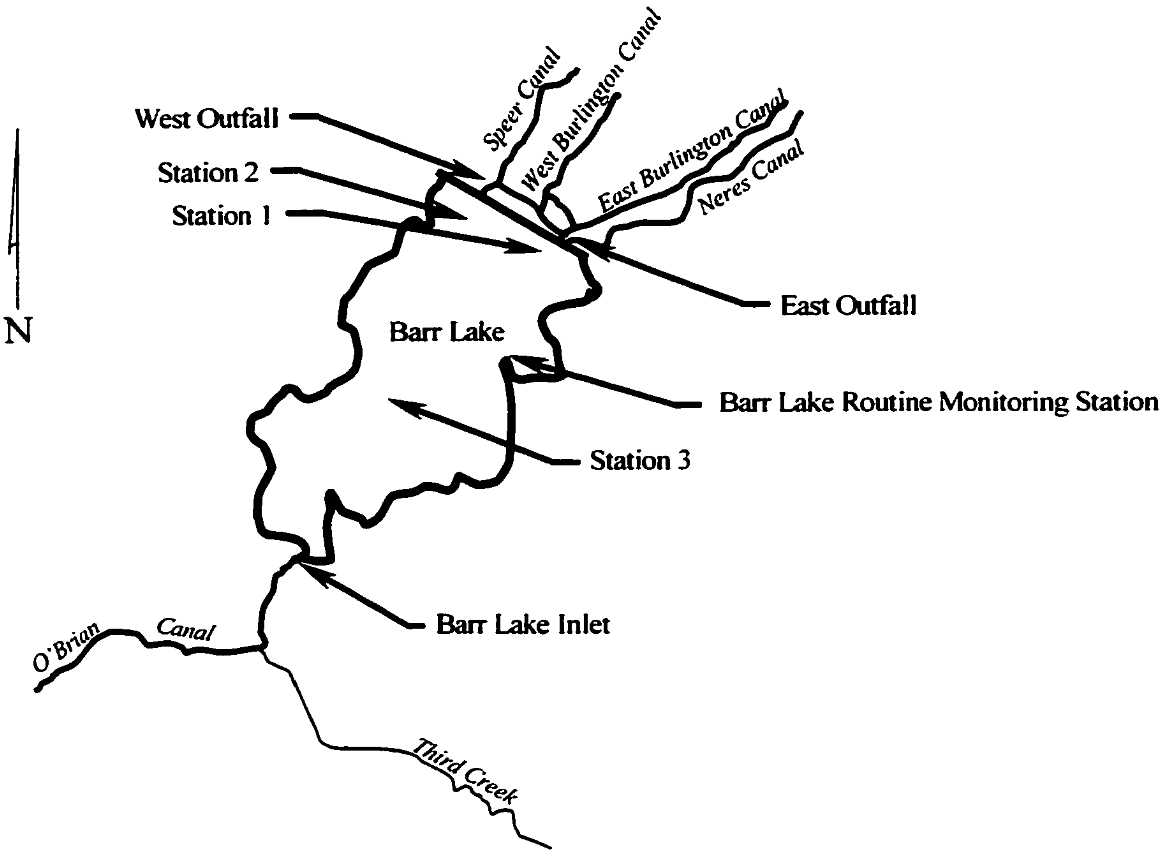


Figure 2. Barr Lake sampling locations

C_p = specific heat of moist air (1.013 kJ kg^{-1} $°C^{-1}$)

P = atmospheric pressure (kPa)

ϵ = ratio of the molecular weight of water vapor to that for dry air (0.622)

T = temperature in °C

Data for input into the Penman Equation were obtained from a Colorado Climate Center weather station located near Fort Lupton, Colorado (approximately 15 km northwest of the study site). Calculated daily evaporation values were multiplied by the daily surface area of Barr Lake to estimate the volume of water lost to evaporation. Because Barr Lake was not subject to complete ice cover during the three years of study, losses due to sublimation were not considered in the hydrologic budget.

Stage measurements in Barr Lake were used to calculate changes in storage using a stage - storage relationship developed by the reservoir operator based on benthic topography.

It was assumed that overland flow to the reservoir is either included in the flow measured at the inlet structure to the reservoir or is negligible given the low lying topography immediately surrounding Barr Lake and generally high infiltration rates.

Daily estimates of water budget components were used in the calculation of hydrochemical fluxes to the Barr Lake system and in error estimation of the hydrochemical budget.

4.1.2. Hydrochemical budget

Chemical constituents used in this analysis were selected on the basis of conservative behavior (sodium) or interest with respect to nutrient loading (calcium, nitrate, orthophosphate, and sulfate). Other nutrient species were included in the overall program (NO_2-N, NH_3-N, NH_4-N, Fe), but a large number of non-detects compromised the calculation of loads. Total phosphorus and total inorganic nitrogen were also included in the overall monitoring program, but are considered to be less important than nitrate and orthophosphate in the Barr Lake system because of short hydraulic retention times.

Water quality samples were taken from the inlet to Barr Lake, the outfall structures from Barr Lake and surficial waters (0.5 m below surface) of Barr Lake (Figure 2). Samples taken at the influent and effluent structures were collected from the approximate centroid of flow. Lateral and vertical variation in concentration is expected to be minimal since all stations are flow measurement structures (i.e. broadcrested weir or flume) located downstream of control structures exhibiting complete mixing and constant velocity cross sections. In-lake samples were collected from approximately 0.5 m below the surface of Barr Lake.

Scheduling for water quality sample collection was based on the schedule of filling and release from Barr Lake. Because Barr Lake is controlled according to water rights, water availability, and is used for irrigation purposes, inlet and outlet canals are often dry.

Samples were collected using 1 L high-density polyethylene (HDPE) bottles or a

1 L VanDorn bottle and transferred to 1 L HDPE bottles, and transported unfiltered and unpreserved (chemically) on ice immediately to the laboratory for analysis.

Major cation (calcium, sodium) concentrations were determined using inductively coupled plasma emission spectroscopy following laboratory filtration. Nitrate, orthophosphate, and sulfate concentrations were determined using ion chromatography.

4.1.2.1. Loading calculations

Because continuous water quality sampling was impractical, the following models were evaluated to extrapolate water quality data between sampling dates:

1. annual mean concentration
2. seasonal mean concentration
3. daily flow versus concentration (regression)
4. time series models (regression)

Models that best fit the data were then used to estimate daily concentrations. Daily modeled concentrations were then multiplied by daily flow and summed over the year using:

$$L_{i,\mathrm{sin}} = \sum_{j=1}^{n} \frac{\hat{c}_{i,j} + \hat{c}_{i,j+1}}{2} \cdot q_j \qquad \text{Equation 3}$$

where:

$L_{i,\mathrm{sin}}$ = the annual load of constituent i based on modeled concentrations

$\hat{c}_{i,j}$ = the modeled concentration value for constituent i at the beginning of period j,

$\hat{c}_{i,j+1}$ = the modeled concentration value for constituent i at the end of period j,

q_j = the total flow for period j.

Annual loading was also calculated using measured concentrations in a moving average method:

$$L_i = \sum_{j=1}^{n} \frac{c_{i,j} + c_{i,j+1}}{2} \cdot q_j \qquad \text{Equation 4}$$

where:

L_i = the annual load for constituent i,

$c_{i,j}$ = the measured concentration of constituent i at the beginning of period j ,

$c_{i,j+1}$ = the measured concentration of constituent i at the end of period j.

Chemical mass inputs from precipitation were considered negligible relative to surface water inputs for all constituents, because both concentrations and volumes are very low compared to influent waters.

4.1.3. Uncertainty analysis

In this research, a bootstrapping method (Efron and Tibshirani, 1993) of estimating concentration uncertainty was combined with Monte Carlo simulation of flow measurement uncertainty. The bootstrapping method consists of random resampling from the set of residuals (from concentration models) with replacement (Efron and Tibshirani, 1986). Residuals used in the bootstrapping procedure were tested for serial correlation using the Durbin-Watson test. Load distributions for each constituent were calculated by substituting the bootstrapped realization for the sampled value, multiplied by the simulated flow during an interval. Monte Carlo simulations of flow were based on published estimates of the uncertainty associated with flow measurement for each component of the hydrologic budget. Error associated with the measurement of the components of the hydrological budget has been estimated at ±5% for flow measurements (flumes), ±10% for precipitation measurements (at the distance to precipitation gages used in this analysis), ±10% for evaporation estimates, and ±50% for groundwater seepage estimates (Winter, 1981; LaBaugh et al., 1997). Interval loads were then summed over the year to yield annual loads for each constituent as given in Equation 5.

$$\hat{L}_i = \sum_{j=1}^{n} \frac{\hat{c}^b_{i,j} + \hat{c}^b_{i,j+1}}{2} \cdot \hat{q}_j \qquad \text{Equation 5}$$

where:

$\hat{c}^b$ = the bootstrapped values of concentration.

$\hat{q}_j$ = total flow simulated for period j

The calculation was repeated for a total of 1000 realizations for both the bootstrapping procedure and the Monte Carlo simulation of flows. The procedure was conducted for the influx, efflux and the budget for each study constituent. The median and 90th percentiles of the 1000 realizations were used to evaluate the input of constituents to Barr Lake.

4.2. Evaluation of in-lake phosphorus retention mechanisms

Once the input-output dynamics of the major chemical constituents were understood in the Barr Lake system, a more detailed analysis of the in-lake nutrient dynamics was undertaken. In this research, both field and laboratory studies were conducted to evaluate possible nutrient retention mechanisms and rates.

4.2.1. Field studies

4.2.1.1. Limnological chemistry

Discrete depth samples were collected from Barr Lake between March 1997 and October 1997. Three profiles were studied, two in the deepest portion of the lake and one in the approximate lake center (Figure 2). Discrete depths studied were: surface, 3 m below surface and at the sediment-water interface. Samples were collected using a 1 L Van Dorn bottle, transferred to 1 L HDPE bottles and transported unfiltered and unpreserved (chemically) on ice immediately to the laboratory for analysis. Cation concentrations (calcium and sodium) were determined using inductively coupled plasma emission spectroscopy following laboratory filtration. Nitrate, orthophosphate, and sulfate concentrations were determined using ion chromatography. In addition to the nutrient and sodium analysis, depth profiles of temperature, pH, Eh, and dissolved oxygen were collected using a YSI Model 6920 Multielectrode at the time of sampling.

4.2.1.2. Groundwater chemistry

To evaluate water quality changes as water from Barr Lake is lost to groundwater, samples of groundwater adjacent to Barr Lake were collected during the period October 1996 - September 1998. Samples were taken from the surface expression of a dewatering drain located at the base of the dam, which represents the chemical condition of the groundwater. Samples were collected in 1-L HDPE bottles, transported unfiltered and unpreserved (chemically) on ice immediately to the laboratory for analysis. Major cation concentrations were determined using inductively coupled plasma emission spectroscopy following laboratory filtration. Nitrate, orthophosphate, and sulfate concentrations were determined using ion chromatography. Field parameters (pH and Eh) were measured at the time of sample collection using a YSI Model 6920 Multielectrode.

4.2.1.3. Physical and chemical properties of lake sediments

To evaluate accumulation of phosphorus in the sediment, samples were collected from two locations in Barr Lake, one littoral and one pelagic. The pelagic sample was collected using an Ekman dredge (Wildco) and the littoral sample was collected directly to a 5 L polyethylene container. Sediment was transported (on ice) to the laboratory where chemical analysis for total phosphorus and total iron and manganese was conducted following perchloric acid digest.

Dry pelagic sediment was evaluated for organic content by gravimetric analysis following ashing, littoral sediment contained only minor amounts of organic material and the organic content was not measured. Pelagic sediment was also evaluated for the presence of clays and other crystalline minerals by X-ray diffraction. Identification of clay minerals was conducted using both air-dried and oriented ethylene glycol solvated samples. Identification of other crystalline phases was conducted using a random powder mounted sample (Moore and Reynolds, 1997).

4.2.2. Laboratory experimentation: sediment extraction using controlled redox conditions

Current models reported in the literature indicate that sediments are expected to control the concentrations of phosphorus and metals in lakes and reservoirs at some level through either solid phase precipitation or surface adsorption (e.g. Mortimer, 1942; Golterman, 1995). To address the affect of solid phase precipitation or dissolution at the sediment-water interface the hypothesis was tested that aqueous phase phosphorus concentrations are not influenced by changes in redox potential.

Sediment samples were collected from Barr Lake during the summer of 1998. Pelagic sediment samples were collected using an Ekman Dredge and included surficial material only from the approximate sediment - water interface at Station 2 (Figure 2). Previous studies have indicated that the uppermost 2 cm of sediment is the most chemically active (Baccini, 1985). Samples were kept wet and on ice for transport to the laboratory. The laboratory procedure for analysis of the sediment included:

1) determination of water content by gravimetric method (desiccation at 105°C until stable weight was obtained) of a homogenized subsample to determine dry equivalent weight;

2) splitting wet sediment into 100 g (dry) aliquots (approximately 1000g wet);

3a) 100 g (dry) sediment was placed in a 2 L modified boiling flask (Figure 3), and 1000 mL deionized water was added (10:1 H_2O:dry sediment ratio (Moore and Reddy, 1994; Brennan, 1994));

3b) flask was sealed and headspace purged with argon gas;

3c) continuous stirring and controlled introduction of atmospheric air;

3d) sampling and filtration using a disposable 60 mL polypropylene syringe fitted with a 47 mm diameter polycarbonate filter holder and 0.4 μm pore filter. Sampling was conducted at discrete pe + pH values while the sediment slurry was allowed to oxidize. The pe, pH and temperature values were recorded on an hourly basis using a data recorder (Campbell Scientific CR10x).

3f) measurement of anions in solution was accomplished using ion chromatography.

4a) for analysis of anoxic conditions, the same sediment slurry was exposed to increasingly reducing conditions (Brennan, 1994; Brennan and Lindsay, 1996). 1% $H_{2(g)}$ (99% $Ar_{(g)}$) was used as the reducing agent according to the equation:

$$\tfrac{1}{2}H_{2(g)} \rightleftharpoons H^{+} + e^{-} \qquad \log K^{o} = 0.0$$

4b) removal of suspension and filtration using a disposable 60 mL polypropylene syringe fitted with a 47 mm diameter polycarbonate filter holder and 0.4 µm pore filter. The pe measurements were taken using three platinum electrodes (Ag/AgCl reference corrected to the standard hydrogen electrode potential). pH measurements were taken using a glass combination electrode (Orion model 91-07). Temperature was measured using a Campbell Scientific model 107 thermistor. All three parameter values were recorded on an hourly basis using a Campbell Scientific CR10x data recorder;

4c) measurement of total anions in solution was conducted using ion chromatography;

4d) measurement of total cations in solution was conducted using inductively coupled plasma argon emission spectroscopy.

Several quality assurance - quality control (QA/QC) procedures were used. Samples consisted of 10 mL of extractant, which was checked for pH immediately upon collection (since continuous pH measurements may drift due to excessive time since electrode calibration) and compared to in-situ pH measurements. Samples for anion analysis were preserved at 4°C in the absence of atmospheric oxygen. Full duplicate sampling was conducted (i.e. two samples per pe + pH value of 10 mL each). This

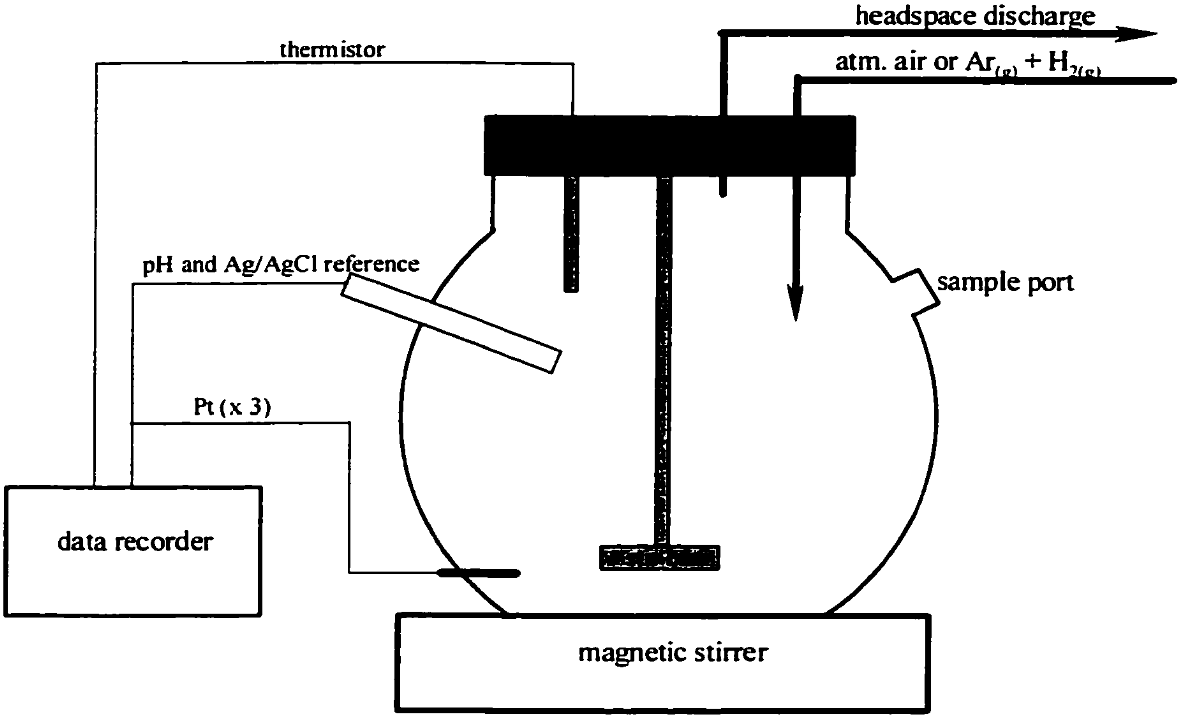


Figure 3. Reaction vessel for redox-manipulation experiments.

sampling schedule allowed for evaluation of equilibrium attainment and potential mixing problems within the reaction vessel.

5. Results

5.1 Calculation of an annual chemical mass budget for Barr Lake

5.1.1. Water budget

Annual water budgets indicate that water volumes entering Barr Lake were greater than the storage volume (approximately 40,705,000 m^3) and effluent volume for each of the three years of study (Table 4). This result is consistent with several other irrigation reservoirs in eastern Colorado, which exhibit flushing rates of less than one year. Mean hydraulic retention times in Barr Lake, calculated as the time between the center of mass of the annual inflow (including precipitation and groundwater gain) versus annual outflow hydrographs (including evaporation and groundwater losses), were approximately 48 days, 49 days and 44 days in water years 1997, 1998, and 1999 respectively (Figure 4 - Figure 6). Minor differences in hydraulic retention time between years are expected due to the controlled nature of Barr Lake and the dependence of flow on water rights.

Comparing the mean hydraulic retention time to the phase shift calculated for Barr Lake and the outfall structures for in-lake and outflow water quality modeling purposes provides insight into control mechanisms on water quality (Equation 5). The calculated phase shift was 78 days in 1997, 77 days in 1998, and 44 days in 1999. The differences between the hydraulic retention time and the phase shift values for water year 1997 and 1998 suggest that in-lake water quality observations or water quality in the outflows from Barr Lake are not strictly related to mean hydraulic retention times, but are more closely related to the influent volume – lake volume relationship.

Table 4. Barr Lake Hydrologic Budget

Component (m^3)	Water Year		
	1997	**1998**	**1999**
surface water influent	57,480,000	64,230,000	49,890,000
precipitation	3,040,000	1,618,000	3,828,000
surface water effluent	32,470,000	52,280,000	40,291,000
evaporation loss	11,610,000	10,840,000	11,345,000
Δ storage	+3,920,000	-1,279,000	+2,877,000
groundwater loss or gain (by calculation)	-12,520,000	-4,003,000	+795,000

Other components of the water budget (precipitation, evaporation, groundwater loss/gain) were minor relative to influent for each of the three years of study, although evaporation loss equaled 20, 17, and 23% of the influent volumes for 1997, 1998, and 1999 respectively. This result would suggest that concentration increases by evaporation might be a significant water quality influence in Barr Lake. Water quality data however, do not suggest that evaporative concentration is a major control on constituent concentration. Precipitation volumes, although comprising only 5, 2, and 8% of the annual influent volume, partially offset evaporative losses (net loss of approximately 15% of the influent volume in each year of study). Evaporative concentration associated with this net loss is probably masked by water quality variability in Barr Lake.

Influent

The midpoint dates for filling of Barr Lake during the three years of study was May 10, 1997, May 14, 1998 and May 25, 1999. Timing of influent flow has significant influence on water quality in the influent waters as well as in-lake and effluent concentrations. Dilution flows associated with stormflow and snowmelt provide the lowest concentrations of chemical constituents observed in the influent waters. The quantity and timing of flows into Barr Lake therefore drive the hydrochemical dynamics to a large extent. The majority of flow into Barr Lake during water years 1997 and 1999 occurred during July (associated with stormflow), compared to May (associated with snowmelt and stormflow) for water year 1998 (Figure 4-Figure 6). This higher proportion of influent volumes in the summer months provides the greatest dilution of treated wastewater and in-part drives the sinusoidal nature of water quality concentrations observed in Barr Lake.

Annual percentage of wastewater input to Barr Lake were approximately 22% in water year 1997, 10% in 1998 and 15% in 1999 (calculated using annual discharge records). Daily wastewater fractional input to Barr Lake was a maximum of 86% in 1997, 31% in 1998 and 68% in 1999, all during wintertime low-flow periods on the South Platte River (February – March). Daily fractional inputs are significantly affected by direct discharge of treated wastewater by the Metropolitan Wastewater Control District (Metro) to the feeder canal to Barr Lake as part of a water rights exchange. Direct discharge of treated wastewater from Metro annually makes up approximately 13,000,000 m^3 of the total influent to Barr Lake.

Barr Lake Volume

Year-to-year differences in storage in Barr Lake were small during the years of study (Table 4) ranging from approximately 2% to 7% of the inflow volume (Figure 10 - Figure 12). This flow regime results in low hydraulic residence times in Barr Lake (on the order of months), which have been shown in other systems to have significant influence on nutrient dynamics. (Walker, 1996). Specifically, inorganic nitrogen (nitrate, ammonia/ium) and orthophosphate have been shown to be better predictors of eutrophication in impoundments with short hydraulic retention times than total nitrogen and total phosphorus which are more commonly used in eutrophication modeling (Walker, 1996).

Intra-year lake stage variation was substantial, ranging by as much as 3 m throughout each year of study, the result of downstream irrigation demands. This range in lake stage not only provides a mixing mechanism, but also results in a sizeable littoral zone in which organic material within the sediment is oxidized. The importance of this condition to the fate of nutrients in Barr Lake is discussed further in Section 6.1.2.

Effluent

Surface-water releases from Barr Lake are entirely controlled by downstream irrigation demand. Releases from Barr Lake typically begin in April and last until October, with the majority of outflow coincident with the irrigation season (Figure 4 - Figure 6). Demand for water was the greatest in 1998 (Table 4), reflected in the highest annual discharge volume observed during the study period. The timing of efflux from Barr Lake is significant in that phytoplanktonic uptake of nutrients significantly alters the water quality during the summer months when irrigation demand is greatest. The result is highly variable aqueous concentrations (with respect to nutrients) in the effluent waters. The highest nutrient concentrations in the effluent waters occur during the early part of the season and the lowest occurring late in the irrigation season. These effects are discussed later in Section 6.1.2.

Precipitation

Precipitation values used in the hydrologic budget are consistent with published values on an annual basis and vary significantly among the three years. In water year 1998, approximately half of the volume of 1997 and 1999 was observed (Figure 7 - Figure 9). The low precipitation input to Barr Lake resulted in the high effluent volume, as demand for irrigation water was highest in 1998. Seasonally, precipitation was highest during the spring and summer months. Precipitation did not appear to have significant influence on the nutrient concentrations or dynamics in Barr Lake (i.e. deviation from mean in-lake concentrations were not observed following precipitation events).

Evaporation

Annual evaporative losses for Barr Lake are consistent with assumptions made by others (HydroTriad, 1974) and with published values for the Front Range of Colorado (approximately 100 cm during the growing season May - October)(Siemer, 1977). Year-to-year variation in evaporation was low (178cm in 1997, 167 cm in 1998, and 168 cm in 1999) consistent with the annual time step used for calculation. Seasonally, evaporation was highest during the irrigation season (Figure 7 - Figure 9).

Groundwater loss/gain

Calculated seepage rates from Barr Lake suggest a losing system for water years 1997 and 1998 (Table 4). The water budget for 1999 indicates groundwater flux into Barr Lake (a gaining condition), but the quantity is considered to be within the error of estimate (795,000 m^3). These findings have hydrochemical significance in that the outward hydraulic gradient tends to minimize the chemical influence of the sediments on the in-lake water column. This will be discussed further in Section 6.1.1.

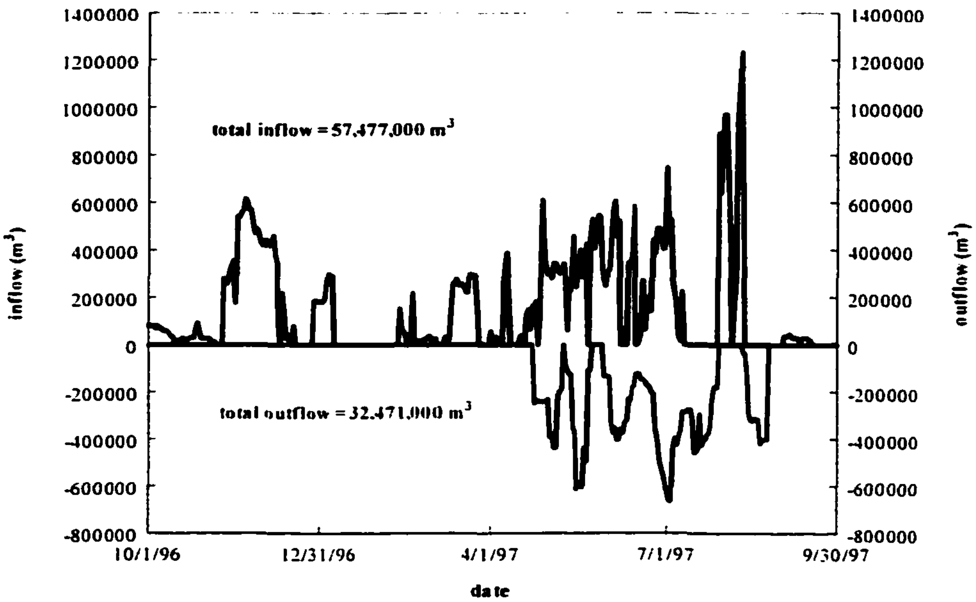


Figure 4. Inflow and outflow hydrographs for Barr Lake - water year 1997.

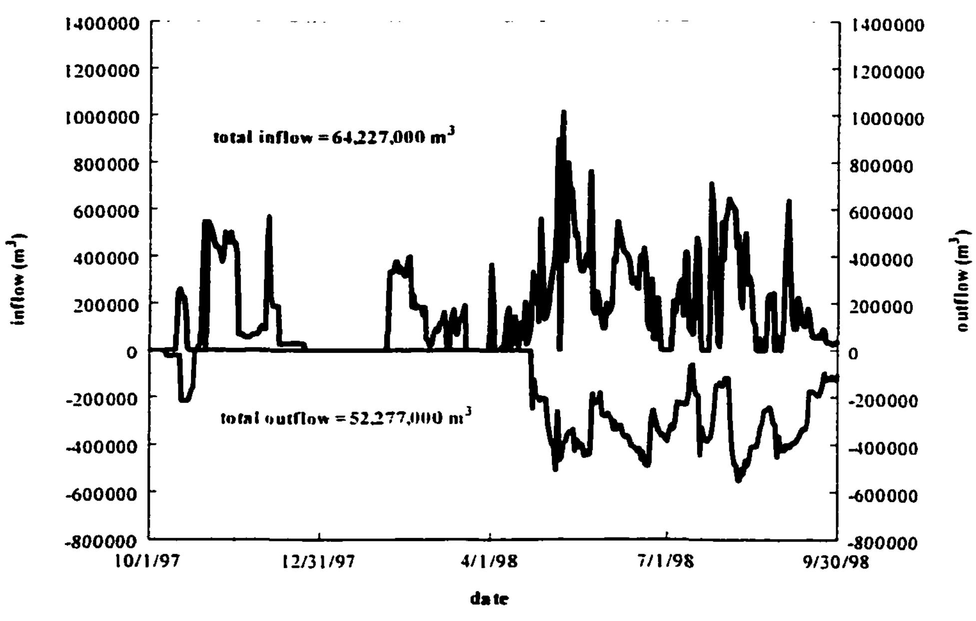


Figure 5. Inflow and outflow hydrographs for Barr Lake - water year 1998.

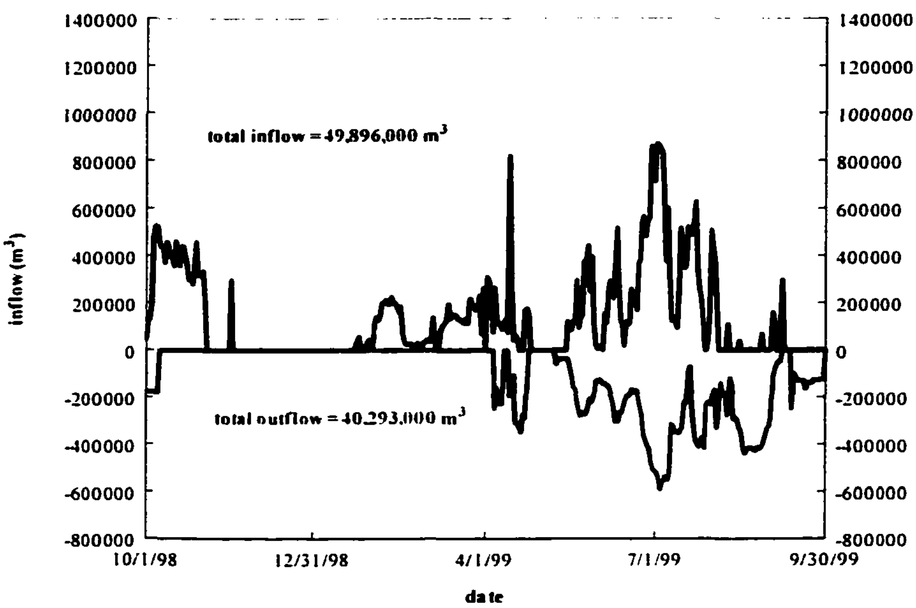


Figure 6. Inflow and outflow hydrographs for Barr Lake - water year 1999.

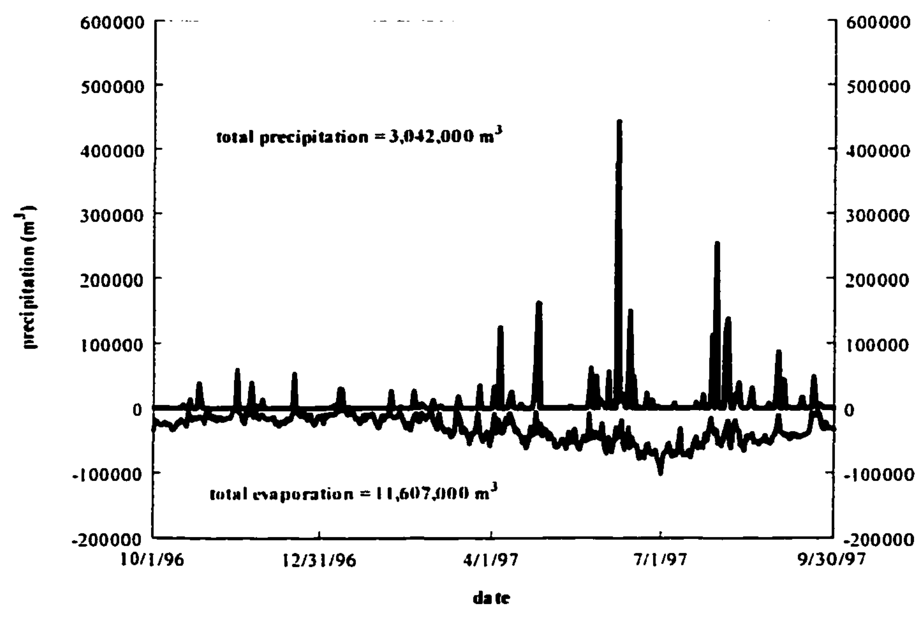


Figure 7. Precipitation and evaporation volumes for Barr Lake - water year 1997.

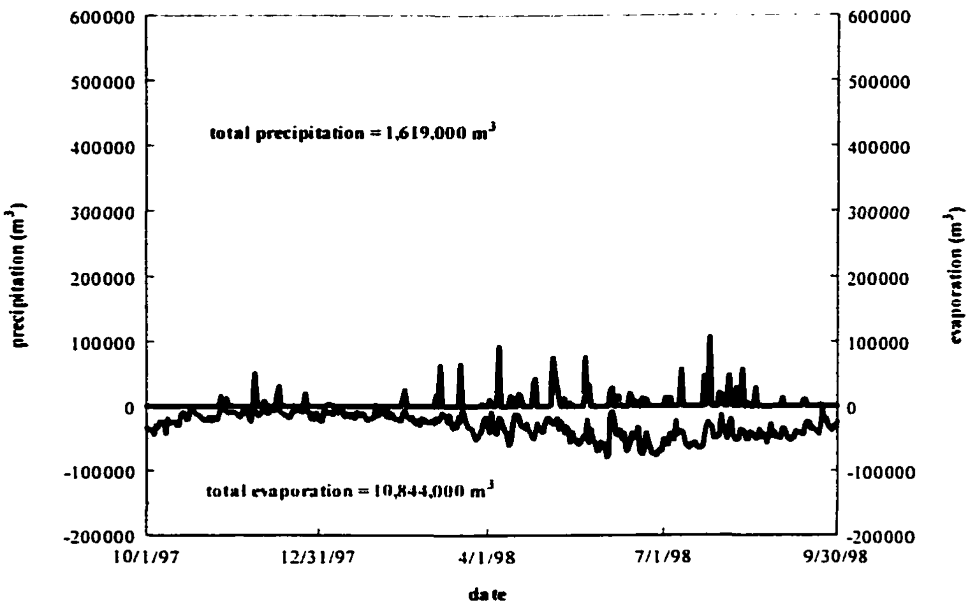


Figure 8. Precipitation and evaporation volumes for Barr Lake - water year 1998.

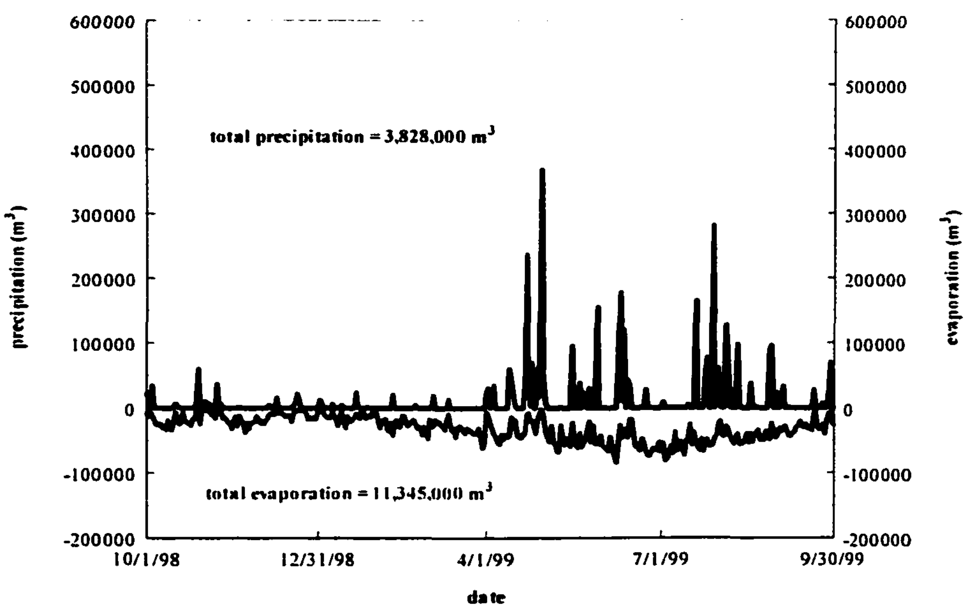


Figure 9. Precipitation and evaporation volumes for Barr Lake - water year 1999.

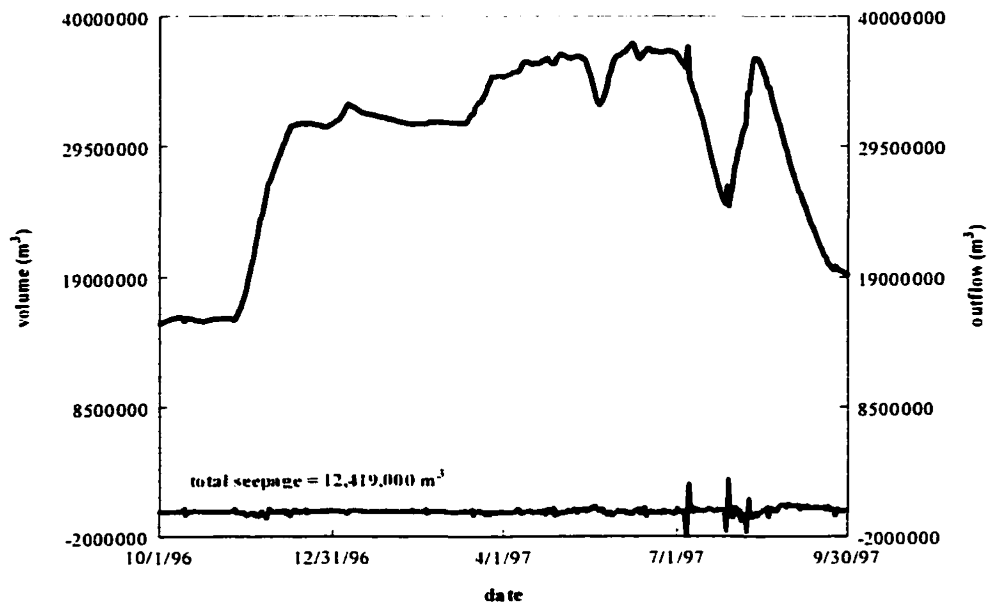


Figure 10. Barr Lake volume and calculated groundwater loss - water year 1997.

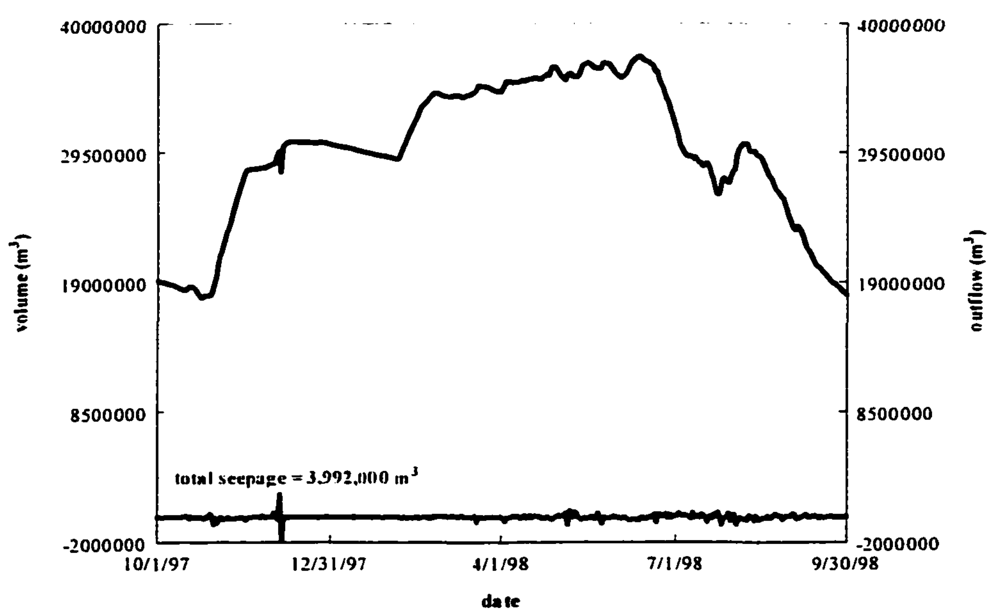


Figure 11. Barr Lake volume and calculated groundwater loss - water year 1998.

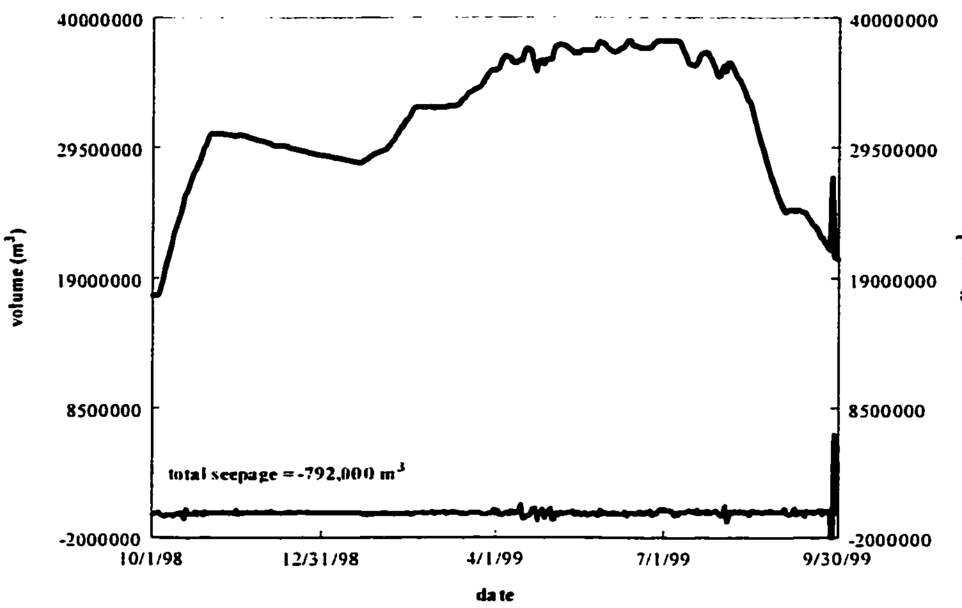


Figure 12. Barr Lake volume and calculated groundwater loss - water year 1999.

5.1.2. Hydrochemical budget

Because flows to and from Barr Lake are controlled, wide ranges of discharge values are not observed; however, variation in concentration for several constituents was observed. Constituent concentrations were initially evaluated versus instantaneous flow in the O'Brian Canal to determine if flow and concentration were correlated. This analysis indicated a poor relationship between canal flow and concentration, making flow based load calculation subject to high uncertainty. Correlations to streamflow measured in the South Platte at Denver (USGS gage) were also evaluated and found to have a good relationship for some constituents, but the spatial distance between the Barr Lake Inlet and the Denver Gage (approximately 60 km) makes any relation difficult to apply.

Time-series data from the influent to Barr Lake, the Barr Lake water column, and the discharge points from Barr Lake revealed a sinusoidal relationship with time based on a period of one year (Appendix A). For this reason, regression models were fit to the time series data (Table 5 - Table 8) and modeled values used to extrapolate between sampling dates for the calculation of hydrochemical loads. The shape parameters (β_1) determined for Barr Lake Inlet concentrations are substantially higher than those calculated for Barr Lake and the outlet structures (Table 5 - Table 8), consistent with the dampened concentration response used in lake water quality models described by others (Chapra, 1997). Intercept terms (β_0), however, tend to be similar in magnitude between sampling locations with the exception of nitrate-N. For each of the three years of data,

Table 5 . Barr Lake Inlet sinusoidal models (τ = radian transformed julian day).

Constituent	1997	1998	1999
Calcium	21.35(sin τ) + 60.29	18.05(sin τ) +59.00	23.19(sin τ) + 61.11
Sodium	34.33(sin τ) + 64.77	38.76(sin τ) + 61.98	28.98(sin τ) + 62.21
Nitrate-N	3.35(sin τ) + 4.28	1.29(sin τ) + 2.82	2.98(sin τ) + 3.88
Orthophosphate-P	0.74(sin τ) + 0.76	0.15(sin τ) + 0.26	0.48(sin τ) + 0.48
Sulfate	111.81(sin τ) + 144.72	52.62(sin τ) + 114.96	51.51(sin τ) + 116.62

Table 6. Barr Lake sinusoidal models (τ = radian transformed julian day).

Constituent	1997 phase shift = 1.35 rad	1998 phase shift = 1.32 rad	1999 phase shift = 1.38 rad
Calcium	8.89(sin τ) + 58.85	6.82(sin τ) +57.94	4.50 (sin τ) + 58.12
Sodium	13.34(sin τ) + 65.13	11.19(sin τ) + 55.59	9.30(sin τ) + 53.92
Nitrate-N	1.81(sin τ) + 1.86	0.69(sin τ) + 0.78	0.96(sin τ) + 1.17
Orthophosphate-P	0.17(sin τ) + 0.44	-0.04(sin τ) + 0.18	-0.001(sin τ) + 0.22
Sulfate	49.95(sin τ) + 133.79	12.60(sin τ) + 103.75	16.96(sin τ) + 107.43

Table 7. East Outfall sinusoidal models (τ = radian transformed julian day).

Constituent	1997 phase shift = 1.35 rad	1998 phase shift = 1.32 rad	1999 phase shift = 1.38 rad
Calcium	12.88(sin τ) + 59.80	5.58(sin τ) +57.22	9.19 (sin τ) + 55.62
Sodium	19.13(sin τ) + 66.31	11.25(sin τ) + 50.85	13.56(sin τ) + 56.32
Nitrate-N	2.18(sin τ) + 2.02	0.66(sin τ) + 0.58	1.24(sin τ) + 1.07
Orthophosphate-P	0.17(sin τ) + 0.43	-0.05(sin τ) + 0.22	-0.03(sin τ) + 0.23
Sulfate	75.32(sin τ) + 140.29	19.99(sin τ) + 99.46	23.10(sin τ) + 105.90

Table 8. West Outfall sinusoidal models (τ = radian transformed julian day).

Constituent	1997 phase shift = 1.35 rad	1998 phase shift = 1.32 rad	1999 phase shift = 1.38 rad
Calcium	11.05(sin τ) + 57.98	7.17(sin τ) +57.90	9.94 (sin τ) + 55.48
Sodium	18.75(sin τ) + 66.19	9.12(sin τ) + 49.29	14.73(sin τ) + 56.82
Nitrate-N	1.80(sin τ) + 1.73	0.59(sin τ) + 0.52	1.16(sin τ) + 1.02
Orthophosphate-P	0.07(sin τ) + 0.36	-0.05(sin τ) + 0.23	-0.09(sin τ) + 0.21
Sulfate	31.11(sin τ) + 103.05	16.59(sin τ) + 100.26	26.81(sin τ) + 107.66

lower intercept values are observed for nitrate-N, consistent with low in-lake nitrate-N concentrations.

The sinusoidal concentration models developed for the Barr Lake Inlet generally reflect the effluent dominance of the influent water. Concentrations observed at the Barr Lake Inlet, for example, are lowest during high flow periods on the South Platte River (when dilution flows are greatest). Conversely, concentrations are highest during periods of low flow on the South Platte River (when dilution flows are low). The sinusoidal nature of concentration with respect to time also caused the residuals from annual and seasonal mean models to be very highly correlated (serially). This serial correlation is a violation of the assumptions necessary for use of annual or seasonal mean models for the calculation of hydrochemical loads or mass budgets. Additionally, use of annual or seasonal mean influent concentrations for predictive purposes, as suggested by several water quality models, is inappropriate.

Estimates of wastewater percentage of flows into Barr Lake range from 5% during the snowmelt period to over 95% during the baseflow period on a daily basis. It is beyond the scope of this research to rigorously evaluate the wastewater loads into the South Platte River, but it is clear from the hydrochemical data collected from the inlet to Barr Lake that the water-quality conditions, as affected by wastewater discharges to the South Platte River, substantially influence the hydrochemical behavior of nutrients in Barr Lake. Annual mass loading values determined using the sinusoidal models (Table 9 - Table 11) were compared to mass loadings calculated using the moving average method (Table 12 - Table 17). Molar concentrations are provided to allow comparisons between constituents and possible reaction mechanisms. The phase shift necessary to fit sinusoidal functions to the data from Barr Lake and the outfall structures were calculated using (Chapra, 1997):

$$\phi(\omega) = \tan^{-1}\left(\frac{\omega}{\lambda}\right) \qquad \text{Equation 6}$$

where:

ϕ = phase shift (radians)

ω = frequency ($year^{-1}$)

λ = eigenvalue = inflow/lake volume ($year^{-1}$).

The phase shifted sinusoidal concentration models were used for calculation of annual mass fluxes of constituents lost or gained from groundwater and lost to effluent from Barr Lake according to Equation 3.

Table 9. Input mass fluxes to Barr Lake for water years 1997 – 1999 using sinusoidal models of concentration.

Constituent	**influx kg/yr (mol/yr)**		
	1997	**1998**	**1999**
Calcium	3,196,000 (79,736,000)	3,465,000 (86,463,000)	2,611,000 (65,147,000)
sodium	3,289,000 (143,065,000)	3,285,000 (142,869,000)	2,565,000 (111,208,000)
nitrate (as N)	203,000 (14,529,000)	158,000 (11,283,000)	138,000 (9,786,000)
orthophosphate (as P)	34,000 (1,134,000)	14,000 (476,000)	15,000 (492,000)
sulfate	6,906,000 (71,937,000)	6,438,000 (67,066,000)	4,846,000 (50,481,000)

Table 10. Output mass fluxes from Barr Lake for water years 1997 – 1999 using sinusoidal models of concentration.

Constituent	**efflux* kg/year (mol/yr)**		
	1997	**1998**	**1999**
calcium	2,523,000 (63,057,000)	3,156,000 (78,877,000)	2,517,000 (62,901,000)
sodium	2,790,000 (121,384,000)	2,693,000 (117,150,000)	2,491,000 (108,353,000)
nitrate (as N)	64,000 (4,574,000)	23,000 (1,644,500)	29,000 (2,089,500)
orthophosphate (as P)	16,000 (521,500)	13,400 (433,500)	11,500 (371,000)
sulfate	4,847,000 (50,455,000)	5,390,000 (56,109,000)	4,728,000 (49,220,000)

*includes losses/gains associated with groundwater seepage

Table 11. Mass budget for Barr Lake for water years 1997 – 1999 using sinusoidal models of concentration.

Constituent	**budget kg/year (mol/yr)**		
	1997	**1998**	**1999**
calcium	673,000 (16,818,000)	309,000 (7,738,000)	94,000 (2,359,000)
sodium	499,000 (21,687,000)	592,000 (25,726,000)	74,000 (2,860,000)
nitrate (as N)	139,000 (9,949,000)	135,000 (9,633,000)	109,000 (9,188,213)
orthophosphate (as P)	18,000 (579,000)	600 (28,000)	3,500 (90,400)
sulfate	2,059,000 (21,435,000)	1,048,000 (10,914,000)	118,000 (1,229,000)

Table 12. Input mass fluxes to Barr Lake for water years 1997-1999 using the moving average method. Difference between the sinusoidal model method and the moving average method are included in parenthesis.

Constituent	**influx (kg/yr)**		
	1997	**1998**	**1999**
calcium	3,064,000 (132,000)	3,515,000 (-50,000)	2,605,000 (6000)
sodium	3,104,000 (185,000)	3,154,000 (131,000)	2,297,000 (268,000)
nitrate (as N)	207,000 (-4000)	164,000 (-6000)	138,000 (0)
orthophosphate (as P)	30,000 (4000)	15,000 (-1000)	13,000 (2000)
sulfate	6,162,000 (744,000)	6,519,000 (-81,000)	4,627,000 (219,000)

Table 13. Output mass fluxes from Barr Lake for water years 1997-1999 using the moving average method. Difference between the sinusoidal model method and the moving average method are included in parenthesis.

Constituent	**efflux (kg/year)**		
	1997	**1998**	**1999**
calcium	2,595,000 (-72,000)	3,111,000 (45,000)	2,605,000 (-88,000)
sodium	2,921,000 (-131,000)	3,309,000 (-616,000)	2,069,000 (422,000)
nitrate (as N)	56,000 (8000)	24,000 (-1000)	13,000 (422,000)
orthophosphate (as P)	17,300 (-1000)	12,700 (400)	10,000 (1500)
sulfate	5,012,000 (-165,000)	6,787,000 (-1,397,000)	3,898,000 (830,000)

Table 14. Hydrochemical mass budget for Barr Lake using the moving average method. Difference between the sinusoidal model method and the moving average method are included in parenthesis.

Constituent	**budget (kg/year)**		
	1997	**1998**	**1999**
calcium	469,000 (204,000)	404,000 (-95,000)	488,000 (-394,000)
sodium	183,000 (315,000)	-155,000 (746,000)	228,000 (-162,000)
nitrate (as N)	151,000 (-12,000)	140,000 (-5000)	125,000 (4000)
orthophosphate (as P)	13,000 (5000)	2300 (1400)	3200 (-400)
sulfate	1,150,000 (909,000)	-268,000 (1,316,000)	729,000 (-611,000)

Table 15. Percentage difference (sinusoidal vs. moving average) between methods for inputs to Barr Lake

Constituent	**influx (percentage)**		
	1997	**1998**	**1999**
calcium	4.13	-1.44	0.23
sodium	5.62	3.99	10.45
nitrate (as N)	-1.97	-3.80	0.00
orthophosphate (as P)	11.76	-7.14	13.33
sulfate	10.77	-1.26	4.52

Table 16. Percentage difference (sinusoidal vs. moving average) between methods for outputs to Barr Lake

Constituent	**efflux (percentage)**		
	1997	**1998**	**1999**
Calcium	-2.85	1.43	-3.50
Sodium	-4.70	-22.87	16.94
nitrate (as N)	12.50	-4.35	55.17
orthophosphate (as P)	-6.25	2.99	13.04
Sulfate	-3.40	-25.92	17.55

Table 17. Percentage difference (sinusoidal vs. moving average) between methods for hydrochemical budgets for Barr Lake

Constituent	**budget (percentage)**		
	1997	**1998**	**1999**
Calcium	30.31	-30.74	-419.15
Sodium	63.25	126.23	-245.45
nitrate (as N)	-8.63	-3.70	3.10
orthophosphate (as P)	27.78	-164.37	-14.29
Sulfate	44.15	125.57	-517.80

Differences in calculation methods were less than 10% for the influent mass loadings, but several constituents among the effluent and budget calculated loadings indicated differences of greater than 10% between methods. These latter differences illustrate the need for rigorous attention to the method used for calculation of hydrochemical loading and underscore the necessity of a reasonable uncertainty analysis.

Mass budgets for sodium indicate that sodium is not behaving conservatively since retention is indicated in each of the three years of study. Only in 1999 can the retention value be considered minor relative to the influx (approximately 2.9%). Possibilities for the lack of conservative behavior of sodium are discussed in Section 6.1.2.

Retention of nutrient species (nitrate-N and orthophosphate-P) is indicated by the mass budgets, although minor for orthophosphate-P in 1998 and 1999. Retention (or loss through denitrification) of nitrate was high in every year of the study. This finding is consistent with the observations of nitrate concentrations in Barr Lake during the late summer in each year of the study (Appendix A). Concurrent retention of orthophosphate was not observed, particularly in water years 1998 and 1999. This finding is significant in that orthophosphate is generally retained in lakes and reservoirs through the adsorptive and solid phase formation mechanisms discussed in Chapter 3.

Comparison of the molar ratio Ca:SO_4 input to and in Barr Lake (1.11 in 1997, 1.29 in 1998 and 1.29 in 1999) suggest that $CaSO_4\ 2H_2O_{(gypsum)}$ may controlling both calcium and sulfate concentrations and may be responsible for most of the calcium removal indicated by the mass budget calculations. Although calcium concentrations support this hypothesis, sulfate concentrations are generally indicative of undersaturation with respect to gypsum (saturation ≈ 4.68×10^{-3} M).

Cumulative daily mass budgets conducted for Barr Lake illustrate the accumulation and/or release of constituents over the water year (Figure 13 – Figure 17). Analysis of these intra-year mass budgets indicates that calcium, sodium and sulfate behave conservatively, accumulating in Barr Lake during the period when inflow >> outflow and releasing from Barr Lake during periods when inflow << outflow. Nitrate (as N) illustrates accumulating behavior for the entire water year (Figure 15) consistent with biomass accumulation during the summer months. Orthophosphate (as P) illustrates an intermediate behavior for water year 1997 (evidence of biomass and/or sediment removal) but exhibits conservative behavior for water year 1998 and 1999 (Figure 16).

Consistently lower mass loadings to Barr Lake observed in water year 1999 were the result of lower inflows in that year. Net retention of all constituents was observed for all years as indicated by a positive budget value (Table 11).

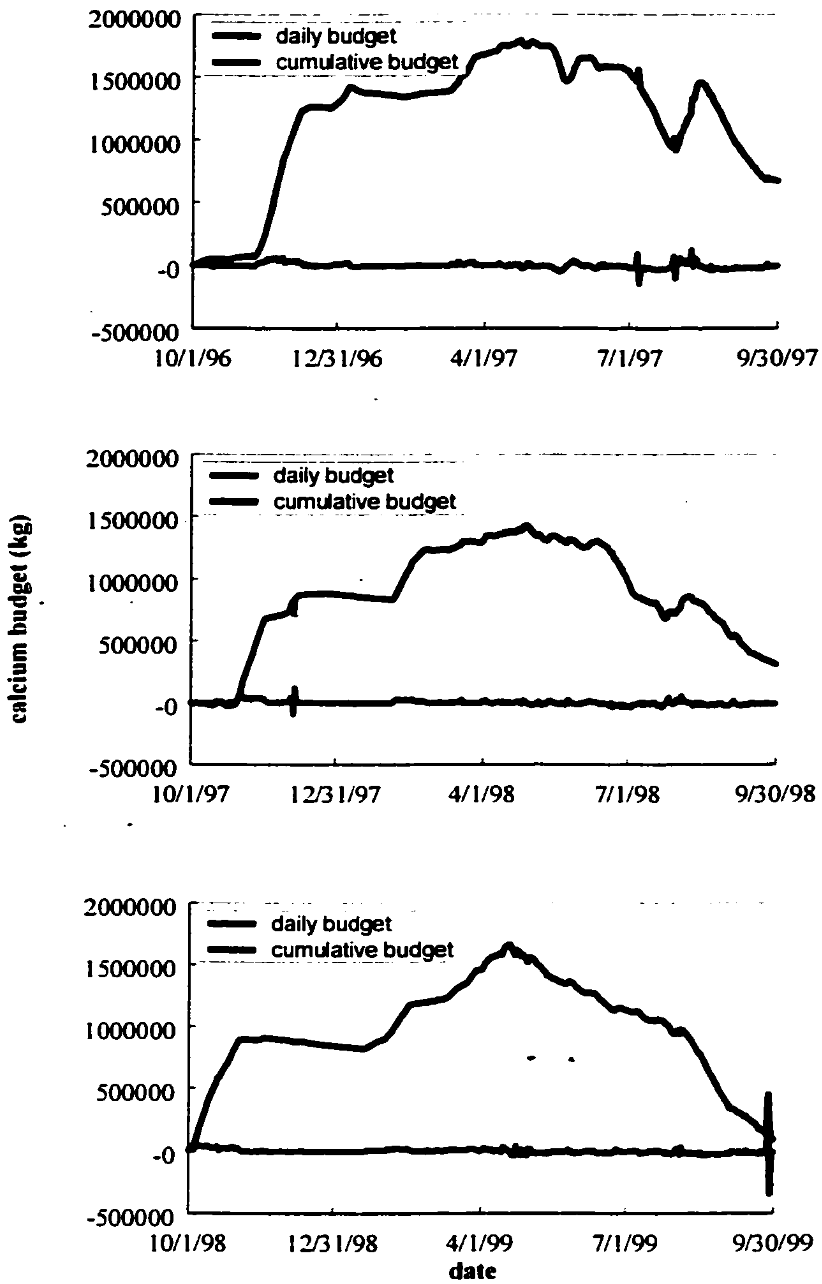


Figure 13. Daily mass and cumulative daily mass budget for calcium in Barr Lake calculated using the sinusiodal model for mass fluxes.

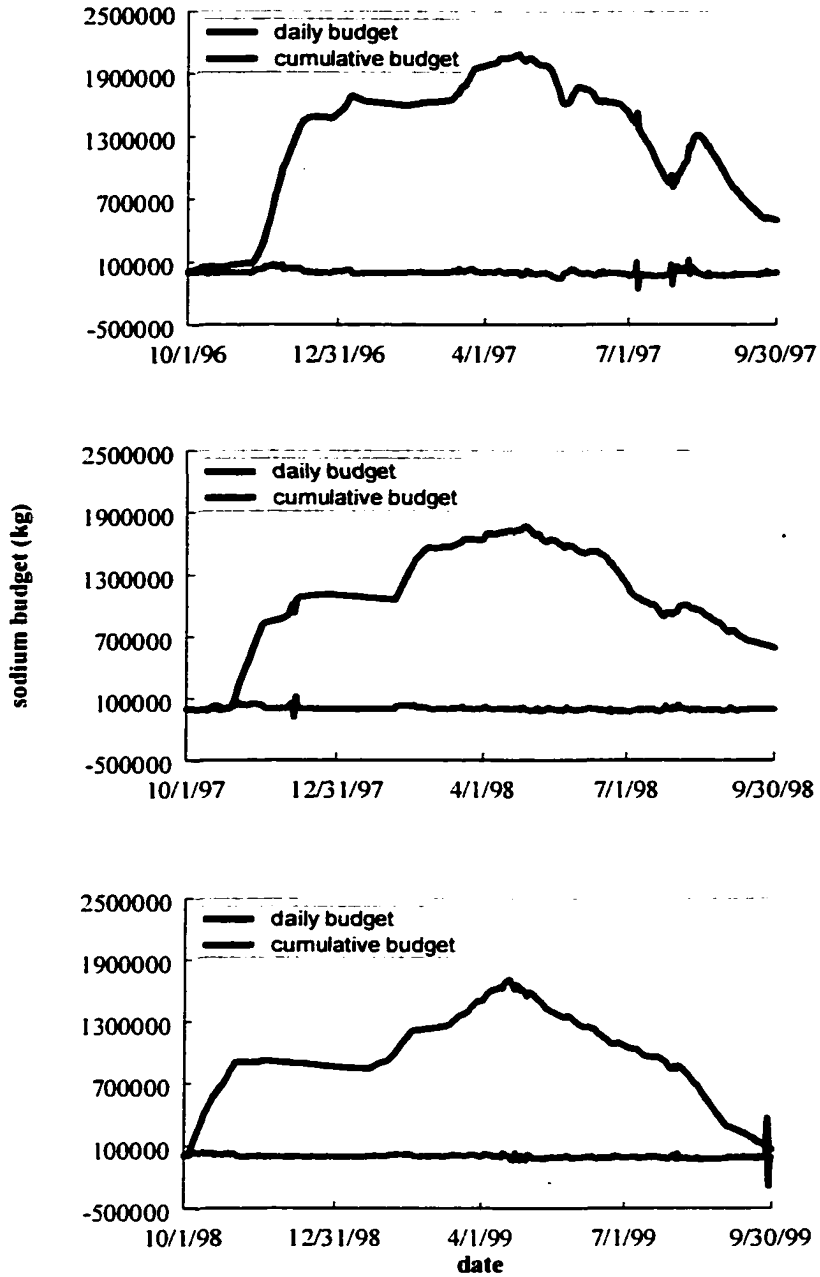


Figure 14. Daily and cumulative daily mass budget for sodium in Barr Lake. Mass fluxes were calculated using sinusoidal concentration models.

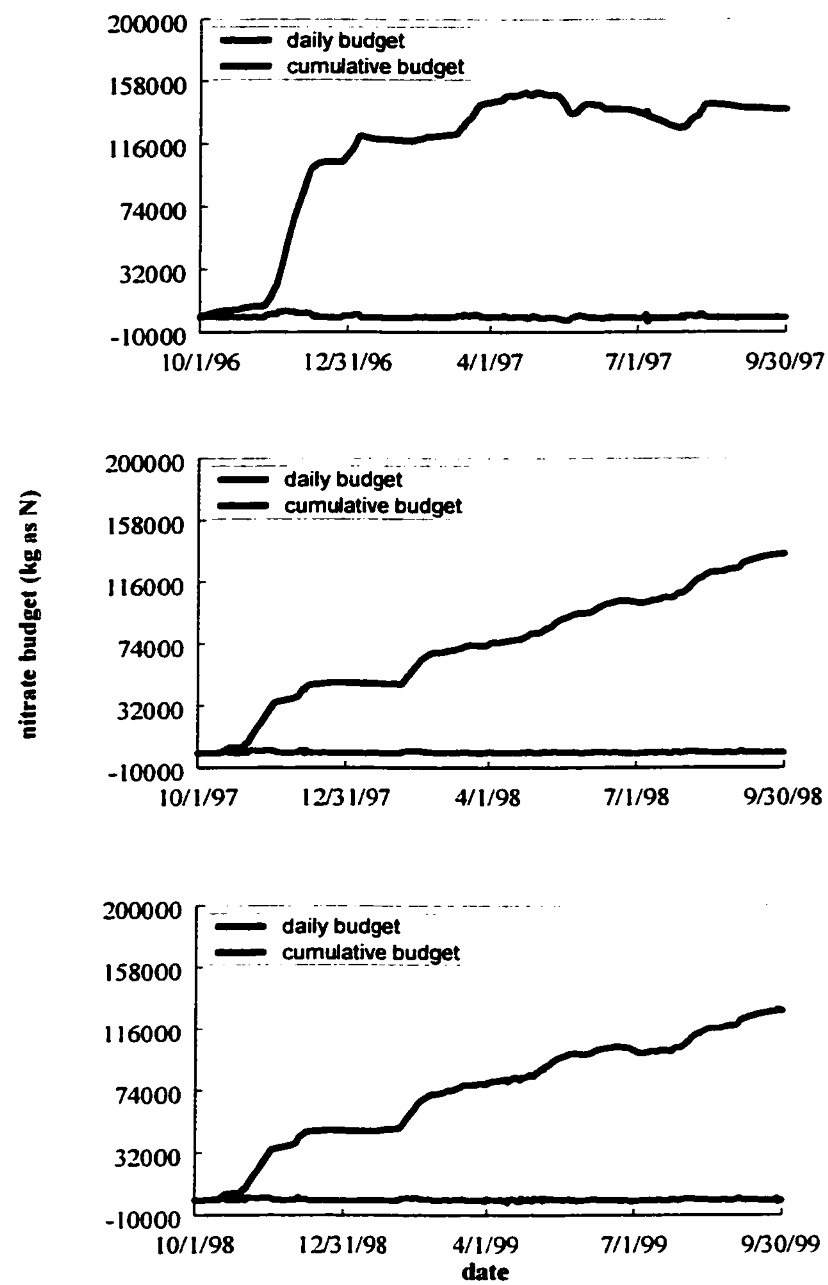


Figure 15. Daily and cumulative daily mass budget for nitrate (as N) in Barr Lake. Mass fluxes were calculated using sinusoidal concentration model.

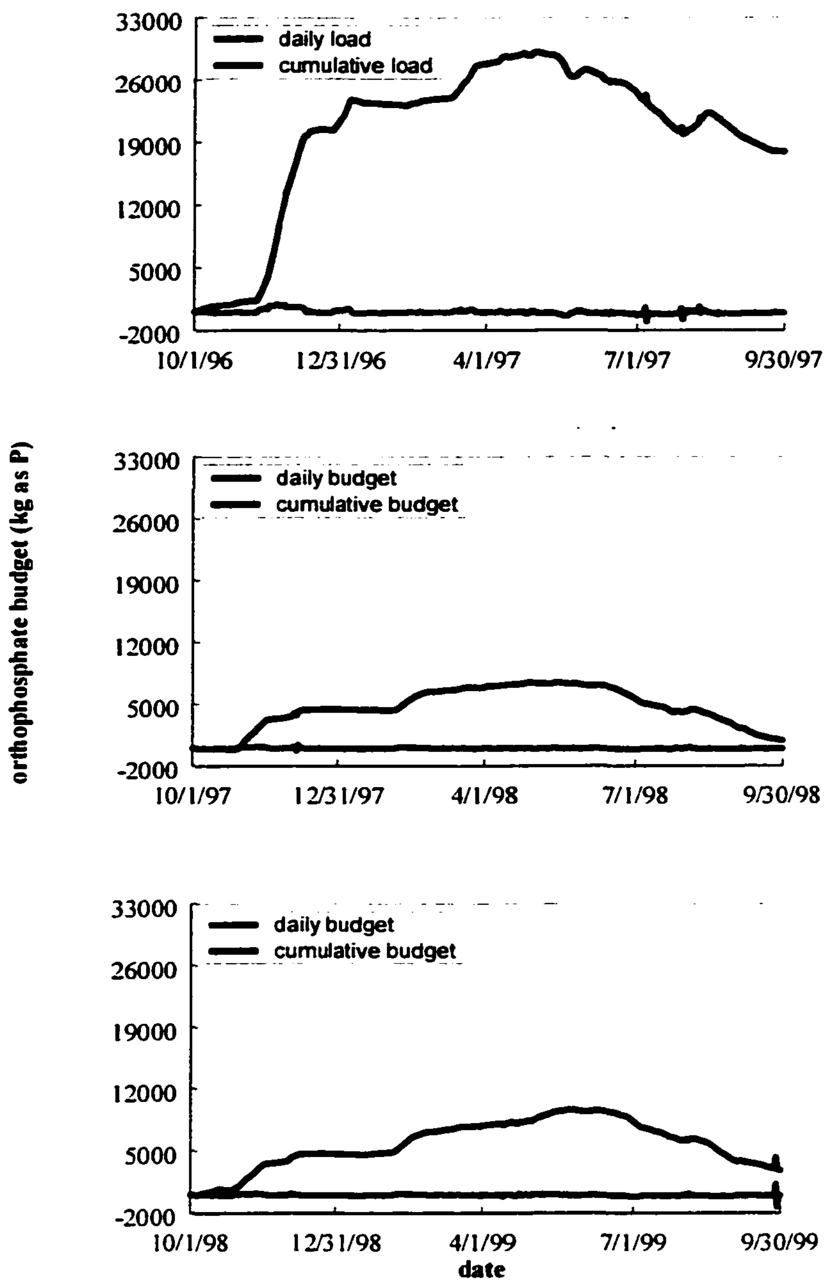


Figure 16. Daily and cumulative daily mass budget for orthophosphate (as P) in Barr Lake. Mass fluxes were calculated using sinusoidal concentration models.

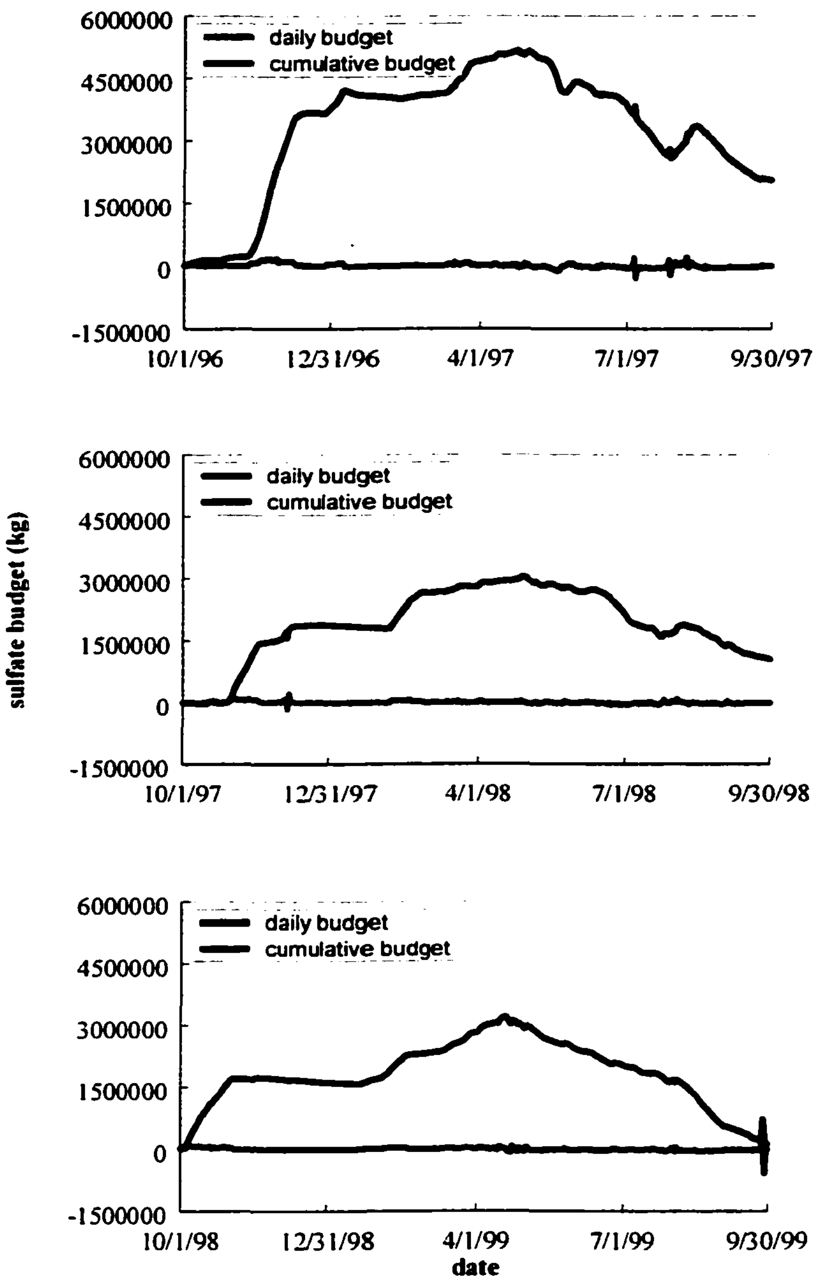


Figure 17. Daily and cumulative daily mass budgets for sulfate in Barr Lake. Mass fluxes were calculated using sinusoidal concentration models.

5.1.3. Uncertainty analysis

Uncertainty estimates for the hydrochemical mass loading for study constituents indicate high variance for each component of the mass budget despite the accumulation suggested by the mass budget calculations alone (Table 18 and Table 19). Comparison of the budget uncertainty estimate to zero (no net accumulation or release) provides a more realistic interpretation of possible retention or release for each constituent (Table 20). Although the results can be used for several purposes (e.g. regulatory limits), the focus of this analysis is to evaluate the retention of phosphorus, nitrate and other constituents in Barr Lake.

For all constituents during the three years of study, the uncertainty analysis resulted in median values that were consistent with the influx values (Table 9) calculated using the sinusoidal models of concentration. Median efflux values were consistent with calculated values with the exception of nitrate flux from Barr Lake (18,000 kg median-efflux in water year 1999 compared to a calculated value of 29,000) (Table 10). Median budget values for several constituents differed from the calculated budget values, reflecting the influence of the influx distribution on the budget calculation. Inclusion of the uncertainty estimate to the mass budgets indicated that calcium in water year 1998 and orthophosphate in water years 1998 and 1999 were not retained by Barr Lake (lower 90th percentile), inferring that the mass budgets alone are insufficient to describe the behavior of these constituents (Table 11).

Table 18. Median loading estimates into Barr Lake including upper and lower 90% values.

Constituent	influx (kg/yr)		
	1997	1998	1999
calcium	median = 3,171,000 upper 90% = 3,449,000 lower 90% = 2,926,000	median = 3,236,000 upper 90% = 3,369,000 lower 90% =2,798,000	median = 2,609,000 upper 90% = 2,798,000 lower 90% =2,426,000
sodium	median = 3,292,000 upper 90% = 3,681,000 lower 90% = 2,904,000	median = 3,136,000 upper 90% = 3,486,000 lower 90% = 2,859,000	median = 2,576,000 upper 90% = 2,832,000 lower 90% = 2,112,000
nitrate (as N)	median = 204,000 upper 90% = 236,000 lower 90% = 172,000	median = 142,000 upper 90% = 166,000 lower 90% = 121,000	median = 136,000 upper 90% = 156,000 lower 90% = 118,000
orthophosphate (as P)	median = 35,000 upper 90%= 56,000 lower 90%= 19,000	median = 13,000 upper 90%= 15,000 lower 90%= 12,000	median = 14,000 upper 90%= 19,000 lower 90%= 9,000
sulfate	median = 6,968,000 upper 90% = 8,607,000 lower 90% =5,550,000	median = 6,022,000 upper 90% = 6,363,000 lower 90% =5,708,000	median = 4,810,000 upper 90% = 5,335,000 lower 90% =4,227,000

Table 19. Median loading estimates from Barr Lake including upper and lower 90% values.

Constituent	**efflux (kg/yr)**		
	1997	**1998**	**1999**
calcium	median = 2.635,000 upper 90% = 2,695,000 lower 90% =2.583,000	median =3,139,000 upper 90% = 3,182,000 lower 90% =3,097.000	median = 2,158,000 upper 90% = 2,253,000 lower 90% = 2,069,000
sodium	median = 2.649,000 upper 90%= 2,715,000 lower 90%= 2,588.000	median = 2,654,000 upper 90%= 2,712,000 lower 90%= 2,602,000	median = 2.089,000 upper 90%= 2,167,000 lower 90%= 2.003,000
nitrate (as N)	median = 56,000 upper 90%= 62,000 lower 90%= 51,000	median = 23,000 upper 90%= 27,000 lower 90%= 20,000	median = 18,000 upper 90%= 22,000 lower 90%= 14,000
orthophosphate (as P)	median = 15,000 upper 90%= 17,000 lower 90%= 14,000	median = 14,000 upper 90%= 15.000 lower 90%= 13.000	median = 10,000 upper 90%= 11,000 lower 90%= 9,000
sulfate	median = 4,898,000 upper 90% = 5,649.000 lower 90% =4.410.000	median = 5,370.000 upper 90% = 5,475.000 lower 90% =5,250,000	median = 4,137,000 upper 90% = 4,335,000 lower 90% = 3,932,000

Table 20. Median hydrochemical budget for Barr Lake including upper and lower 90% values.

Constituent	budget (kg/yr)		
	1997	1998	1999
calcium	median = 541,000 upper 90% = 818,000 lower 90% =283,000	median = 97,000 upper 90% = 236,000 lower 90% =-20,000	median = 448,000 upper 90% = 659,000 lower 90% = 250,000
sodium	median = 651,000 upper 90%= 1,031,000 lower 90%= 244,000	median = 477,000 upper 90%= 835,000 lower 90%= 206,000	median = 480,000 upper 90%= 765,000 lower 90%= 7,000
nitrate (as N)	median = 147,000 upper 90%= 179,000 lower 90%= 114,000	median = 118,000 upper 90%= 142,000 lower 90%= 99,090	median = 117,000 upper 90%= 137,000 lower 90%= 99,000
orthophosphate (as P)	median = 20,000 upper 90%= 41,000 lower 90%= 3,000	median = 0 upper 90%= 1,000 lower 90%= -2,000	median = 4,000 upper 90%= 9,000 lower 90%= -1,000
sulfate	median = 2,014,000 upper 90% = 3,845,000 lower 90% = 452,000	median = 656,000 upper 90% = 1,019,000 lower 90% = 327,000	median = 667,000 upper 90% = 1,259,000 lower 90% = 60,000

The majority of the residuals used to estimate uncertainty associated with water quality were not found to be serially correlated using the Durbin-Watson test (Table 21). The residuals associated with losses of Ca, Na, PO_4-P and SO_4 to groundwater (from the Barr Lake models) were found to be serially correlated however. Significant serial correlation is indicated by test statistics below 1.5 (Weisberg, 1985). Residuals used in the bootstrapping procedure are included (in graphical form) in Appendix B. There is some disagreement regarding the validity of bootstrapping procedures using serially correlated residuals. The extent to which the residuals (used for the estimate of uncertainty associated with fluxes to groundwater) are serially correlated, compromised estimates of uncertainty for the overall mass budget may have occurred.

Table 21. Durbin-Watson test statistics for serial correlation of residuals used in bootstrapping procedure.

Consituent	**Influent**	**Barr Lake (groundwater fluxes)**	**East Outfall**	**West Outfall**
Calcium	2.35	0.73*	1.96	2.06
Sodium	2.09	0.71*	1.61	1.58
Nitrate (as N)	1.96	1.69	1.54	1.59
Orthophosphate	2.29	1.27*	1.75	1.63
Sulfate	2.04	1.20*	1.83	1.50

*indicates significant serial correlation

5.2. Evaluation of in-lake phosphorus-retention mechanisms

5.2.1. Field studies

5.2.1.1. Limnological chemistry

Limnological studies on Barr Lake indicate that the lake can be considered polymictic (mixes throughout the year), and does not thermally stratify for significant periods of the year (Table 22 and Figure 18). The general lack of a thermal or chemical stratification in Barr Lake allows for complete mixing during most months of the year, limiting the potential for anoxic conditions to develop at the sediment-water interface, thereby minimizing release of iron bound phosphorus from the sediment as suggested by the Fe:P model. This degree of mixing also minimizes the potential for abiotic denitrification to occur to a significant extent.

High water column pH is observed for most of the summer season, resulting in deprotonation of orthophosphoric acid to the form HPO_4^{2-}. The high pH acts to minimize surface adsorption of phosphate by two mechanisms:

1) HPO_4^{2-} has been shown to adsorb only minimally to iron (hydr)oxides (Golterman, 1995), and
2) Competition for adsorption sites by OH^-.

The pH measurements collected from the sediment-water interface indicate slightly lower values than observed in the bulk water column (Figure 19). This result is important because it suggests the adsorption of OH^- to the surface sites of iron (hydr)oxides present in the sediment may influence pH at the sediment-water interface.

Dissolved oxygen concentrations at the sediment-water interface have been observed to be very low during summer months (Figure 20), but the lack of a strong thermocline allows oxidizing conditions to exist at the sediment water interface for most of the year.

No samples taken from the sediment-water interface indicated release of phosphorus from the sediment to the water column. Water quality profiles are consistent with complete mixing with respect to orthophosphate-P (Figure 24). The high water-column concentrations of orthophosphate-P observed throughout the summer months probably limit any flux of orthophosphate-P from the sediment to the water column, due to the lack of a strong chemical gradient. Minor increases in orthophosphate-P observed on 11 September 97 and 21 March 97 at the sediment-water interface, but are not considered to be significantly different than the bulk water-column concentrations. Seasonal differences in profiles are the result of phosphorus uptake by biota (particularly between the 21 March 97 profile and the 17 July 97 profile). The lack of difference in profiles during the late summer (July-October) is consistent with nitrogen or light limitation occurring in Barr Lake.

Table 22. Mean temperature, dissolved oxygen, calcium, sodium, nitrate, orthophosphate and sulfate profiles taken from Barr Lake. Mean values are calculated using data collected at Stations 1, 2, and 3.

Date	depth (m)	temperature °C	dissolved oxygen (mg/L)	Calcium (mg/L)	Sodium (mg/L)	Nitrate (mg/L as N)	Orthophosphate (mg/L as P)	Sulfate (mg/L)
21 March 97	0	8.1	9.0	65	75	3.30	0.57	125
	1	7.9	9.5	65	75	3.42	0.56	132
	3	6.9	9.6	65	76	3.34	0.57	125
	7	5.9	9.2	65	77	3.25	0.57	132
17 July 97	0	22.9	14.3	51	57	0.42	0.24	82
	1	22.5	11.5	51	57	0.47	0.37	80
	3	22.3	9.8	52	58	0.51	0.27	84
	6	21.7	6.6	52	58	0.51	0.35	82
26 August 97	0	22.8	9.4	46	46	0.13	0.27	70
	1	22.2	8.0	48	47	<0.02	0.28	73
	3	22.0	8.0	47	48	<0.02	0.28	74
	6	21.7	6.5	47	48	<0.02	0.30	65
11 September 97	0	21.1	7.2	49	50	0.04	0.25	72
	1	22.1	9.3	49	51	<0.02	0.30	70
	3	21.4	8.0	49	51	<0.02	0.31	73
	6	21.1	6.1	49	51	<0.02	0.30	73
09 October 97	0	19.3	9.9	50	50	0.04	0.25	72
	1	16.5	8.8	49	51	0.06	0.26	64
	3	16.5	8.0	51	51	0.06	0.26	77
	5	15.3	7.8	51	54	0.07	0.26	75

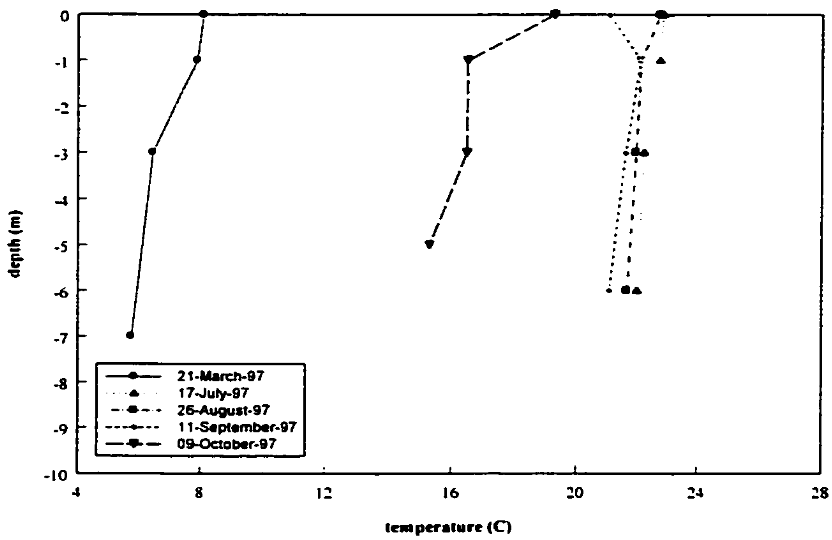


Figure 18. Temperature profiles from Station 1, Barr Lake - water year 1997.

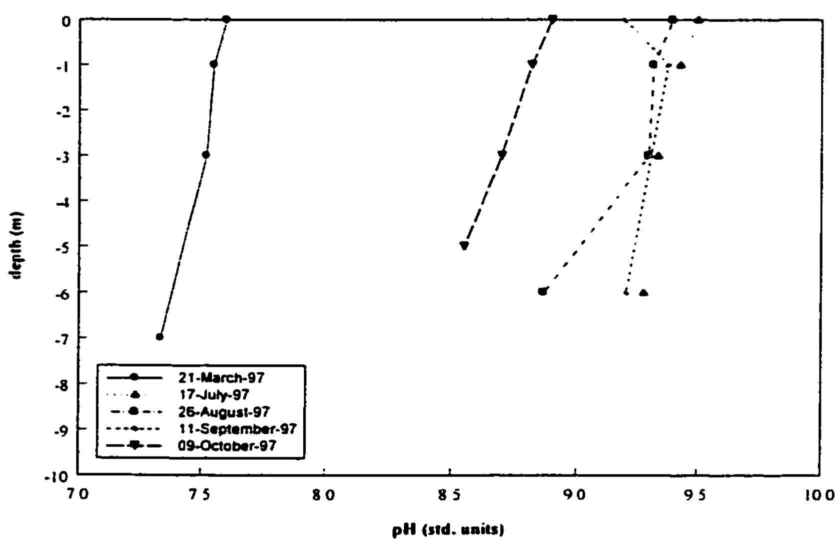


Figure 19. pH profiles from Station 1, Barr Lake - water year 1997.

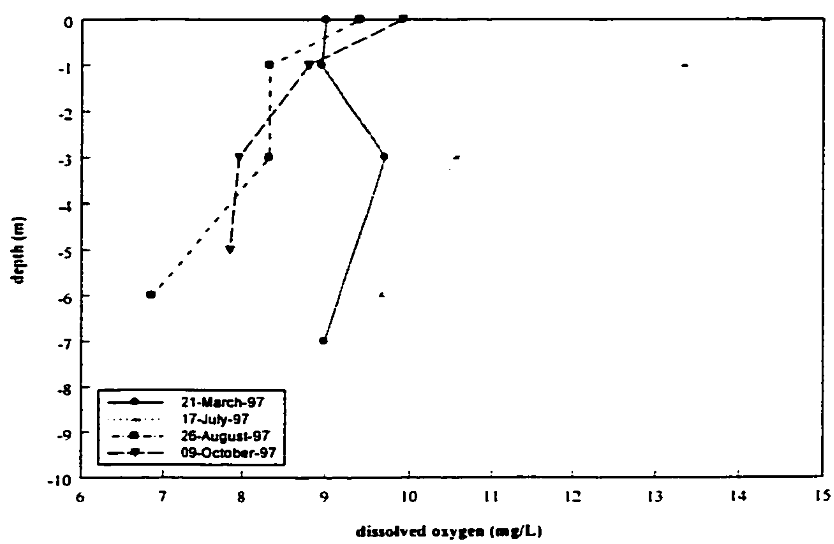


Figure 20. Dissolved oxygen profiles from Station 1, Barr Lake - water year 1997.

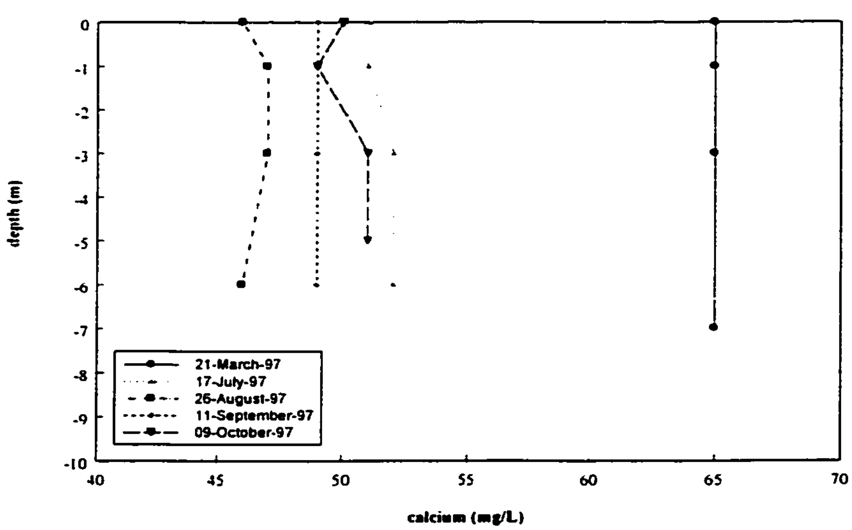


Figure 21. Calcium profiles from Station 1, Barr Lake - water year 1997.

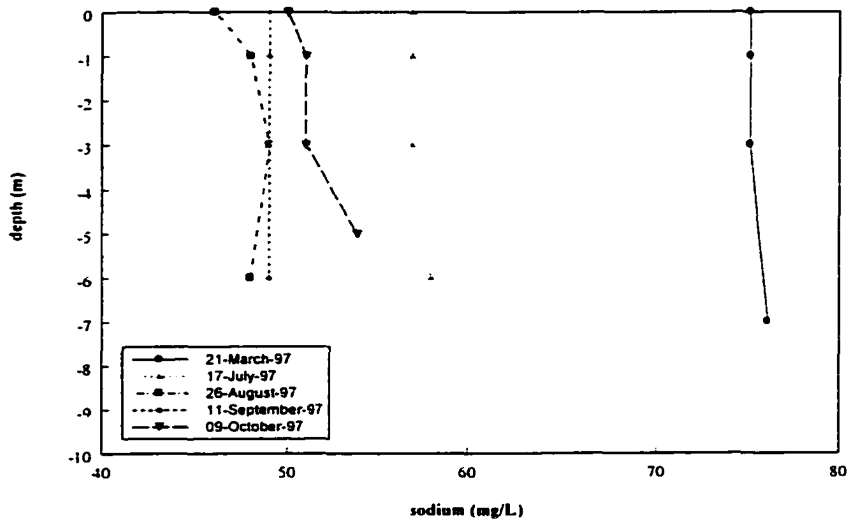


Figure 22. Sodium profiles from Station 1, Barr Lake - water year 1997.

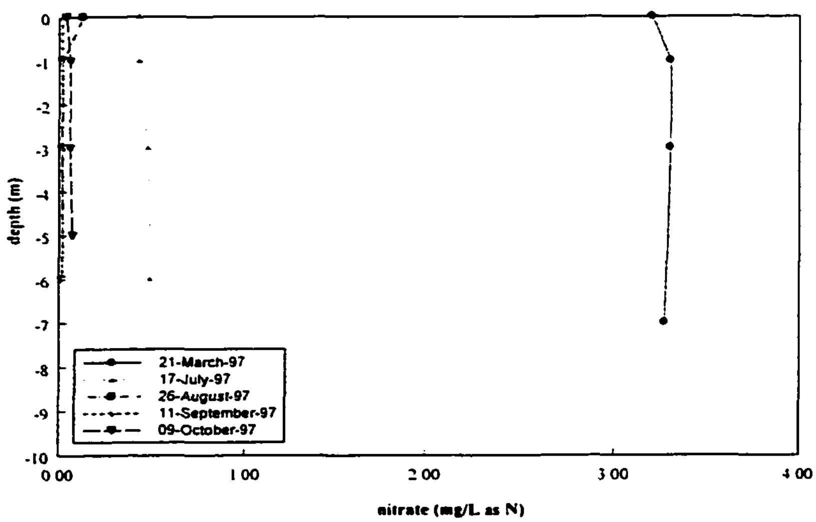


Figure 23. Nitrate (as N) profiles from Station 1, Barr Lake - water year 1997.

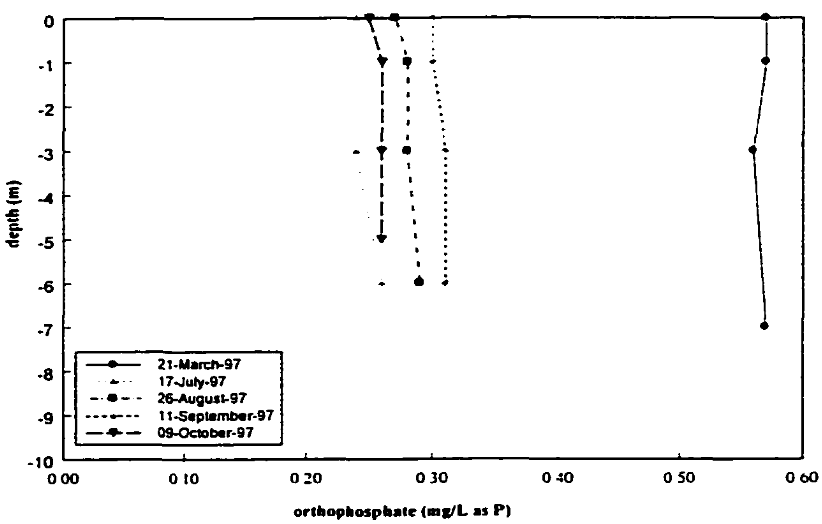


Figure 24. Orthophosphate (as P) profiles from Station 1, Barr Lake - water year 1997.

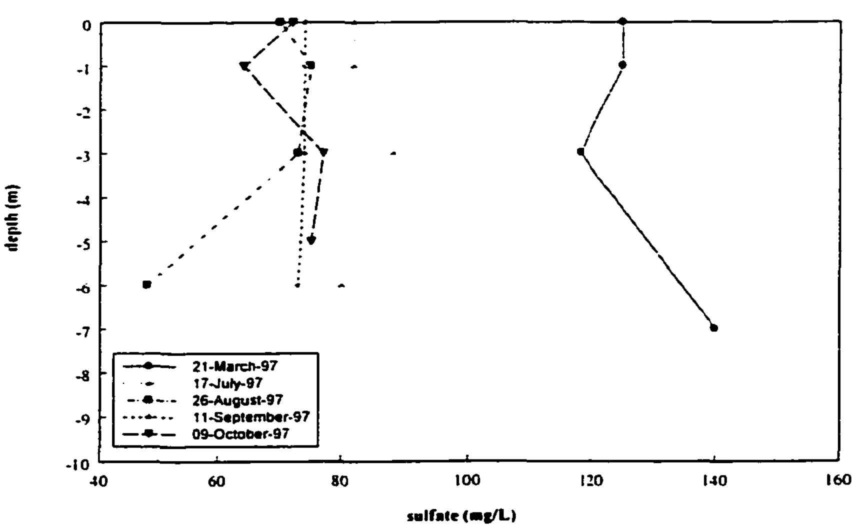


Figure 25. Sulfate profiles from Station 1, Barr Lake - water year 1997.

Seasonal differences in profiles for nitrate-N reflect biotic uptake, the highest concentrations observed in the 21 March 97 profile decreasing throughout the growing season to values below detection in the late summer. Nitrate reduction (to ammonia/ium) was not observed at depth, consistent with mixing of dissolved oxygen to the sediment-water interface for most periods of the year. The lack of direct evidence of denitrification in Barr Lake limits water-column nitrogen cycling to organic and aqueous nitrate forms, and suggests that loss of nitrogen though gaseous phase (e.g. $N_{2(g)}$, $N_2O_{(g)}$) losses is probably minimal. The possibility exists however, that denitrification could occur following mineralization of organic matter within the sediment and subsequent loss of reduced nitrogen species.

Calcium, sodium and sulfate profiles are also indicative of the lack of chemical stratification (Figure 21, Figure 22, Figure 25) and consistent decreases observed between successive sampling dates for all three constituents is indicative of the dilution flows associated with the filling of Barr Lake during the snowmelt/stormflow period.

Comparison of sodium profiles with the orthophosphate profiles however, clearly illustrates the dynamic behavior of orthophosphate in the water column associated with biotic uptake and release. Although sodium concentrations in the water column decrease steadily throughout the season, orthophosphate concentrations decrease rapidly early in the summer season and increase in subsequent profiles, followed by minor decreases suggesting initial uptake by biota until nitrogen/light limitation results in the observed increases in water column orthophosphate. Low nitrate concentrations for the remainder of the season likely results in short-term orthophosphate uptake and release by the organic phase, causing short-lived increases and decreases in water column orthophosphate concentrations (Figure 24). This behavior is reflected in water-column nitrate concentrations, probably due to a combination of factors including N:P ratio and algal species composition. Water quality data indicate that, during the growing season, when nitrate concentrations in the water column are above detection, the orthophosphate concentrations are the lowest measured (17 July 97 and 09 October 97). When nitrate concentrations are very low, orthophosphate concentrations tend to be high (26 August 97 and 11 September 97). This opposing behavior may be explained through changing N:P ratios removed from the water column later in the season compared to early season. Early season algal communities are expected to uptake N:P in a ratio of approximately 16:1 and deplete the water column of both nitrogen and phosphorus. Under nitrogen-limiting conditions later in the season, the algal community is expected to change to low nitrogen-tolerant or nitrogen-fixing species (Shapiro, 1972). Release of nitrogen and phosphorus through mineralization of biomass containing high N:P ratios and uptake at a lower ratio later in the season should result in increasing nitrogen concentrations in the water column later in the season. This effect could explain nitrate increases and concurrent orthophosphate decreases observed in the 09 October 97 sample.

5.2.1.2. Groundwater chemistry

Constituent concentrations in groundwater samples collected from the drain at the base of Barr Lake dam indicated little variation throughout the year (Figure 26 - Figure 33). Orthophosphate concentrations observed in the drain were the lowest in the Barr

Lake system (median = 0.05 mg/L and 0.04 mg/L or $10^{-5.79}$ M and $10^{-5.88}$ M in 1997 and 1998 respectively). This finding suggests that as water moves from Barr Lake through the sediment, significant retention of PO_4-P by the sediment/groundwater matrix occurs.

Nitrate concentrations were also low in the groundwater samples, but ammonia/ium concentrations were the highest observed in the Barr Lake system, indicating reduction of nitrate as water moves from the lake to the groundwater. The reduction of nitrate to ammonia/ium is consistent with the observation of high manganese concentrations in the groundwater (Figure 27 - Figure 33). Iron concentrations, however were below the detection limit (0.05 mg/L) for the entire sampling period, indicating that only moderately reducing conditions are present in the groundwater. Eh measurements (Figure 34 - Figure 35) indicated only moderately reducing conditions consistent with both manganese and nitrate reduction. The high total inorganic nitrogen concentrations present in the groundwater are inconsistent with in-lake concentrations observed for large parts of the summer season. Although the low nitrate (and non-detect ammonia/ium) concentrations observed in Barr Lake are suggested by the variability in nitrate and ammonia/ium concentrations in the groundwater, high total inorganic nitrogen concentrations suggest that the sediment is acting as a source of nitrogen to the aqueous phase of the groundwater seeping from Barr Lake. This opposing behavior to orthophosphate in the groundwater is probably the result of organic phase release of both nitrogen and phosphorus in the sediment followed by adsorption or precipitation of solid phase phosphate and migration and reduction of nitrate through the groundwater matrix.

Because Barr Lake tends to be a losing system, groundwater chemistry has little influence on in-lake nutrient concentrations and therefore little influence on nutrient dynamics in Barr Lake. It is important, however to understand the fate of nutrients in groundwater with regard to potential re-release to the water column of adsorbed or solid phase constituents.

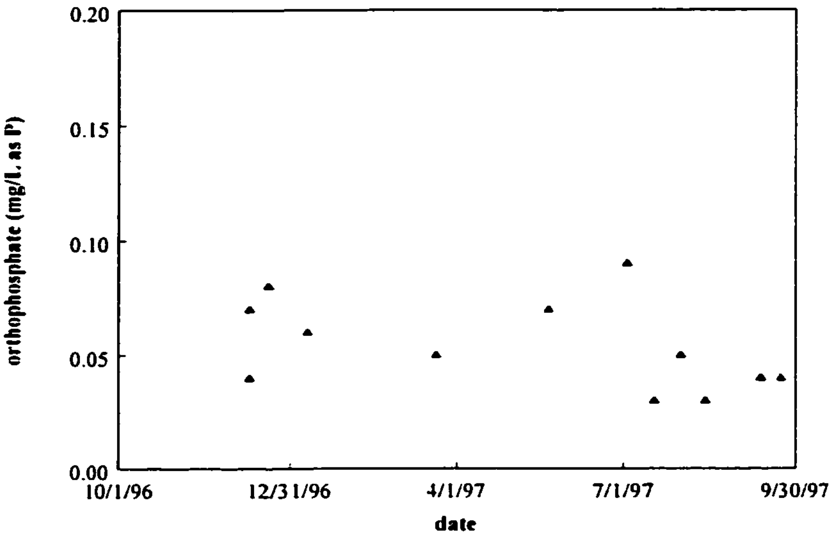


Figure 26. Orthophosphate (as P) concentrations in groundwater - water year 1997.

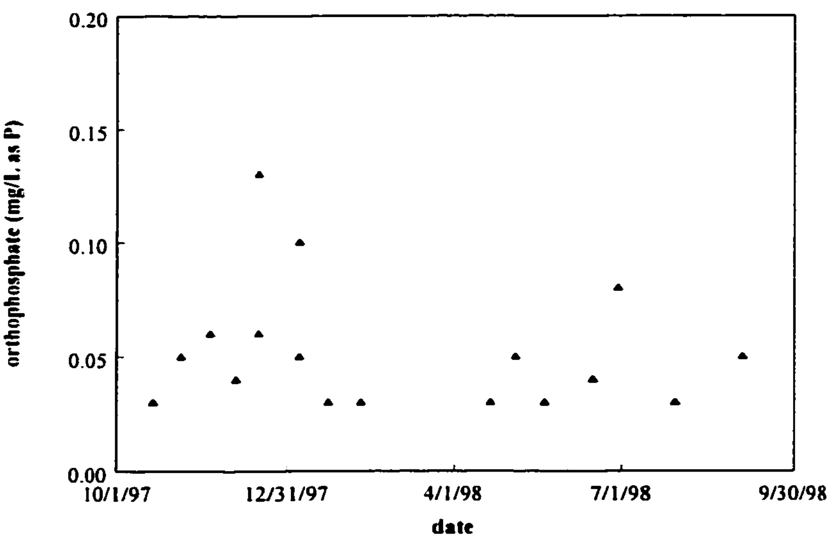


Figure 27. Orthophosphate (as P) concentrations in groundwater - water year 1998.

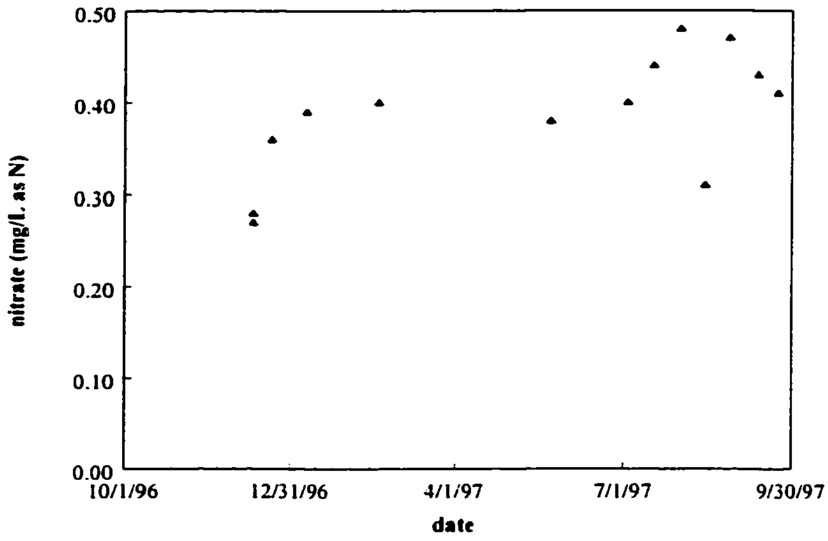


Figure 28. Nitrate (as N) concentration in groundwater - water year 1997.

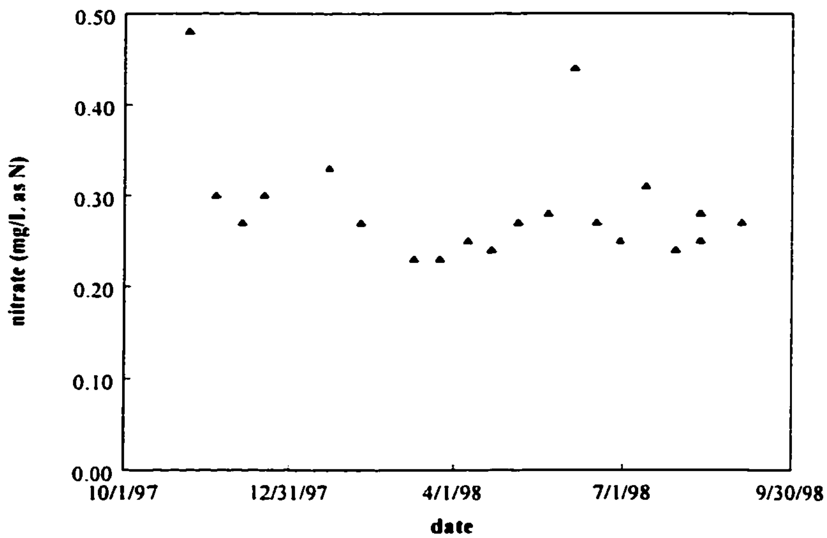


Figure 29. Nitrate (as N) concentrations in groundwater - water year 1998.

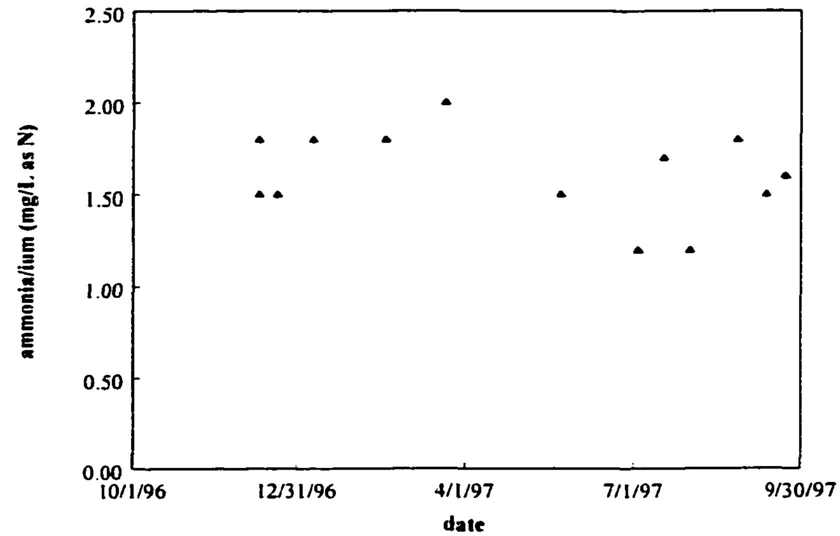


Figure 30. Ammonia/ium (as N) concentration in groundwater - water year 1997.

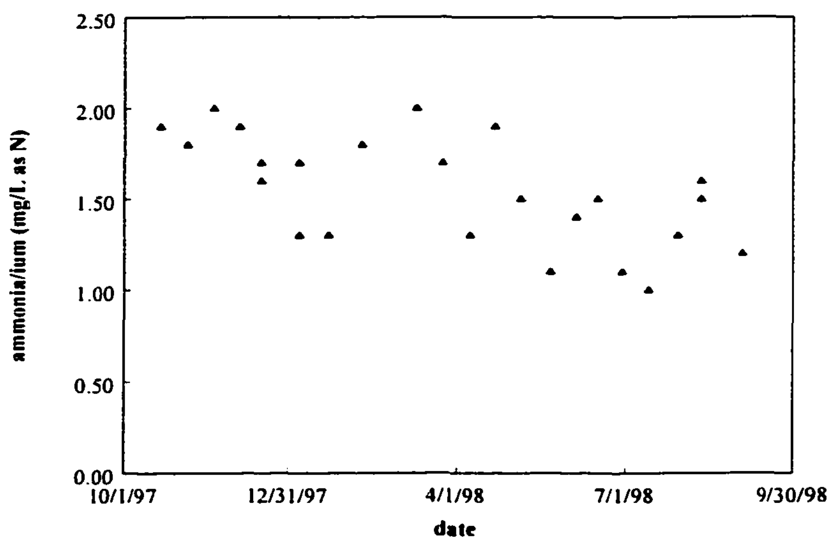


Figure 31. Ammonia/ium (as N) concentration in groundwater - water year 1998.

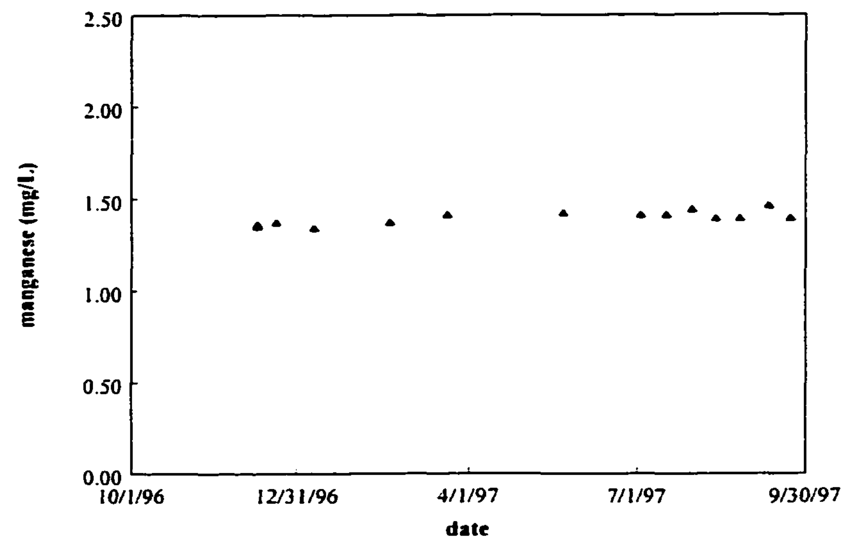


Figure 32. Manganese concentrations in groundwater - water year 1997.

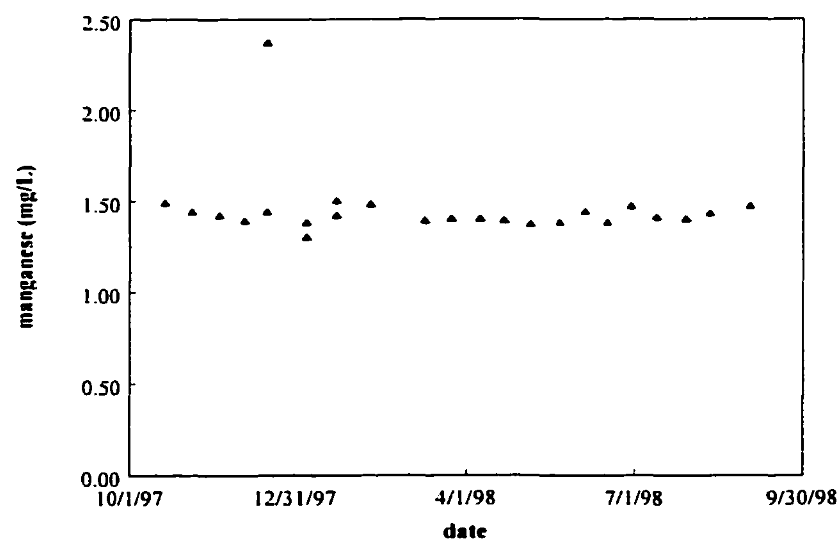


Figure 33. Manganese concentrations in groundwater - water year 1998.

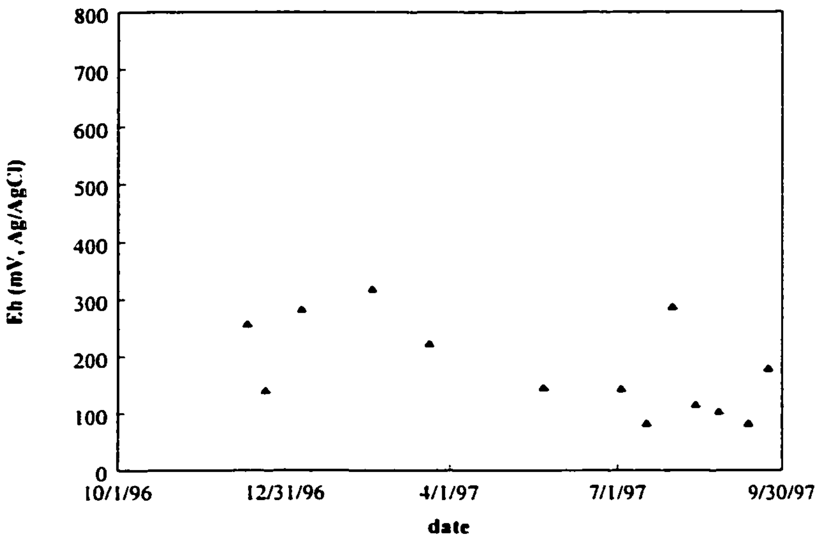


Figure 34. Eh measurements in groundwater - water year 1997.

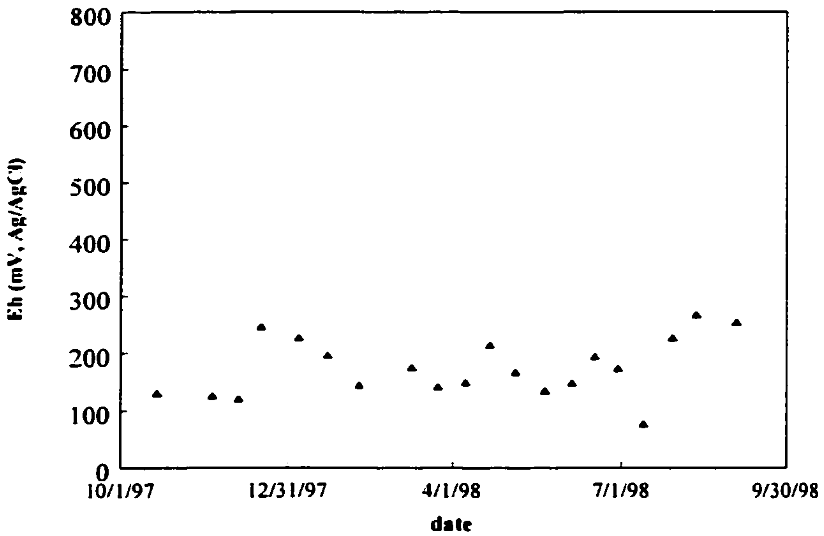


Figure 35. Eh measurements in groundwater - water year 1998.

5.2.1.3. Physical and chemical properties of lake sediments

Results from the chemical extraction of the littoral and pelagic sediment indicate that the pelagic sediment contains substantially higher concentrations of phosphorus, iron and manganese (Table 23). Sediment from the pelagic zone of Barr Lake contained approximately 16% organic matter by weight, which suggests that the higher phosphorus is related to the organic phase.

Chemical differences between the littoral and pelagic sediment (lower iron, manganese and phosphorus in the littoral sediment) reflect changes that occur as sediment becomes oxidized. Significant to this change is that the Fe:P ratio remains approximately 30:1 for both sediment types. This finding suggests that adsorption of phosphate to iron is not a significant removal mechanism. If iron were a significant control, a difference in the Fe:P ratio would be expected (e.g. decreasing as the sediment becomes oxidized). In contrast, ratios of Mn:P increase as sediment becomes oxidized (from 0.35:1 to 0.63:1 by weight), suggesting that retention of phosphorus by manganese may be occurring in the sediment of Barr Lake. Molar Mn:P ratios suggest that authigenic solid phase manganese phosphate may be forming in both the pelagic and littoral sediment, but other sinks of phosphorus are likely given the ratios of less than 1. Adsorbed phase phosphate (to either iron or manganese (hydr)oxides) may be occurring at some level, but Metal:P ratios suggest that this removal mechanism is either not significant or not behaving as suggested by literature (i.e. Fe:P ratio of 2:1).

Table 23. Sediment analysis after perchloric digestion

Constituent	**Total extractable (mg/kg)**	
	littoral sediment	**pelagic sediment**
Iron	7780	24400
Manganese	162	296
Phosphorus	257	838
Fe:P (weight)	30:1	29:1
Mn:P (weight)	0.63:1	0.35:1
Mn:P (mol)	0.35:1	0.20:1

X-ray diffraction analysis (XRD) using random powder packed mounts of the sediment indicated presence of crystalline quartz and feldspar, consistent with the geologic conditions in the Front Range of Colorado (Trimble and Machette, 1979). Crystalline phase phosphorus minerals were not identified by XRD. Clay minerals identified using glycolated and air dried mounts of the sediment included kaolinite, illite, and montmorillonite. X-ray diffraction spectra are included in Appendix C.

The low overall quantities of iron, manganese and phosphorus in the sediments of Barr Lake, both littoral and pelagic, suggests that the sediments play only a minor role in the nutrient dynamics of Barr Lake.

5.2.2. Laboratory experimentation: sediment extraction using controlled redox conditions

The sediment extraction experiment under controlled redox conditions was conducted continuously for a period of approximately 120 days. The initial appearance of the sediment suggested reducing conditions, but measured pe+pH values at the beginning of the experiment were approximately 12.9. It is likely that actual conditions in the Barr Lake sediment are more reducing, but experiment setup resulted in sediment oxidation.

The initial phase of the experiment consisted of addition of atmospheric air to the sediment slurry to achieve oxidizing conditions. This initial oxidation required a period of approximately 30 days to achieve a maximum pe+pH of 15.8. The reduction phase of the experiment consisted of addition of 1% $H_{2(g)}$ and required approximately 75 days to

Table 24. Constituent concentrations at pe and pH values during the sediment extraction under controlled redox conditions.

pe+pH	pH (std. units)	Orthophosphate (mg/L as P)	Nitrate (mg/L as N)	Sulfate (mg/L)	Iron (mg/L)	Manganese (mg/L)
12.9	6.6	2.23	<0.02	107	2.45	8.92
12.9	6.6	1.77	0.02	121	2.45	8.92
14.7	5.6	<0.03	14.01	636	0.39	8.89
15.8	3.4	<0.03	8.91	892	0.39	8.89
12.6	3.8	<0.03	5.63	837	No determination	No determination
11.6	4.4	<0.03	0.20	858	58.76	9.97
8.3	6.2	<0.03	<0.02	1070	155.90	8.24
7.7	6.7	<0.03	<0.02	1047	153.00	7.13
5.5	6.8	<0.03	<0.02	994	146.60	7.19

achieve the minimum pe+pH value measured in the experiment of 5.5. The third phase of the experiment consisted of reoxidation of the sediment to a pe+pH of 15.5 through addition of atmospheric air. The reoxidation phase required approximately 15 days.

Phosphorus concentrations observed during the experiment suggested that organic-phase phosphorus is the primary source of orthophosphate reintroduced to the water column from the sediments (Table 24). Orthophosphate concentrations in the aqueous phase were present in concentrations above the detection limit of 0.03 mg/L only during the initial oxidation. Controlled pe+pH values of 12.9 resulted in PO_4 - P concentrations of 2.23 and 1.77 mg/L in successive samplings. This result suggests that as organic phase phosphorus was released, it was removed from the aqueous phase by either solid phase precipitation or surface adsorption to sediment particles.

Subsequent reduction of the sediment did not result in release of phosphorus to the aqueous phase, phosphorus was below the detection limit. This result is inconsistent with work by others that indicated that reducing conditions leads to phosphorus release from sediments through iron reduction (e.g. Mortimer, 1942; Lijklema, 1977). This result implies that adsorption of phosphate to iron (hydr)oxides in the sediment is either insignificant in terms of mass or is readsorbed to a reduced form of iron (hydr)oxide, such as amorphous magnetite. Subsequent reoxidation did not result in phosphorus release, nor was phosphorus release observed under the low pH condition developed during the oxic phase of the experiment. This result suggests that pH sensitive precipitation or adsorption of phosphorus did not occur.

The presence of clay minerals in the sediments of Barr Lake raises the possibility of phosphorus adsorption to the surface of particularly montmorillonite and illite. which have the potential for adsorption at pH values observed in Barr Lake. Kaolinite is not expected to provide significant adsorption of phosphorus at the pH values typically observed in reservoirs on the eastern plains of Colorado (i.e. pH values >8.0).

Nitrate by contrast, was released from the organic material following phosphorus at a pe+pH value of approximately 12.6 reaching a maximum value at pe+pH 14.7 (Table 24). Nitrate-N concentrations observed during the experiment were either below detection (<0.02 mg/L) or at detection (0.02 mg/L) while measurable PO_4-P was in solution (Table 24). Nitrate-N concentrations increased at higher pe+pH values (14.01 mg/L at pe+pH 14.7), followed by decreased concentration at the maximum pe+pH value (8.91 mg/L at pe+pH 15.8).

Subsequent reduction of the sediment resulted in nitrate reduction (probably to ammonia/ammonium) and a decreased nitrate-N concentration at pe+pH 12.6 (5.63 mg/L). Nitrate was not detected at pe+pH values lower than 11.6.

The reoxidation of the sediment did not result in measurable concentrations of nitrate-N. Loss of nitrogen from the water column by off gassing of nitrogen oxides and or ammonia probably explains this result.

Sulfate concentrations increased steadily throughout the entire experiment under both oxidizing and reducing conditions. Concentrations of sulfate were the lowest at the beginning of the experiment (107 mg/L), suggesting that either solid phase sulfides were present, or that dissolution rates of sulfate minerals (e.g. gypsum) present in the sediment were slow. Sulfate concentration (892 mg/L) at the most oxidizing condition (pe+pH

15.8) approached saturation with gypsum and remained high for the remainder of the experiment. Minor decreases in sulfate concentration were observed under reducing conditions (pe+pH 7.7 and 5.5) but sulfate-reducing conditions were not achieved during the experiment.

Cations were measured for selected portions of the experiment and redox sensitive constituents (e.g. iron and manganese) were speciated using MINTEQA2 (Allison, et al., 1991) (Figure 36- Figure 37). Maximum iron concentration (155 mg/L) was measured when pe+pH was approximately 8.3 (Table 24). Iron concentrations decreased with increasing pe+pH as expected (Lindsay, 1979). Manganese concentrations remained relatively stable (between 7 and 10 mg/L) over a wide range of pe+pH values (Table 24).

Calcium concentrations observed in the reaction vessel during the experiment did not suggest pH dependence (Figure 38). This result is consistent with the sulfate concentrations measured during the experiment (i.e. equilibrium with gypsum), although crystalline phase gypsum was not identified by XRD.

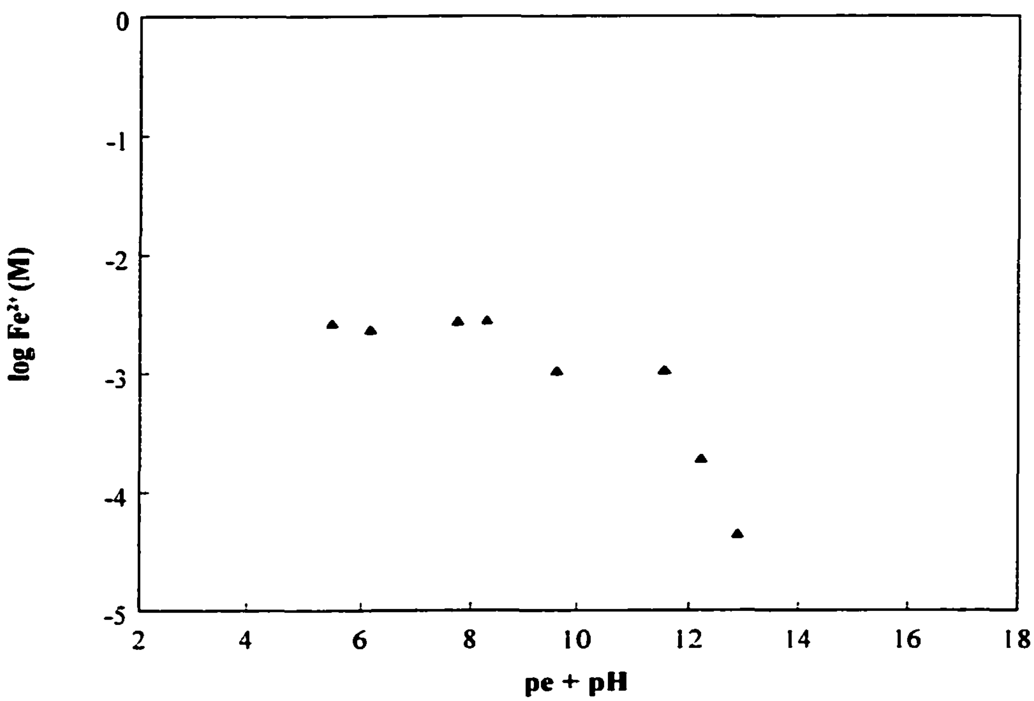


Figure 36. Fe^{2+} activity measured during the sediment extraction experiment.

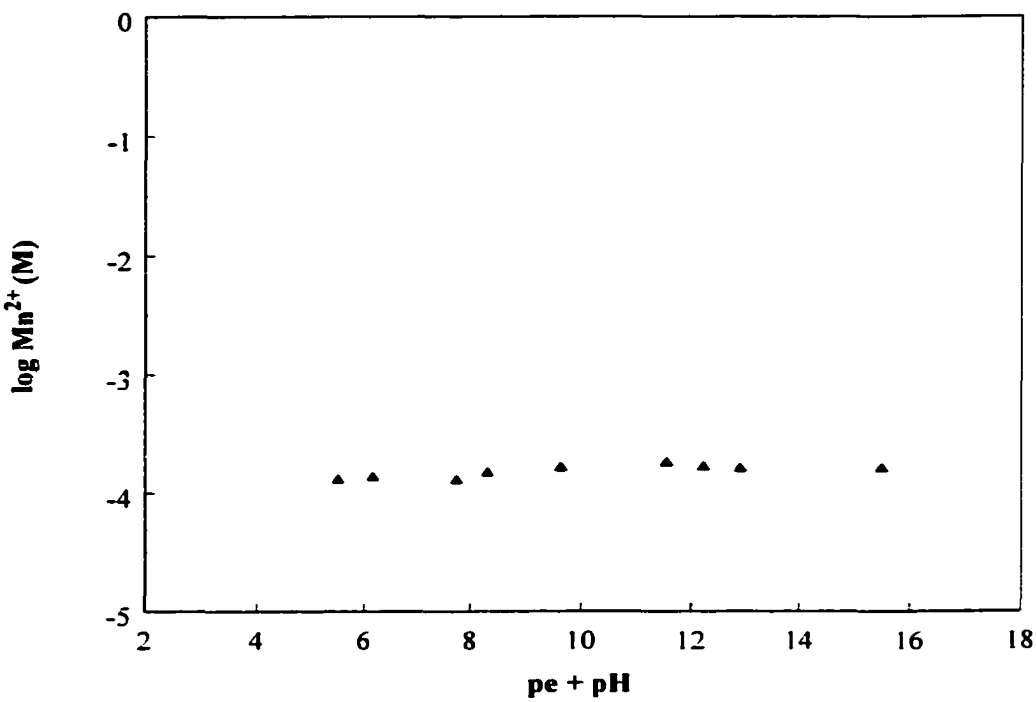


Figure 37. Mn^{2+} activity measured during the sediment extraction experiment.

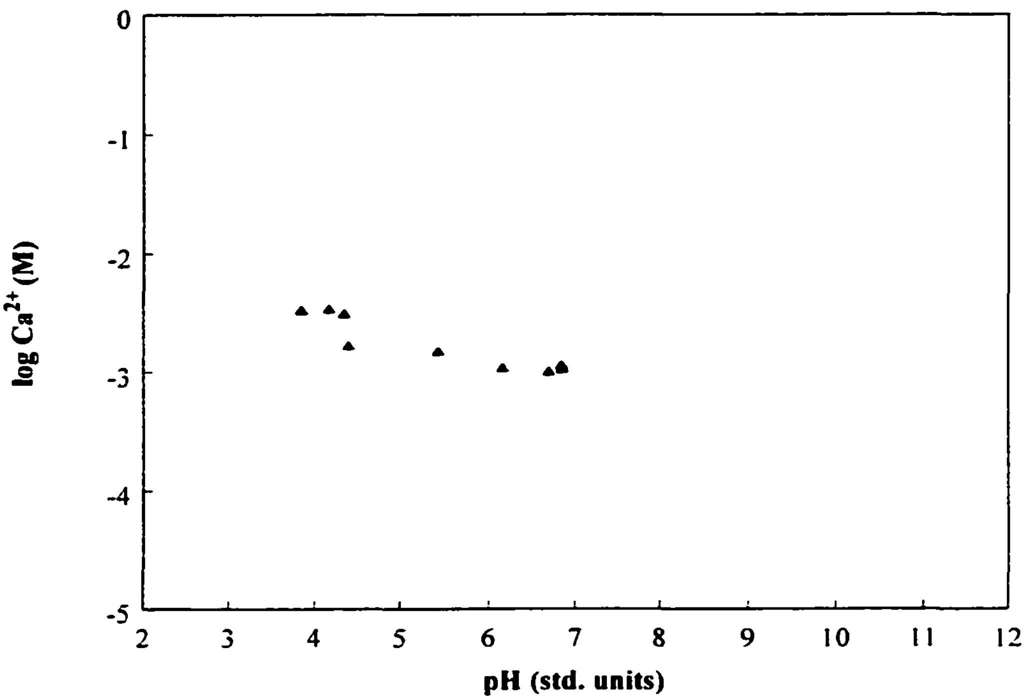


Figure 38. Ca^{2+} activity measured during the sediment extraction experiment.

6. Discussion

6.1. Calculation of an annual mass balance for Barr Lake

6.1.1. Water budget

To accurately assess chemical dynamics in reservoirs, accurate water budgets are a critical first step. Each component of the water budget should be evaluated and understood in terms of measurement precision and accuracy. The water budget components for Barr Lake consist of:

1. surface water inflows and outflows,
2. volume measurements (storage),
3. precipitation inputs,
4. evaporation losses, and
5. groundwater losses or gains.

For Barr Lake and many other reservoirs on the eastern plains of Colorado, the major components of the water budget are controlled and measured accurately. Flows through the gaging structure (and into Barr Lake) are rigorously controlled and measured by FRICO based on water rights and water availability. Intra-day variability in inflow to Barr Lake is therefore minimal, and the reported values for inflow to Barr Lake are subject to relatively low uncertainty. However, the accuracy of the inflow measurement may be compromised during flow extremes. In particular, any flows associated with seepage through the control gates are not recorded as inflows to Barr Lake. Also, extremely high flows, when accompanied by high surface elevation in the lake floods the measurement weir, likely resulting in overestimates of inflow to the lake. No attempt to account for these potential inaccuracies was conducted.

While daily flow variability is low, annual differences in water availability resulted in inflow volumes to Barr Lake that varied substantially between years of study. To a large extent, water availability dictates the timing of flows into Barr Lake, and timing of inflows also varied substantially between water years. During water year 1998, water availability was greatest, and a high volume of waters with low concentration was diverted to Barr Lake during the snowmelt/stormflow season (Figure 4 - Figure 6). In water years 1997 and 1999, when water availability was less, lower volumes were diverted during this period, and a greater portion of annual inflow occurred during fall and winter months. In an effluent dominated system like Barr Lake, one might expect annual nutrient loads to be highest in a water year where inflows are highest. However, because substantial filling occurred during the snowmelt/stormflow period, this was not the case for inflows to Barr Lake during water year 1998. Rather, the highest loads were found in water year 1997, when hydraulic fluxes were substantially less. This result suggests that both the timing and amount of water available have a significant effect on hydrochemical loads into Barr Lake.

Surface outflows from Barr Lake were not subject to the same level of inaccuracy in measurement as the surface inflows. Specifically, the two outflow structures did not exhibit seepage and the measurement flumes are not subject to flooding. The controllability of the surface-water outflows makes these measurements of discharge subject to low variability, high precision and low uncertainty. The amount and timing of discharges from Barr Lake are determined by downstream irrigation demand. As with the inflow, the amount and timing of outflow from Barr Lake appears to have a substantial influence on the nutrient budgets for Barr Lake. Specifically, discharges during the later portion of the irrigation season tend to have the lowest nitrate concentrations. This result is consistent with lower in-lake nitrate concentrations during the later part of the irrigation season.

Storage measurements in Barr Lake are measured by a staff-gage, read by FRICO personnel. Translation to volume stored in the lake is therefore subject to any inaccuracies associated with the stage-volume relationship, which is not updated annually. The relationship for Barr Lake has been determined by bathymetric survey and is of the exponential form:

$$Volume_{(acre\ feet)} = \left[stage_{(feet)}\right]^{1.9} \cdot 35.84$$

The relationship indicates that at high lake levels, in particular, a small error in measurement would result in a large error in reporting of lake volume or change in storage. On an annual basis however, this error is probably not large since all other components of the water budget must be considered. Years in which storage in Barr Lake was positive (water years 1997 and 1999) are generally coincident with years in which precipitation was high, consistent with lower irrigation demand. Positive annual storage does not appear to substantially influence nutrient retention, probably because the increase in storage is a small volume relative to the influent and effluent volumes observed for Barr Lake on an annual basis (less than 10%). Estimates for water gained to Barr Lake by precipitation were derived by multiplying the measured precipitation depth at Denver International Airport (DIA) (approximately 5 km from Barr Lake) and the surface area of Barr Lake on the date in which the precipitation occurred. The results indicate that precipitation has a minor influence on the water budget for Barr Lake (less than 10% of the inflow volume for each of the three years of study). Nonetheless, the estimate is subject to error associated with extrapolation of precipitation data from the DIA gage to Barr Lake, the stage-surface area relationship for Barr Lake and the assumption that overland flow to Barr Lake is an insignificant volume relative to other components of the hydrologic budget (only direct precipitation is included in the water budget). On an annual basis, the extrapolation of precipitation depths from the DIA gage is consistent with annual averages reported for the eastern plains of Colorado. The surface area-stage relationship is linear of the form:

$$Surface\ Area_{acres} = 51.9 \cdot (Stage_{feet}) + 62.07$$

This relationship is only somewhat sensitive to errors in stage measurement and error is probably minor in terms of volume on an annual basis. The assumption that no volume is added to Barr Lake by overland flow is likely valid based on the observation that the area surrounding Barr Lake is bordered by a levy road, which isolates the lake hydrologically. Estimates of evaporation were conducted using data from the Fort Lupton, Colorado Agricultural Meteorological Network Station located approximately 10 km from Barr Lake. Error associated with extrapolation of data over space is expected to be the main error component on a daily basis, but is probably minor on an annual basis. Other sources of error to the evaporation estimate are associated with the stage-surface area relationship (as described above), extrapolation of water temperature between actual measurements and, the assumption that sublimation from ice cover is accurately described using Equation 2. Application of Equation 2 required several assumptions:

1. Energy advected to the water body was assumed to be zero
2. Surface water temperature was assumed to be constant over a day
3. Wind speed was determined by dividing the daily wind run by 86,400
4. The psychrometric constant (γ) was assumed to be 0.055
5. The latent heat (λ) was calculated based on mean daily temperatures

Sensitivity analysis conducted on the components of Equation 2 indicated that temperature differences in the range observed seasonally in Barr Lake had little influence on the overall calculation of E_p. Energy advected to Barr Lake by inflows from the O'Brian Canal may have resulted in an underestimate of evaporation, but on an annual basis, the evaporation calculated for Barr Lake is consistent with reported values for the Eastern Plains of Colorado (approximately 60 in/year)(Siemer, 1977). Although evaporation loss from Barr Lake is a substantial part (approximately 20%) of the annual water budget, site-specific data are not expected to improve the estimate because of inherent difficulties associated with other methods (e.g. pan-evaporation measurements). One potential improvement that could be made would be to include a sublimation estimate for periods of ice cover.

Groundwater losses or gains were calculated by residual of all other components of the water budget. The estimate therefore contains the combined error associated with the measurement or calculation of each other component of the water budget. The high degree of daily fluctuation in calculated groundwater loss or gain reflect the uncertainty associated with the residual approach, although annual totals of groundwater loss agree with estimates made previously (Hydro-Triad, 1974). The high daily variability of groundwater loss or gain (Figure 10 - Figure 12) is probably an artifact of the method of calculation because the greatest variability is observed on days when other components of the water budget are highly variable (e.g. precipitation events and errors in storage measurement). It is possible, however, that bank storage and discharge may be responsible for part of this variability, given that water-surface elevation in Barr Lake is subject to a high degree of variability associated with reservoir operations. The between-year variability is also very high (ranging from losses of 12,520,000 m^3 to gains of 795,000 m^3). High groundwater loss in water year 1997 coincides with the highest nutrient retention observed during the period of study (see Section 6.2.1.3). The groundwater gain observed during water year 1999 is suspect, given the lower regional groundwater elevation around Barr Lake, although 1999 was a year of high precipitation.

Based on the water budget, the main hydrologic factors affecting chemical loads in the Barr Lake system are timing and quantity of the inflow and outflows. Precipitation and evaporation, although important in the hydrochemical budgets of many aquatic systems both in terms of volume and chemical influence, are minor relative to the surficial flows associated with the operation of Barr Lake.

6.1.2. Hydrochemical budget

The annual wastewater inputs to Barr Lake were lower during the period of study than estimated historically due to higher annual precipitation and the result of limited direct discharge of treated wastewater by Metro during the period of study.

Models fit for Barr Lake and the outfall structures mimic the inflow models with a phase shift based on residence time in Barr Lake. This result is consistent with published lake models (Chapra, 1997). Comparison of annual mean concentrations for total phosphorus with other hypereutrophic reservoirs indicates that Barr Lake total phosphorus concentrations tend to be higher by three to five times. The threshold value published for classification of a lake or reservoir as hypereutrophic is 0.1 mg/L total phosphorus. Values published in limnological literature are rarely reported above 0.15 mg/L total phosphorus (Annual mean values calculated for Barr Lake range from 0.29 mg/L to 0.52 mg/L). Annual mean values are misleading however, given the serial correlation of the data (e.g. non-normal distributions, lack of homogeneity of variance).

The lack of sodium balance (calculated retention) during water years 1997 and 1998 may be explained by cation exchange of clay minerals present. The extent to which this process occurs in Barr Lake is unknown and the magnitude would require laboratory investigation.

With respect to nutrient relationships in Barr Lake, higher NO_3-N loading in water year 1997 coincided with higher retention of PO_4-P in 1997, when compared to water years 1998 and 1999. Although rigorous nutrient limitation studies were not conducted, evidence from in-lake concentrations of NO_3-N for water year 1997 suggests that NO_3-N was available throughout the growing season (in low concentrations). Measured in-lake NO_3-N concentrations in water years 1998 and 1999, however, suggest possible nitrogen limitation during the summer months (Appendix A). Conversely, in-lake PO_4-P concentrations suggest available phosphorus for the entire water year. Mass balance analysis indicates that when nitrogen concentrations are low in Barr Lake, PO_4-P is not retained and the lake behaves as steady-state (input = output). The nature of operation of the reservoir allows for this phenomenon to occur. The timing of irrigation releases from Barr Lake (May through September) when in-lake nitrogen concentrations are low, result in outputs of phosphorus that can equal the inputs.

Removal of aqueous phase phosphorus by aquatic biota is expected to be greatest when other nutrients (i.e. nitrogen) are not limiting algal growth. In-lake nitrogen to phosphorus ratios tend to be below the 16:1 Redfield ratio during most parts of the year and particularly during the late summer (Figure 39). This variation in N:P ratio throughout the summer season is indicative of preferential removal of nitrogen relative to phosphorus. If aquatic biomass were consuming both nitrogen and phosphorus at a ratio of 16:1, as suggested by the Redfield ratio, N:P ratio would remain unchanged (in the aqueous phase) until either nitrogen or phosphorus became limited. This behavior is most clear during 1999, when the N:P ratio decreased abruptly in July to values that could not be calculated due to non-detection of inorganic nitrogen in Barr Lake during the late summer.

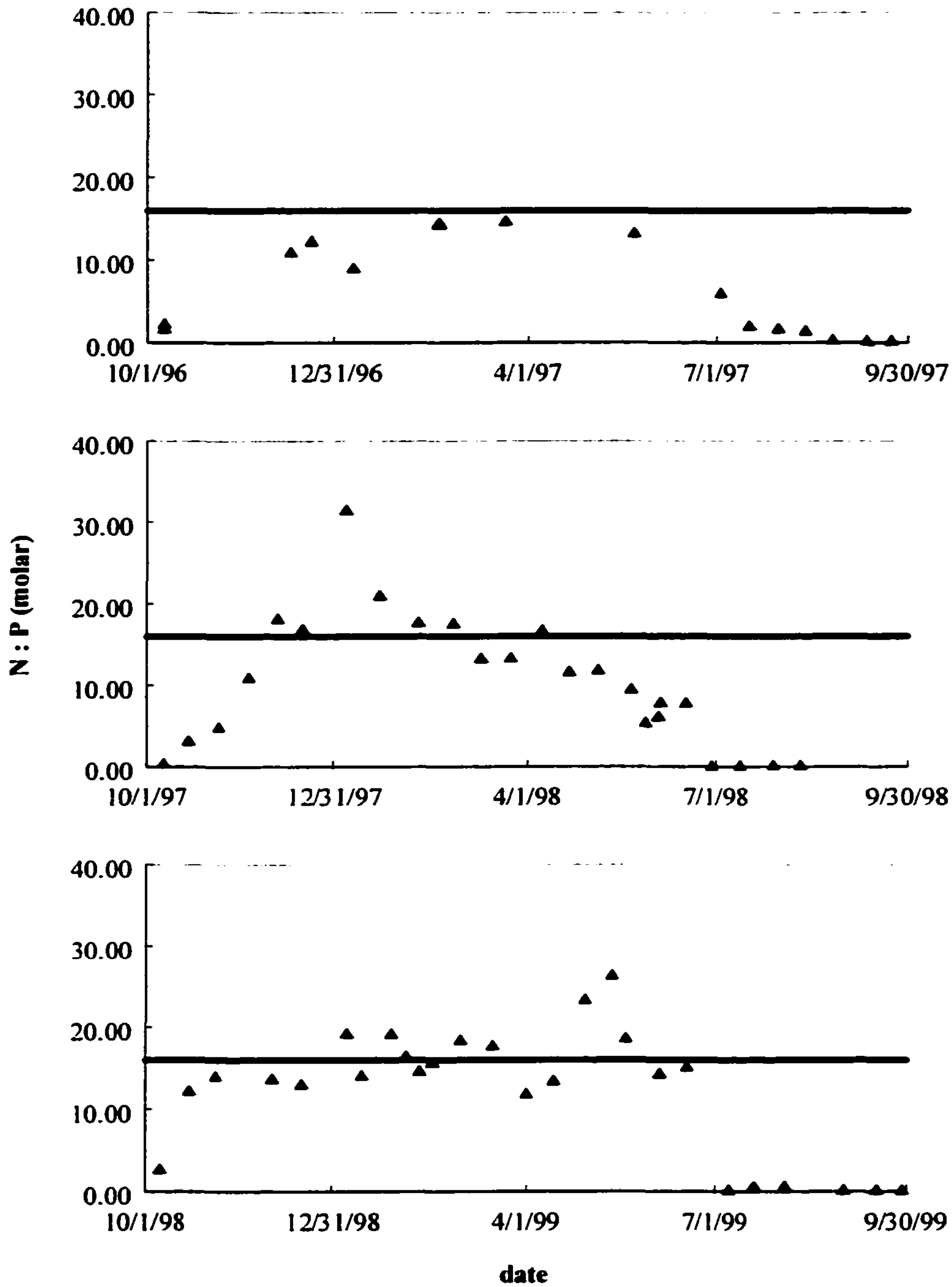


Figure 39. N:P (molar) ratios for Barr Lake.

It is likely that Barr Lake undergoes nitrogen limitation for parts of the growing season and algal species shifts occur. Water quality data and algal species observations suggest that shifts to blue-green algae occur in Barr Lake throughout the summer months. Shifts to nitrogen fixing species are likely to result in light limitation on algal growth (decreased photic zone due to high productivity), resulting in the lack of phosphorus removal by incorporation into the organic phase as observed in Barr Lake during water years 1998 and 1999.

Precipitation of calcite is possible at the pH values measured in Barr Lake (and by geochemical modeling of hypolimnetic waters) and several researchers have discussed phosphorus removal from the water column through coprecipitation with calcite at high pH values observed in eutrophic systems (Kleiner, 1988). This phosphorus removal mechanism is apparently not significant in Barr Lake given the minimal phosphorus removal calculated by mass budget in water years 1998 and 1999. This result is further supported by the lack of phosphorus release from the sediment during the low pH phase of the laboratory extraction, since calcite solubility is redox (pe+pH) independent, but pH dependent. It is likely that although the increased pH values observed in Barr Lake would normally result in supersaturation of and precipitation of calcite, in-lake processes reduce the partial pressure of $CO_{2(aq)}$ (by photosynthetic consumption) possibly resulting in calcium control by gypsum rather than calcite.

6.1.3. Uncertainty analysis

Inclusion of the uncertainty estimate in this study is intended to provide more rigorous treatment of the calculated loads than is typically included in the mass balance approach. Few studies have rigorously discussed uncertainty in terms of chemical loading and no studies have been identified that specifically include a hydrologic component combined with a water quality component as described here. The uncertainty estimate is helpful in the interpretation of hydrochemical loads, but because there are two distinct sources of uncertainty (flow and concentration measurement), both models used must accurately describe the nature of uncertainty in the system.

For the hydrologic component of the analysis, published uncertainty estimates were used. Normal distributions were assumed and Monte Carlo analysis was used to randomly sample from the distribution of periodic mass flux of the hydrologic component. No attempt was made to ascertain the actual distribution or extent of the uncertainty. Misrepresentation of the normality of the distribution could result in significant changes to the extent and shape of the resultant loading distribution.

For the water quality component of the uncertainty analysis, results from the Durbin - Watson test for serial correlation of residuals indicated that only calcium, sodium, nitrate and sulfate in Barr Lake were significantly correlated. This serial correlation is expected to have only a minor influence on the loading distribution, since the data from Barr Lake was used only in the calculation of seepage loss (or gain), which is not a major part of the hydrochemical budget.

The decision to aggregate individual sources of uncertainty in this analysis is based on the intractability of the explicit quantification of each source. As an example, sampling error and natural system variability may be impossible to evaluate explicitly.

Given that using an aggregate uncertainty will result in an imprecise evaluation, it is recommended that future effort in this area be focused on explicit evaluation of each component of the aggregate uncertainty.

The assumptions required for the use of traditional methods of uncertainty estimation (first order methods or Monte Carlo simulation) are inappropriate for serially correlated concentration data such as those observed for Barr Lake (requiring the use of time series based sinusoidal concentration models). For example, first order analysis requires linearity (in x or transformed x), and the variance is calculated at the mean value of the independent variable (Cornell, 1972, Berthouex, 1975), which is not appropriate for the Barr Lake data set. Other assumptions associated with regression analysis (e.g. homoscedacity, normality of residuals) are also required and were found to be violated by many of the Barr Lake data (Appendix B). ARIMA modeling (with uncertainty estimation) was also considered for use with the Barr Lake data set, but the nature of reservoir operations (discontinuous flows resulting in irregular sampling intervals) required filling in missing values. Therefore a method that requires fewer assumptions was required for use in estimation of uncertainty in the Barr Lake system.

One significant advantage of this approach over first order error analysis is that each component of the outflow was considered independently (i.e. east outfall, west outfall, groundwater seepage) and the uncertainty associated with each component was weighted accordingly.

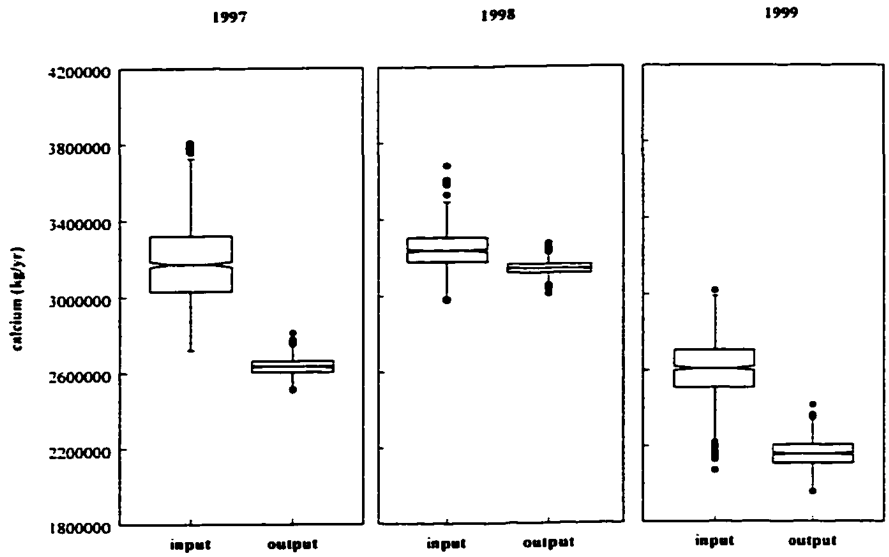
The explicit inclusion of the main sources of uncertainty (flow measurement and water quality measurement uncertainty) resulted in a more realistic interpretation of the calculated mass loading than previously discussed in the literature and provided a more realistic assessment of the fate of orthophosphate and nitrate in Barr Lake.

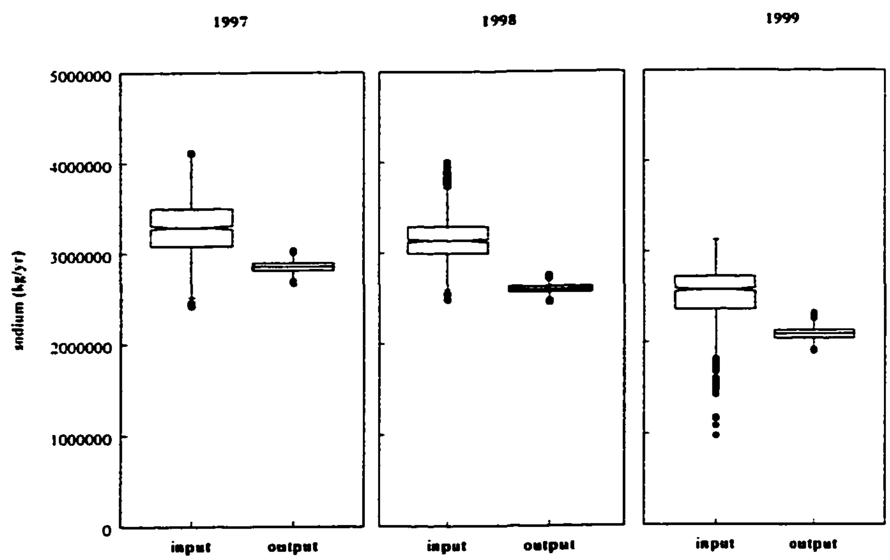
Influx and efflux boxplots of chemical loadings are included to provide graphical comparison of the distributions of loading between locations and between years (Figure 40 - Figure 44). In addition to graphical representation, the realizations were ranked and tested using a general linear model approach and a multiple comparison of means was conducted using the Ryan – Einot - Gabriel - Welsch Multiple Range Test (to control the type I experimentwise error rate). Use of this procedure is equivalent to using the Kruskal-Wallis procedure to determine between year differences in influx and efflux. Using this procedure, influent loads were highest in 1997 for sodium, nitrate, orthophosphate and, sulfate. Influent loads for calcium were highest in 1998. Influent loads for all constituents except orthophosphate were lowest in 1999. The lowest influent load for orthophosphate was in 1998. This analysis indicated that for all constituents for all years, the effluent loads were lower than the influent loads with the exception of orthophosphate in 1998.

Effluent loads mimicked the influent loads in terms of between year rankings, with the exception of orthophosphate and sulfate. Effluent loads of orthophosphate were lowest in 1999, consistent with all other constituents studied (i.e. all other constituent loads were lowest in 1999). This result is of significance because the lowest effluent load was not observed in 1998 when the lowest influent load of orthophosphate was observed. Effluent loads of sulfate were highest in 1998, which is inconsistent with the influent load, which was highest in 1997. The Kruskal-Wallis procedure outlined above can also be applied to influent and effluent loads for each year to assess if the effluent load is (as indicated by the nominal budgets) statistically lower than the influent load.

To evaluate the annual budgets more completely, each output realization was subtracted from the corresponding input realization resulting in a distribution of budgets for each constituent for each year. This inclusion of uncertainty to the mass budgets for Barr Lake results in the observation of phosphorus flushing in water years 1998 and 1999, when zero is included within the lower limit (90%) of the budget realizations. Boxplots of the budget realizations also illustrate this phenomenon, as 90% percent of data is included within the whiskers (Figure 45 -Figure 49) note: center line in box is median value, 50% of data lies within the box, outliers are denoted by points outside the whiskers. This analysis also suggests that phosphorus is accumulated in Barr Lake only during water year 1997, when median budgets for all constituents reflect the highest accumulation observed during the three years of study. This analysis also suggests that nitrate (and other nitrogen species) is accumulated or lost in Barr Lake in each of the three years of study.

Ca:SO_4 molar ratios suggest that $CaSO_{4(gypsum)}$ is the controlling phase for both calcium and sulfate in Barr Lake which is inconsistent with the high pH values suggesting calcite ($CaCO_{3(s)}$) control on calcium. The precipitation of calcite is expected to result in coprecipitation of orthophosphate, but the budget for orthophosphate does not reflect significant removal of orthophosphate during water years 1998 and 1999. The median calcium budget for water year 1999 indicates high removal of calcium, which is not reflected in the orthophosphate budget.


1997
1998
1999
4200000
3800000
3400000
3000000
2600000
2200000
1800000
calcium (kg/yr)
input
output
input
output
input
output


1997
1998
1999
5000000
4000000
3000000
2000000
1000000
0
sodium (kg/yr)
input
output
input
output
input
output

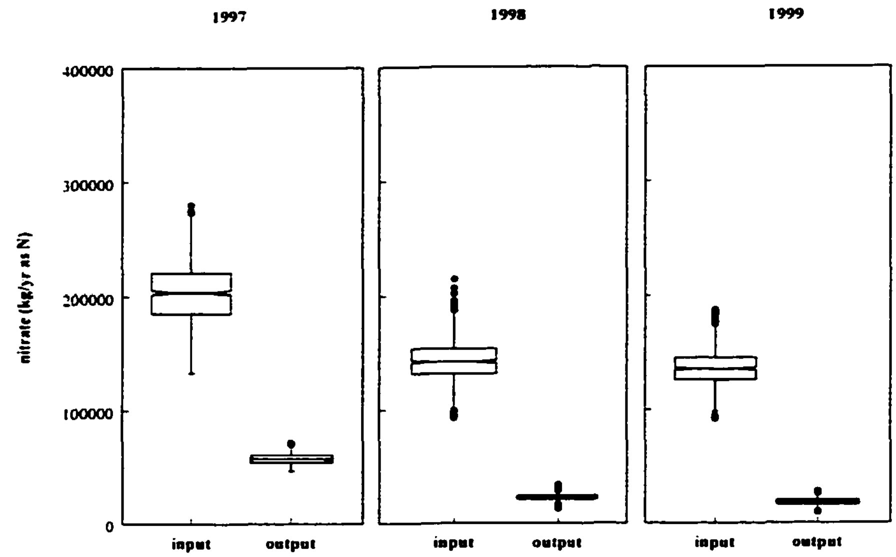


Figure 42. Nitrate (as N) input and output load boxplots for Barr Lake.

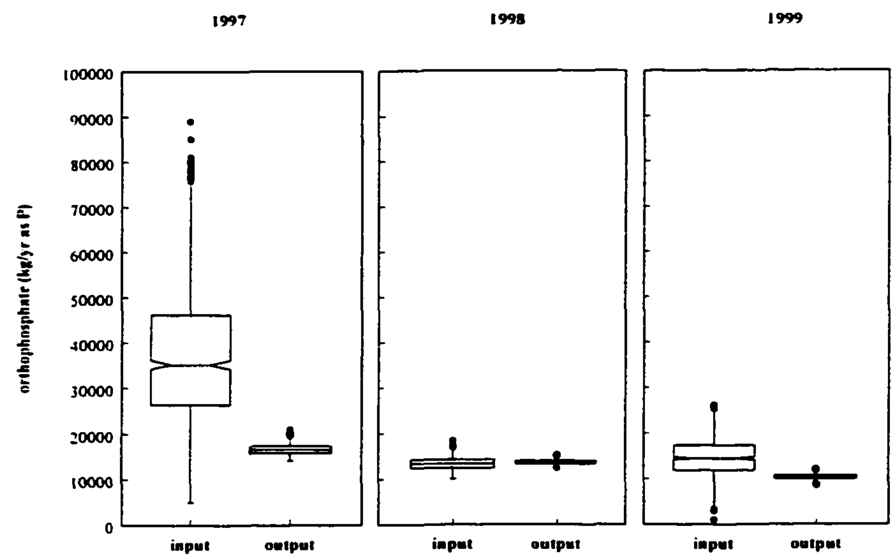


Figure 43. Orthophosphate (as P) input and output load boxplots for Barr Lake.

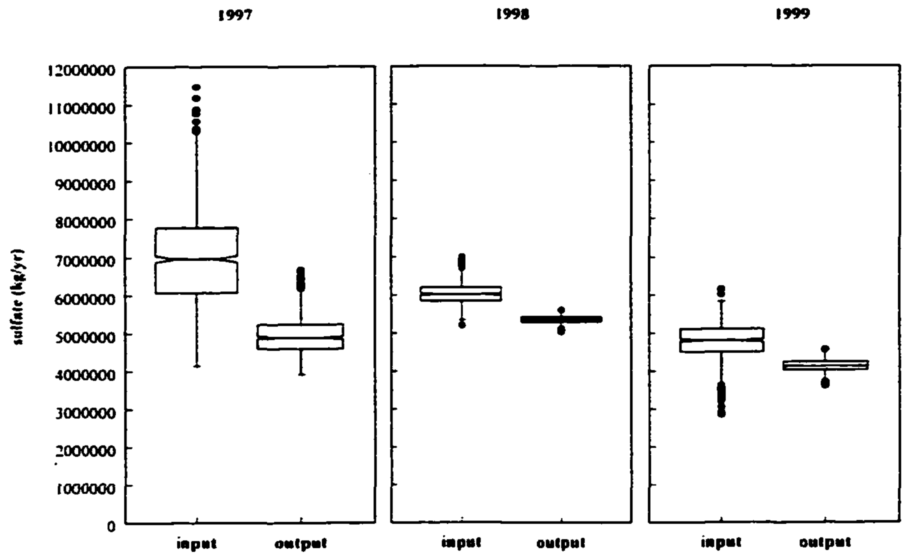


Figure 44. Sulfate input and output load boxplots for Barr Lake.

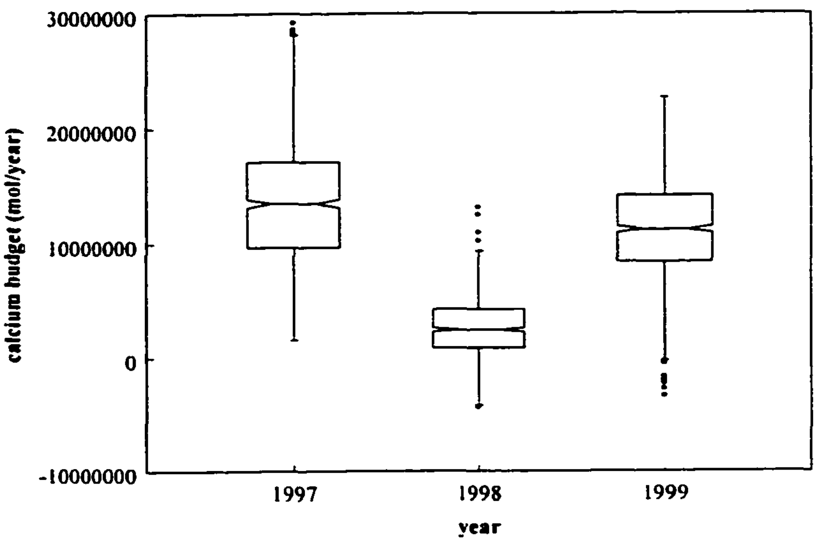


Figure 45. Calcium budget distribution for Barr Lake.

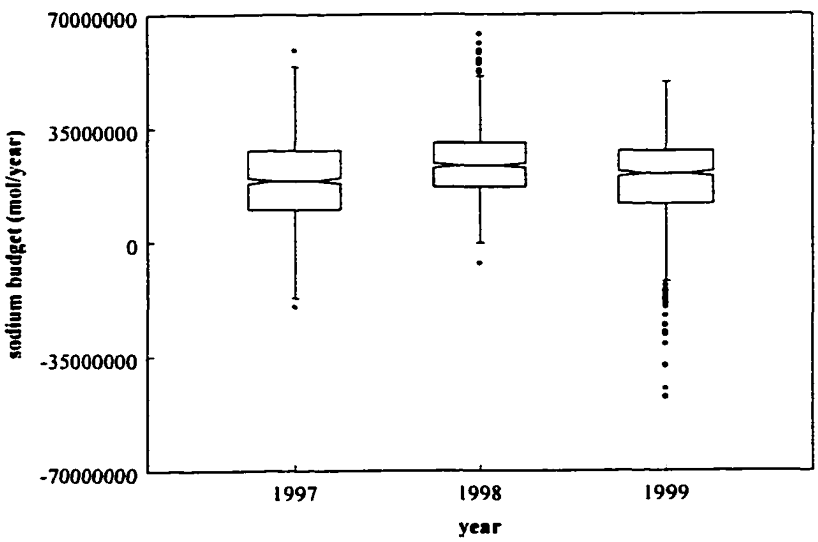


Figure 46. Sodium budget distribution for Barr Lake.

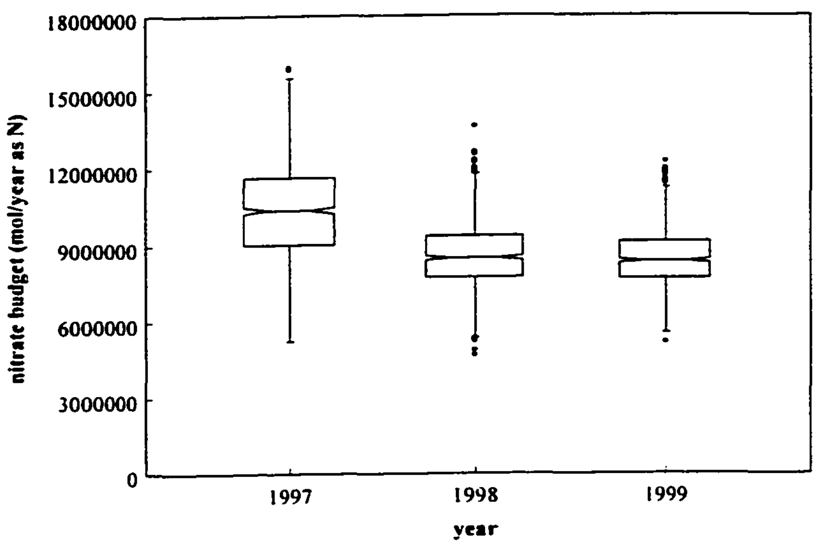


Figure 47. Nitrate (as N) budget distribution for Barr Lake

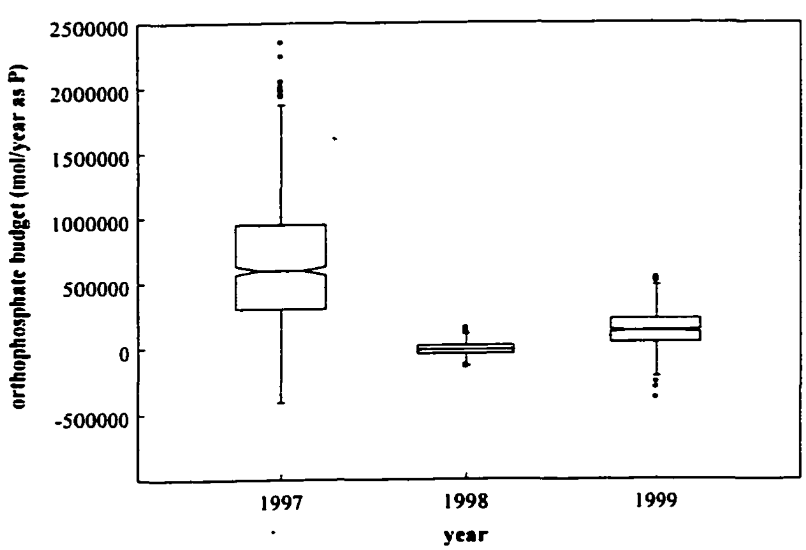


Figure 48. Orthophosphate (as P) budget distribution for Barr Lake.

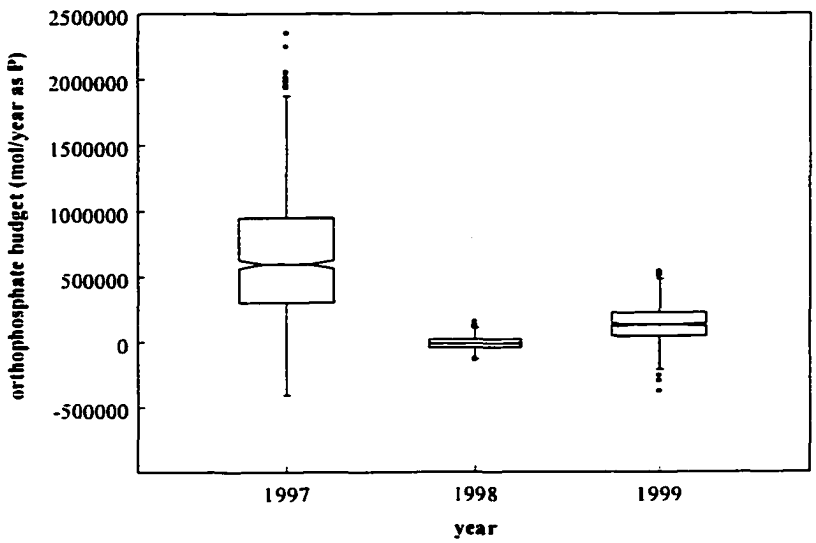


Figure 49. Sulfate budget distribution for Barr Lake.

6.2. Evaluation of in-lake phosphorus retention mechanisms

6.2.1. Field studies

6.2.1.1. Limnological chemistry

Elevated hypolimnetic phosphorus concentrations in Barr Lake were observed only twice during the study period. The 17 July 97 sample contained elevated concentrations of orthophosphate as well as elevated concentrations of Mn and NH_4^+. Iron concentrations were below detection limit (50 ug/L) for this sample indicating that conditions may have been only moderately reducing. This is consistent with low dissolved oxygen measured at the time of sampling (1.1 mg/L) and moderately low pe values measured at the time of sampling (5.5). The pe + pH value for this sample was 14.0, which suggests manganese reduction but not sufficient for iron reduction. This result conflicts with the generally accepted model of phosphorus release associated with iron reduction (which would also yield elevated iron concentrations). All other water quality samples from the hypolimnion have indicated consistency with the accepted model however. August 26,1997 results indicated high iron concentrations and slightly elevated orthophosphate concentrations. Manganese concentrations were also elevated. pe + pH for this sample was 9.8, consistent with Fe(III) reduction. Considering the high Fe:P ratio found in the sediment chemical analysis (30:1) only minor release of phosphorus would be expected following reduction of Fe(III) to Fe(II). Nitrogen species in general, were low throughout the water column making an analysis of the redox couple NH_4^+/NO_3^- not possible. Dissolved oxygen concentration in this sample was low (4.7

mg/L) but not indicative of anoxia. The lowest concentration of orthophosphate observed in Barr Lake during the three years of study occurred on September 11, 1997 in a sample from the hypolimnion (<0.03 mg/L) (Figure 24). The sample contained a slightly elevated manganese concentration (0.04 mg/L), low iron concentration (<0.05 mg/L) and a high pe + pH value (14.6) which is consistent with Mn(IV) reduction but not Fe(III) reduction. Dissolved oxygen measured at the time of the sampling was not indicative of anoxia (4.7 mg/L). Ammonia concentrations measured in the hypolimnion indicated that nitrate was acting as an electron acceptor in the absence of dissolved oxygen. This result is consistent with research by others, which identified reduction of nitrate (to ammonia/ium as a process inhibiting release of phosphorus from sediment (Bostrom, et al. 1988; Kleeberg and Kozerski, 1997). The proposed mechanism being that adequate electron acceptors exist at the sediment water interface such that iron reduction (and concomitant phosphorus release) is not favored thermodynamically.

Reservoir operations may also limit the release of phosphorus from the sediment through oxidation of littoral sediments (and adsorption of phosphate to oxic solid phases). Subsequent filling of the reservoir does not result in release of phosphorus because adequate electron acceptors are reintroduced to the aqueous phase during refilling (i.e. dissolved oxygen and nitrate).

Research by others has indicated that release of phosphorus from oxic sediments can be a significant process, particularly under high pH conditions (Boers, 1991). This release mechanism may be significant in Barr Lake given high pH values resulting from photosythetically driven CO_2 consumption. The mechanism proposed for oxic release is anion exchange (primarily OH^-), and has been shown to result in phosphorus release on the order of 5-10 $mg/m^2/day$ (Penn, et al., 2000). The composition of the littoral sediment (oxidized) provides information regarding potential for release of phosphorus under oxic conditions in Barr Lake.

6.2.1.2. Groundwater chemistry

Groundwater monitoring data indicate that the groundwater is moderately reduced and low in orthophosphate consistent with either adsorption onto metallo (hydro)xides or solid phase precipitation. High concentrations of manganese and NH_4^+ are consistent with moderately reducing conditions. The calculated (Nernstian) pe (based on the NH_4^+/NO_3^- redox couple) was consistent with the measured pe (6.39 vs. 6.67 respectively). The resultant (measured) pe + pH is approximately 13.8, which is consistent with rhodochrosite control on manganese (Lindsay, 1979). This condition is also inadequate to cause release of phosphorus from adsorbed ferric hydroxides since the conditions are not sufficiently reducing to affect Fe^{3+}/Fe^{2+}. This result illustrates the potential of the sediment to adsorb phosphorus to a much greater extent than in-lake concentrations of orthophosphate would suggest.

The data collected from the groundwater may also suggest solid phase phosphate mineral control on aqueous phosphate activities. A comprehensive solid phase phosphate mineral solubility diagram has not been presented in current literature. Figure 50 and Figure 51 were developed to provide information regarding solid phase phosphate mineral solubility under the range of conditions expected, as water from Barr Lake is lost to groundwater. Following is a discussion of the assumptions made and equilibria used in the development of Figure 50 and Figure 51.

Under the moderately reducing conditions observed in groundwaters in the vicinity of Barr Lake (pe + pH approximately 14.5), $MnOOH_{(manganite)}$ is expected to control manganese which, in turn controls orthophosphate as follows:

$$MnOOH_{(manganite)} + 3H^+ + e^- \rightleftharpoons Mn^{2+} + 2H_2O \qquad \log K^0 = 25.27$$

$$MnPO_4 \cdot 1.5H_2O + 2H^+ + e^- \rightleftharpoons Mn^{2+} + H_2PO_4^- + 1.5H_2O \qquad \log K^0 = 10.28$$

The resulting equilibrium expression follows:

$$MnPO_4 \cdot 1.5H_2O + 0.5H_2O \rightleftharpoons MnOOH_{(manganite)} + H^+ + H_2PO_4^- \qquad \log K^0 = -14.99$$

At pe + pH values less than 14.58, $MnCO_{3(rhodochrosite)}$ is expected to control manganese (using partial pressure $CO_{2(g)} = 10^{-2.61}$) as follows:

$$MnPO_4 \cdot 1.5H_2O + 2H^+ + e^- \rightleftharpoons Mn^{2+} + H_2PO_4^- + 1.5H_2O \qquad \log K^0 = 10.28$$

$$MnCO_{3(rhodochrosite)} + 2H^+ \rightleftharpoons Mn^{2+} + CO_{2(g)} + H_2O \qquad \log K^0 = 8.08$$

resulting in the equilibrium:

$$MnPO_4 \cdot 1.5H_2O + e^- + CO_{2(g)} \rightleftharpoons MnCO_{3(rhodochrosite)} + H_2PO_4^- + 1.5H_2O \quad \log K^0 = 2.20$$

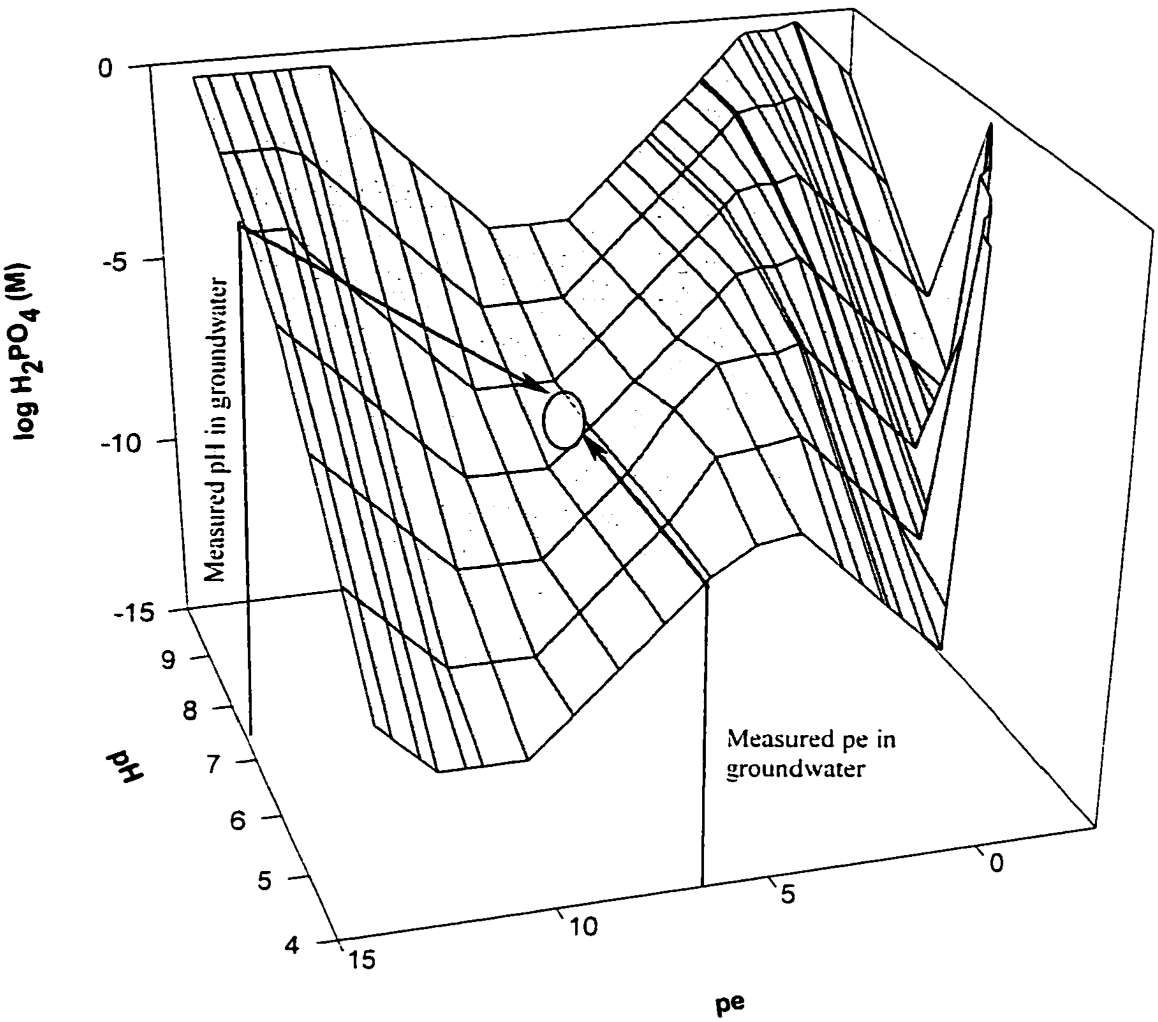


Figure 50. Isothermal solubility surface for orthophosphate solid phases

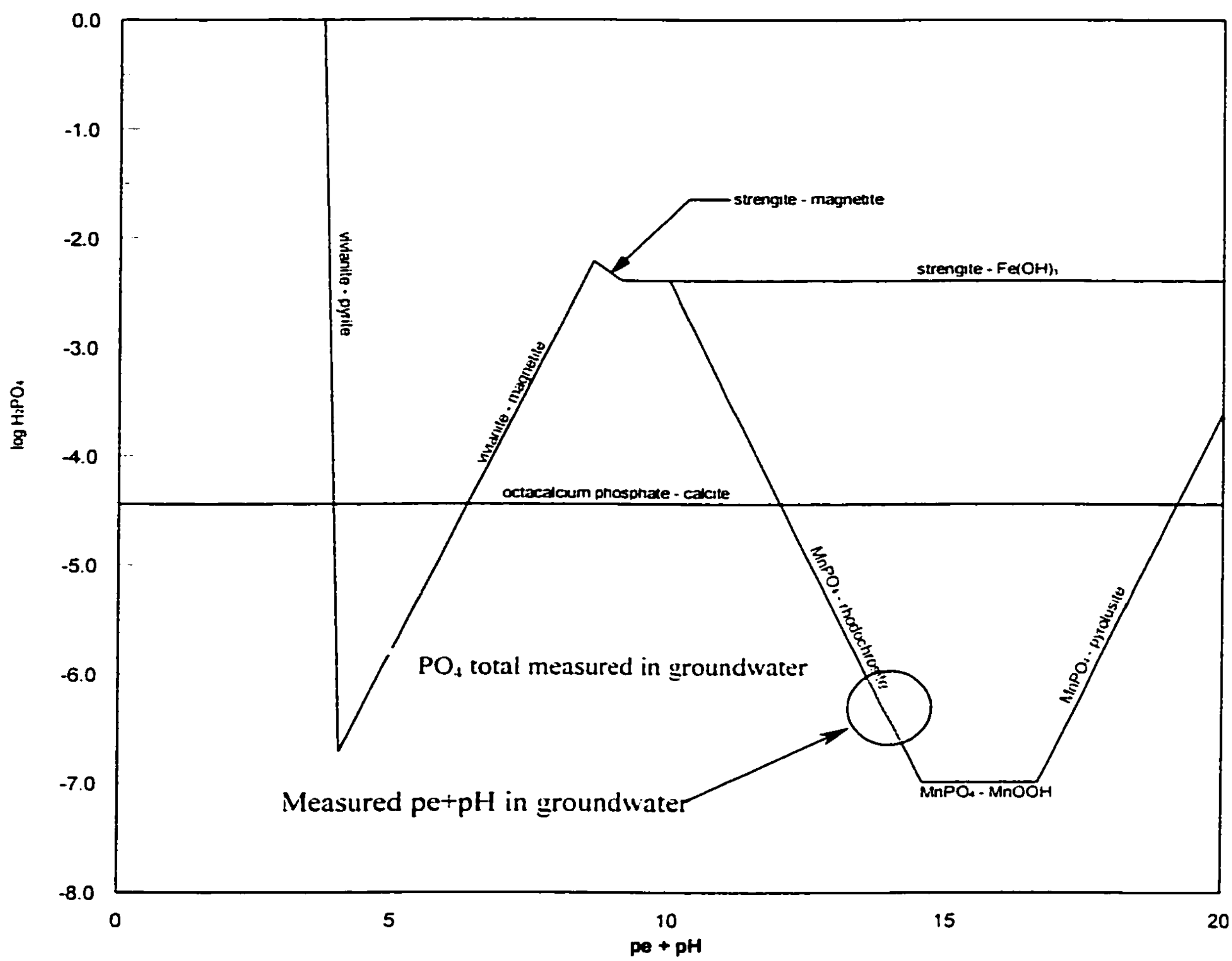


Figure 51. Solid phase orthophosphate control at pH 8

6.2.1.3. Physical and chemical properties of lake sediments

The accumulation of phosphorus within the organic fraction of the sediment provides an exchangeable source of phosphorus and nitrogen with the overlying waters in Barr Lake and is discussed further in Section 6.2.2.2. Transfer of phosphorus from the organic phase to the mineral sediment is illustrated through comparison of the pelagic to littoral sediment phosphorus. On a unit weight basis, approximately two-thirds of the phosphorus is released (0.838 mg/g to 0.257 mg/g) to the aqueous phase during oxidation of pelagic sediment. Both values of total sediment phosphorus are low relative to other hypereutrophic systems indicating lower than expected adsorption/removal. Sediment from Stone Lake (Michigan) and Lake Charles East (Indiana), both hypereutrophic systems, have reported total P values of 3.42 mg/g and 2.28 mg/g, respectively (Theis and McCabe, 1978). Sediment from Lake Sobygaard (Denmark) is reported to contain 6.8 mg/g total P (Jensen, et al., 1992). The relatively low phosphorus values observed in the Barr Lake sediment may be attributable to the lack of adsorption due to competition for adsorption sites by either OH^- or SO_4^{2-} as suggested by other researchers (Caraco, et al., 1989). Highly calcareous hypereutrophic systems also exhibit higher total sediment phosphorus, although generally in the range of 1.2 – 2.0 mg/g total phosphorus. Total sediment phosphorus in the hypereutrophic Onondaga Lake (New York) is reported to be 1.8 mg/g (Penn, et al., 2000). Sediment from Lake Apopka and Lake Okeechobee (Florida) also hypereutrophic, are reported to contain approximately 1.6 mg/g and 1.2 mg/g total phosphorus, respectively (Olila and Reddy, 1997; Moore, et al., 1998). The lower sediment phosphorus content observed in calcareous systems is probably the result of lower adsorption efficiency of calcite relative to iron (hydr)oxides.

Total iron content in the sediment of Barr Lake is also low relative to other hypereutrophic systems. Lake Sobygaard sediment contains 58 mg/g total Fe (Jensen, et al., 1992) compared to 24 mg/g in the pelagic and 7.8 mg/g in the littoral sediment in Barr Lake. Although the correlation of sorption of phosphorus to iron solid phases has been indicated by several studies to be spurious, sediment with low total iron content is generally considered to result in low phosphorus adsorption on percentage basis (Bortleson and Lee, 1974).

Both littoral and pelagic sediment from Barr Lake indicate a Fe:P ratio of approximately 30:1. This result is consistent with iron dominated sediment chemistry, but is inconsistent with the high orthophosphate concentrations found in Barr Lake. In a study of 47 European lakes, a mean Fe:P in sediment was found to be approximately 17:1 (van der Molen and Boers, 1994). Comparison of Fe:P in hypereutrophic systems indicated a substantially lower Fe:P than observed in Barr Lake. Lake Sobygaard is reported to contain Fe:P of approximately 8.5:1 reflecting the high P loading (Jensen, et al. 1992). The difference between observations made in Barr Lake sediment and those reported in the literature suggest that the Barr Lake sediment has a greater capacity to retain phosphorus and that adsorption sites associated with iron in the sediment are unavailable. This behavior suggests competition (probably by OH^- or SO_4^{2-}) for sorption sites, resulting in the high Fe:P ratio observed in Barr Lake sediment. Previous studies have found that lakes in which the sediment Fe:P ratio was greater than 15:1 were less likely to release soluble reactive phosphorus (orthophosphate) than sediment with a lower

Fe:P (Jensen, et al., 1992). Other research indicates that low P:Fe (high Fe:P) ratios tend to show lower P release rates at high pH values (Lijklema, 1977).

Manganese quantities in the sediment tend to be low, but differences in Mn:P ratio between the pelagic (0.20) and littoral (0.35) suggest that oxidation of manganese results in lower P retention by manganese which is more consistent with solid phase manganese control than adsorptive controls. The low Mn:P ratios observed in the sediments however do not indicate that Mn solid phase can control P completely.

The presence of kaolinite in the sediment of Barr Lake is significant in that adsorption of orthophosphate to kaolin group minerals has been identified in previous literature. The general formula for kaolin group minerals is $Al_4Si_4O_{10}(OH)_8$ and includes the specific minerals kaolinite, dickite, nacrite, and halloysite all of which are similar in composition. Although the specific kaolin group mineral is difficult to ascertain from the XRD spectra, it is likely that kaolinite is the dominant kaolin group mineral in the sediment of Barr Lake. Although the zero point of charge for kaolinite is approximately 3.5 (Drever, 1988) and has been reported as high as 4.6 (Stumm and Morgan, 1996) (as expected with nonhomogeneity of chemical composition) several studies have indicated that phosphate adsorption by kaolin group clays is significant in natural systems (Kuo and Lotse, 1972). It is clear from the low reported values of the isoelectric points, that clays in the kaolin group will tend to adsorb phosphate mainly at low pH values, however a small amount of adsorption is expected to be pH independent (Newman and Brown, 1987). Kaolin group minerals have been shown to significantly adsorb phosphate at pH values below 5 (Martynova, 1981), consistent with values of the zero point of charge discussed above. Other studies have indicated maximum adsorption (frequently referred to as the adsorption envelope) of phosphate on kaolinite occurs between pH 4 and 5 with decreasing adsorption at low and high pH values. This behavior is attributed to $CaPO_{4(solid)}$ precipitation at high pH values and presence of $H_3PO_4^0$ at low pH values ($p_{k1} = 2.1$)(Edzwald, et al., 1976).

Degree of crystallization has also been shown to influence adsorption on kaolinites. Poorly crystallized clay minerals tend to have more surface imperfections and more exposed hydroxyl groups leading to higher anion exchange capacity (Grim, 1953). Solid phases that are poorly crystalline are consistent with XRD results observed in sediments taken from Barr Lake, which indicated the presence of kaolinite and may explain in part the lack of orthophosphate release observed in the laboratory redox manipulations, particularly at the low pH values observed in the reaction vessel (Section 6.2.2.2). In-lake pH values observed throughout the study period were higher than 7.5 standard units, probably minimizing the influence of orthophosphate adsorption to kaolinite.

X-ray diffraction of sediment taken from Barr Lake has also identified the presence of mica minerals, which are also expected from the weathering of granitic parent material in the upper South Platte Basin. Mica group minerals have also been identified as phosphate adsorbing. The micas-illite group have the general formula:

$$X_2Y_{4\text{-}6}Z_8O_{20}(OH,F)_4$$

where: X = interlayer cation (K_2 or Ca_2)

Y = octahedral cation (Al_4, $Fe^{3+}{}_2$, $Fe^{2+}{}_3$, Mg, Li)

Z = tetrahedral cation (Si or Al)

The mica-illite group includes specific minerals as muscovite, biotite, phlogopite and the clay mineral illite (containing less K and more H_2O than the mica minerals. Adsorption of phosphate to illites has been shown to be strongly pH dependent with a maximum adsorption occurring in the pH range 4-5 (Edzwald, et al., 1976). Other studies have indicated that phosphate adsorption to illites is significant at low pH values (Martynova, 1981; Gunatilaka, 1982). The affect of the competing ions SO_4^{2-} and Cl^- has been shown to be largely insignificant at moderate pH values (Edzwald, et al., 1976). Like kaolinite, adsorption of phosphorus to illite may have been in part responsible for the low aqueous phase orthophosphate concentrations observed in the laboratory redox manipulations (particularly at the pH values observed during the extraction), but the lack of orthophosphate release at higher pH values observed later in the experiment suggest that adsorption to illite is probably minor.

X-ray diffraction of glycolated samples also indicated the presence of montmorillonite, a smectite group clay mineral. It is likely from the comparison of glycolated to air dried samples, that the smectite group clays are interstratified illite/smectite. Smectite group minerals are classified as 2:1 structures including the specific minerals montmorillonite, beidellite, saponite and vermiculite. Formulae are given below:

$$(Al_{3.15}Mg_{0.85})(Si_{8.00})O_{20}(OH)_4X_{0.85}nH_2O_{(montmorillonite)}$$

$$(Al_{4.00})(Si_{7.15}Al_{0.85})O_{20}(OH)_4X_{0.85}nH_2O_{(beidellite)}$$

$$(Mg_{6-z}R_z^{3+})(Si_{8-y}Al_y)O_{20}(OH)_4X_x^-nH_2O_{(saponite)}$$

where X is typically an interlayer monovalent or divalent cation.

Surface charges typically develop on montmorillonite from the substitution of Mg^{2+} in the octahedral layer, in beidellite and saponite from the substitution of Al^{3+} in the tetrahedral layer. The value reported for the zero point of charge for montmorillonite is approximately 2.5 (Drever, 1988; Stumm and Morgan, 1996), although montmorillonite clays have been shown to adsorb phosphate at pH values greater than 10 (Martynova, 1981) and have exhibited increasing adsorption over the pH range observed in natural systems (Edzwald, et al., 1976). The proposed mechanism for this behavior is not explained by increased absorption, but by the high amount of exchangeable Ca^{2+} within the montmorillonite interlayer that can react with phosphate to form a relatively insoluble $CaPO_4$ mineral phase. Apparently, the kinetics of precipitation of solid phase calcium phosphate mineral are difficult to discern from adsorption under experimental conditions. Removal of water column phosphorus by montmorillonite may be responsible for a portion of the phosphorus removed from the aqueous phase during the redox manipulation experiment, given the apparently wide range of conditions under which phosphorus removal by montmorillionite occurs. Lack of release under variable pe and pH conditions however, suggest that removal by any of the clay minerals is probably small.

Overall, the relatively low phosphorus content of the sediment in Barr Lake appears to contradict the groundwater chemistry, which indicated phosphorus retention by the sediments. To evaluate if these findings are consistent with retention of phosphorus in the sediments, as suggested by the groundwater chemistry, an orthophosphate mass comparison between water loss from Barr Lake (calculated using water quality data from Barr Lake and water flux calculated using seepage volumes) and groundwater (calculated using water quality collected from groundwater monitoring and water flux calculated using seepage volumes) indicates that while nitrogen is gained as water moves through the sediment and groundwater, phosphorus is retained (Table 25). This result suggests mineralization of organic matter causing increased nitrogen in water as it exits Barr Lake via seepage. Orthophosphate, however, is retained as seepage exits Barr Lake, in approximate mass of 3100 and 400 kg/yr in water years 1997 and 1998 respectively. Normalized to an areal loading is approximately 0.43 and 0.05 $g/m^2/year$ in 1997 and 1998. These values suggest annual accumulation of orthophosphate in the sediment in low quantities consistent with the low measured phosphorus following perchloric digest.

Table 25. Mass comparison between Barr Lake seepage and groundwater.

Water year	**Total nitrogen (kg/yr)**		**Orthophosphate (kg/yr)**	
	Lake loss	**Groundwater**	**Lake loss**	**Groundwater**
1997	8000	25.000	3800	700
1998	4000	15.000	700	300

6.2.2. Laboratory experimentation: sediment extraction using controlled redox conditions

Initial oxidation of sediment resulted in release of orthophosphate as the pe increased (Figure 52). The pe+pH of the suspension at the outset of the experiment was high (pe+pH = 12.9) relative to stability of organic phase constituents (pe+pH 4.15 for the $CO_2 \rightleftharpoons CH_2O$ redox couple [Lindsay, 1979]). This overpotential leads to rapid oxidation and increase in pe (Segment 1, Figure 52). Orthophosphate concentrations were at the maximum observed for the experiment ($10^{-4.1}$ M) during this oxidation phase, consistent with the release of organic phase phosphorus during the oxidation of organic matter. Nitrate remained low during the initial phase of the oxidation, but increased to very high concentrations, reaching an experiment maximum of approximately 10^{-3} M under the pe+pH conditions 14.2. The lag time of release nitrate relative to orthophosphate from the organic phase may explain the cycling behavior described by many researchers in which organic phosphorus is bound to iron in sediments following mineralization of the organic matter rather than cycled back to the organic pool (Moore, et al. 1998).

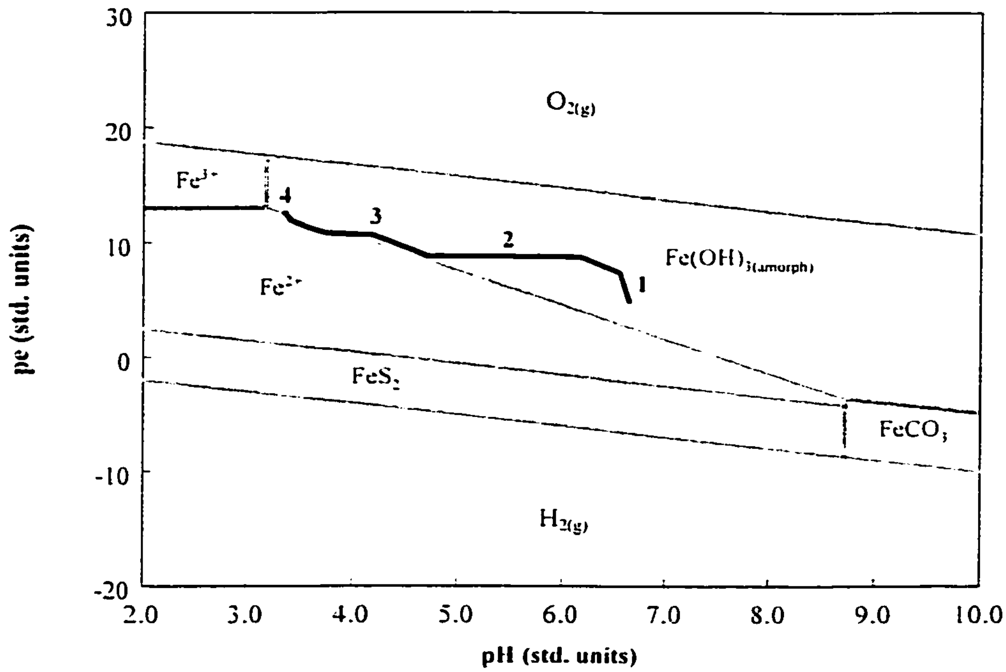


Figure 52. Initial oxidation of Barr Lake pelagic sediment relative to iron stability diagram. $Fe_{total} = 10^{-3}$ M, $S_{total} = 10^{-3}$ M, $CO_2 = 10^{-3.53}$ atm.

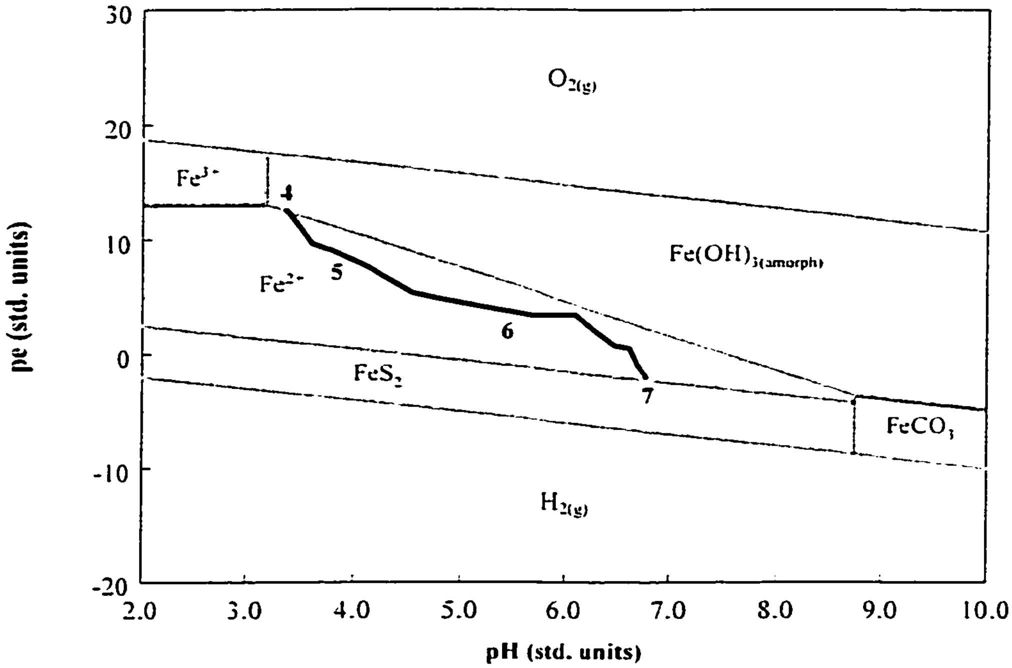


Figure 53. Reduction of Barr Lake pelagic sediment relative to iron stability diagram. $Fe_{total} = 10^{-3}$ M, $S_{total} = 10^{-3}$ M, $CO_2 = 10^{-3.53}$ atm.

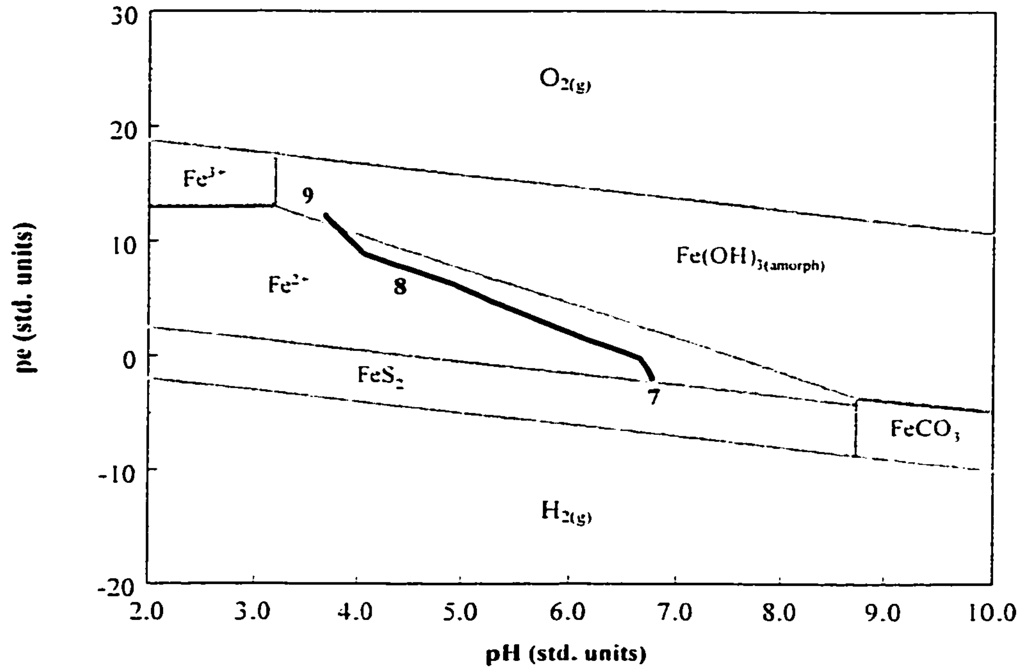


Figure 54. Reoxidation of Barr Lake pelagic sediment relative to iron stability diagram. $Fe_{total} = 10^{-3}$ M, $S_{total} = 10^{-3}$ M, $CO_2 = 10^{-3.53}$ atm.

Further oxidation of the sediment suspension resulted in precipitation of $FeOH_3$ and adsorption or coprecipitation of orthophosphate (Segment 2, Figure 52). pH decreased as expected during this precipitation, while pe remained constant. The endpoint pe+pH value for this step in the oxidation phase was approximately 13.6 which is consistent with precipitation of $Fe(OH)_{3(amorphous)}$. Data collected from the reaction vessel is consistent with the precipitation of $Fe(OH)_3$ and adsorption of orthophosphate to the surface. Important to the analysis of this result is that following precipitation of $Fe(OH)_3$ pH of the bulk solution is low as expected from:

$$Fe(II) + 3H_2O \rightleftharpoons Fe(OH)_3 + e^- + 3H^+$$

Comparison of this result to observations in Barr Lake indicate that photosynthetically driven pH values in the range of pH 9 will likely result in minimization of adsorption to any precipitated $Fe(OH)_3$. Additional oxidation (Segment 3, Figure 52) resulted in increase in pe + pH to approximately 15.9, consistent with manganese oxide formation (pe+pH 15.6 [Lindsay, 1979]). The maximum pe+pH value achieved through the addition of atmospheric air was approximately 16.0 (Point 4, Figure 52). The first phase of the experiment (oxidizing under atmospheric conditions) resulted in orthophosphate concentrations below the detection limit ($<10^{-6}$ M) for the majority of conditions. This result is inconsistent with observations in Barr Lake and other eastern Colorado reservoirs where aqueous orthophosphate concentrations above the detection limit ($>10^{-6}$ M) are observed throughout the year. Extrapolation of results from the laboratory experiment to field conditions is difficult for several reasons, primarily the presence of photosynthetic organisms (which will control aqueous pH) and the high volume of inflow relative to storage volume on an annual basis (adding both high orthophosphate and pH waters). However, the experiment did indicate that the sediments are behaving as literature would predict, controlling aqueous phase orthophosphate. The discrepancy between observations made in Barr Lake and the groundwater quality are consistent with the observations made in the experiment. Groundwater samples collected, although reduced relative to experimental conditions during the oxidizing phase, were also low in orthophosphate and lower in pH than observed in Barr Lake.

The reduction of the sediment suspension following the oxidation phase was intended to provide information on the release of orthophosphate from the sediment, as described in the literature (e.g. Mortimer, 1941). Initial reduction of the sediment suspension resulted in a steady decline in pe and an increase in pH (Segment 5, Figure 53). This path was hysteretic relative to the oxidation phase of the experiment, probably the result of differing reaction kinetics associated with manganese and iron redox behavior. Further reduction resulted in a poise (Segment 5, Figure 53) at pe approximately 6 and an increasing pH (pe+pH value of approximately 9.5, consistent with $Fe_3O_4 \rightleftharpoons Fe(OH)_{3(amorphous)}$ equilibria at pe+pH 9.1 [Brennan and Lindsay, 1996]). Further reduction resulted in a sharp decrease in pe and a steady increase in pH (Segment 6, Figure 53). The reduction minimum was reached at a pe+pH value of 4.8 (Point 7, Figure 53). This pe+pH value, although not the minimum achievable from a theoretical standpoint, was considered to be the minimum practically achievable using the current apparatus. Fugitive infiltration of atmospheric air and/or impurities in the $H_{2(g)}$ -$Ar_{(g)}$ source may have contributed to difficulties in achieving lower pe+pH values. Regardless. aqueous phase orthophosphate concentrations remained below the detection limit for the entire reduction phase of the experiment. a result that is inconsistent with existing hypotheses regarding orthophosphate release from sediment under reducing conditions. This observed insensitivity of orthophosphate concentrations in the aqueous phase to decreases in redox condition suggests that in this system. adsorption to iron hydroxide surfaces may not control orthophosphate. Similarly. redox manipulation resulting in pH variation ranging from 6.8 to 3.4 suggests that adsorption to other minerals may be limited. since adsorption to kaolin group and montmorillonite/mica group clay minerals is strongly pH dependent. The subsequent oxidation phase of the experiment resulted in a hysteretic return to lower pH values under oxidizing conditions (Segment 8. Figure 54 to Point 9. Figure 54). Both the reducing phase and the reoxidation phase pH and pe values followed the Fe(III)-Fe(II) boundary suggesting iron control on redox conditions within the sediment slurry. This behavior of the sediment is somewhat unexpected given the relatively low iron content of the sediment. It does however reflect the influence of iron on the redox cycle in these sediments. Speciation of iron measurements taken during a portion of the experiment suggest that $Fe(OH)_3$ and $FeCO_{3(siderite)}$ control iron concentrations within the interstitial waters of Barr Lake (Figure 55). In order for siderite to control iron at low pe+pH conditions however requires increased CO_2 partial pressure relative to atmospheric conditions (Figure 55). This condition is possible in the sediment of Barr Lake given the high organic load (releasing CO_2 upon mineralization).

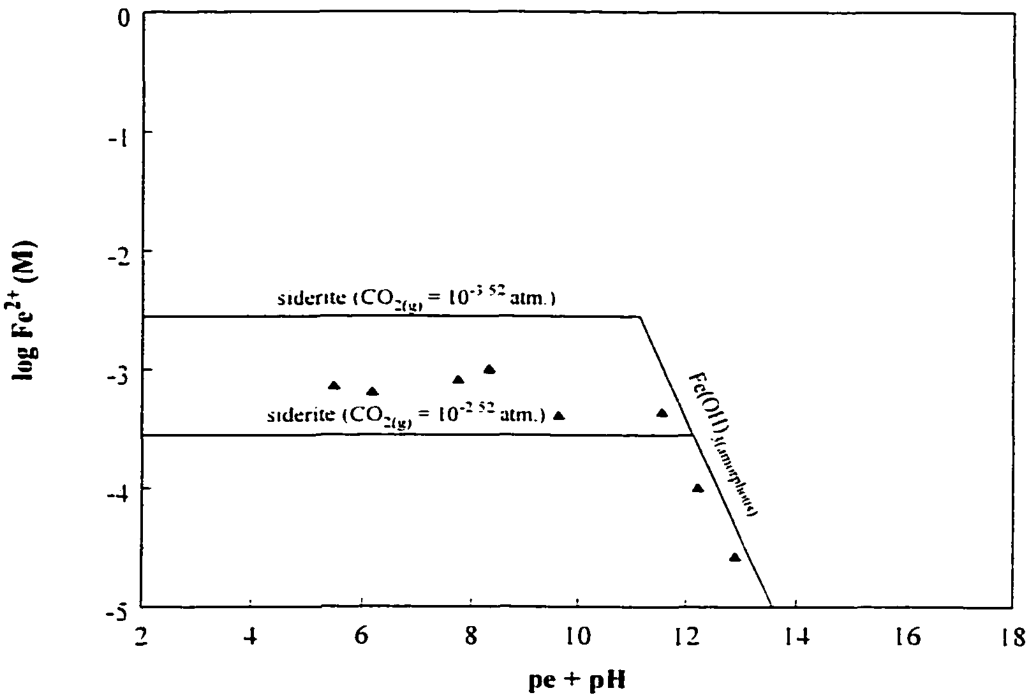


Figure 55. Fe^{2+} activity vs pe+pH measured during the sediment extraction using controlled redox conditions. Included are potential controlling mineral phases.

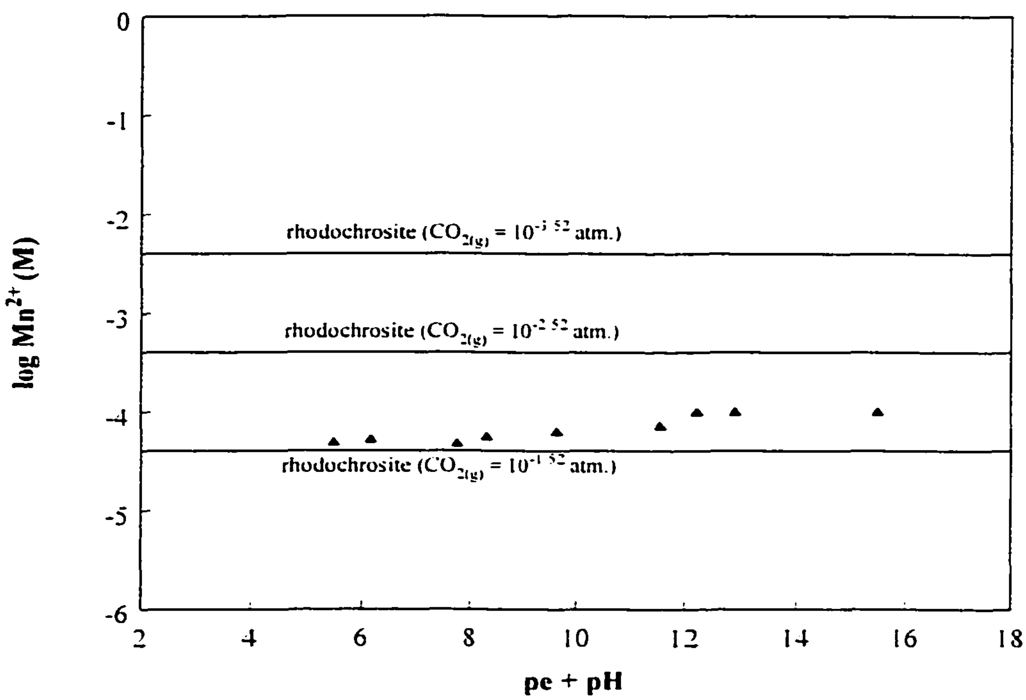


Figure 56. Mn^{2+} activity vs pe+pH measured during the sediment extraction using controlled redox conditions. Included are potential controlling mineral phases.

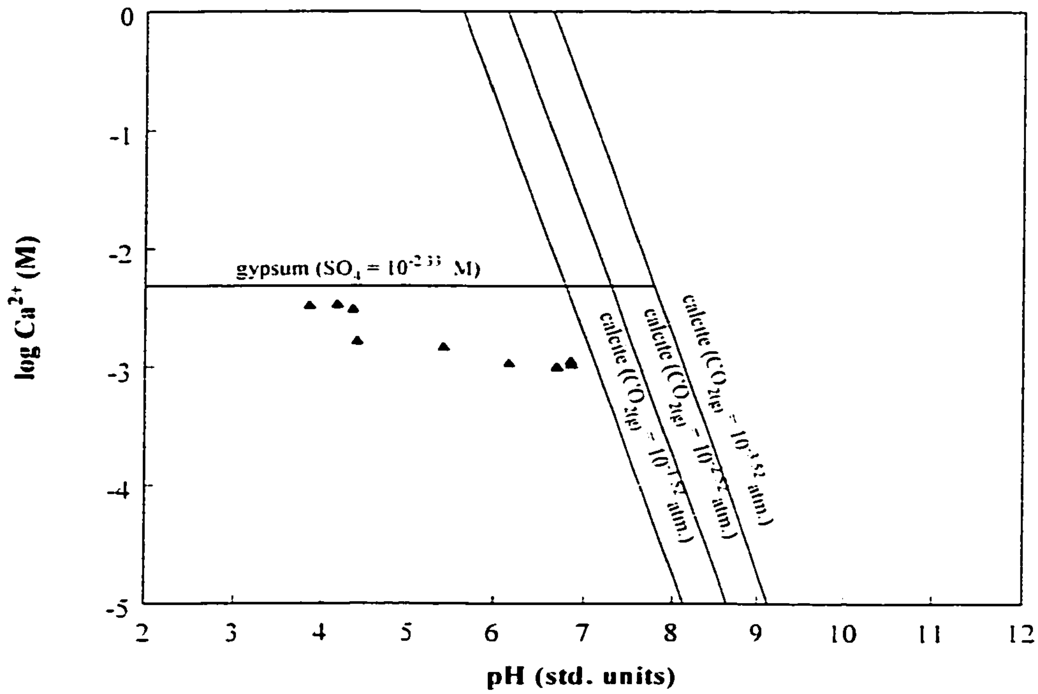


Figure 57. Ca^{2+} activity vs pH measured during the sediment extraction using controlled redox conditions. Included are potential controlling mineral phases. SO_4 activity is assumed to be $10^{-2.33}$ M based on measured values during the experiment.

Manganese activity measured during the experiment supports the contention of high CO_2 partial pressure relative to atmospheric conditions (Figure 56). The relatively stable manganese activities measured over the range of pe+pH values suggest insensitivity to redox condition and possible control by rhodochrosite. Rhodochrosite control on manganese is significant in that manganese activity supported by rhodochrosite suggests solid phase manganese phosphate may be forming (Figure 51). This result is consistent with measurements from groundwater samples.

Calcium control in the sediment appears to be controlled mainly by gypsum, despite potentially high partial pressures of CO_2 (Figure 57). As discussed in Section 5.2.2., sulfate concentrations do not support precipitation of gypsum from the water column. This discrepancy may be explained by sulfide formation at the sediment water interface resulting in the low sulfate concentrations observed at the beginning of the experiment (Table 24). Subsequent oxidation of the sulfide minerals (e.g. $FeS_{2(pyrite)}$) resulted in increasing concentrations of sulfate which were eventually controlled by precipitation of gypsum. The extent to which this process may occur in Barr Lake is unknown.

Speciation modeling of data collected from the vessel indicated typically supersaturated concentrations of Al^{3+} with respect to the expected phase aluminum mineral $Al(OH)_{3(amorphous)}$. Aluminum phosphate control on aqueous phase phosphorus has been documented in the literature (Olila and Reddy, 1997) and is used in efforts to reduce phosphate concentrations in eutrophic surface waters. If $AlPO_4$ were formed in the reaction vessel, orthophosphate concentrations would be redox and pH independent.

There is no evidence that this is a significant process in Barr Lake.

The redox manipulation experiment provided insight into the adsorptive capacity of the sediment in Barr Lake, and the range of conditions under which sediment bound phosphorus is stable. The lack of release of sediment bound phosphorus under the range of redox conditions imposed during the redox manipulation, combined with the apparent phosphorus adsorption/solid phase precipitation as water moves through the sediment and into groundwater, indicates the high potential of the sediment in Barr Lake to remove phosphorus from the aqueous phase. Observations to the contrary from the mass budgets and the aqueous phase concentrations of orthophosphate, are an indication that competing processes to the removal of phosphorus from the water column must be occurring in Barr Lake.

7. Conclusions

Barr Lake receives high annual loads of nutrients and other wastewater related constituents. The high fraction of treated wastewater entering the reservoir results in nutrient cycling that is different from reservoirs discussed in the classic limnological literature. The chemical composition of Barr Lake is related to a baseline of secondary treatment plant effluent onto which dilution flows from stormwater or snowmelt are superimposed.

Inflow, in-lake and outflow nutrient concentrations follow sinusoidal time series models that require nontraditional methods to calculate hydrochemical budgets and to estimate uncertainty than are generally reported in limnological literature. Mass loadings of nitrate to Barr Lake were 203,000, 158,000, and 138,000 kg/year (as N) for water years 1997, 1998 and 1999, respectively. Loadings for orthophosphate to Barr Lake were 34,000, 14,000, and 15,000 kg/year (as P) for water years 1997, 1998 and 1999, respectively. These values are high relative to values reported in current literature.

Use of a combined Monte Carlo and bootstrapping procedure allowed for rigorous evaluation of the uncertainty associated with the hydrochemical budgets for Barr Lake. The uncertainty analysis indicated that orthophosphate behaved as a conservative constituent for two of the three years of study. Calculated mass budgets for orthophosphate (as P) were 18,000, 600, and 3500 kg/year in 1997, 1998, and 1999 respectively. The values for 1998 and 1999 were found to be not significantly different than zero (within 45% of the median budget value). This behavior has not been reported in literature describing hypereutrophic systems. Nitrate, by contrast, is removed in significant quantities (139,000, 135,000, and 109,000 kg/year for 1997, 1998, and 1999, respectively) through organic removal and/or denitrification, to concentrations that suggest nitrogen limitation and/or colimitation by photic zone compression. Intra-year variation in N:P ratio in the Barr Lake water column supports this finding, but significant retention of orthophosphate was not observed on an annual basis.

The Einsele-Mortimer model for orthophosphate adsorption to amorphous iron (hydr)oxides in lake sediments may be adequate to describe orthophosphate concentrations observed in groundwater studies and in laboratory manipulations of redox potential in sediments from Barr Lake. The model is insufficient, however, to describe observed aqueous phase orthophosphate concentrations in Barr Lake or the lack of phosphorus retention in Barr Lake observed during 1998 and 1999. This lack of orthophosphate retention by the sediment in Barr Lake can be explained by high Fe:P ratios in both oxidized and reduced sediment suggesting that phosphorus removal by adsorption to iron precipitates is not a significant removal or release mechanism for phosphorus to or from the aqueous phase. Although the laboratory experiments suggested that the redox behavior of the sediments is probably controlled by iron chemistry, the high pH observed in Barr Lake probably results in competition for sorption sites on iron (hydr)oxides by OH^-. This result, combined with the relatively low iron content of the sediments suggests that the phosphorus dynamics in Barr Lake are more related to manganese chemistry. Since the redox conditions in Barr Lake are rarely sufficient to reduce Fe(III) to Fe(II), but are commonly sufficient to reduce Mn(IV) to Mn(III) or Mn(II), manganese is apparently very active in the sediment and groundwater of Barr Lake. Overall manganese content of the sediment is low, however, resulting in low overall phosphorus removal by manganese in the sediment.

Retention of large quantities of phosphorus in the sediment of Barr Lake is expected given the history and magnitude of nutrient loading to the lake. Water column chemical composition, in lake processes and nitrate dynamics, however, combine to limit the amount of phosphorus retained in Barr Lake, resulting in a phosphorus saturation condition. This condition has somewhat negative effects on the use of water from Barr Lake for irrigation purposes since the phosphorus concentrations are high and nitrogen concentrations tend to be low during the irrigation season. This result has positive implication for attempts to improve the water quality in Barr Lake, however, since the potential for long term internal loading of phosphorus is low.

8. Recommendations

This research quantified mass fluxes and chemical dynamics in an irrigation reservoir receiving a high percentages of treated wastewater. Although this study included three years of data and research is ongoing, most research into lake and reservoir chemical dynamics involves decades of data collection and analysis. Nonetheless, this study revealed several unique characteristics and dynamics that require additional research and pose difficult questions regarding the water quality management of these systems.

Specific Recommendations:

1. Additional annual mass budgets should be conducted to evaluate long-term changes in mass loading and chemical retention and/or flushing.
2. Additional sediment surveys should be conducted to better quantify spatial and seasonal variation in sediment chemistry.
3. Research into the wastewater volumes input to the South Platte River compared to the dilution flows should be quantified to a greater extent. The data included here did not include all wastewater inputs and did not quantify other potential fugitive sources of wastewater.
4. Comparison of sediment extraction methods should be conducted. Chemical extractions used in most studies indicate phosphorus release under reducing conditions. The data presented here using a redox manipulation extraction suggested that reduction of sediment did not result in phosphorus release.

In the area of water quality management, it is clear that the chemical dynamics in Barr Lake (i.e. nitrogen limitation or colimitation, limited adsorption to sediment) provide a mechanism by which nuisance algal blooms are not as extreme as the phosphorus loading would suggest. Attempts to achieve substantial reductions in algal biomass production by limiting phosphorus loading would therefore require extreme levels of control.

9. Literature Cited

Allison, J.D., D.S. Brown and K.J Novo-Gradac. 1991. MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems. EPA/600/3-91/021. 106 p.

Baccini, P., 1985. Phosphate interactions at the sediment-water interface. in Chemical Processes in Lakes. W. Stumm ed. John Wiley & Sons. New York. pp. 189-205.

Bar-Yosef, B. and, U. Kafkafi, 1978. Phosphate desorption from kaolinitic suspensions. Soil Science Society of America Journal 42: 570-572.

Barrow, N.J. and T.C. Shaw, 1975. The slow reactions between soil and anions. Soil Science, 119(4):311-320.

Berner, E.K. and R.A. Berner, 1996. Global Environment: Water, Air, and Geochemical Cycles. Prentice Hall, Inc. Upper Saddle River, NJ. 376 p.

Berthouex, P.M., 1975. Modeling concepts considering process performance, variability and uncertainty. In: Mathematical Modeling for Water Pollution Control Processes. T.M. Keinath and M.P. Wanielista, eds. Ann Arbor Science Publishers, Ann Arbor, MI. pg 405-440.

Boers, P.C.M., 1991. The influence of pH on phosphate release from lake sediments. Water Research 25(3):309-311.

Boers, P.C.M., W. Van Raaphorst, and D.T. Van der Molen, 1998. Phosphorus retention in sediments, Water Science and Technology 37(3): 31-39.

Bortleson, G.C. and G.F. Lee, 1974. Phosphorus, iron, and manganese distribution in sediment cores of six Wisconsin lakes. Limnology and Oceanography 19(5): 794-801.

Boström, B., J.M. Andersen, S. Fleischer and M. Jansson, 1988. Exchange of phosphorus across the sediment - water interface. Hydrobiologia 170: 229-244.

Brennan, E.W., 1994. Effect of redox on the solubility and mineral transformations of Fe, Zn, Pb, and Cd in soils. Ph.D. Dissertation, Colorado State University. 129 pg.

Brennan, E.W. and W.L. Lindsay, 1996. The role of pyrite in controlling metal ion activities in highly reduced soils. Geochimica et Cosmochimica Acta 60(19): 3609-3618.

Brinkman, A.G., 1993. A double layer model for ion adsorption onto metal oxides, applied to experimental data and to natural sediments of Lake Veluwe, the Netherlands. Hydrobiologia 253: 31-45.

Bulgakov, N.G. and A.P. Levich, 1999. The nitrogen:phosphorus ratio as a factor regulating phytoplankton community structure. Archiv fur Hydrobiologie 146(1):3-22.

Caraco, N.F., J.J. Cole and G.E. Likens, 1993. Sulfate control of phosphorus availability in lakes. Hydrobiologia 253: 275-280.

Caraco, N.F., J.J. Cole and G.E. Likens, 1989. Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. Nature 341: 316-318.

Chapra, S.C. 1997. Surface Water-Quality Modeling. McGraw-Hill, Boston. 844 pg.

Cornell, C.A., 1972. First-order analysis of model and parameter uncertainty. Proceedings of the International Symposium on Uncertainties in Hydrologic and Water Resource Systems. Vol. 3. C.C. Kisiel and L. Duckstein, eds. University of Arizona, December 11-14, 1972. pg. 1245-1274.

Cornett, R.J. and F.H. Rigler, 1980. The areal hypolimnetic oxygen deficit: an empirical test the model. Limnology and Oceanography 25(4): 672-679.

Danen-Louwerse, H., L. Lijklema and M. Coenraats, 1993. Iron content of sediment and phosphate adsorption properties. Hydrobiologia 253: 311-317.

Dann, M.S., J.A. Lynch, and E.S. Corbett, 1986. Comparison of methods for estimating sulfate export from a forested watershed. Journal of Environmental Quality 15(2): 141-145.

Davis, J.A. and D.B. Kent, 1990. Surface complexation modeling in aqueous geochemistry. In Mineral - Water Interface Geochemistry, M.F. Hochella and A.F. White eds. Reviews in Mineralogy Volume 23. Mineralogical Society of America, Washington D.C. p. 177-260.

de Mesquita Filho, M.V. and J. Torrent, 1993. Phosphate sorption as related to mineralogy of a hydrosequence of soils from the Cerrado Region (Brazil). Geoderma 58: 107-123.

Dennehy, K.F., D.W. Litke, C.M. Tate, and J.S. Heiny, 1993. South Platte River Basin-Colorado, Nebraska, and Wyoming. Water Resources Bulletin 29:647-683.

Dillon, P.J. and F.H. Rigler, 1974. The phosphorus-chlorophyll relationship in lakes. Limnology and Oceanography 19(5):767-773.

Downing and McCauley, 1992. The nitrogen: phosphorus relationship in lakes. Limnology and Oceanography 37(5):936-945

Drever. J.I.. 1988. The Geochemistry of Natural Waters. Prentice Hall, N.J. 437 p.

Edmondson, W.T. and J.T. Lehman, 1981. The effect of changes in the nutrient income on the condition of Lake Washington. Limnology and Oceanography 26(1):1-29.

Edzwald, J.K., D.C. Toensing, and M.C. Lewis, 1976. Phosphate adsorption reactions with clay minerals. Environmental Science and Technology 10(5): 485-491.

Efron, B. and R. Tibshirani, 1986. Bootstrap methods for standard errors, confidence intervals, and other measures of statistical accuracy. Statistical Science 1(1): 54-75.

Efron, B. and R. Tibshirani, 1993. An Introduction to the Bootstrap. Chapman and Hall, New York. 436 p.

Emerson, S., 1976. Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geochemica et Cosmochemica Acta 40: 925-934.

Emerson, S. and G. Widmer, 1976. Early disgenesis in anaerobic lake sediments-II. Thermodynamic and kinetic factors controlling the formation of iron phosphate. Geochimica et Cosmochimica Acta 42: 1529-1538.

Farmers Reservoir and Irrigation Company, 1994. The Barr Lake Plan. unpublished.

Gale, P.M. and K.R. Reddy, 1994. Carbon flux between sediment and water column of a shallow subtropical, hypereutrophic lake. Journal of Environmental Quality 23:965-972.

Gibson, C.E., 1971. Nutrient limitation. Journal of the Water Pollution Control Federation 43(12): 2436-2440.

Gilbert, R.O., 1987. Statistical Methods for Environmental Pollution Monitoring. VonNostrand Reinhold, New York. 320 pg.

Golterman, H.L., 1995. Theoretical aspects of adsorption of ortho-phosphate onto iron-hydroxide. Hydrobiologia 315: 59-68.

Grim, R.E., 1953. Clay Mineralogy. McGraw Hill. N.Y., 384 p.

Guildford. S.J. and R.E. Hecky, 2000. Total nitrogen. total phosphorus. and nutrient limitation in lakes and oceans: Is there a common relationship? Limnology and Oceanography 45(6): 1213-1223.

Gunatilaka, A., 1982. Phosphate adsorption kinetics of resuspended sediments in a shallow lake, Neusuedlersee, Austria. Hydrobiologia 91: 293-298.

Haraughty. S.J. and S.L. Burks, 1996. Nutrient limitation in Lake Tenkiller. Oklahoma. Journal of Freshwater Ecology 11(1): 91-100.

Hasler. A.D. and W.G. Einsele, 1948. Fertilization for increasing productivity of natural inland waters. Transactions of the thirteenth North American Wildlife Conference. pp. 527-555.

Hecky. R.E., P. Campbell, and L.L. Hendzel. 1993. The stoichiometry of carbon. nitrogen. and phosphorus in particulate matter of lakes and oceans. Limnology and Oceanography, 38(4):709-724.

Hem. J.D., 1992. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water Supply Paper 2254. 263 p.

Hingston. F.J., R.J. Atkinson, A.M. Posner, and J.P. Quirk. 1967. Specific adsorption of anions. Nature 215: 1459-1461.

Hydro-Triad. Ltd., 1974. Barr Lake hydrology study. Unpublished Report. Hydro-Triad Ltd., Denver. Colorado.

Jensen, H.S., P. Kristensen, E. Jeppesen. and A Skytthe. 1992. Iron:phosphorus ratio is surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. Hydrobiologia 235/236: 731-743.

Jensen, H.S. and F.O. Andersen, 1992. Importance of temperature. nitrate. and pH for phosphate release from aerobic sediments of four shallow. eutrophic lakes. Limnology and Oceanography 37(3): 577-589.

Kawashima, M., Y. Tainaka. T. Hori, M. Koyama. and T. Takamatsu. 1986. Phosphate adsorption onto hydrous manganese oxides in the presence of divalent cations. Water Research 20(4): 471-475.

Kleeberg, A. and H.P. Kozerski, 1997. Phosphorus release in Lake Grosser Mueggelsee and its implications for lake restoration. Hydrobiologia 242/243:9-26.

Kleiner, J., 1988. Coprecipitation of phosphate with calcite in lake water: a laboratory experiment modeling phosphorus removal with calcite in Lake Constance. Water Research, 22(10):1259-1265.

Knowlton, M.F. and J.R. Jones, 1996. Nutrient addition experiments in a nitrogen-limited high plains reservoir where nitrogen-fixing algae seldom bloom. Journal of Freshwater Ecology 11(2):123-130.

Kopacek, J., L. Prochazkova, E. Stuchlik, and P. Blazka, 1995. The nitrogen-phosphorus relationship in mountain lakes: influence of atmospheric input, watershed, and pH. Limology and Oceanography 40(5): 930-937.

Ku, W.C., F.A. DiGiano, and T.H. Feng, 1978. Factors affecting phosphate adsorption equilibria in lake sediments. Water Research 12(12): 1069-1074.

Kuo, S. and E.G. Lotse, 1972. Kinetics of phosphate adsorption by calcium carbonate and Ca-kaolinite. Soil Science Society of America Proceedings 36:725-729.

Kuo, S. and E.G. Lotse, 1974. Kinetics of phosphate adsorption and desorption by lake sediments. Soil Science Society of America Proceedings 38(1):50-54.

LaBaugh, J.W., 1985. Uncertainty in phosphorus retention, Williams Fork Reservoir, Colorado. Water Resources Research, 21(11):1684-1692.

LaBaugh, J.W. and T.C. Winter, 1984. The impact of uncertainties in hydrologic measurement on phosphorus budgets and empirical models for two Colorado Reservoirs. Limnology and Oceanography, 29(2):322-339.

LaBaugh, J.W., T.C. Winter, D.O. Rosenberry, P.F. Schuster, M.M. Reddy, and G.R. Aiken, 1997. Hydrological and chemical estimates of the water balance of a closed-basin lake in north central Minnesota. Water Resources Research, 33(12):2799-2812.

Larsen, D.P., J. Van Sickle, K.W. Malueg, and P. D. Smith, 1979. The effect of wastewater phosphorus removal on Shagawa Lake, Minnesota: phosphorus supplies, lake phosphorus and chlorophyll a. Water Research 13: 1259-1272.

Lasenby, D.C. 1975. Development of oxygen deficits in 14 Southern Ontario lakes. Limnology and Oceanography 20(6): 993-999.

Lee, G.F., W.C. Sonzogni, and R.D. Spear, 1977. Significance of oxic vs. anoxic conditions for Lake Mendota sediment phosphorus release. in H.L Golterman (ed) Interactions Between Sediment and Freshwater, Junk, The Hague. pp. 294-306.

Levine. S.N. and D.W. Schindler. 1989. Phosphorus. nitrogen. and carbon dynamics of experimental lake 303 during recovery from eutrophication. Canadian Journal of Fisheries and Aquatic Sciences 46:2-10.

Levine. S.N. and D.W. Schindler, 1992. Modification of the N:P ratio in lakes by in situ processes. Limnology and Oceanography 37(5): 917-935.

Lijklema. L. 1977. The role of iron in the exchange of phosphate between water and sediments. In Interactions Between Sediments and Fresh Water. Proceedings of an International Symposium held at Amsterdam, the Netherlands. September 6-10, 1976. pg. 313-317.

Lijklema. L.. 1980. Interaction of orthophosphate with iron (III) and aluminum hydroxides. Environmental Science and Technology 14(5): 537-541.

Lijklema. L.. 1976. Phosphorus flux across the sediment-water interface. In Interactions between sediments and fresh water. H.L golterman ed.. Dr W. Junk B.V. Publishers. The Hague. p 313-323.

Lijklema, L. 1993. Considerations in modeling the sediment - water exchange of phosphorus. Hydrobiologia 253: 1-16.

Lijklema. L. 1994. Nutrient dynamics in shallow lakes: effects of changes in loading and the role of sediment-water interactions. Hydrobiologia 275/276: 335-348.

Likens. G.E.. 1977. Biogeochemistry of a forested ecosystem. Springer Verlag. New York. 146 pg.

Lind. O.T.. 1987. Spatial and temporal variation in hypolimnetic oxygen deficits of a multidepression lake. Limnology and Oceanography 32(3): 740 - 744.

Lindsay,W.L.. 1979. Chemical Equilibria in Soils. Wiley and Sons. New York.

Livingstone. D.A.,1963. Chemical composition of rivers and lakes. Data of geochemistry (6th ed.) U.S. Geological Survey Professional Paper 440-G. 64 pg.

Lotse. E.G., 1973. Phosphate retention by lake sediments. Maine University Land and Water Resources Center, Project Completion Report. June 1973.

Malueg. K.W., D.P. Larsen. D.W. Shults, H.T. Mercier. 1975. A six-year water. phosphorus. and nitrogen budget for Shagawa Lake Minnesota. Journal of Environmental Quality 4(2): 236-242.

Martynova, M.V., 1981. Bottom sediments as a source of nitrogen and phosphorus in water. Water Resources 8(1):91-106.

McCallister, D.L. and T.J. Logan. 1978. Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio. Journal of Environmental Quality 7(1): 87 - 92.

McMahon, P.B., J.A. Tindall, J.A. Collins, and K.J. Lull, J.R. Nuttle. 1995. Hydrologic and geochemical effects on oxygen uptake in bottom sediments of an effluent-dominated river. Water Resources Research 31(10):2561-2569.

Molot, L.A. and P.J. Dillon. 1991. Nitrogen/Phosphorus ratios and the prediction of chlorophyll in phosphorus limited lakes in central Ontario. Canadian Journal of Fisheries and Aquatic Science 48: 140-145.

Moore, D.M. and R.C. Reynolds. 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press. 2nd edition. 332 p.

Moore, P.A. and K.R. Reddy. 1994. Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. Journal of Environmental Quality 23(5): 955-964.

Moore, P.A., K.R. Reddy, and M.M. Fisher. 1998. Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: spatial and temporal variations. Journal of Environmental Quality 27:1428-1439.

Mortimer, C. H., 1941. The exchange of dissolved substances between mud and water in lakes. Journal of Ecology 29(2): 280 - 329.

Mortimer, C.H., 1942. The exchange of dissolved substances between mud and water in lakes. Journal of Ecology, 30(1): 147 - 201.

Newman, A.C.D. and G. Brown, 1987. The chemical constitution of clays. In Chemistry of Clays and Clay Minerals. A.C.D. Newman ed.. Mineralogical Society Monograph #6. John Wiley, N.Y.

Nurnberg, G. K., 1988. Prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments. Can. Journal of Fisheries and Aquatic Science 45:453-462.

Olila, O.G. and K.R. Reddy, 1997. Influence of redox potential on phosphate-uptake by sediments in two sub-tropical eutrophic lakes. Hydrobiologia 345:45-57.

Otsuki. A. and R.G. Wetzel. 1972. Coprecipitation of phosphate with carbonates in a marl lake. Limnology and Oceanography 17:763-767.

Parfitt, R.L., 1977. Phosphate adsorption on an oxisol. Soil Science Society of America Journal 41:1064-1067.

Parfitt, R.L., R.J. Atkinson and R.St.C. Smart, 1975. The mechanism of phosphate fixation by iron oxides. Soil Science Society of America Proceedings 38: 837-841.

Penn, M.R., M.T. Auer, S.M. Doerr, C.T. Driscoll, C.M. Brooks, and S.W. Effler, 2000. Seasonality in phosphorus release rates from the sediments of a hypereutrophic lake undera matrix of pH and redox conditions. Can. Journal of Fisheries and Aquatic Science 57:1033-1041.

Pettersson, K., B. Bostrom, and O. Jacobsen, 1988. Phosphorus in sediments – speciation and analysis. Hydrobiologia 170: 91-101.

Portielje, R. and L. Lijklema, 1993. Adsorption of phosphate by sediments as a result of enhanced external loading. Hydrobiologia 253: 249-261.

Rast, W. and G.F. Lee, 1978. Summary analysis of the North American (U.S. portion) OECD Eutrophication Project: Nutrient loading – lake response relationships and trophic state indices. USEPA-600/3-78-008.

Reckhow, K.H., 1979. The use of a simple model and uncertainty analysis in lake management. Water Resources Bulletin, 15(3):601-611.

Reckhow, K.H. and S.C. Chapra, 1979. A note on error analysis for a phosphorus retention model. Water Resources Research, 15(6):1643-1646.

Redfield, A.C., B.A. Ketchum, and F.A. Richards, 1963. The influence of organisms on the chemical composition of sea-water. In M.N. Hill (ed.), The Sea. V. 2, p 26-77. Wiley.

Rhee, G.Y., 1978. Effects of N:P atomic ratios and nitrate limitation on algal growth, cell composition, and nitrate uptake. Limnology and Oceanography 23(1):10-25.

Rigler, F.H., 1964. The phosphorus fractions and the turnover time of inorganic phosphorous in different types of lakes. Limnology and Oceanography 9:511-518.

Seitzinger, S.P., 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnology and Oceanography 33:702-724.

Shapiro. J., 1972. Blue Green algae: why they become dominant. Science 179: 382-384.

Shuttleworth. W.J., 1993. Chapter 4 Evaporation. In Handbook of Hydrology, D.R. Maidment, ed. McGraw-Hill, New York.

Siemer, E.G., 1977. Colorado Climate. Colorado Experiment Station Report.

Sibanda, H.M. and S.D. Young. 1986. Competitive adsorption of humic acids and phosphate on goethite, gibbsite and two tropical soils. Journal of Soil Science 37: 197-204.

Smith, V.H., 1979. Nutrient dependence of primary productivity in lakes. Limnology and Oceanography 24(6):1051-1064.

Sondergaard, M., E. Jeppesen, P. Kristensen, and O. Sortkjaer, 1990. Interactions between sediment and water in a shallow and hypereutrophic lake: a study on phytoplankton collapses in Lake Sobygaard, Denmark. Hydrobiologia 191:139-148.

Sposito, G., 1990. Molecular models of ion adsorption on mineral surfaces. In Mineral - Water Interface Geochemistry, M.F. Hochella and A.F. White eds. Reviews in Mineralogy Volume 23. Mineralogical Society of America, Washington D.C. p. 261-279.

Spear, R.D. 1970. The release of phosphorus from lake sediments. PhD dissertation. University of Wisconsin - Madison.

Stednick, J.D. and D.M. Gilbert, 2000. Unpublished data.

Stumm, W. and J.J. Morgan, 1996. Aquatic Chemistry. Wiley -Interscience, New York. 1022 p.

Swistock, B.R., P.J. Edwards, F. Wood, D.R. Dewalle, 1997. Comparison of methods for calculating annual solute exports from six forested Appalachian watersheds. Hydrological Processes, 11(7):655-669.

Theis, T.L. and P.J. McCabe, 1978. Phosphorus dynamics in hypereutrophic lake sediments. Water Research 12:677-685.

Trimble, D.E. and M.N. Machette, 1979. Geologic map of the greater Denver area, Front Range urban corridor, Colorado. U.S. Department of Interior. U.S. Geological Survey, Miscellaneous Investigations Series.

Van der Molen, D.T. and P.C.M. Boers, 1994. Influence of internal loading on phosphorus concentration in shallow lakes before and after reduction of the external loading. Hydrobiologia, 275/276:379-389.

Walker, W.W., 1996. Simplified procedures for eutrophication assessment and prediction: User manual. Instruction Report W-92-2 (Updated April 1999), U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Weisberg, S., 1985. Applied Linear Regression. Wiley, New York. 324 p.

Welch, E.B. and M.A. Perkins, 1979. Oxygen deficit - phosphorus loading relation in lakes. Journal of the Water Pollution Control Federation 51(12): 2823-2828.

Winter, T.C., 1981. Uncertainties in estimating the water balance of lakes. Water Resources Bulletin, 17(1):82-115.

APPENDIX A

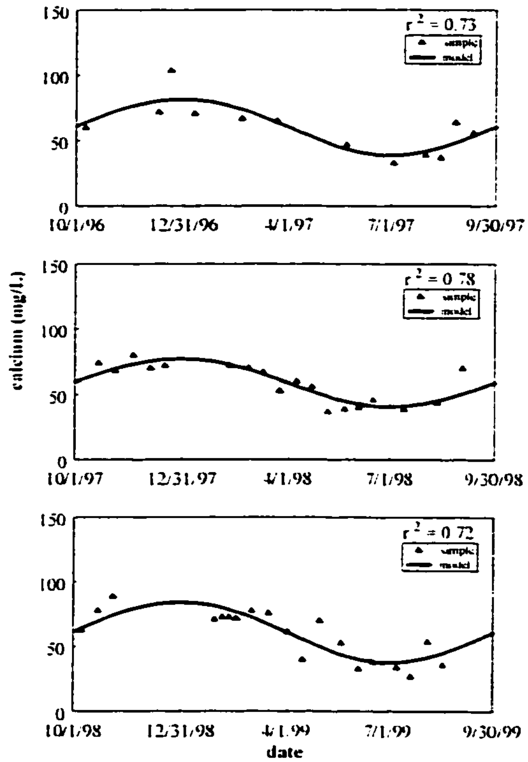


Figure A - 1. Calcium concentration - Barr Lake Inlet

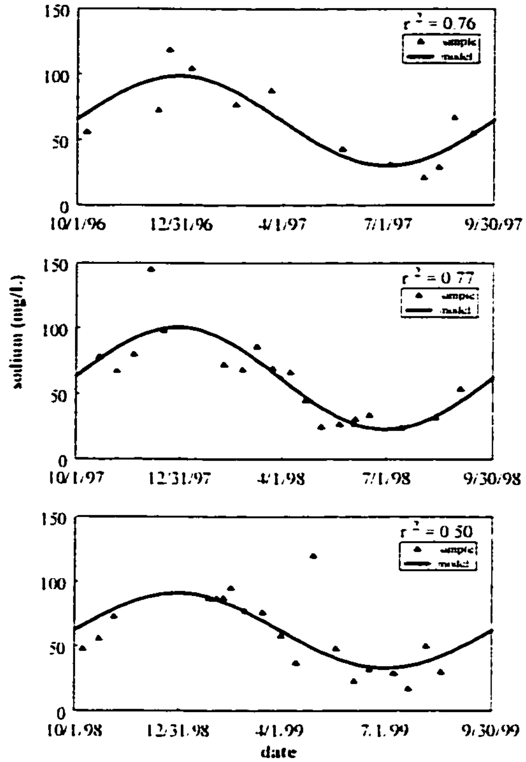


Figure A - 2. Sodium concentration - Barr Lake Inlet

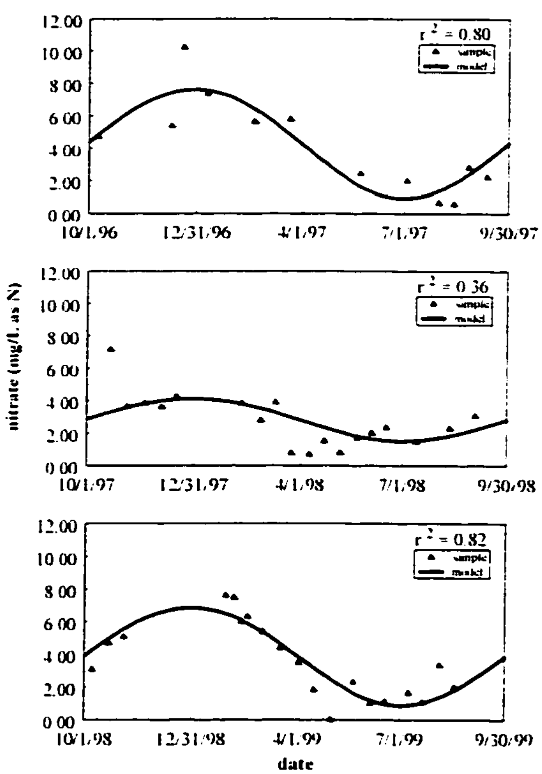


Figure A - 3. Nitrate concentration - Barr Lake Inlet

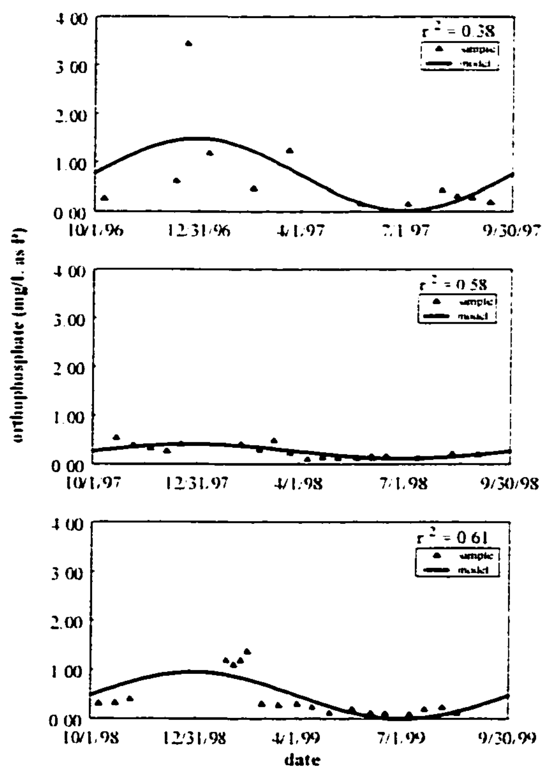


Figure A - 4. Orthophosphate concentration - Barr Lake Inlet

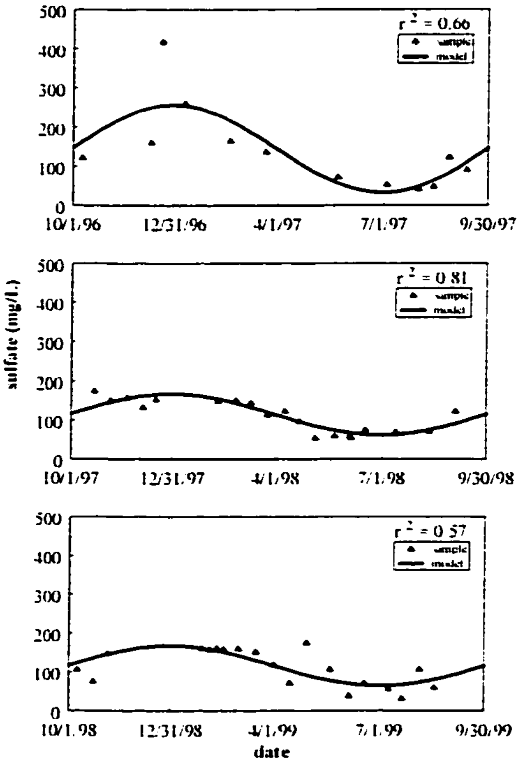


Figure A - 5. Sulfate concentration - Barr Lake Inlet

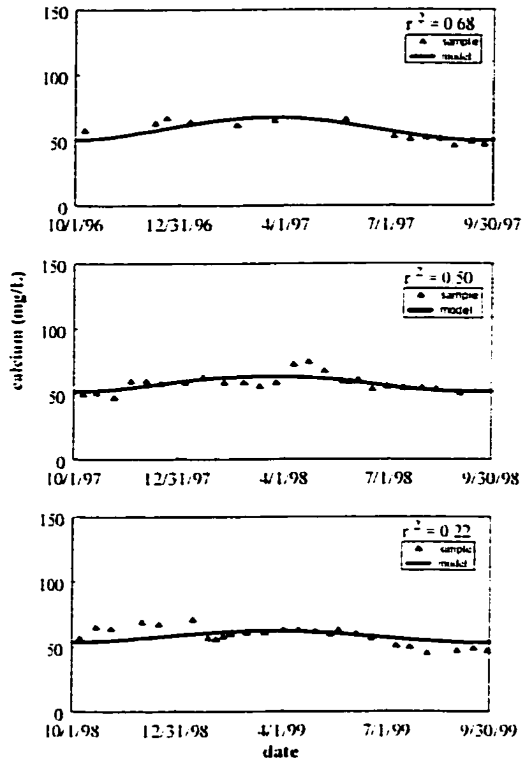


Figure A - 6. Calcium concentration - Barr Lake

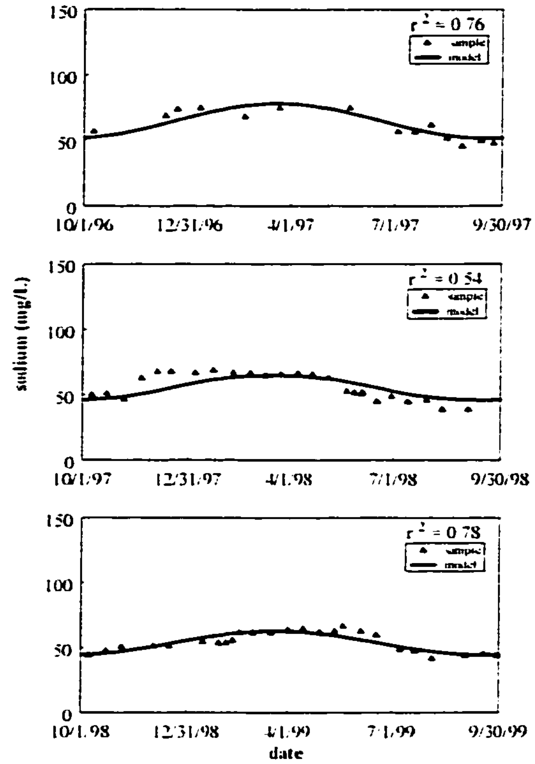


Figure A - 7. Sodium concentration - Barr Lake

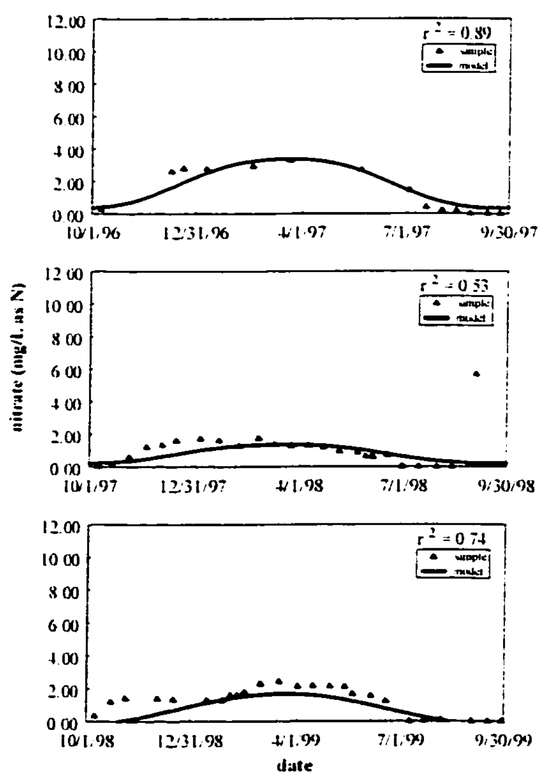


Figure A - 8. Nitrate concentration - Barr Lake

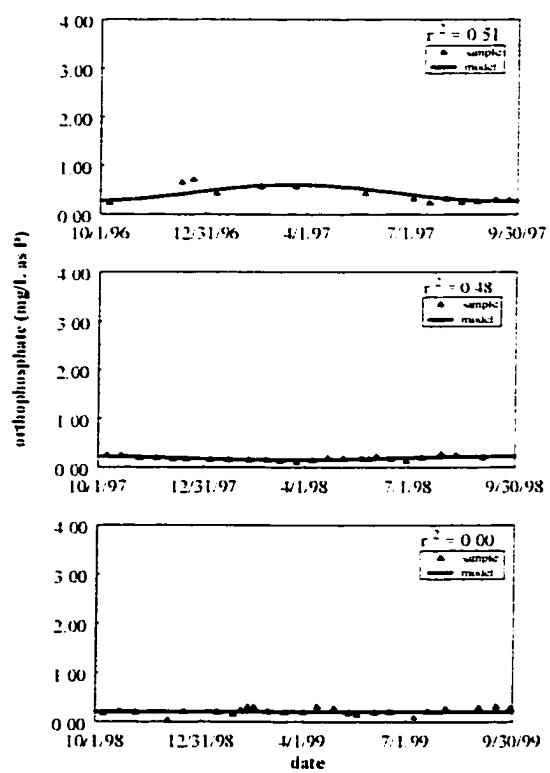


Figure A - 9. Orthophosphate concentration - Barr Lake

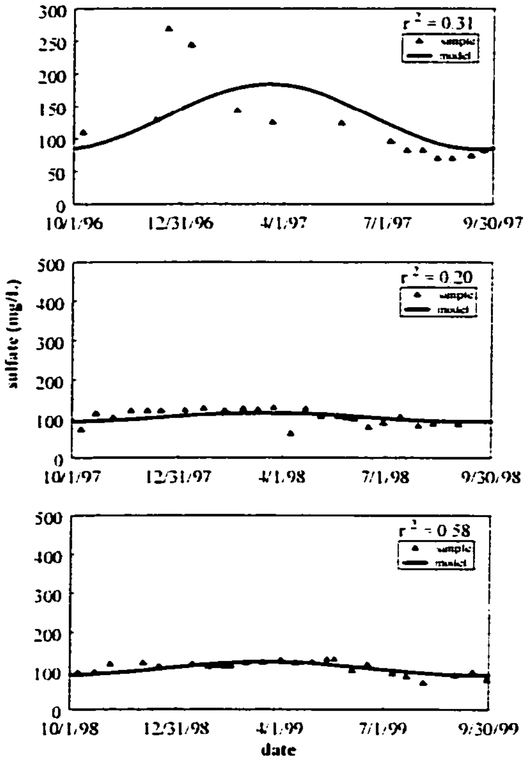


Figure A - 10. Sulfate concentration - Barr Lake

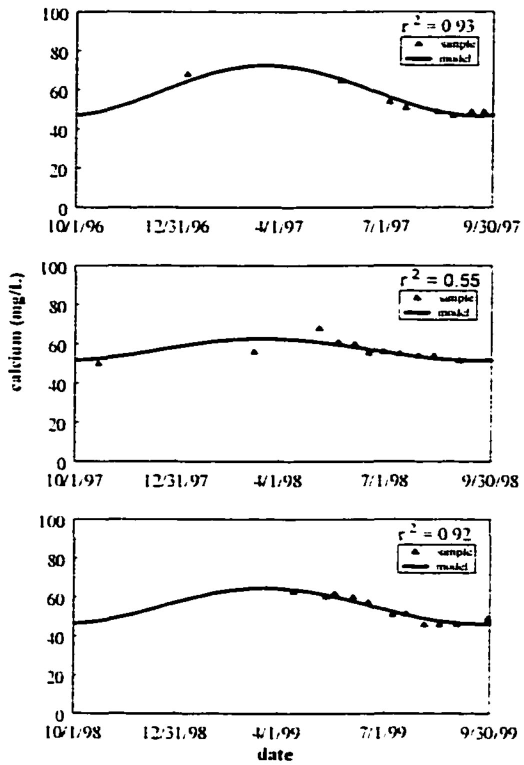


Figure A - 11. Calcium concentration – East Outfall

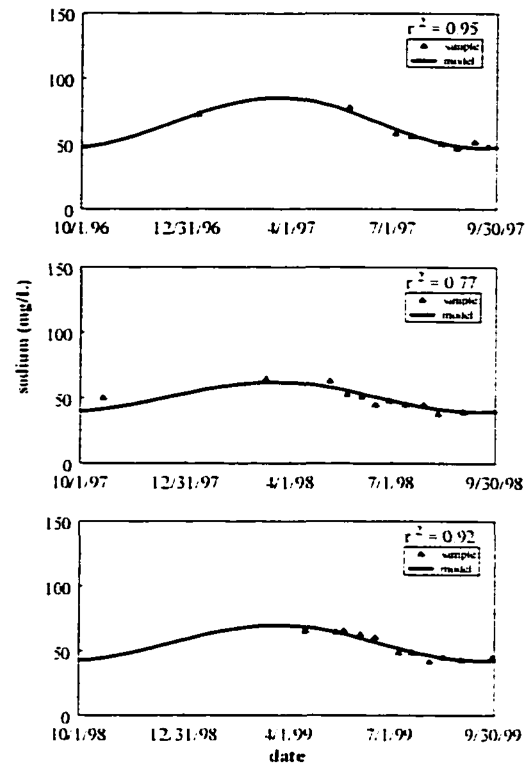
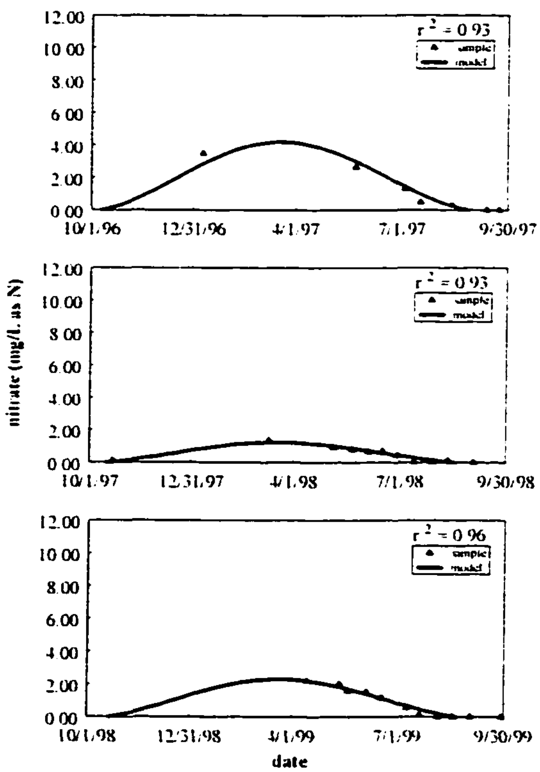


Figure A - 12. Sodium concentration – East Outfall



A - 13. Nitrate concentration – East Outfall

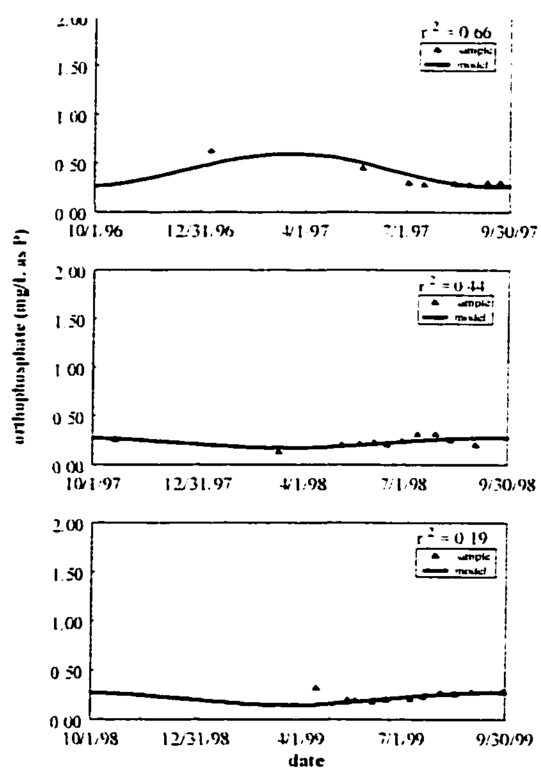
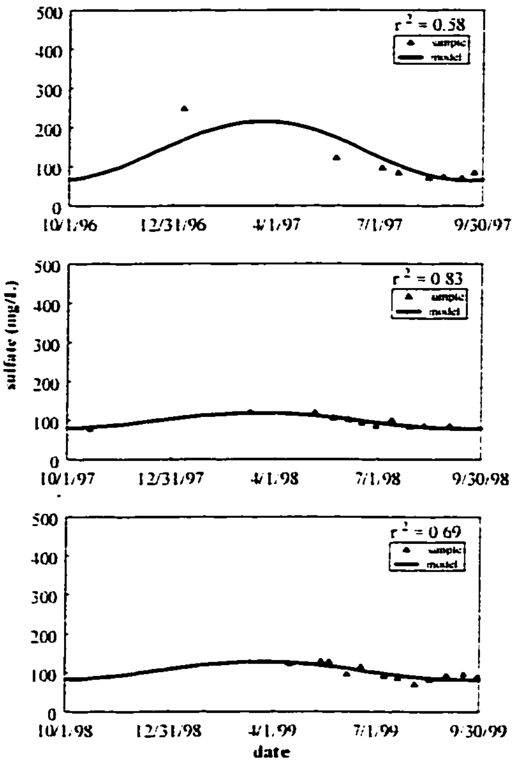


Figure A - 14. Orthophosphate concentration – East Outfall



A - 15. Sulfate concentration – East Outfall

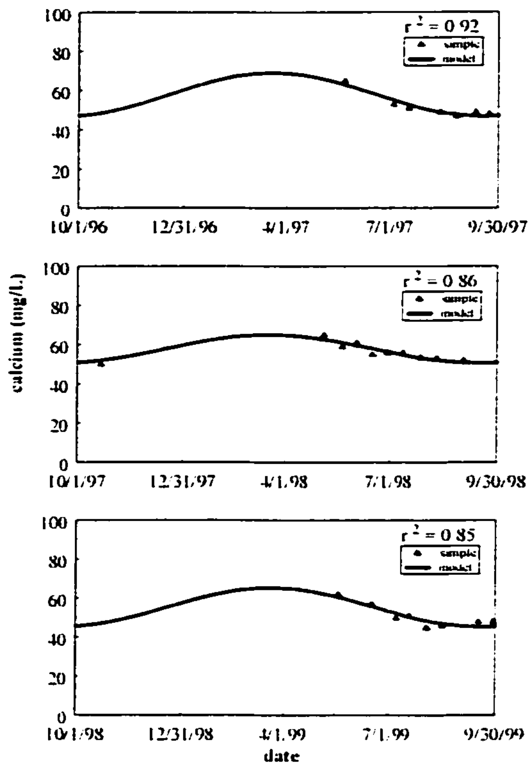


Figure A - 16. Calcium concentration – West Outfall

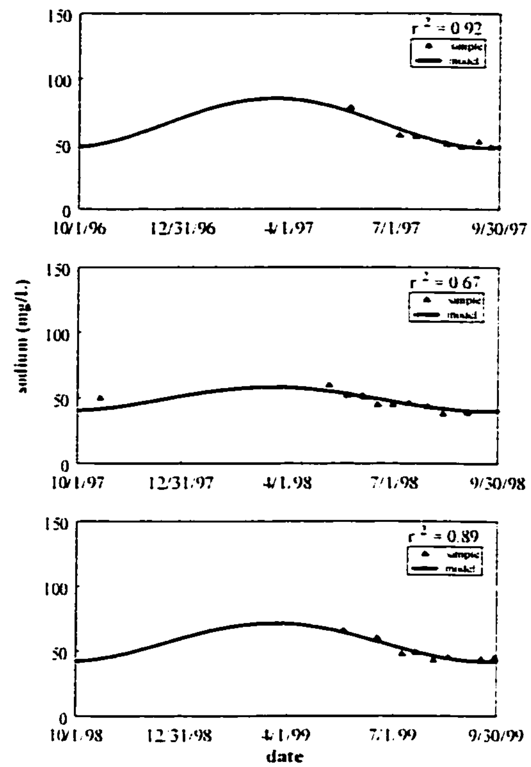


Figure A - 17. Sodium concentration – West Outfall

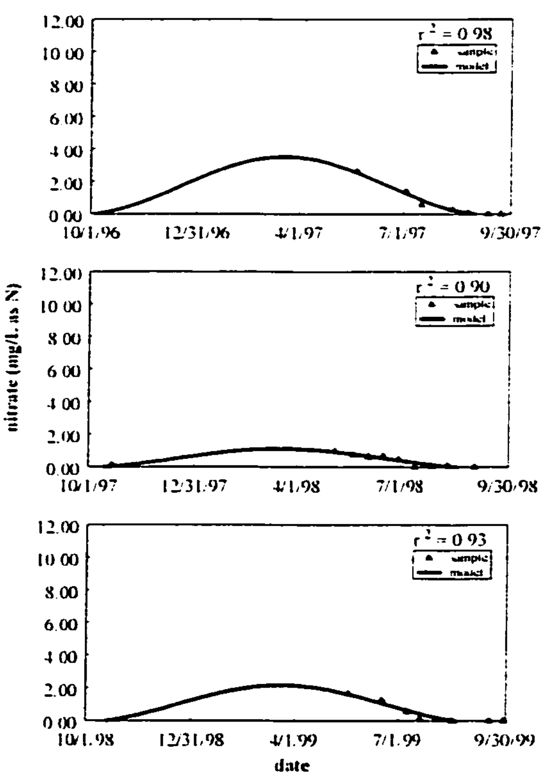


Figure A - 18. Nitrate concentration – West Outfall

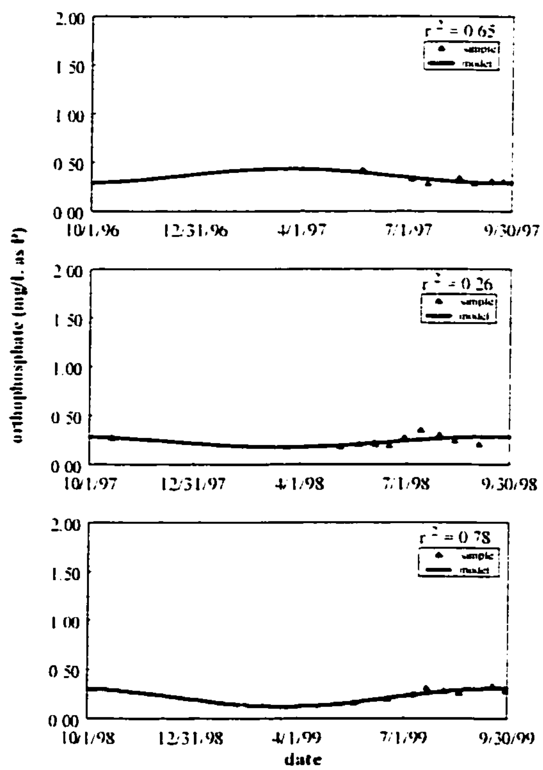


Figure A - 19. Orthophosphate concentration – West Outfall

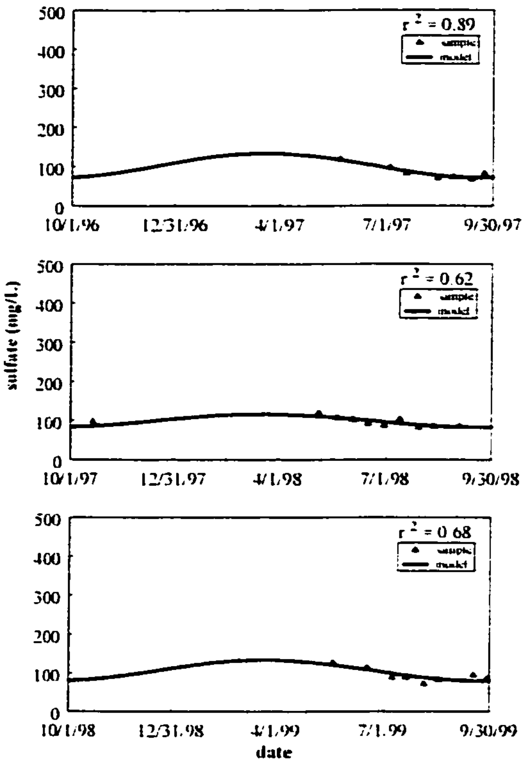


Figure A - 20. Sulfate concentration – West Outfall

Barr Lake Hydrochemical Budget Data

		calcium	sodium	nitrate	orthophosphate	sulfate
units		mg/L	mg/L	mg/L as N	mg/L as P	mg/L
EPA method		200.7	200.7	353.2	365.1	375.1
MDL		1	1	0.02	0.02	1

Location	date	calcium	sodium	nitrate	orthophosphate	sulfate
Barr Lake Inlet	09-Oct-96	60	56	4.73	0.27	122
Barr Lake Inlet	10-Dec-96	72	73	5.38	0.62	161
Barr Lake Inlet	20-Dec-96	104	119	10.24	3.44	417
Barr Lake Inlet	09-Jan-97	72	103	7.36	1.2	266
Barr Lake Inlet	09-Jan-97	70	106	7.42	1.18	256
Barr Lake Inlet	18-Feb-97	67	77	5.66	0.47	165
Barr Lake Inlet	21-Mar-97	65	88	5.79	1.25	137
Barr Lake Inlet	22-May-97	47	43	2.45	0.16	72
Barr Lake Inlet	03-Jul-97	33	31	2	0.15	53
Barr Lake Inlet	31-Jul-97	39	21	0.67	0.43	42
Barr Lake Inlet	13-Aug-97	37	29	0.59	0.31	48
Barr Lake Inlet	26-Aug-97	64	67	2.83	0.28	123
Barr Lake Inlet	11-Sep-97	56	55	2.25	0.19	91
Barr Lake Inlet	21-Oct-97	74	78	7.16	0.54	175
Barr Lake Inlet	05-Nov-97	68	67	3.67	0.39	152
Barr Lake Inlet	20-Nov-97	78	78	3.84	0.33	160
Barr Lake Inlet	20-Nov-97	81	81	3.86	0.32	156
Barr Lake Inlet	04-Dec-97	70	145	3.63	0.27	133
Barr Lake Inlet	16-Dec-97	72	98	4.25	0.41	153
Barr Lake Inlet	09-Feb-98	72	72	3.86	0.41	151
Barr Lake Inlet	09-Feb-98	71	72	3.84	0.42	147
Barr Lake Inlet	25-Feb-98	70	68	2.84	0.29	144
Barr Lake Inlet	25-Feb-98	69	67	2.78	0.3	156
Barr Lake Inlet	10-Mar-98	67	86	3.91	0.49	144
Barr Lake Inlet	24-Mar-98	53	69	0.79	0.23	114
Barr Lake Inlet	08-Apr-98	60	66	0.72	0.1	123
Barr Lake Inlet	21-Apr-98	56	45	1.52	0.14	97
Barr Lake Inlet	05-May-98	37	25	0.82	0.12	54
Barr Lake Inlet	21-May-98	39	27	1.75	0.12	60
Barr Lake Inlet	03-Jun-98	40	27	2.02	0.16	59
Barr Lake Inlet	04-Jun-98	42	31	2.04	0.12	62
Barr Lake Inlet	04-Jun-98	42	31	1.95	0.12	47
Barr Lake Inlet	16-Jun-98	46	34	2.37	0.17	75
Barr Lake Inlet	13-Jul-98	39	24	1.5	0.12	70
Barr Lake Inlet	11-Aug-98	44	32	2.31	0.21	72
Barr Lake Inlet	02-Sep-98	70	54	3.1	0.2	123
Barr Lake Inlet	08-Oct-98	63	48	3.10	0.31	107
Barr Lake Inlet	22-Oct-98	78	56	4.71	0.32	76
Barr Lake Inlet	04-Nov-98	89	73	5.09	0.38	149
Barr Lake Inlet	28-Jan-99	71	87	7.62	1.19	161
Barr Lake Inlet	04-Feb-99	73	87	7.49	1.10	158

Location	date	calcium	sodium	nitrate	orthophosphate	sulfate
Barr Lake Inlet	10-Feb-99	73	87	6.03	1.19	162
Barr Lake Inlet	16-Feb-99	72	95	6.33	1.37	158
Barr Lake Inlet	01-Mar-99	78	77	5.42	0.34	160
Barr Lake Inlet	16-Mar-99	76	76	4.41	0.28	152
Barr Lake Inlet	01-Apr-99	62	58	3.52	0.32	119
Barr Lake Inlet	14-Apr-99	40	37	1.85	0.24	72
Barr Lake Inlet	29-Apr-99	70	120	0.02	0.12	176
Barr Lake Inlet	19-May-99	53	48	2.35	0.19	107
Barr Lake Inlet	04-Jun-99	33	23	1.03	0.12	39
Barr Lake Inlet	17-Jun-99	38	32	1.14	0.11	71
Barr Lake Inlet	08-Jul-99	34	29	1.67	0.09	57
Barr Lake Inlet	20-Jul-99	27	17	1.10	0.19	32
Barr Lake Inlet	04-Aug-99	54	50	3.35	0.23	107
Barr Lake Inlet	17-Aug-99	36	30	2.01	0.12	60
Barr Lake	09-Oct-96	58	57	0.27	0.24	110
Barr Lake	09-Oct-96	57	57	0.24	0.24	109
Barr Lake	10-Dec-96	63	69	2.6	0.66	129
Barr Lake	20-Dec-96	67	75	2.84	0.73	252
Barr Lake	20-Dec-96	67	73	2.77	0.7	285
Barr Lake	09-Jan-97	64	75	2.76	0.43	244
Barr Lake	18-Feb-97	60	74	2.95	0.57	142
Barr Lake	18-Feb-97	63	63	2.93	0.56	145
Barr Lake	21-Mar-97	65	75	3.3	0.57	125
Barr Lake	22-May-97	66	75	2.7	0.43	124
Barr Lake	03-Jul-97	53	57	1.45	0.32	96
Barr Lake	17-Jul-97	51	57	0.42	0.24	82
Barr Lake	31-Jul-97	52	62	0.21	0.32	82
Barr Lake	13-Aug-97	51	52	0.22	0.25	70
Barr Lake	26-Aug-97	46	46	0.04	0.27	70
Barr Lake	11-Sep-97	49	50	0.02	0.3	74
Barr Lake	22-Sep-97	47	48	0.02	0.29	82
Barr Lake	09-Oct-97	50	50	0.06	0.25	72
Barr Lake	21-Oct-97	51	51	0.12	0.24	113
Barr Lake	05-Nov-97	46	47	0.62	0.19	102
Barr Lake	05-Nov-97	49	47	0.59	0.2	102
Barr Lake	20-Nov-97	60	63	1.22	0.19	120
Barr Lake	04-Dec-97	60	69	1.35	0.18	120
Barr Lake	04-Dec-97	60	67	1.35	0.16	121
Barr Lake	16-Dec-97	58	68	1.61	0.17	120
Barr Lake	06-Jan-98	59	67	1.73	0.16	121
Barr Lake	22-Jan-98	63	69	1.63	0.16	126
Barr Lake	09-Feb-98	59	67	1.29	0.15	121
Barr Lake	25-Feb-98	59	67	1.76	0.16	126
Barr Lake	10-Mar-98	56	65	1.38	0.13	123
Barr Lake	24-Mar-98	59	67	1.28	0.1	128
Barr Lake	24-Mar-98	59	65	1.29	0.11	128
Barr Lake	08-Apr-98	74	67	1.32	0.15	3
Barr Lake	08-Apr-98	72	66	1.27	0.14	121
Barr Lake	21-Apr-98	75	66	1.18	0.2	125

Location	date	calcium	sodium	nitrate	orthophosphate	sulfate
Barr Lake	05-May-98	68	63	0.97	0.19	106
Barr Lake	21-May-98	60	53	0.88	0.18	106
Barr Lake	28-May-98	60	52	0.65	0.17	103
Barr Lake	03-Jun-98	60	51	0.65	0.22	101
Barr Lake	04-Jun-98	61	52	0.6	0.21	100
Barr Lake	16-Jun-98	54	45	0.73	0.17	78
Barr Lake	29-Jun-98	56	49	0.02	0.13	89
Barr Lake	13-Jul-98	55	45	0.02	0.2	104
Barr Lake	29-Jul-98	55	46	0.02	0.28	82
Barr Lake	11-Aug-98	54	39	0	0.25	87
Barr Lake	02-Sep-98	51	39	5.71	0.2	86
Barr Lake	08-Oct-98	56	44	0.35	0.18	96
Barr Lake	22-Oct-98	65	48	1.21	0.22	97
Barr Lake	04-Nov-98	64	51	1.43	0.19	118
Barr Lake	02-Dec-98	69	51	1.41	0.03	121
Barr Lake	16-Dec-98	68	52	1.34	0.21	112
Barr Lake	14-Jan-99	71	55	1.30	0.20	118
Barr Lake	28-Jan-99	57	54	1.30	0.16	112
Barr Lake	04-Feb-99	56	54	1.63	0.24	114
Barr Lake	10-Feb-99	58	56	1.62	0.31	113
Barr Lake	16-Feb-99	60	62	1.79	0.29	114
Barr Lake	01-Mar-99	61	62	2.32	0.21	122
Barr Lake	16-Mar-99	61	62	2.43	0.19	123
Barr Lake	01-Apr-99	63	64	2.14	0.19	128
Barr Lake	14-Apr-99	63	65	2.17	0.31	121
Barr Lake	29-Apr-99	62	62	2.15	0.28	123
Barr Lake	12-May-99	60	63	2.12	0.18	130
Barr Lake	19-May-99	63	67	1.68	0.15	131
Barr Lake	04-Jun-99	60	63	1.57	0.19	102
Barr Lake	17-Jun-99	57	60	1.26	0.20	117
Barr Lake	08-Jul-99	51	49	0.02	0.09	94
Barr Lake	20-Jul-99	50	48	0.06	0.22	86
Barr Lake	04-Aug-99	45	42	0.10	0.27	70
Barr Lake	01-Sep-99	47	44	0.02	0.29	89
Barr Lake	16-Sep-99	49	46	0.02	0.31	97
Barr Lake	28-Sep-99	47	44	0.02	0.28	78
East Outfall	09-Jan-97	68	73	3.5	0.63	248
East Outfall	22-May-97	65	78	2.67	0.45	122
East Outfall	03-Jul-97	54	58	1.32	0.3	97
East Outfall	17-Jul-97	51	56	0.5	0.28	84
East Outfall	13-Aug-97	49	50	0.3	0.29	71
East Outfall	26-Aug-97	47	47	0.02	0.28	73
East Outfall	11-Sep-97	49	52	0.02	0.3	72
East Outfall	11-Sep-97	49	51	0.02	0.3	70
East Outfall	22-Sep-97	49	48	0.02	0.3	85
East Outfall	21-Oct-97	50	50	0.12	0.26	78
East Outfall	10-Mar-98	56	65	1.39	0.13	121
East Outfall	05-May-98	68	63	0.95	0.2	120
East Outfall	21-May-98	61	53	0.81	0.21	106

Location	date	Calcium	sodium	nitrate	orthophosphate	sulfate
East Outfall	04-Jun-98	60	51	0.67	0.23	102
East Outfall	16-Jun-98	56	45	0.74	0.2	94
East Outfall	16-Jun-98	55	45	0.68	0.21	94
East Outfall	29-Jun-98	56	48	0.46	0.24	86
East Outfall	13-Jul-98	55	45	0.03	0.31	101
East Outfall	29-Jul-98	54	45	0.04	0.31	84
East Outfall	11-Aug-98	54	38	0.14	0.25	86
East Outfall	02-Sep-98	52	40	0.02	0.2	86
East Outfall	02-Sep-98	51	39	0.02	0.2	86
East Outfall	14-Apr-99	63	66	2.21	0.32	123.5
East Outfall	12-May-99	60	64	2.04	0.20	130
East Outfall	19-May-99	62	66	1.62	0.19	129
East Outfall	04-Jun-99	60	63	1.54	0.18	97
East Outfall	17-Jun-99	57	60	1.18	0.20	116
East Outfall	08-Jul-99	51	49	0.55	0.21	92
East Outfall	20-Jul-99	52	49	0.15	0.23	87
East Outfall	04-Aug-99	46	42	0.02	0.27	71
East Outfall	17-Aug-99	46	45	0.02	0.26	83
East Outfall	01-Sep-99	46	43	0.02	0.28	93
East Outfall	16-Sep-99	49	45	0.02	0.29	96
East Outfall	28-Sep-99	49	45	0.02	0.28	88
West Outfall	22-May-97	65	78	2.62	0.42	119
West Outfall	03-Jul-97	53	57	1.39	0.33	98
West Outfall	17-Jul-97	51	56	0.58	0.28	83
West Outfall	13-Aug-97	49	50	0.3	0.35	75
West Outfall	13-Aug-97	49	50	0.3	0.32	69
West Outfall	26-Aug-97	47	48	0.08	0.28	74
West Outfall	11-Sep-97	49	52	0.02	0.31	69
West Outfall	22-Sep-97	48	48	0.03	0.3	83
West Outfall	21-Oct-97	50	50	0.14	0.27	98
West Outfall	05-May-98	65	60	1	0.18	120
West Outfall	21-May-98	59	52	0.74	0.2	108
West Outfall	03-Jun-98	61	52	0.65	0.22	103
West Outfall	04-Jun-98	60	51	0.63	0.2	103
West Outfall	16-Jun-98	55	45	0.68	0.19	93
West Outfall	29-Jun-98	56	45	0.48	0.27	88
West Outfall	13-Jul-98	56	46	0.02	0.35	104
West Outfall	29-Jul-98	54	44	0.05	0.3	86
West Outfall	29-Jul-98	53	43	0.06	0.3	80
West Outfall	11-Aug-98	53	38	0.1	0.24	86
West Outfall	02-Sep-98	52	39	0.02	0.2	86
West Outfall	19-May-99	62	66	1.68	0.16	128
West Outfall	17-Jun-99	57	60	1.27	0.20	114
West Outfall	08-Jul-99	50	48	0.57	0.24	90
West Outfall	20-Jul-99	51	49	0.16	0.31	90
West Outfall	04-Aug-99	45	43	0.09	0.28	73
West Outfall	17-Aug-99	46	45	0.02	0.26	84
West Outfall	16-Sep-99	48	44	0.02	0.33	96
West Outfall	28-Sep-99	48	45	0.02	0.28	87

Barr Lake Groundwater Monitoring Program

		temperature	pH	Eh	calcium	sodium	nitrate	orthophosphate	sulfate	iron	manganese
units		degrees celcius	std. units	mV	mg/L	mg/L	mg/L as N	mg/L as P	mg/L	mg/L	mg/L
EPA method		170.1	150.1	na	200.7	200.7	353.2	365.1	375.1	200.7	200.7
MDL		0.1	0.01	1	1	1	0.02	0.02	1	0.05	0.02

Location	date	temperature	pH	Eh	calcium	sodium	nitrate	orthophosphate	sulfate	iron	manganese
Center Drain	10-Dec-96	11.0	7.0	257	74	76	0.27	0.07	91	<0.05	1.36
Center Drain	10-Dec-96	11.0	7.0	257	73	76	0.28	0.04	94	<0.05	1.35
Center Drain	20-Dec-96	10.8	7.1	140	76	78	0.36	0.08	169	<0.05	1.37
Center Drain	9-Jan-97	10.7	7.4	282	73	78	0.39	0.06	157	<0.05	1.34
Center Drain	18-Feb-97	10.6	7.3	318	69	75	0.40	<0.03	89	<0.05	1.37
Center Drain	21-Mar-97	10.7	7.4	222	71	78	0.54	0.05	78	<0.05	1.41
Center Drain	22-May-97	11.2	7.4	145	72	78	0.38	0.07	77	<0.05	1.42
Center Drain	3-Jul-97	11.6	7.3	143	70	80	0.40	0.09	81	<0.05	1.41
Center Drain	17-Jul-97	11.8	7.4	82	69	79	0.44	0.03	74	<0.05	1.41
Center Drain	31-Jul-97	11.9	7.3	287	70	78	0.48	0.05	71	<0.05	1.44
Center Drain	13-Aug-97	11.9	7.4	115	73	79	0.31	0.03	73	<0.05	1.39
Center Drain	26-Aug-97	11.9	7.7	103	69	77	0.47	<0.03	72	<0.05	1.39
Center Drain	11-Sep-97	11.9	7.2	82	70	83	0.43	0.04	68	<0.05	1.46
Center Drain	22-Sep-97	11.9	7.6	179	67	77	0.41	0.04	77	<0.05	1.39
Center Drain	21-Oct-97	11.8	7.4	130	67	76	0.55	0.03	62	<0.05	1.49
Center Drain	5-Nov-97	11.6	7.3	610	66	47	0.48	0.05	86	<0.05	1.44
Center Drain	20-Nov-97	11.4	7.1	125	70	79	0.30	0.06	92	<0.05	1.42
Center Drain	4-Dec-97	11.1	7.3	120	67	75	0.27	0.04	86	<0.05	1.39
Center Drain	16-Dec-97	10.9	7.3	245	66	81	0.30	0.06	86	<0.05	1.44
Center Drain	16-Dec-97	10.9	7.3	245	66	88	4.76	0.13	97	<0.05	2.37
Center Drain	6-Jan-98	10.7	7.3	226	68	77	35.35	0.05	87	<0.05	1.3
Center Drain	6-Jan-98	10.7	7.3	226	65	99	7.22	0.1	135	<0.05	1.38
Center Drain	22-Jan-98	10.6	7.5	195	67	80	0.33	<0.03	87	<0.05	1.42

Location	date	temperature	pH	Eh	calcium	sodium	nitrate	orthophosphate	sulfate	iron	manganese
Center Drain	22-Jan-98	10.6	7.5	195	70	80	0.33	0.03	84	<0.05	1.5
Center Drain	9-Feb-98	10.6	7.5	144	67	79	0.27	0.03	82	<0.05	1.48
Center Drain	25-Feb-98	10.6	7.4	153							
Center Drain	10-Mar-98	10.6	7.5	175	60.0	71	0.23	<0.03	82	<0.05	1.39
Center Drain	24-Mar-98	10.7	7.4	141	63	72	0.23	<0.03	73	<0.05	1.4
Center Drain	8-Apr-98	10.8	7.6	149	77	72	0.25	<0.03	73	<0.05	1.40
Center Drain	21-Apr-98	10.9	7.1	213	81	73	0.24	0.03	84	<0.05	1.39
Center Drain	5-May-98	11.1	7.6	167	76	72	0.27	0.05	83	<0.05	1.37
Center Drain	21-May-98	11.3	7.5	134	78	70	0.28	0.03	85	<0.05	1.38
Center Drain	4-Jun-98	11.5	7.4	148	84	76	0.44	<0.03	89	<0.05	1.44
Center Drain	16-Jun-98	11.6	7.5	193	81	74	0.27	0.04	89	<0.05	1.38
Center Drain	29-Jun-98	11.7	7.3	173	84	75	0.25	0.08	70	<0.05	1.47
Center Drain	13-Jul-98	11.9	7.6	76	83	74	0.31	<0.03	98	<0.05	1.41
Center Drain	29-Jul-98	12.1	7.5	226	83	77	0.24	0.03	83	<0.05	1.4
Center Drain	11-Aug-98	12.1	7.1	266	88	75	0.25	<0.03	89	<0.05	1.43
Center Drain	11-Aug-98	12.1	7.1	266	90	76	0.28	<0.03	89	<0.05	1.43
Center Drain	2-Sep-98	12.1	7.3	253	80	74	0.27	0.05	86	<0.05	1.47

Barr Lake In-Lake Monitoring Program

	depth	temperature	pH	dissolved oxygen	calcium	sodium	nitrate	orthophosphate	sulfate
units	meters	degrees celcius	std. units	mg/L	mg/L	mg/L	mg/L as N	mg/L as P	mg/L
EPA method	na	170.1	150.1	360.1	200.7	200.7	353.2	365.1	375.1
MDL	0.01	0.1	0.01	0.1	<1 mg/L	<1 mg/L	<0.02	<0.02 mg/L	<1 mg/L

location	date	depth	temperature	pH	dissolved oxygen	calcium	sodium	nitrate	orthophosphate	sulfate
Station 1	21-Mar-97	1	7.9	7.6	9.0	65	75	3.30	0.57	125
Station 1	21-Mar-97	3	6.4	7.5	9.7	65	75	3.30	0.56	118
Station 1	21-Mar-97	7	5.7	7.3	9.0	65	76	3.27	0.57	140
Station 2	21-Mar-97	1	7.6	7.6	9.5	65	76	3.40	0.55	138
Station 2	21-Mar-97	3	7.2	7.5	9.4	65	77	3.42	0.57	140
Station 2	21-Mar-97	7	6.1	7.5	9.4	65	78	3.35	0.57	138
Station 3	21-Mar-97	1	8.1	7.7	9.8	66	76	3.43	0.57	142
Station 3	21-Mar-97	1	8.1	7.7	9.8	65	75	3.56	0.55	125
Station 3	21-Mar-97	3	7.1	7.6	9.8	66	77	3.29	0.58	118
Station 3	21-Mar-97	7	5.9	7.4	9.3	65	77	3.12	0.58	118
Station 1	17-Jul-97	1	22.8	9.4	13.4	51	57	0.42	0.52	82
Station 1	17-Jul-97	3	22.3	9.3	10.6	52	57	0.47	0.24	88
Station 1	17-Jul-97	6	22.0	9.3	9.7	52	58	0.48	0.26	80
Station 2	17-Jul-97	1	22.4	9.4	11.1	51	56	0.49	0.27	79
Station 2	17-Jul-97	3	22.1	9.3	9.6	52	60	0.51	0.24	80
Station 2	17-Jul-97	5.7	21.9	9.3	9.0	52	59	0.54	0.33	82
Station 3	17-Jul-97	1	22.4	9.4	10.0	52	59	0.49	0.31	78
Station 3	17-Jul-97	3	22.0	9.3	9.4	52	56	0.54	0.32	83
Station 3	17-Jul-97	7	21.0	8.5	1.1	53	58	0.45	0.47	83
Station 3	17-Jul-97	7	21.0	8.5	1.1	51	56	0.54	0.42	84
Station 1	26-Aug-97	1	22.2	9.3	8.3	47	48	<0.02	0.28	75
Station 1	26-Aug-97	3	22.0	9.3	8.3	47	49	<0.02	0.28	73
Station 1	26-Aug-97	6	21.7	8.9	6.9	46	48	<0.02	0.29	48

location	date	depth	temperature	pH	dissolved oxygen	calcium	sodium	nitrate	orthophosphate	sulfate
Station 2	26-Aug-97	1	22.1	9.3	8.5	50	47	<0.02	0.28	73
Station 2	26-Aug-97	3	22.0	9.3	8.3	47	47	<0.02	0.27	73
Station 2	26-Aug-97	6	21.9	9.3	8.0	47	48	<0.02	0.27	74
Station 2	26-Aug-97	8	21.6	8.1	3.1	48	48	<0.02	0.29	72
Station 3	26-Aug-97	1	22.3	9.2	7.2	47	46	<0.02	0.29	71
Station 3	26-Aug-97	3	21.9	9.2	7.4	46	47	<0.02	0.28	75
Station 3	26-Aug-97	7	21.4	8.7	4.7	47	47	<0.02	0.33	74
Station 1	11-Sep-97	1	22.1	9.4	9.9	49	50	<0.02	0.30	74
Station 1	11-Sep-97	3	21.7	9.3	8.9	49	51	<0.02	0.31	74
Station 1	11-Sep-97	6	21.1	9.2	7.2	49	52	<0.02	0.31	73
Station 2	11-Sep-97	1	22.2	9.3	8.9	49	51	<0.02	0.31	70
Station 2	11-Sep-97	3	21.4	9.2	7.5	49	52	<0.02	0.32	72
Station 2	11-Sep-97	5.7	21.0	9.0	4.7	49	48	<0.02	<0.03	74
Station 3	11-Sep-97	1	22.0	9.3	9.1	48	53	<0.02	0.30	67
Station 3	11-Sep-97	3	21.2	9.2	7.7	48	51	<0.02	0.31	74
Station 3	11-Sep-97	5.7	21.1	9.1	6.3	48	52	<0.02	0.32	72
Station 1	9-Oct-97	1	16.5	8.8	8.8	49	51	0.06	0.26	64
Station 1	9-Oct-97	3	16.5	8.7	8.0	51	51	0.06	0.26	77
Station 1	9-Oct-97	5	15.3	8.6	7.8	51	54	0.07	0.26	75

APPENDIX B

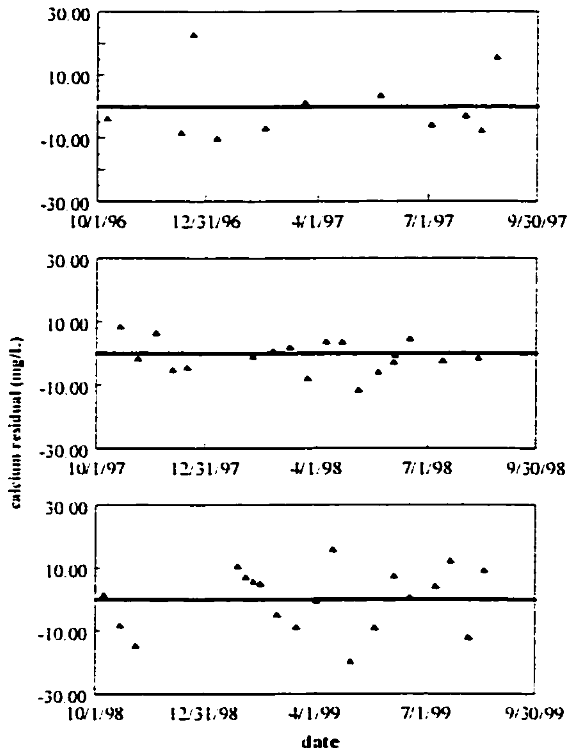


Figure B - 1. Calcium residual Barr Lake Inlet

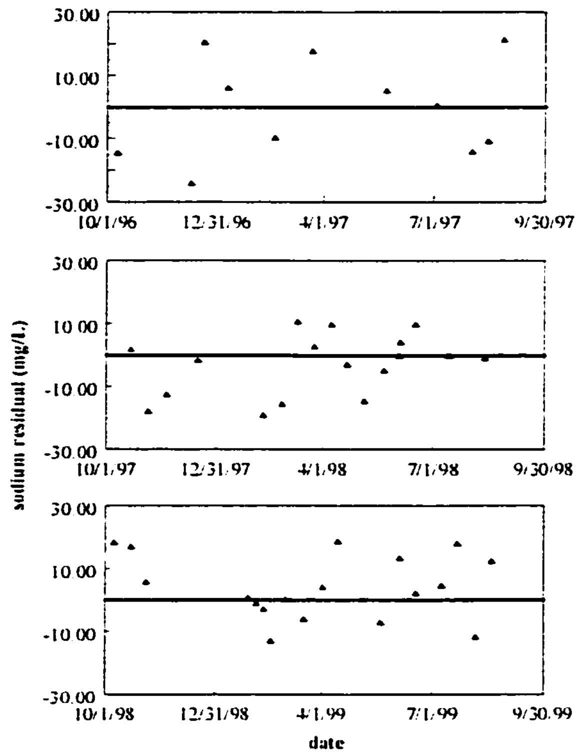


Figure B - 2. Sodium residual Barr Lake Inlet

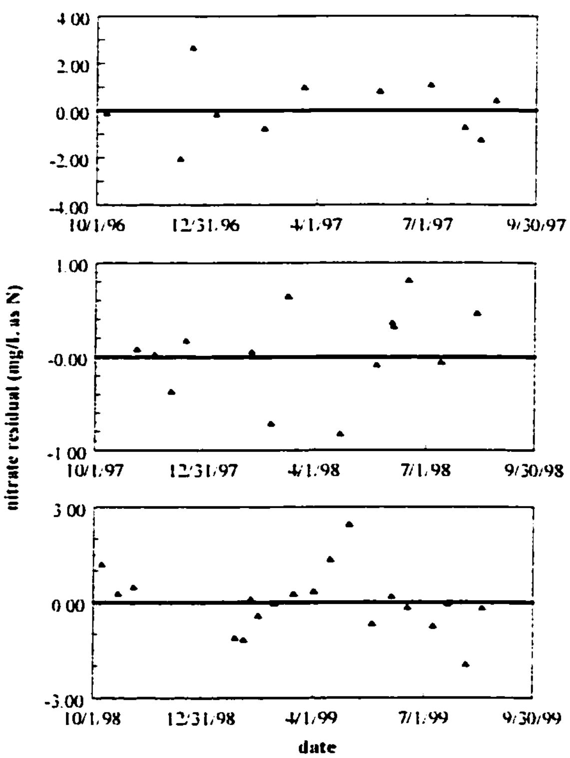


Figure B - 3. Nitrate residual Barr Lake Inlet

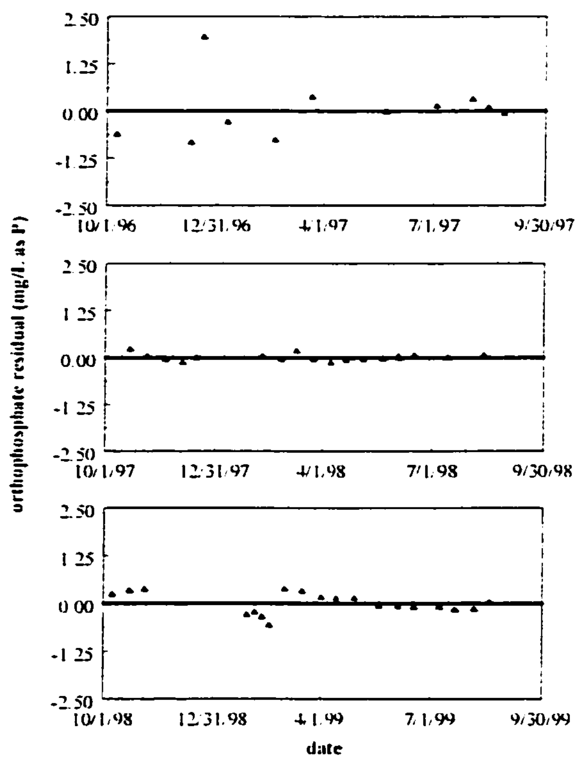


Figure B - 4. Orthophosphate residual Barr Lake Inlet

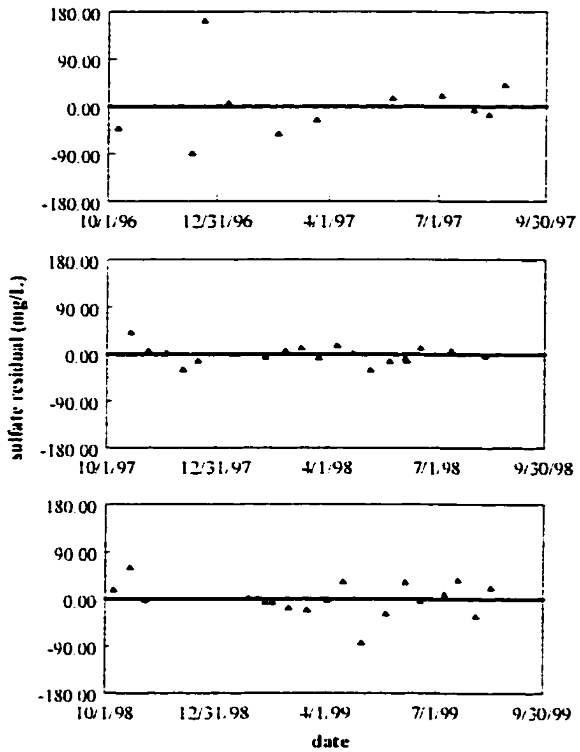


Figure B - 5. Sulfate residual Barr Lake Inlet

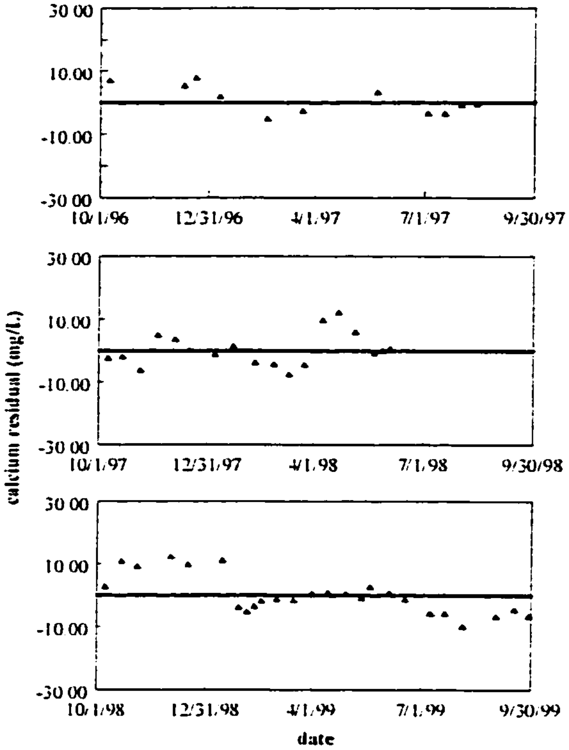


Figure B - 6. Calcium residual Barr Lake

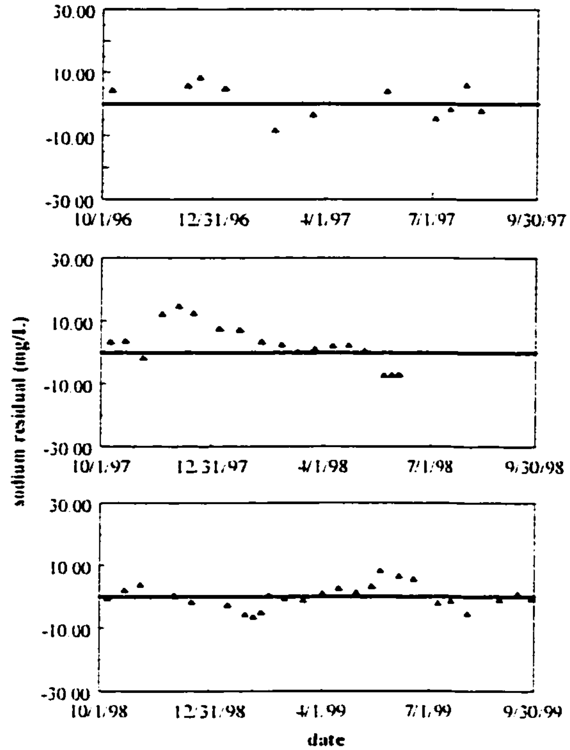


Figure B - 7. Sodium residual Barr Lake

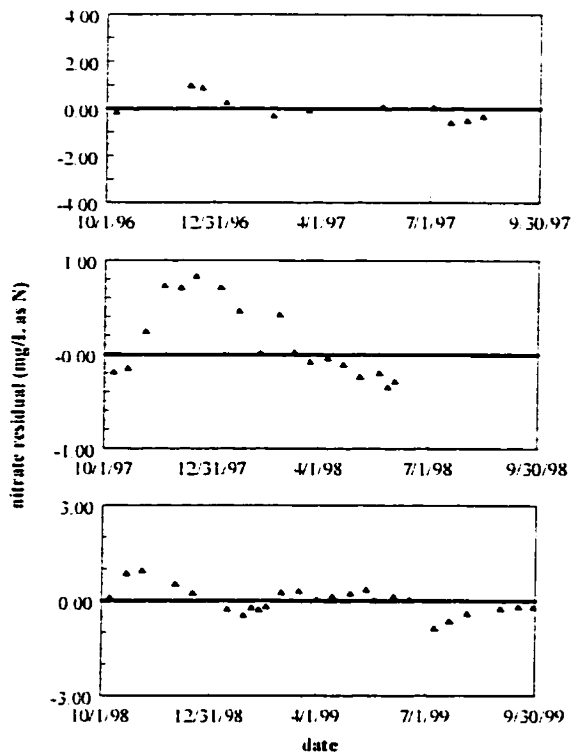


Figure B - 8. Nitrate residual Barr Lake

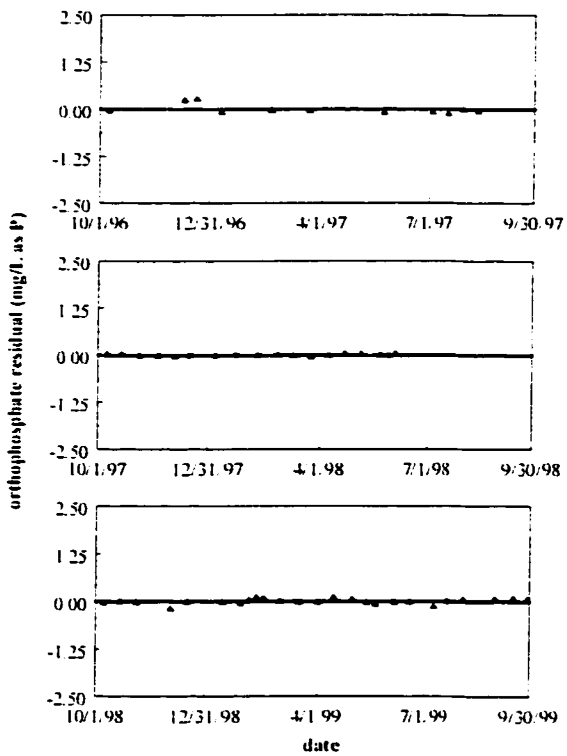


Figure B - 9. Orthophosphate residual Barr Lake

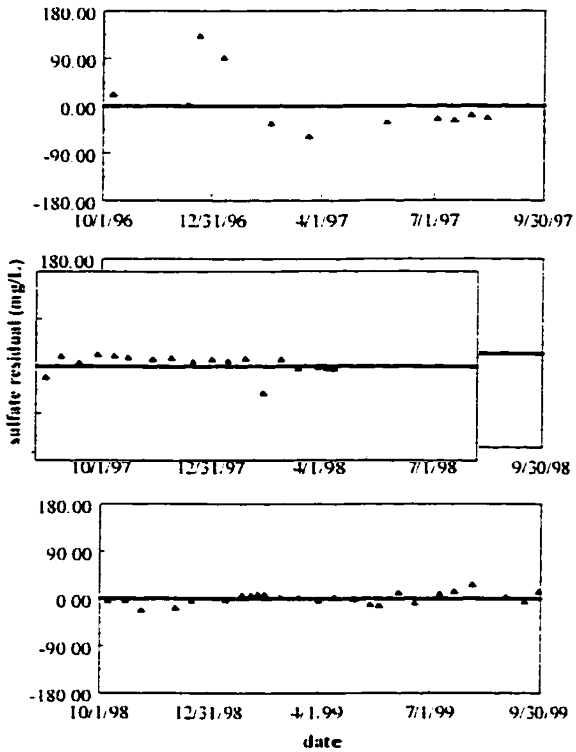


Figure B - 10. Sulfate residual Barr Lake

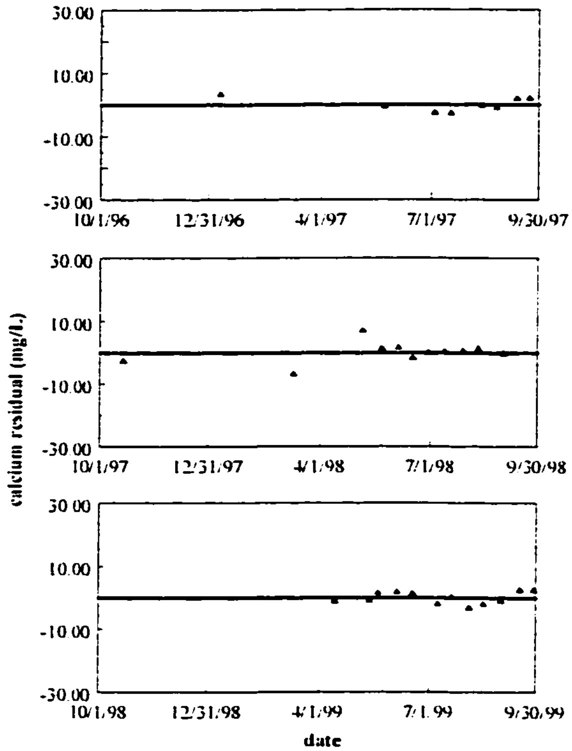


Figure B - 11. Calcium residual East Outfall

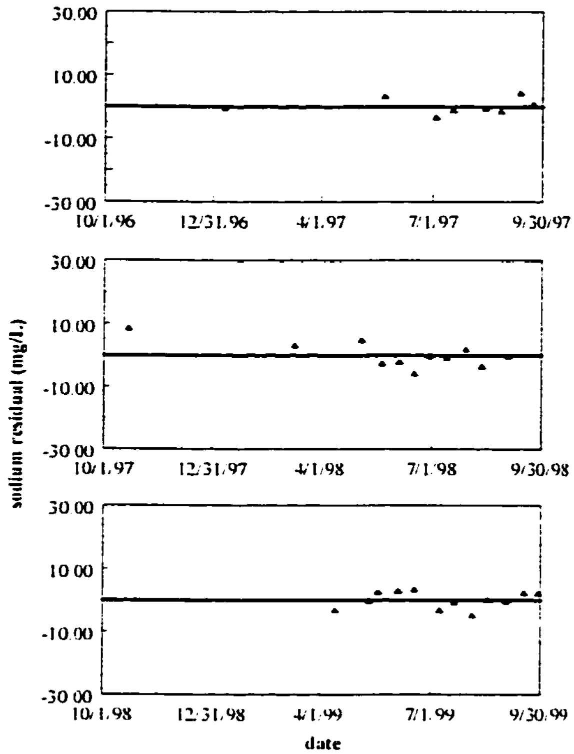


Figure B - 12. Sodium residual East Outfall

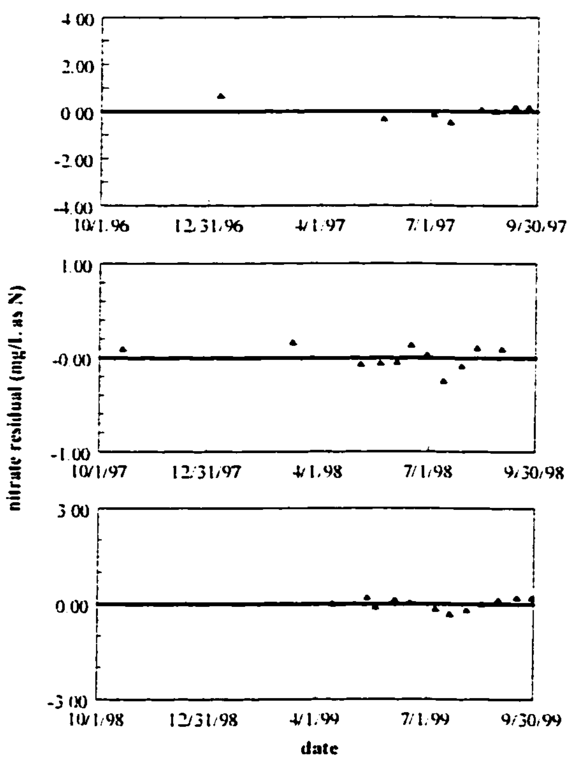


Figure B - 13. Nitrate residual East Outfall

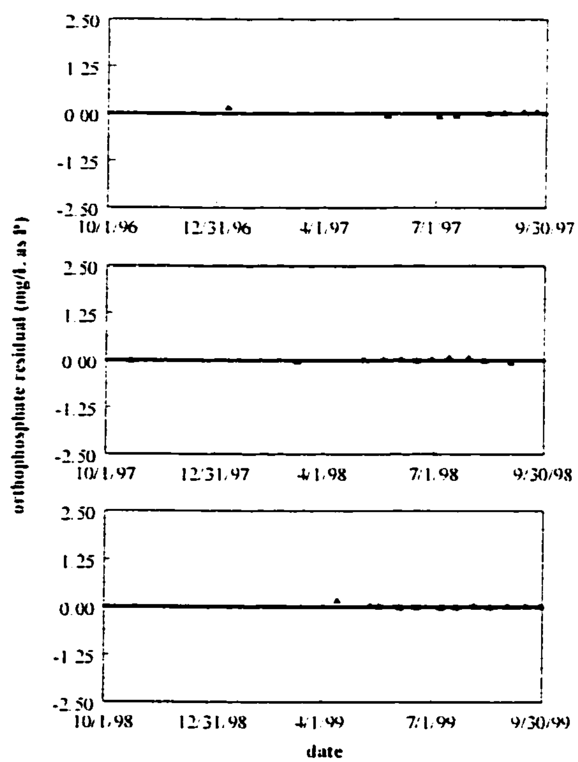


Figure B - 14. Orthophosphate residual East Outfall

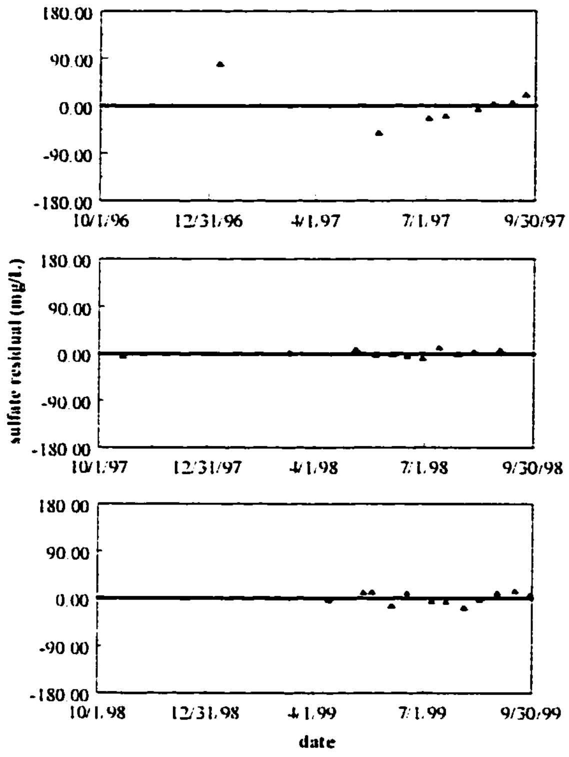


Figure B - 15. Sulfate residual East Outfall

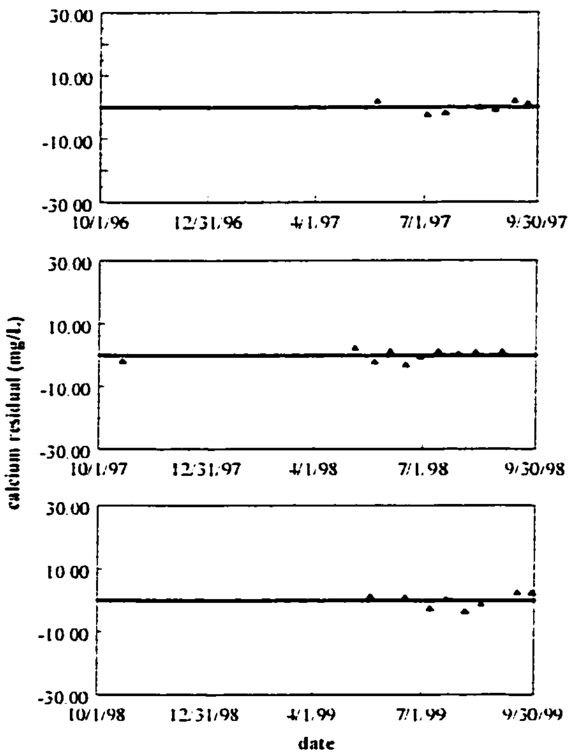


Figure B - 16. Calcium residual West Outfall

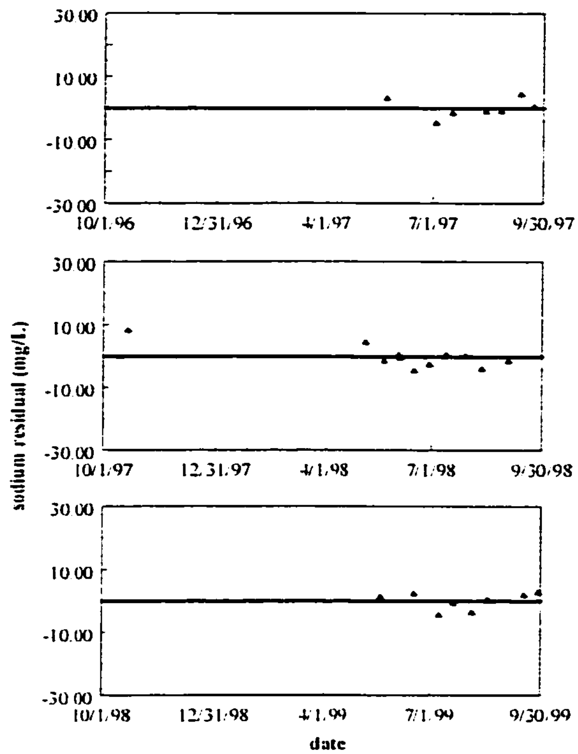


Figure B - 17. Sodium residual West Outfall

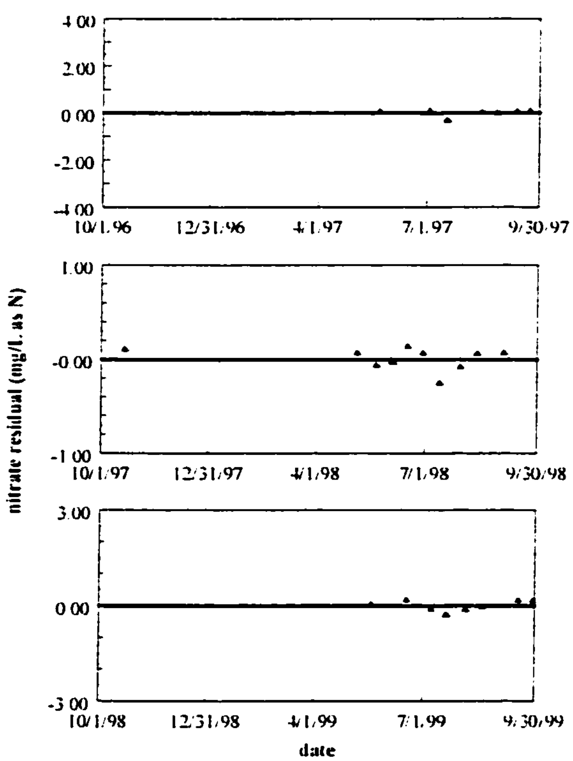


Figure B - 18. Nitrate residual West Outfall

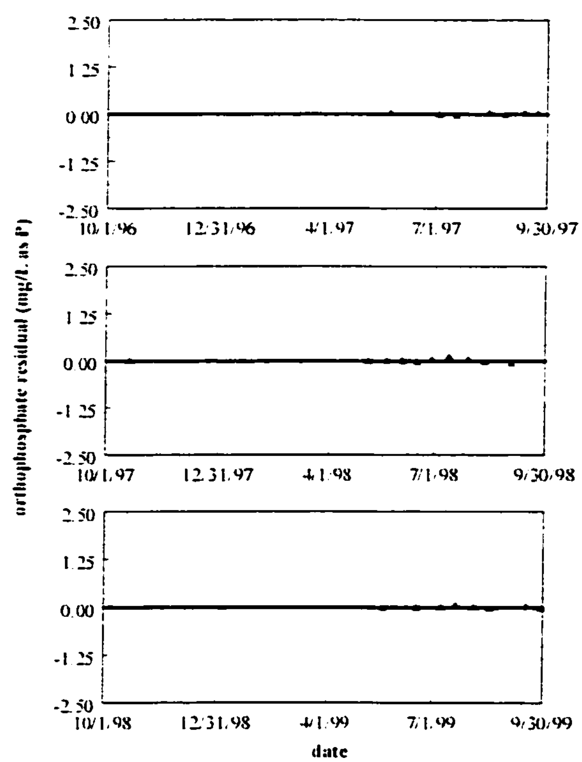


Figure B - 19. Orthophosphate residual West Outfall

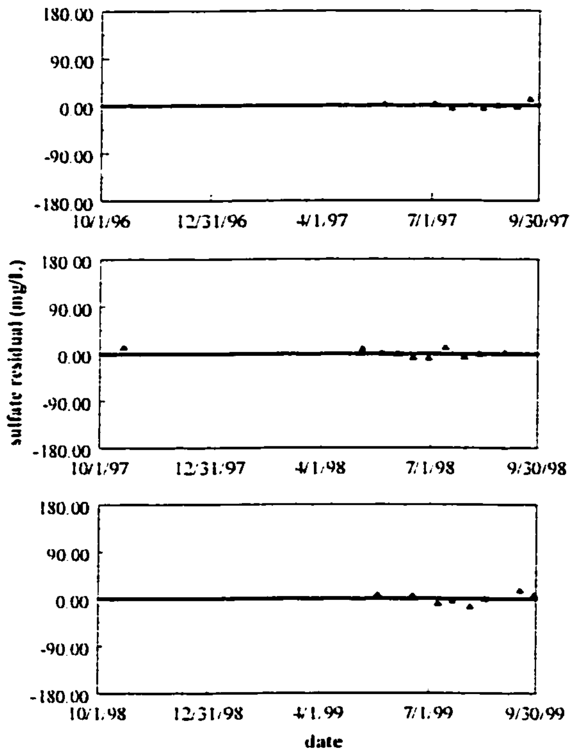


Figure B - 20. Sulfate residual West Outfall

APPENDIX C

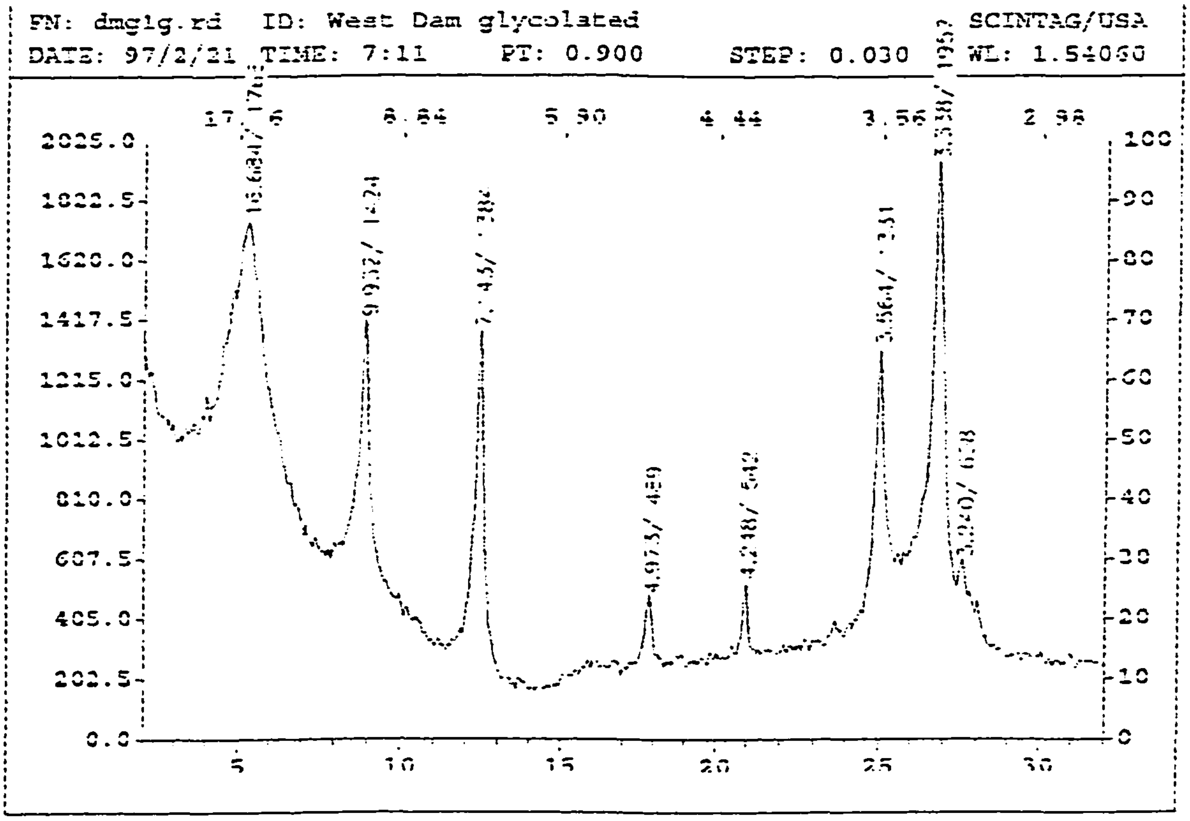


Figure C - 1. X-ray diffraction spectra from pelagic sediment – gycolated sample.

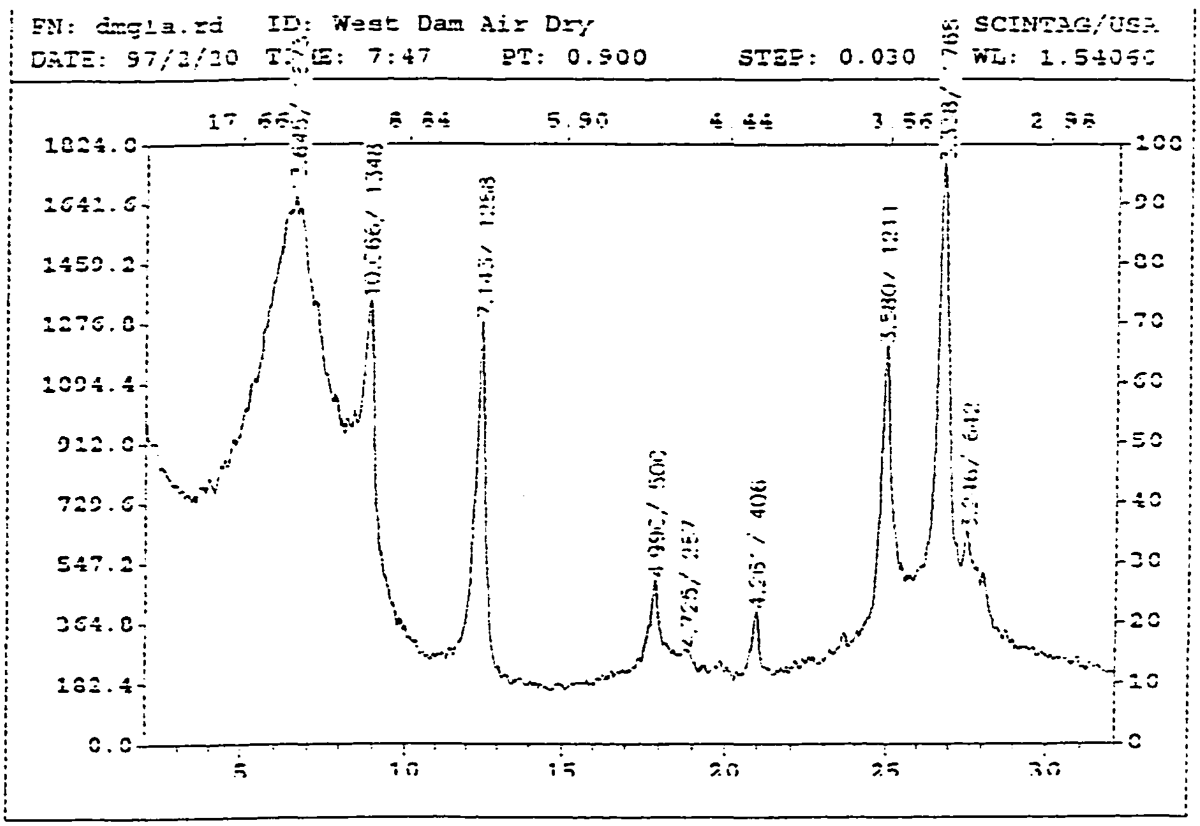


Figure C - 2. X-ray diffraction spectra from pelagic sediment – air-dried sample.

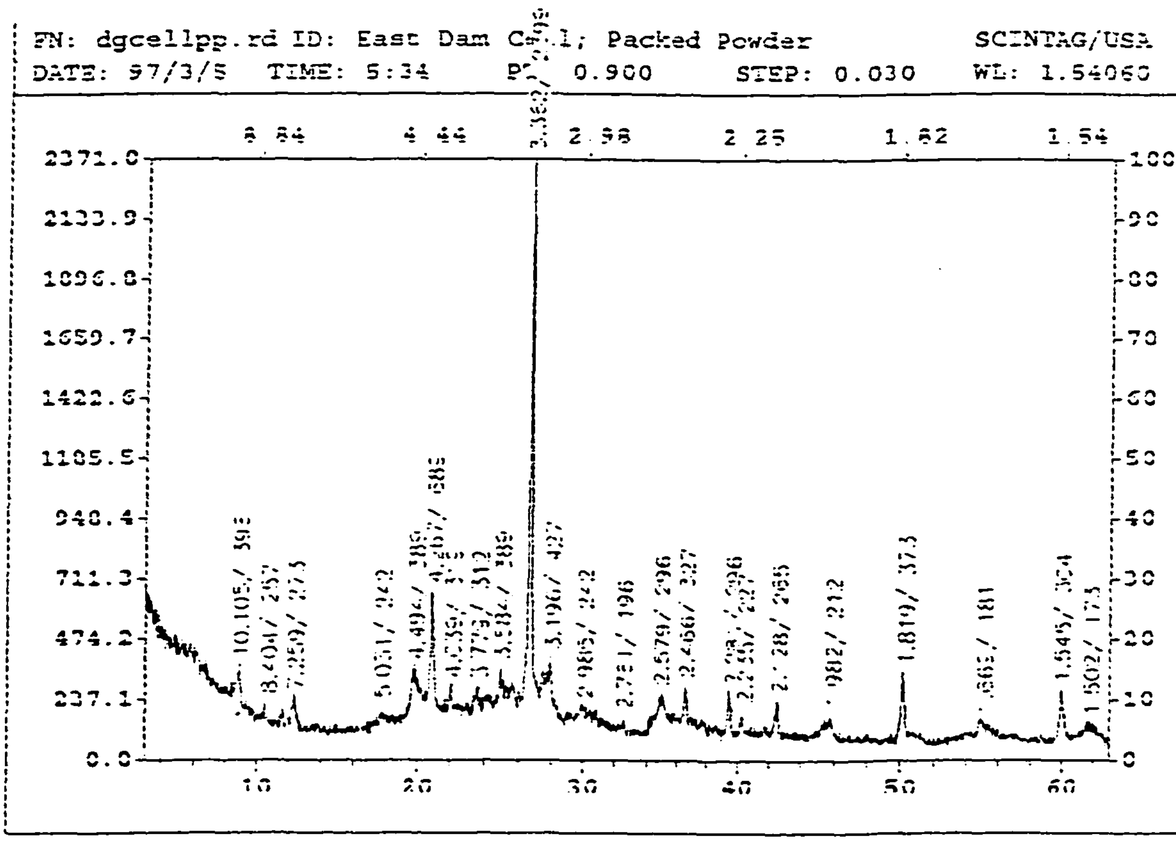


Figure C - 3. X-ray diffraction spectra from pelagic sediment – packed powder sample.