PHOSPHORUS RELEASE
FROM A SLOW-RELEASE FERTILIZER
UNDER SIMULATED STREAM CONDITIONS

by

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Abstract

A new slow-release fertilizer has been developed to restore productivity in nutrient deficient streams. The product (7-40-0; N-P_2O_5-K_2O) was studied to determine physical and chemical conditions which might inhibit phosphate release. In laboratory analyses, hardness (> 40 mg $Ca^{2+} \cdot L^{-1}$) and humic material (> 100 colour units) complexed phosphate and inhibited its dissolution from the pellets; pH, alkalinity and iron had less effects on phosphate solubility. A series of indoor trough experiments indicated fertilizer dissolution was independent of velocity (0.15-0.30 m/s), pellet size (2-9 g) and water temperature (8-14.5 °C). Fertilizer treatments (0.5-5 μg $P \cdot L^{-1}$) in outdoor trough experiments increased periphyton abundance and altered the dominant diatom species. A saturation level for periphyton growth and biomass was achieved at ~ 1.0 $\mu g \cdot L^{-1}$ orthophosphate from May-June; in June-July growth and biomass increased proportionally to fertilizer additions. Relationships developed during these controlled experiments demonstrate streams having < 40 $mg \cdot L^{-1}$ calcium, < 100 colour units and ranges within other variables tested are optimal for slow-release fertilizer additions.

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Acknowledgments

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1. Introduction

Adult salmonids (salmon, trout, char and grayling) continue to form a staple for native British Columbians, as well as provide economic benefits through the commercial and sport fisheries. Historical salmonid production in B.C. has been high despite the oligotrophic nature of many streams; however, over time human intervention has upset nature's delicate equilibrium.

Over the past hundred years, numerous wild salmonid stocks in B.C. and the Yukon have deteriorated to extinction, with approximately one thousand at a moderate to high risk status (Slaney et al., 1996). Causes of these impacts include overharvesting by recreational and commercial fisheries, and industrial activity in watersheds which includes logging, road construction and hydroelectric development. For example, destruction of habitat reduces productivity and survival of juvenile salmonids, and reservoirs created by the impoundment of rivers can act as upstream sediment traps for nutrients, causing an oligotrophication of downstream fish habitat (Stockner and MacIsaac, 1996). The limiting nutrient in freshwater habitats is phosphorus but nitrogen and metals such as iron and manganese can become limiting if phosphorus levels are solely increased (Vymazal, 1995).

Productivity of migratory salmon stocks can be further affected through a reduction in spawning adults which 'naturally' fertilize the streams for their progeny. Adults transport nutrients from the marine to freshwater habitats in the form of excretion, gametes, and carcass decomposition (Richey et al., 1975; Mathisen et al., 1988; Minshall et al., 1991; Schuldt and Hershey, 1995). These marine nutrients are significant and are important to the productivity of the oligotrophic streams in which the salmon spawn. For example, an adult salmon weighing 2.5 kg releases about 12 g P, 70 g N, 9 g K and 21 g Ca upon decomposition (Shearer et al., 1994).

Limited nutrients in streams causes a reduction in primary production which in turn reduces the food supply and causes a decrease in growth and health of the hatchlings. Survival of salmonids in coastal streams is size-related (Hume and Parkinson, 1988). Thus increased salmonid fry sizes resulting from fertilization treatment could affect smolt output from the river,

since overwinter survival increases with salmonid fry size (Hager and Noble, 1976; Hume and Parkinson, 1988; Ward and Slaney, 1988). One reason for increased survival is that swimming speed, which affects the ability to obtain food and escape predators, increases sharply with increased size of fish (Scott, 1985; Simonson and Swenson, 1990). Also, a larger body size helps males to defend their territories and is advantageous in feeding hierarchies; in females, fecundity increases with body size and leads to higher egg production (Deegan and Peterson, 1992).

Although whole-lake fertilization experiment work in Alaska in the 1950's, and research on limiting nutrients since the early 1970's as part of B.C.'s Salmonid Enhancement Program has been conducted, a significant surge of interest in using nutrient enrichment techniques to enhance or restore the productivity of freshwater fish habitat has occurred since the development of the Watershed Restoration Program in the early 1980's (Ashley and Slaney, 1997).

The main goal of fertilization is to speed up the recovery of habitat and fish stocks through introduction of the limiting nutrients. Application of fertilizer to oligotrophic streams increases algal growth, stimulates insect growth and provides more food for hatchling salmonids which subsequently enhances salmonid growth and survival (Figure 1.1). Other benefits of fertilization include salmon carcasses which serve as a food source for non-target animals such as eagles and scavengers (Cederholm et al., 1989). Effects of fertilizer additions are reversible; however, for damaged streams undergoing long-term fertilization treatment and habitat rehabilitation, it is expected that inorganic fertilizer additions would be replaced by natural fertilization from riparian vegetation and anadromous salmonids once the system equilibrates to historic nutrient levels.

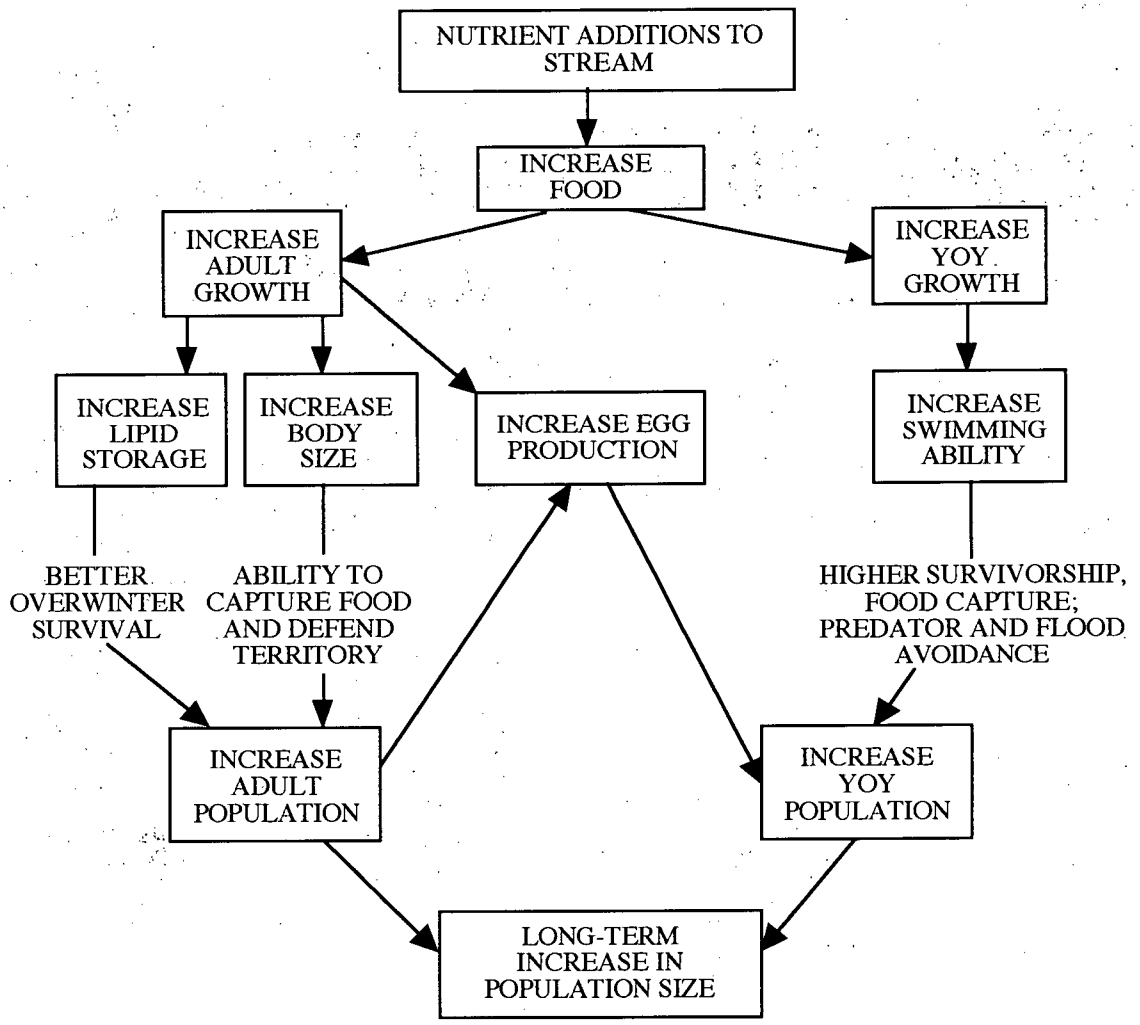


Figure 1.1 An overview of the long-term grayling response to stream fertilization, provided grayling production was limited solely by food availability during the summer; YOY = young-of-the-year (adapted from Deegan and Peterson, 1992).

Oligotrophic total phosphorus and nitrogen levels range from < 1 - 5 μg/L and < 1 - 250 μg/L respectively (Wetzel, 1975). The requirement of a productive freshwater stream habitat for nitrogen and phosphorus is currently under debate, but ranges from approximately 0.1 - 10 μg/L phosphorus and 250 - 400 μg/L nitrogen, with > 10 μg/L phosphorus resulting in excessive periphyton biomass (Bothwell, 1989). Limits for algal biomass set by the Ministry of Environment are 50 mg/m^2 as chlorophyll *a* for recreation and aesthetic considerations, and 100 mg/m^2 for aquatic life in streams (Nordin, 1985).

In the past few years (1994 to present), the B.C. Environment has been testing a solid slow release pellet fertilizer developed by I.M.C. Vigoro Inc., Winter Haven, Florida. Initial laboratory testing of the pellets was done by Anne Pons, field testing was conducted by Sarah Mouldey and further laboratory testing and controlled field studies are presented in this thesis.

In order to safely but effectively fertilize a stream, an understanding of how the nutrients cycle in the water column is critical. Nitrogen present as oxides or ammonium ions tend to remain in solution and biologically available; however, phosphorus forms many complexes making it unavailable to aquatic biota. Knowledge of release rates of the fertilizer pellets under various physical water conditions is important to achieve desired nutrient levels.

The purpose of this research was to provide a means for estimating the amount of slow release pellet fertilizer needed to achieve a desired nutrient concentration in provincial oligotrophic streams exhibiting various chemical and physical characteristics. Laboratory jar tests were used to examine the biological availability of phosphorus when exposed to different chemical characteristics of water. Indoor trough studies were used to determine the dissolution rates of the pellets under different velocities and temperatures. Outdoor trough studies determined periphyton, or attached algae, growth rates exposed to various fertilizer amounts and nutrient effects on algal species abundance.

A literature review of previous fertilization experiments and phosphorus chemistry in Chapter 2 leads to the development of the experimental design. The methodology in Chapter 3 specifies the jar testing and trough study approaches, Abbotsford well water characteristics, outdoor trough dimensions, analytical techniques used for water quality determination, and statistical analysis methods.

Results and discussion (Chapter 4) are presented in one chapter because of the many subsections involved. Finally, the conclusions and recommendations for future research are proposed in Chapter 5. The appendices contain raw data tables, and are referred to throughout the thesis.

2. Literature Review

2.1 Introduction

Fertilization effects on stream productivity and algal community will be discussed, followed by the history of fertilizers and amounts used. Characteristics of the new slow-release fertilizer will be presented. Finally, the freshwater cycling of nitrogen and phosphorus in freshwater systems, along with three types of phosphorus removal in provincial streams will be reviewed.

2.2 Productivity Effects from Stream and River Fertilization

Inorganic fertilization has been shown to increase productivity throughout the food chain culminating in increased salmonid growth and production. For example, whole-river fertilization of the Keogh River, B.C. during 1983-86 to increase summer average nutrient concentrations, from < 1 μg P/L and 25 μg N/L to 10-15 μg P/L and 30-100 μg N/L, resulted in five- to ten-fold increases in periphyton standing crops on artificial substrata and 1.4- to 2.0-fold increases in late-September salmonid fry weights (Johnston et al., 1990).

A number of studies have shown that the addition of nitrogen and phosphorus to nutrient deficient streams results in increased autotrophic production with diatoms, a suitable food for stream invertebrates, predominating (Stockner and Shortreed, 1978; Peterson et al., 1985; Perrin et al., 1987; Johnston et al., 1990). Fertilization of the Kuparuk River initially resulted in a five- to ten-fold increase in periphyton accrual as chlorophyll *a,* similar to the Keogh River (Peterson et al., 1985). At the upper Nechako River, whole-river fertilization was effective at very low levels (3-5 μg/L P and 4-10 μg/L N); enrichment for two months with N and P resulted in 10-fold increases in peak chlorophyll *a* (Slaney et al., 1994).

A study of a small woodland stream in Tennessee (Elwood et al., 1981) demonstrated that both leaf decomposition and primary production were stimulated by phosphorus additions, suggesting a competition for phosphorus between heterotrophs (bacteria) processing nutrient-poor detrital material and periphyton (Peterson et al., 1983). Bacteria colonies on the Kuparuk River, Alaska, flourished on the diatoms and responded to additions of phosphorus (Hershey et al., 1988).

Gregory (1983) and Murphy et al. (1986) found that the numbers of aquatic herbivores / benthic insects were regulated by the amount of algae available; thus stream insect abundance is increased by inorganic fertilization. This theory was verified when Mundie et al. (1991) found that benthic insect communities responded strongly to low level (2-4 μg/L) increases in phosphorus and nitrate nitrogen. In addition, fertilization of a tundra stream (Kuparuk River) with phosphorus showed an increase in the size and development of the dipterans *Orthocladius* and *Prosimulium* (Hershey et al., 1988) along with elevated densities for the caddisfly *Brachycentrus* (Hershey and Hiltner, 1988). Mundie et al. (1991) also showed that an addition of 10 μg P/L increased chlorophyll *a* biomass by 3.5 times, with a subsequent doubling of insects' survival to emergence due to an increase in food abundance.

Reed (1964) determined that aquatic and terrestrial insects comprise most of the Arctic grayling (*Thymallus arcticus*) diet in streams; later, Johnston et al. (1990) verified that the diet of juvenile salmonids was primarily benthic insects. Several studies have determined that fish density and growth correlate with nutrient status and food supply in a stream (McFadden and Cooper, 1962; Slaney and Northcote, 1974; Mason, 1976; Wilzbach, 1985; Wilzbach et al., 1986; Bowlby and Roff, 1986; Deegan and Peterson, 1992). For example, Johnston et al. (1990) increased the growth of steelhead (*Oncorhynchus mykiss*), coho (*O. kisutch*), and Dolly Varden (*Salvelinus malma*) fry in the Keogh River with nutrient enrichment, and Murphy et al. (1981) found that growth rates of salmonid fry varied directly with insect drift in several Oregon streams. Slaney and Ward (1993) discovered that, as in the Keogh and the Kuparuk Rivers, the response in fish at the Salmon River was associated with both increased periphyton accrual and

benthic insects. Also, fertilization of the Kuparuk River, Alaska, during 1985-90 resulted in a 1.4- to 1.9-fold increase in the size of age 0+ fish and a 1.5- to 2.4-fold increase in the weight gain of adult grayling in some years (Deegan and Peterson, 1992). Thus addition of fertilizer to enhance autochthonous primary production can increase salmonid growth in nutrient poor streams.

However, salmonid growth is highly influenced by food availability and fish density (Wilzbach, 1985). The ultimate size of the salmonid population would likely be limited at an equilibrium level established through 'top-down control' as described by Peterson et al. (1993), Figure 2.1. For example, after three years at both the Kuparuk River, Alaska and Salmon River, B.C., the effect of nutrient input on the peak chlorophyll response dropped. The lower response was probably related to increased grazing by benthic insects: as the aquatic insects responded to increased algal biomass, the algae was grazed down to slightly elevated control levels. Miller et al. (1992) also suggested that the increase of algal biomass from fertilization could reduce the concentration of SRP to low levels.

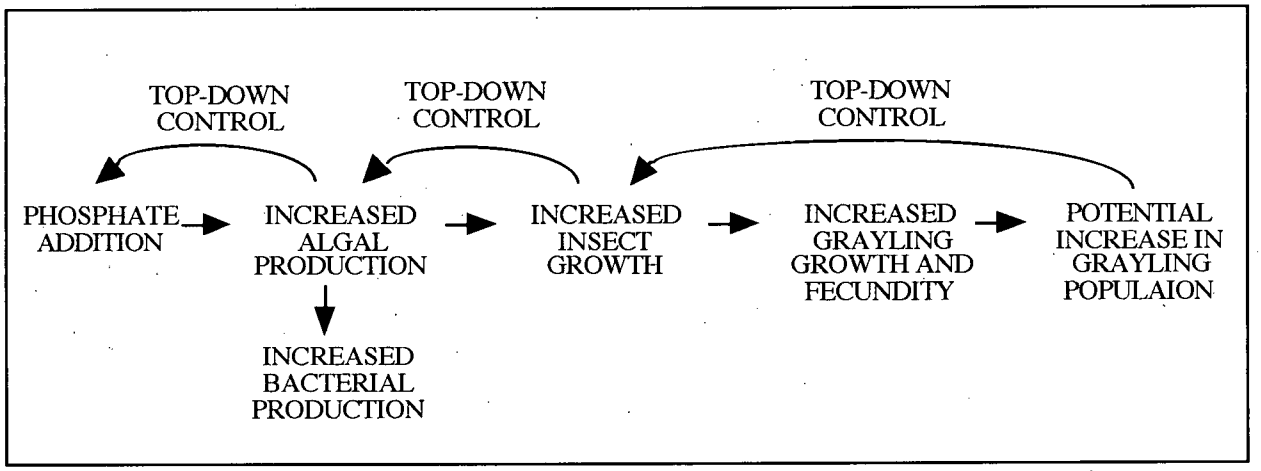


Figure 2.1 A summary of the responses of riverine biota to phosphorus enrichment (adapted from Peterson et al., 1993).

Thus fertilization replenishes stream productivity through increased algal biomass and invertebrates, causing an increase in smolt size and subsequent survival, and greater numbers of adults returning to spawn.

2.3 Optimal Nutrient Level Additions

Phosphorus concentrations of 10-30 μg/L used to experimentally enhance algal production in experimental troughs at Carnation Creek, B.C. (Stockner and Shortreed, 1978), whole-river sites at Kuparuk River, Alaska (Peterson et al., 1983, 1985), and Keogh River, B.C. (Perrin et al., 1987) were well above inferred growth rate saturation concentrations (Bothwell, 1988). Nitrogen levels added to the Keogh and Salmon Rivers from 1981 to 1991 ranged from 0 to 400 μg N/L (Slaney and Ward, 1993); levels above 100 μg N/L are determined to be high.

To determine relative specific growth rates, Bothwell (1988) studied the diatom communities as a function of soluble reactive phosphate concentration in the South Thompson River. The growth rates were nearly constant throughout the year with saturation occurring at an ambient phosphate level of around 0.3 to 0.6 μg P/L. He found areal periphyton biomass could be further stimulated by higher phosphorus concentrations, but excessive periphyton biomass occurred when phosphate levels were > 10 μg/L. Levels of phosphorus enrichment needed in rivers to produce dense algal accumulations vary in the literature. This discrepancy was due partly to the difference between concentrations required to saturate cellular growth rates, and the levels needed to maximize growth of an entire benthic mat. Therefore, Bothwell determined that the concentrations of dissolved orthophosphate required to saturate specific cellular growth rates of periphytic riverine diatoms were well under 1 μg P/L, recognizing that overestimation of true orthophosphate levels occurs using standard SRP measurements (Bothwell, 1988).

2.4 Algal Community

According to Wetzel (1975), the outstanding feature of phytoplankton communities is that a number of species populations can co-occur within a habitat, with each species having a niche based on physiological requirements. A species may be able to survive indefinitely provided that a suitable combination occurs with sufficient frequency and duration. Even though competitive interactions are in effect, coexistence can occur because the interactions are so complex and variable (Wetzel, 1975).

Physical, chemical and biological factors such as light, turbidity, temperature, current velocity, nutrient concentration, nutrient ratios, immigration, grazing and catastrophic disturbance can all cause a change in the algal community (Miller et al., 1992).

Elevated *light* intensities, altered through colour, turbidity and depth of water, inhibit chlorophyll *a* accumulations (Talling, 1971) but seasonal variation in light levels do not influence algal growth or biomass (Bothwell, 1988). *Turbidity* refracts light, and when the particulates are transported at elevated velocities they scour periphyton standing crops.

Temperature (T) controls the rate of photosynthesis in all plants. In general, growth rate increases exponentially with temperature up to an optimum T, then declines rapidly as T exceeds this optimum. Different species have significantly different temperature optima, although cold-water forms generally have lower optima (Vymazal, 1995).

Current velocity can reduce colonization from shear stress (> 50 cm/s) and low growth rates (< 10 cm/s), but can also increase algal metabolism and abundance at rates of 10-50 cm/s (Horner and Welch, 1981; Whitford and Schumacher, 1964; Reisen and Spencer; 1970).

Nutrient enrichment generally leads to increased dominance, reduced species diversity, loss of rare species and higher biomass (Miller et al., 1992). Characteristics of planktonic algal associations occurring among lakes of increasing nutrient enrichment and cycling from oligotrophy to eutrophy are in Table 2.1.

Table 2.1 Characteristics of common major algal associations of the phytoplankton in relation to increasing lake fertility (Wetzel, 1975).

General Lake Trophy	Water Characteristics	Dominant Algae	Other Commonly Occurring Algae
Oligotrophic	Slightly acidic; very low salinity	Desmids *Staurodesmus, Staurastrum*	*Sphaerocystis, Gloeocystis, Rhizosolenia, Tabellaria*
Oligotrophic	Neutral to slightly alkaline; nutrient-poor lakes	Diatoms, especially *Cyclotella* and *Tabellaria*	Some *Asterionella* spp., some *Melosira* spp., *Dinobryon*
Oligotrophic	Neutral to slightly alkaline; nutrient-poor lakes or more productive lakes at seasons of nutrient reduction	Chrysophycean algae, especially *Dinobryon*, some *Mallomonas*	Other chrysophyceans, e.g., *Synura, Uroglena*; diatom *Tabellaria*
Oligotrophic	Neutral to slightly alkaline; nutrient-poor lakes	Chlorococcal *Oocystis* or chrysophycean *Botryoccocus*	Oligotrophic diatoms
Oligotrophic	Neutral to slightly alkaline; generally nutrient-poor; common in shallow Arctic lakes	Dinoflagellates, especially some *Peridinium* and *Ceratium* spp.	Small chrysophytes, cryptophytes, and diatoms
Mesotrophic or Eutrophic	Neutral to slightly alkaline; annual dominants or in eutrophic lakes at certain seasons	Dinoflagellates, some *Peridinium* and *Ceratium* spp.	*Glenodinium* and many other algae
Eutrophic	Usually alkaline lakes with nutrient enrichment	Diatoms much of the year, especially *Asterionella* spp., *Fragilaria crotonensis, Synedra, Stephanodiscus*, and *Melosira granulata*	Many other algae, especially greens and blue-greens during warmer periods of the year; desmids if dissolved organic matter is fairly high
Eutrophic	Usually alkaline; nutrient enriched; common in warmer periods of temperate lakes or perennially in enriched tropical lakes	Blue-green algae, especially *Anacystis* (=*Microcystis*), *Aphanizomenon, Anabaena*	Other blue-green algae; euglenophytes if organically enriched or polluted

High *nutrient ratios* (N:P > 30) indicate phosphorus deficiency but enhanced blue-green algae growth in algal cultures (Vymazal, 1995). For example, Mundie et al. (1991) observed the taxonomic change of an increase in blue-green algae (cyanophytes) proportions that occurred with fertilization of a mesocosm at Carnation Creek, B.C.

Invertebrate *grazers* reduce biomass, increase algal productivity per unit biomass in the survivors, and increase or decrease the number of species surviving depending on the type and severity of grazing, but they also act as a food source for other biota in the food chain (Hershey et al., 1988; Miller et al., 1992).

Finally, *catastrophic disturbances*, including storm events and desiccation, and *immigration* of algal species from sloughing may selectively or completely alter the algal species composition.

2.5 History of Stream Fertilizers Used

Experimental streams and troughs exposed to organic enrichment have demonstrated consistent increases in the standing stocks of stream zoobenthos (Williams et al., 1977; Mundie et al., 1983), but until recently, there have been few studies of the effects of inorganic enrichment. It has been previously believed that the main source of nutrients to forested stream ecosystems is from allochthonous inputs of organic material to the stream, such as leaf litter (Hynes, 1969; Boling et al., 1975); however, a source of inorganic nutrients within the stream's food chain (autochthonous energy) has also been found to be significant (Huntsman, 1948; Minshall, 1978; Johnston et al., 1990).

Stream fertilization in British Columbia was pioneered in the Keogh River, northern Vancouver Island, in 1981 and has continued on the Salmon River and Adam River on Vancouver Island, the Big Silver Creek north of Harrison Lake, the Mesilinka River north of Prince George and the Nechako River in the central interior of the province (Perrin et al., 1987; Johnston et al., 1990; Slaney and Ward, 1993; Mouldey and Ashley, 1996; Ashley and Slaney, 1997). Primary objectives of fertilization were to determine the effect of nutrient additions on the growth and abundance of anadromous salmonids in oligotrophic streams, as well as to determine if controlled seasonal fertilization is a cost-effective enhancement or habitat compensation option (Slaney and Ward, 1993).

Initially, the response of the food chain levels to additions of crushed barley and agricultural fertilizer pellets were examined in the Keogh River (Perrin et al., 1987). Nutrient effect of the barley was found to be less than with fertilizers and it was labour intensive to introduce. In 1983 a solid prill, slow-release fertilizer with a soybean resin coating (Osmocote™, Sierra Chemical Ltd., Milpitas, California) was used but it had a few shortcomings (Johnston et al., 1990). The pellets dissolved quickly and released the nutrients immediately after application, even with the thickest coating. They also fractured during aerial application, and the cost was 2 - 4 times higher than conventional granular agricultural blends.

In 1990 a new liquid fertilizer formulation was tested (a mixture of ammonium polyphosphate, 10-34-0, and ammonium nitrate, 34-0-0) with excellent results at the Upper Salmon River on Vancouver Island and then at the Nechako River (Slaney and Ward, 1993; Slaney et al., 1994). It was subsequently used in other rivers around the province. However, some difficulties arose with using the liquid fertilizer. To facilitate monitoring, its use is limited to more accessible streams and rivers. Also, application is expensive due to high maintenance required to check for plugged lines or to carry heavy equipment such as fertilizer or batteries to the site needed by the automated dosage stations.

Finally, in 1995, a small amount of custom made slow-release pellet fertilizer (I.M.C. Vigoro Inc., Florida; used for experiments discussed in this thesis) was placed in a tributary of the Big Silver Creek near Harrison Lake and was successful in enhancing the diatom and invertebrate production in a matter of weeks (Mouldey and Ashley, 1996). Preliminary tests using the slow-release fertilizer briquettes aimed for a dissolved inorganic phosphorus concentration of 3 μg/L. The slow-release pellet fertilizer is a low-maintenance alternative to the mechanical dispensers using liquid fertilizer for smaller streams since the fertilizer needs to be applied only once a year, significantly reducing labour and costs. However, liquids would still be more efficient for larger rivers because of the magnitude of fertilizer required.

2.6 Characteristics of the Slow-Release Fertilizer

Ideal slow-release fertilizer characteristics include biodegradable coatings with no heavy metal contaminants. The pellets need to be large enough to sink rapidly to bottom of stream riffles (0.1 - 2 m deep) in current velocities of 0.5 - 1 m/s, and have a release rate ranging from 3 - 5 months depending on the stream (P.A. Slaney, 1994, pers. comm.). It is the preferred method for nutrient additions in most streams and smaller rivers having mean summer flows < 10 m^3/s due to its annual application, low maintenance costs, and 'low profile vandal-proof design' (Ashley and Slaney, 1997).

A slow-release fertilizer pellet was developed in 1994-95 by I.M.C. Vigoro Inc., Winter Haven, Florida and contains 14 % magnesium, 7 % nitrogen and 40 % P_2O_5 by weight existing in the form of the $MgNH_4PO_4 \cdot H_2O$ compound. The fertilizer compound was compressed into ~10 g pellets with an unpolymerized Saran™-like binder called Daratak® XB-3631, or vinylidene chloride-acrylic acid-2-ethylhexyl acrylate polymer, which slowly releases nutrients while dissolving under aqueous conditions.

Although magnesium is not normally a limiting nutrient, use of it as a binding metal in the fertilizer is sensible since plants require it to form the active center of the chlorophyll *a* molecule (Horne and Goldman, 1994). Studies of river systems have shown nitrogen to be present in high enough levels to be non-limiting (e.g. Salmon River, 1992), but its presence in the fertilizer ensures that it will not become limited after P is increased (Slaney and Ward, 1993). Nitrogen limitation of freshwater algal growth is less common than phosphorus limitation because blue-green algae (cyanobacteria) are able to fix nitrogen from the atmosphere.

Phytoplankton growth is mostly controlled by the presence of orthophosphate which is used in energy transfer and for cell components such as cell membranes and genetic material, and most plants use ammonia, nitrite or nitrate for protein synthesis (McCarty, 1970). Living matter generally requires an N:P ratio of 7:1 by weight or 16:1 by element, so phosphorus depletion is likely in fresh waters where nitrate levels are > 100 μg/L. In general, if the ratio of N:P > 10, by

weight, then phosphorus is considered to limit phytoplankton growth (Horne and Goldman, 1994).

2.7 Nitrogen Cycling in Freshwater Ecosystems

Natural external nitrogen inputs to rivers and lakes are in the form of ammonia and nitrates that are introduced from land drainage and direct precipitation on the water. Once nitrogen enters the aquatic ecosystem it exists mainly as inorganic forms of ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) ions which are of biological interest. Ammonia is the preferred form for plant growth, however, nitrate is usually the predominant form of nitrogen. With a few exceptions, nitrogen based inorganic salts are generally highly soluble in water.

Organic nitrogen consists of dissolved and particulate materials. Dissolved organic nitrogen is mainly in the form of polypeptides and complex organics with a smaller portion present as free amino nitrogen (Nordin, 1985). Particulate organic nitrogen consists of plankton and detritus and is much smaller than the dissolved fraction, with the exception of turbid streams. It is also much less available to algae than the dissolved forms. Another nitrogen component involves ions (NH_4^+) that may be adsorbed to particulate matter.

The nitrogen cycle (Figure 2.2) describes the steady state for aquatic chemical transformations which are for the most part biologically mediated (Vymazal, 1995); however, in streams and rivers the water residence time is shorter than lakes, and there is less opportunity for mineralization of the nutrients by biochemical processes.

Nitrate (NO_3^-) and ammonia (NH_3, NH_4^+) are taken up by phytoplankton, via ammonia and nitrate assimilation and hydrolysis, and used for growth in the form of proteins. These organic forms can either be deposited to the sediments as detritus and / or transferred to a higher trophic level (zooplankton, fish). Organic N from excretion products and sediments is converted to inorganic N, especialy ammonium (NH_4^+), via the ammonification process. Ammonia is oxidized by chemolithotrophic bacteria to nitrate, which use the energy for growth, and recycled

back to the algae. *Nitrosomonas* bacteria oxidize ammonium to nitrite ($NH_4^+ \rightarrow NO_2^- + 5e^-$) and *Nitrobacter* oxidize nitrite to nitrate ($NO_2^- \rightarrow NO_3^- + 2e^-$). Denitrification occurs in the anoxic sediments or stagnant waters by denitrifying bacteria (e.g. *Pseudomonas*) in which the nitrogen oxides serve as terminal electron acceptors

($NO_3^- \xrightarrow{+2e^-} NO_2^- \xrightarrow{+1e^-} NO \xrightarrow{+1e^-} N_2O \rightarrow N_2$). Nitrogen fixation involves the transformation of N_2 to ammonia by blue-green algae or bacteria ($N_2 \xrightarrow{+3e^-} NH_3$). In oligotrophic streams, the main source of nitrogen for plankton in the summer is from the recycling of nitrogen from plants and animals back to ammonia or nitrate.

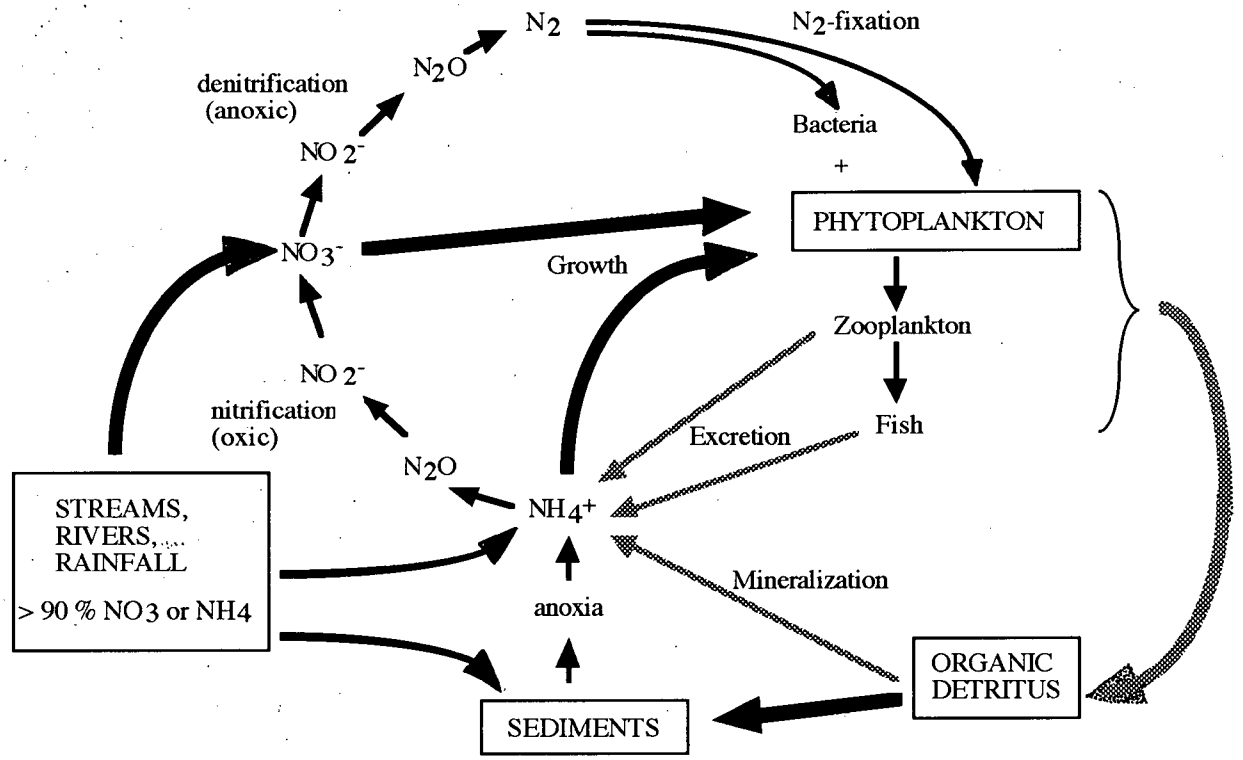


Figure 2.2 The nitrogen cycle in freshwater aquatic ecosystems (adapted from Horne and Goldman, 1994). Thick black lines indicate the main pathways in terms of mass transfer; grey lines indicate pathways involving recycling and mineralization in the water column.

2.8 Phosphorus Cycling in Freshwater Ecosystems

The geochemical cycle of phosphorus is essentially a one-way transport of weathered rock fragments from land to aquatic sediments. In natural waters 90 to 95 percent of phosphorus is inert and moves as sediment particles; the rest is carried in soluble form. (Horne and Goldman, 1994). Soluble phosphorus inputs in natural waters result from the weathering and solution of crystalline and/or amorphous particulate phosphate minerals contained in the water or present in the minerals of the soil. (McCarty, 1970). The phosphate minerals are relatively insoluble and rates of solution are slow. As with the nitrogen cycle, the kinetics of mineralization in streams having short water residence times are unlikely to be a factor in making forms of phosphorus other than dissolved and inorganic available to algae (Nordin, 1985).

Phosphorus is limited in freshwater systems for four main reasons: (1) the small amount of phosphate released from rock breakdown in the watershed is readily immobilized by most soils so leachates and ground waters in general are much lower in phosphate than in nitrate; (2) soluble phosphorus compounds are retained by plant roots on land; (3) there is no gaseous phase in the phosphorus cycle and thus rainwater contains little phosphorus; and (4) and soluble phosphate released into water is rapidly adsorbed onto particles or precipitated with other compounds and is not readily available to algae (Horne and Goldman, 1994).

Phosphate is present in all known minerals as orthophosphate. The apatite family represents the majority of phosphorus in the earth's crust, with hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$ being an important component. Other solid phase forms that make phosphorus biologically unavailable are presented in Table 2.2.

In natural waters phosphorus occurs as orthophosphate (PO_4^{3-}), condensed phosphates (pyro-, meta- and other polyphosphates) and organically bound phosphates; they occur in solution, in particles or detritus, or in the bodies of aquatic organisms (Figure 2.3).

In most aquatic environments, total particulate phosphorus is present in much larger quantities than soluble phosphorus. *Particulate* phosphorus includes bacterial, plant, and animal phosphorus, as well as that absorbed onto or complexed with suspended inorganic particles, such

as clays and other minerals (Horne and Goldman, 1994). Inorganic solid phosphate phases are formed by direct precipitation with calcium, aluminum, and iron, while clay particles 'scavenge' phosphate by sorption (Horne and Goldman, 1994). Because phosphate is both quickly released and absorbed by particles, an equilibrium arises between phosphate ions and mineral particles in streams and rivers whereby phosphate is adsorbed or desorbed from particles depending on the relative concentrations of the phosphates and the metal ions, the pH, and the presence of other ligands (sulfate, carbonate, fluoride, organic species) in the water (McCarty, 1970).

The bulk of the total *soluble* phosphorus pool includes soluble reactive phosphorus but is primarily composed of dissolved organic phosphorus. It is thought to comprise of numerous compounds, ranging from low molecular weight, highly labile compounds to large, biologically refractory compounds (Tarapchak and Nalewajko, 1986). The portion available for algal growth depends on the origin of the material and its rate of mineralization.

Table 2.2 Solid phase forms of phosphorus of possible significance in natural water; ROP = refractory organic phosphate systems (adapted from McCarty, 1970).

Form	Representative Compounds or Substances
Soil and Rock Mineral Phases	
Hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$
Brushite	$CaHPO_4 \cdot 2H_2O$
Carbonate fluorapatite	$(Ca, H_2O)_{10}\ (F, OH)_2\ (PO_4, CO_3)_6$
Varsicate, Stringite	$AlPO_4 \cdot 2H_2O$, $FePO_4 \cdot 2H_2O$
Wavellite	$Al_3(OH)_3(PO_4)_2$
Mixed Phases, Solid Solutions, Sorbed Species, Etc.	
Clay-phosphate (e.g. kaolinite)	$[Si_2O_5Al_2(OH)_4 \cdot (PO_4)]$
Metal hydroxide-phosphate	$[Fe(OH)_x(PO_4)_{3-x/3}]$, $[Al(OH)_x(PO_4)_{3-x/3}]$,
Clay-organophosphate	$[Si_2O_5Al_2(OH)_4 \cdot ROP]$, clay-pesticide, etc.
Metal hydroxide-inositol phosphate	$[Fe(OH)_3 \cdot$inositol hexaphosphate]
Suspended or Insoluble Organic Phosphorus	
Bacterial cell material	Inositol hexaphosphate or phytin; Phospholipid;
Plankton material	Phosphoprotein; Nucleic acids; and/or
Plant debris	Polysaccharide phosphate

Biological availability (as PO_4) of insoluble phosphorus in lakes, reservoirs, and rivers is achieved through slow physical or biological dissolution of the various insoluble minerals and organics (McCarty, 1970). Desorption from particles releases biologically available phosphorus,

which is available as PO_4 for phytoplankton growth. Since input of phosphorus in summer is often low, recycling comprises much of the activity in the aquatic phosphorus cycle (Horne and Goldman, 1994).

Soluble orthophosphates (PO_4) are readily assimilated by plants and other aquatic organisms forming particulate organic phosphorus. Either during growth or death of these organisms, soluble compounds that contain organic phosphorus may be excreted into solution. These compounds are either reassimilated to form particulate organic phosphorus or are converted back to inorganic orthophosphates through degradation.

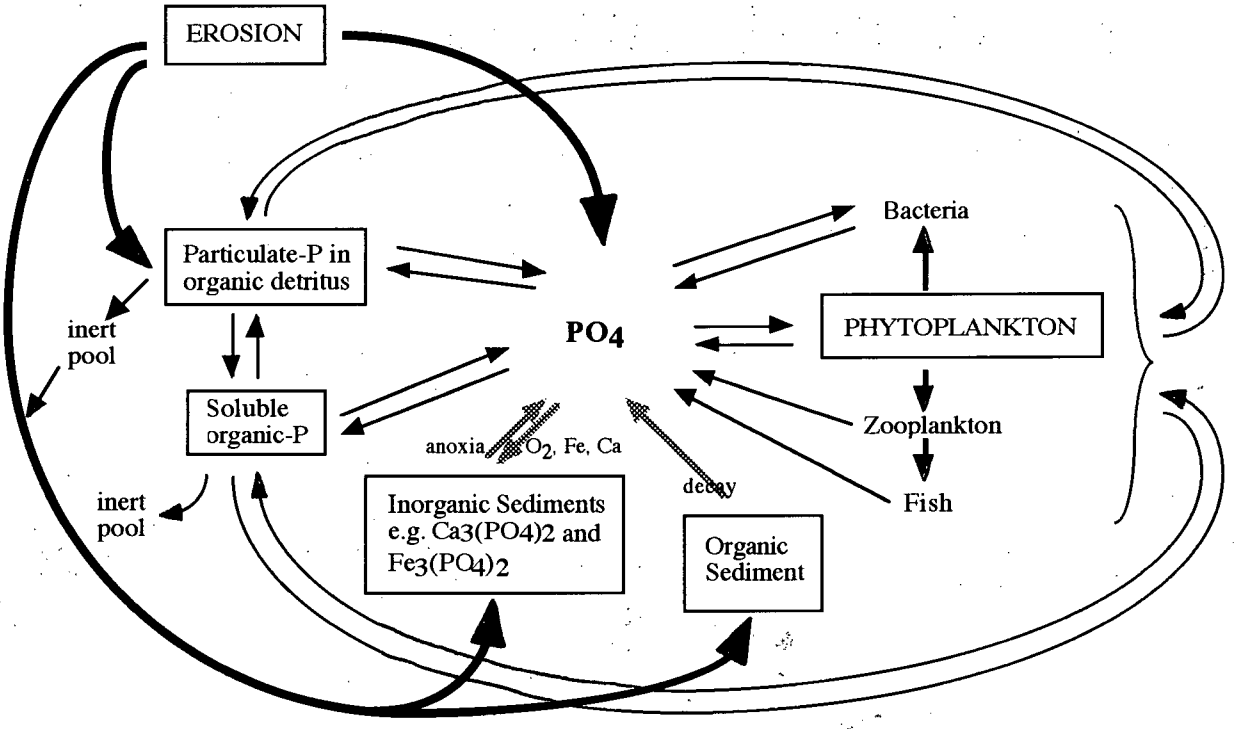


Figure 2.3 The phosphorus cycle in freshwater aquatic ecosystems, excluding sewage inputs (adapted from Horne and Goldman, 1994). Thick black lines indicate external loading, and grey lines indicate internal loading, other lines indicate internal recycling.

A certain portion of the organic phosphorus becomes incorporated into refractory biological materials, a further parallel with the nitrogen cycle. The refractory organic phosphorus

is relatively unavailable for subsequent biological growth and may settle to form part of the sludge deposits and organic muds of rivers and lakes (McCarty, 1970).

The major loss of phosphorus from open water is sedimentation of the biota or from chemically formed precipitates. For example, phosphates are removed from solution by adsorption to freshly precipitated ferric and aluminum hydroxides, section 1.9.2 (McCarty, 1970). Most of this phosphorus becomes part of the permanent accumulation of sediments. However, in anoxic sediments reduction of ferric to ferrous iron may release phosphorus from iron phosphate complexes. Lower pH's in these conditions may also release phosphorus by solubilizing precipitates.

2.9 Three Types of Phosphorus Removal in B.C. Streams

At normal lake pH ranges most soluble phosphate is present in three ionic forms: orthophosphate (PO_4^{3-}), monohydrogen (HPO_4^{2-}) and dihydrogen ($H_2PO_4^-$) phosphate ions. Changes between these forms occur rapidly with pH.

Sorption and desorption of phosphate onto organic and inorganic, such as $CaCO_3$, particle surfaces dominates phosphorus chemistry in natural waters. Insoluble phosphorus compounds such as calcium hydroxyapatite and iron phosphate are also formed. Phosphate may be removed from solution by the presence of both calcium and iron at high concentrations as well as humic material.

2.9.1 Calcium Complexes

Calcium and phosphate form the insoluble calcium hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$:

$$Ca_{10}(OH)_2(PO_4)_{6\,(s)} \Leftrightarrow 10Ca^{2+} + 6PO_4^{3-} + 2OH^-$$

where $K_{sp} = [Ca^{2+}]^{10}[PO_4^{3-}]^6[OH^-]^2 = 10^{-56}$.

Hydroxyapatite is a thermodynamically stable solid in typical natural water conditions of solution concentration, pH and temperature (Snoeyink and Jenkins, 1980). Elevation of pH of natural water containing typical levels of calcium increases apatite formation (McCarty, 1970).

The calcium phosphate system is very complex. Other calcium and phosphorus inorganic compounds likely to be of some significance in natural waters are presented in Table 2.3.

Table 2.3 Heterogeneous and complexation phosphate equilibria (adapted from Snoeyink and Jenkins, 1980).

Compound	Equation	pK_{sp}
Heterogeneous Equilibria		
Calcium hydrogen phosphate	$CaHPO_4$ (s) $\Leftrightarrow Ca^{2+} + HPO_4^{2-}$	6.66
Calcium dihydrogen phosphate	$Ca(H_2PO_4)_2$ (s) $\Leftrightarrow Ca^{2+} + 2H_2PO_4^-$	1.14
β-Tricalcium phosphate	β-$Ca_3(PO_4)_2$ (s) $\Leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	24.0
Tetracalcium pyrophosphate	$Ca_2P_2O_7$ (s) $\Leftrightarrow 2Ca^{2+} + P_2O_7^{4-}$	13.5
Complexation Equilibria		
Orthophosphate complex	$CaHPO_4^0 \Leftrightarrow Ca^{2+} + HPO_4^{2-}$	2.2
"	$CaH_2PO_4^+ \Leftrightarrow Ca^{2+} + HPO_4^{2-} + H^+$	- 5.6
Pyrophosphate complex	$CaP_2O_7^{2-} \Leftrightarrow Ca^{2+} + P_2O_7^{4-}$	5.6
"	$CaHP_2O_7^- \Leftrightarrow Ca^{2+} + HP_2O_7^{3-}$	2.0
Tripolyphosphate complex	$CaP_3O_{10}^{3-} \Leftrightarrow Ca^{2+} + P_3O_{10}^{5-}$	8.1

The phase diagram in Figure 2.4 is useful in predicting some of the stable calcium phosphate phase(s), listed in Table 2.3, under varying pH and degree of saturation conditions with respect to calcium and inorganic phosphate ions (LeGeros, 1991). For example, at 25 °C, pH 6, and calcium concentration of 10^{-2} M, $CaHPO_4 \cdot 2H_2O$ would be the most stable phase; however, at pH > 4.2 calcium hydroxyapatite, $Ca_5(PO_4)_3OH$, is the most stable. Limitations include experimental observation of the predicted formation of monetite, $CaHPO_4$, at 60 °C and above but not at 25 °C. Also, mixing rates and the presence of different ions affects the type of stable Ca-phases.

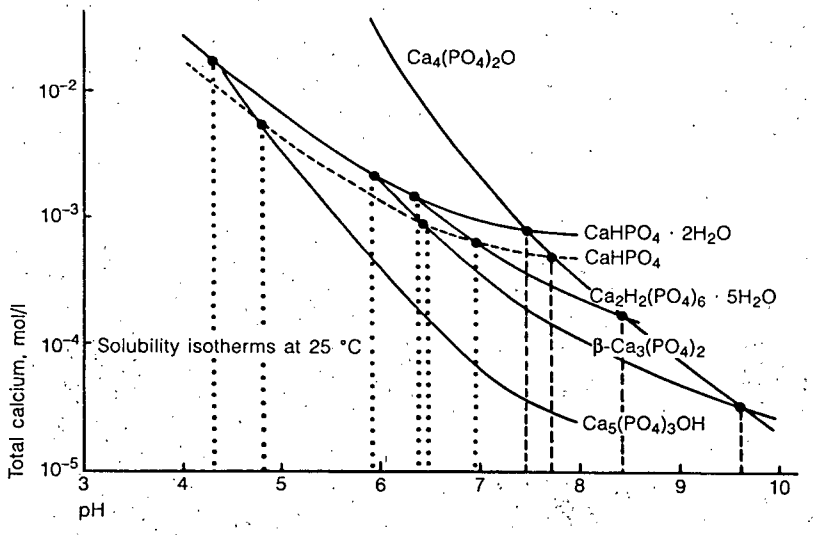


Figure 2.4 Solubility phase diagram for the system: $Ca(OH)_2$-H_3PO_4-H_2O at 25 °C showing the stable calcium phosphate phases at different pH and different calcium concentrations (LeGeros, 1991).

2.9.2 Iron Complexes

Phosphate can be removed from solution by precipitation or sorption onto the outside of complex iron-containing particles. Ferric iron and phosphate precipitate to form $FePO_4$:

$$FePO_4 \Leftrightarrow Fe^{3+} + PO_4^{3-}$$

where $K_{sp} = [Fe^{3+}][PO_4^{3-}] = 10^{-23}$.

Precipitation to remove phosphate as iron phosphate (or mixed hydroxyphosphate, $Fe_x(OH)_y(PO_4)_z$) is increased by depression of the pH (McCarty, 1970). The indirect process of coprecipitation is a more viable removal mechanism than direct precipitation. Insoluble ferric hydroxide can coprecipitate phosphate from solution whereby phosphate anions enter the solid oxides or hydroxides of iron via isomorphic replacement or solid solution (McCarty, 1970). Isomorphous replacement and solid solution (a mixed crystal) involve introduction of atoms into a complex molecule without affecting its structure.

Other iron and phosphorus inorganic compounds likely to be of some significance in natural waters are presented in Table 2.4.

Table 2.4 Complexation phosphate equilibria (Snoeyink and Jenkins, 1980).

Compound	Equation	pK_{sp}
Complexation Equilibria		
Orthophosphate complex	$FeHPO_4^+ \Leftrightarrow Fe^{3+} + HPO_4^{2-}$	9.75
Pyrophosphate complex	$Fe(HP_2O_7)_2^{3-} \Leftrightarrow Fe^{3+} + 2HP_2O_7^{3-}$	22

2.9.3 Humic Complexes

Humic substances is a general term referring to the persistent fraction of organic matter present in all terrestrial and aquatic environments. They are the residues from plants and animals that do not become completely mineralized, and are more or less resistant to microbial decomposition. More specifically, humic substances are often described as refractory, yellow to black organic substances, of high molecular weight, heterogeneous and naturally occurring in the environment. They do not have a definite chemical composition, but one that changes constantly as a result of the decomposition process (Aiken et al., 1985; Thurman, 1985).

Aquatic humus is chiefly formed from allochthonous plants brought in by wind and water currents, by soil humus carried by flowing water, and also from organic material produced from the decomposition of aquatic plant and animal residues. Humic substances contain carboxylic, hydroxyl and phenolic groups which interact with elements and compounds present in the aquatic system. Aquatic humus exists in dissolved and colloidal states, as well as in organic detritus and have a molecular weight range of 1000 - 100 000 daltons (Ghassemi and Christman, 1968). Most finds its way to the sediments by adsorption onto settling particles of clay or other mineral particles, but a significant portion remains in soluble form giving a yellow-brown colour to the water.

The involvement of humic materials in complexing phosphorus is complicated, and is influenced by the amount of complexed iron, pH and the presence of Ca^{2+} ions in the water (Figure 2.5). Gerke and Hermann suggested that phosphorus is bound via Fe- and Al-bridges to the humic surface by substitution of H_2O and OH^-:

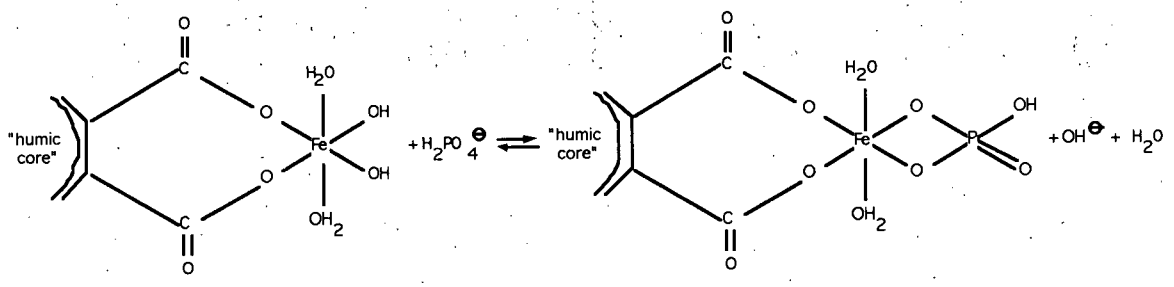


Figure 2.5 Scheme of orthophosphate adsorption by humic-Fe-surfaces (Gerke and Hermann, 1992).

The pH and ionic composition of humic waters are key factors in the complexation and release of PO_4^{3-}, and would also affect its speciation (i.e. $H_2PO_3^-$, HPO_3^{2-}, etc.) and cycling in the water column, and its availability for uptake by planktonic organisms (Jones et al., 1993). The pH affects the acid-base properties of the functional groups on the humic substances, while in hard water the divalent cations, especially calcium, compete for metal binding sites with iron and inhibit the orthophosphate binding processes.

2.10 Conclusion

All potential nutrient interactions and their subsequent effects on the ecosystem should be considered in detail before fertilizers are added to oligotrophic streams. Although the long-term consequences of fertilization for the habitat and salmonid populations is not fully known, results from many experiments indicate that addition of small amounts of nutrients may be a way to enhance and restore fisheries production in nutrient-poor streams and rivers.

3. Methodology

This chapter describes the procedures for the laboratory batch testing at the University of British Columbia, the indoor trough testing in the Fraser Valley Trout Hatchery, the outdoor periphyton growth studies at the Cultus Lake Salmon Research Laboratory, the analytical techniques that were used for water quality measurements, and finally the statistical analyses performed.

3.1 Laboratory Tests

I.M.C. Vigoro Inc., Winter Haven, Florida provided fertilizer granules for the preliminary solubility experiments. These experiments were undertaken in a temperature controlled room (11 °C) in the Environmental Engineering laboratory at U.B.C. The reactors were 1 L square Nalgene bottles mixed by a rotating tumbler to simulate river conditions. Fertilizer granules (100 mg) were bundled by polyester thread in 5 cm diameter circles of 118 μm Nitex mesh and placed in bottles containing water of varying chemical conditions. Mesh bundles containing no fertilizer were used for blanks. New bundles were made for each set of experiments, with weights of fertilizer granules in Appendix I . The bottles were placed on a rotating tumbler at 10 rpm for two weeks (Figure 3.1) and the water was changed and analyzed for soluble reactive phosphorus (SRP), total phosphorus (TP) and pH at two day intervals (Table 3.1). Both SRP and TP values were measured to determine whether the changes in phosphorus availability were due to either an impedance in phosphorus release from the fertilizer, or precipitation of the phosphorus after its release from the pellets. Make-up water (distilled water or distilled water of various alkalinities) was kept in the cold room. Just prior to changing the bottles the make-up water was measured into acid-washed 1 litre containers, chemicals were added and final pH adjustments were made.

Table 3.1 Sampling program for laboratory experiments.

Batch Number	Day	Cumulative Hours	Hours on Tumbler	Notes
0	0	0	0	Place solutions on tumbler
1	1	24	24	Change solutions
2	2	48	24	"
3	4	96	48	"
4	6	144	48	"
5	8	192	48	"
6	10	240	48	"
7	12	288	48	Remove solutions

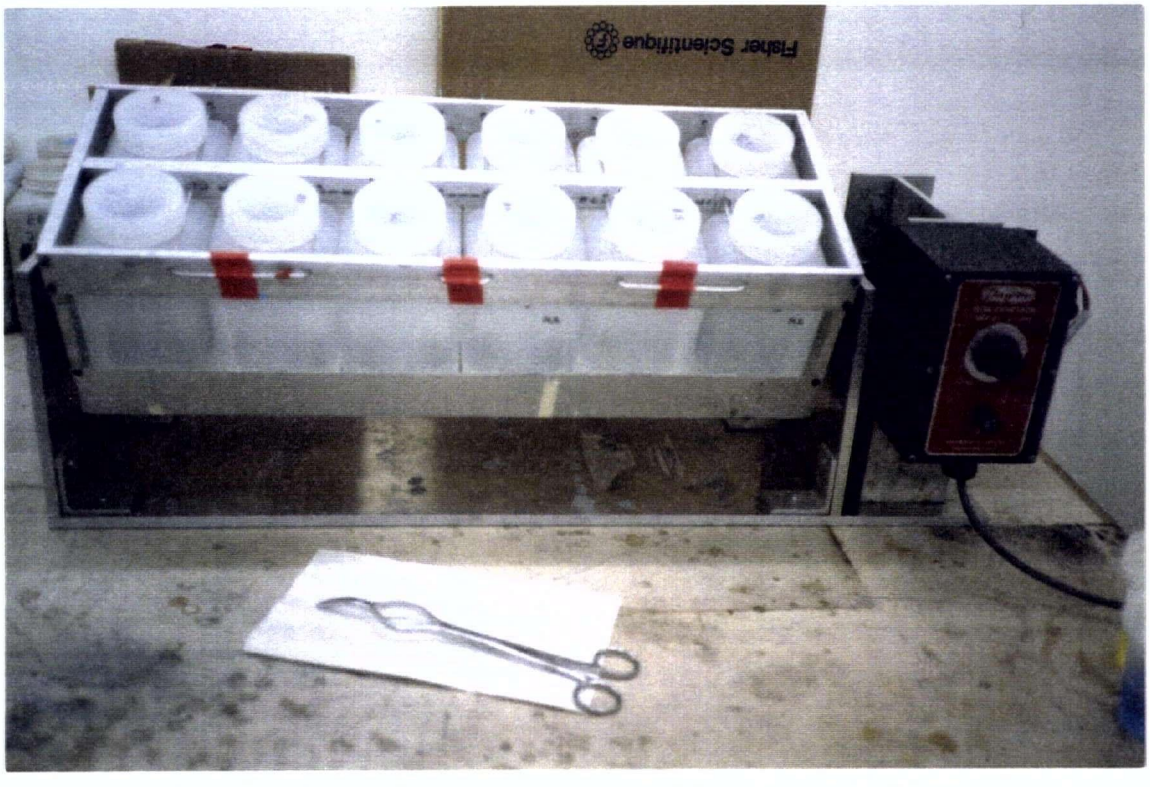


Figure 3.1 Tumbler apparatus containing 12 Nalgene bottles.

3.1.1 Experiment 1

The first of four experiments of this type was designed to determine if there is a potential for phosphorus precipitation under various water chemistry conditions typical of B.C. streams (K. Hall, 1994, pers. comm.). Water chemistry levels included: pH 7.8 or 8.5, alkalinity of 160 mg/L as $CaCO_3$, and Ca^{2+} (hardness) of 25, 100 or 175 mg/L as $CaCO_3$ (Figure 3.2). Alkalinity and pH 7.8 were chosen to be consistent with Pons' (1994) report, and hardness was chosen for soft to moderately hard water (Benefield et al. 1982) characteristic of B.C.'s streams (Table 3.2).

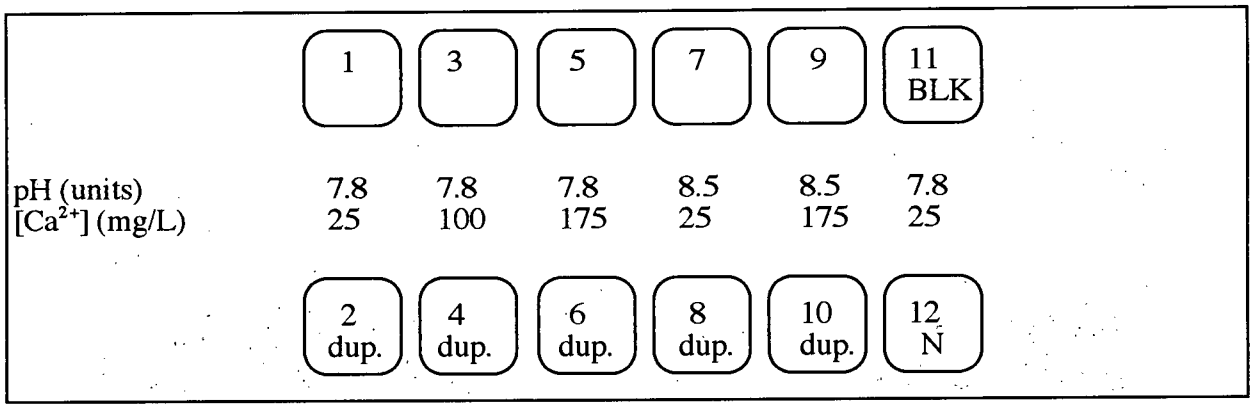


Figure 3.2 Tumbler set up for the first experiment which compared phosphorus release in water of varying pH and hardness. Variables included pH = 7.8, 8.5, $[Ca^{2+}]$ = 25, 100, 175 mg/L as $CaCO_3$ and alkalinity = 160 mg/L as $CaCO_3$. Each variable had a duplicate except for the blank and bottle 12 which was for ammonia release over 2 weeks. Numbered boxes represent sample jars.

Table 3.2 Hardness levels used in the experiment based on Benefield et al.'s (1982) international classification of hard waters.

Experiment		Classification	
Hardness (mg/L as Ca^{2+})	Hardness (mg/L as $CaCO_3$)	Hardness Range (mg/L as $CaCO_3$)	Hardness Description
10	25	0-50	Soft
		50-100	Moderately Soft
40	100	100	Moderately Soft / Slightly Hard
		100-150	Slightly Hard
70	175	150-200	Moderately Hard
		200-300	Hard
		>300	Very Hard

Distilled water (995 mL) at 11 °C was measured into clean labeled bottles, 5 mL of 55.0024 g/L $NaHCO_3$ was added and 0.428, 1.809 or 3.000 mL of 84.666 g/L $CaCl_2 \cdot 2H_2O$ was added by adjustable pipette. The bottles were shaken and pH was adjusted to 7.80 or 8.50 ± 0.02 units using 0.01 - 0.2 N HCl and NaOH. Tongs were used to remove fertilizer bundles from the bottles in the cold room and to transfer them to the fresh water solutions. The ammonia concentration in bottle 12 (pH 7.8, alkalinity of 160 mg/L as $CaCO_3$ and Ca^{2+} of 25 mg/L as $CaCO_3$) was analyzed at the end of the experiment to determine the %N released after leaving a fertilizer bundle tumbling in the same water for 286 hours (2 weeks) at 11 °C. All of the nitrogen present in the fertilizer pellets is in the form of ammonia (I.M.C. Vigoro Inc.).

3.1.2 Experiment 2

This experiment compared effects of alkalinity on the release of phosphorus using the same pH and hardness levels as in the previous experiment but having alkalinities of 20 and 95 mg/L as $CaCO_3$ (Figure 3.3). The duplicate results in the previous experiment were very close, so were not run again due to bottle limitations. The set up was similar except that 1000 mL of distilled water was added to the bottles, followed by 0.633 mL or 3.000 mL of 55.0024 g/L $NaHCO_3$. The 12th bottle was used as a preliminary experiment for phosphorus release in humic water having pH 7.6, alkalinity = 115 mg/L as $CaCO_3$ and colour = 80 colour units. The water was collected from Crescent Slough in Delta, filtered through a GF/F filter to remove large particulate matter and stored at 4 °C.

3.1.3 Experiment 3

A third experiment measured the reproducibility of phosphorus release in water containing the highest and lowest values of pH, alkalinity and hardness from the first two experiments (Figure 3.4). Five replicates plus one blank were tested in water two types having:

pH 7.8, alkalinity = 20 mg/L as $CaCO_3$ and Ca^{2+} = 25 mg/L as $CaCO_3$, and

pH 8.5, alkalinity = 160 mg/L as $CaCO_3$ and Ca^{2+} = 175 mg/L as $CaCO_3$.

Water solutions were made weekly and kept in the cold room. pH was the only parameter that needed to be adjusted before placing solutions on tumbler, and greater accuracy was found when adjusting pH for larger volumes of solutions instead of 1 L at a time.

	1 BLK	2	3	4	5	6
pH	7.8	7.8	7.8	7.8	7.8	7.8
$[Ca^{2+}]$ (mg/L $CaCO_3$)	25	100	175	25	175	25
alk (mg/L $CaCO_3$)	20	20	20	95	95	20

	7	8	9	10	11	12 humic
pH	8.5	8.5	8.5	8.5	8.5	7.6
$[Ca^{2+}]$ (mg/L $CaCO_3$)	25	100	175	25	175	-
alk (mg/L $CaCO_3$)	20	20	20	95	95	115

Figure 3.3 Tumbler set up for second experiment which compared alkalinity changes to release of phosphorus. Variables included pH 7.8, 8.5, $[Ca^{2+}]$ = 25, 200, 175 mg/L $CaCO_3$ and alkalinity = 20, 95 mg/L as $CaCO_3$.

	1	2	3	4	5	6 BLK
pH	7.8	7.8	7.8	7.8	7.8	7.8
$[Ca^{2+}]$ (mg/L $CaCO_3$)	25	25	25	25	25	25
alk (mg/L $CaCO_3$)	20	20	20	20	20	20

	7	8	9	10	11	12 BLK
pH	8.5	8.5	8.5	8.5	8.5	8.5
$[Ca^{2+}]$ (mg/L $CaCO_3$)	175	175	175	175	175	175
alk (mg/L $CaCO_3$)	160	160	160	160	160	160

Figure 3.4 Tumbler set up for replication experiment. Variables included pH 7.8, 8.5, $[Ca^{2+}]$ = 25, 175 mg/L as $CaCO_3$ and alkalinity = 20, 160 mg/L as $CaCO_3$.

3.1.4 Experiment 4

This last experiment investigated the effect of humic material and soluble iron levels on the dissolution rate of phosphorus in natural bog water. The water contained colour resulting from humic substances at 50, 100 and 200 colour units, pH = 5.85, and alkalinity = 4.4, 11 and 20 mg/L as $CaCO_3$ for each colour respectively. Fe^{3+}, in addition to what was present in natural bog water, was added at 0.2 or 1.0 mg/L to give cumulative additions of 0, 1.4 or 7.0 mg/L after two weeks (Figure 3.5).

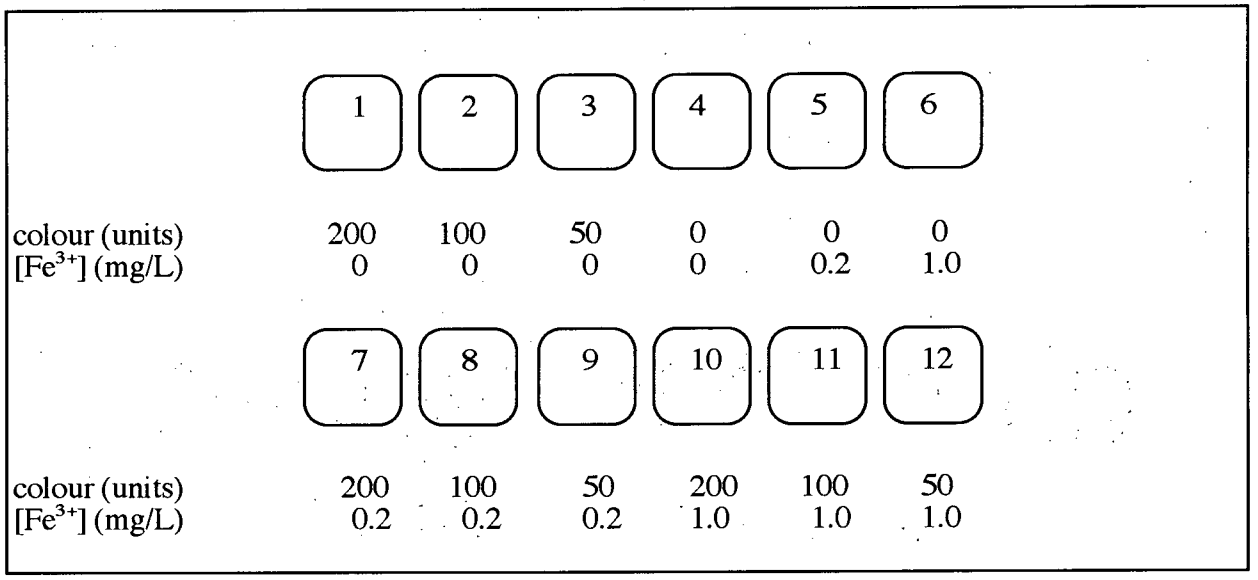


Figure 3.5 Tumbler set up for experiment comparing effects of humic water and iron content on phosphorus release. Variables included pH 5.85, median alkalinity = 7.6 mg/L as $CaCO_3$, colour = 200, 100, 50 units, and $[Fe^{3+}]$ added = 0, 0.2, 1.0 mg/L.

The Burns Bog (humic) water was filtered after sampling through Whatman 43 filters (medium-fast, ashless, 125 mm ∅) to remove large particulate material such as twigs, leaves, large plankton and insects. The filtration apparatus was acid washed and rinsed three times with distilled water prior to filtering. The humic water was diluted in 20 L batches to 50, 100 and 200 colour units, adjusted to the original bog water pH value of 5.85 units and stored with the dilution water at 4 °C. Since the post dilution alkalinity of the coloured water was very low (4.4 - 20 mg/L as $CaCO_3$), it was assumed that distilled water was approximately equal in alkalinity and no adjustment was made.

When setting up the tumbler apparatus, 1000 mL of sample water (shaken) was measured into the 1 L acid washed bottles in order of increasing colour level. Ferric iron (1000 mg/L) was added by adjustable pipet in 0.2 or 1.0 mL doses, the bottles were shaken, pH was measured (after addition of iron), and fertilizer bundles were transferred as in previous experiments.

3.2 Indoor Trough Studies

The second phase of research used channels located at the Ministry of Environment's Fraser Valley Trout Hatchery to determine release rates of pellet fertilizer (approximately 2, 6 and 9 g sizes) under various water temperatures (8, 10 and 14.5 °C) and velocities (0.03, 0.15 and 0.30 m/s). Specially constructed plexiglass troughs (dimensions 0.17 m x 0.17 m x 2.4 m) containing the pellets were placed in hatchery rearing troughs. The plexiglass troughs were modelled after ones used by Bothwell (1983, 1988). There were a total of ten troughs including a duplicate.

Twelve hundred and sixty pellets were cut into sizes of approximately 2, 6 and 9 g at the Mechanical Shop at U.B.C.'s Department of Civil & Mechanical Engineering. 1/16" diameter holes were drilled in the centre of the pellets using B.C. Building Corporation's drill press at the Fraser Valley Trout Hatchery. The pellets were rinsed, oven dried, desiccated, individually weighed and strung, separated by 5 mm diameter plastic beads, onto 30 cm lengths of 18 gauge galvanized wire. Two to three beads were strung on each end of the wire to keep the pellets away from the slower moving water at the sides of the trough. The wire and the order of the pellets on the wire were numbered and fastened to the sides of the troughs with Duct Tape.

Temperature of the oven and drying time was determined by soaking pellets in water for 12 hours and drying the pellets for up to 24 hours in a 105 °C and 70 °C oven. The drying time and weights (after desiccation) of the pellets were plotted and revealed that the pellets decomposed in the 105 °C oven. Optimum drying time for the three sizes of the pellets was 18 hours in the 70 °C oven (Appendix II).

The plexiglass troughs (Figure 3.6 & 3.7) were constructed using 3 minute epoxy resin; bonds using a hot glue gun became loose. Different water speeds required different numbers and heights of dams at the beginning and/or end of the troughs (Figure 3.6) to reduce visible turbulence. Each trough contained fourteen wires strung with three pellets of each size. The furthest wire downstream was removed each sampling date, oven dried, desiccated and weighed to determine the amount of pellet dissolved over time. Sampling took place over a period of three months and occurred 2, 4, 7, 11, 14, 18, 26, 32, 47, 60, 74 and 88 days after the pellets were introduced to the troughs.

Three water temperatures of 6.5, 9.5 and 17.5 °C were available for use but had a maximum flow restriction. Appropriate water temperatures and velocities were obtained by mixing water of various temperatures and head tank sources as well as adjusting slopes of troughs. There was also a need to watch for temperature gradients across the troughs. The velocities were measured by a Marsh McBirney, Inc. Model 2000 Portable Flowmeter which required a minimum of 1" of water depth to make measurements. The groundwater had the following water chemistry (Table 3.3).

Table 3.3 Selected water chemistry parameters of Fraser Valley Trout Hatchery well #4 and head tank.

Parameter	Value
pH	8.0
Hardness	160 mg/L as $CaCO_3$
Alkalinity at pH 4.5	88 mg/L as $CaCO_3$
Dissolved Ammonia	0.007 mg/L
Calcium	49 mg/L
Iron	< 0.05 mg/L
Magnesium	9 mg/L

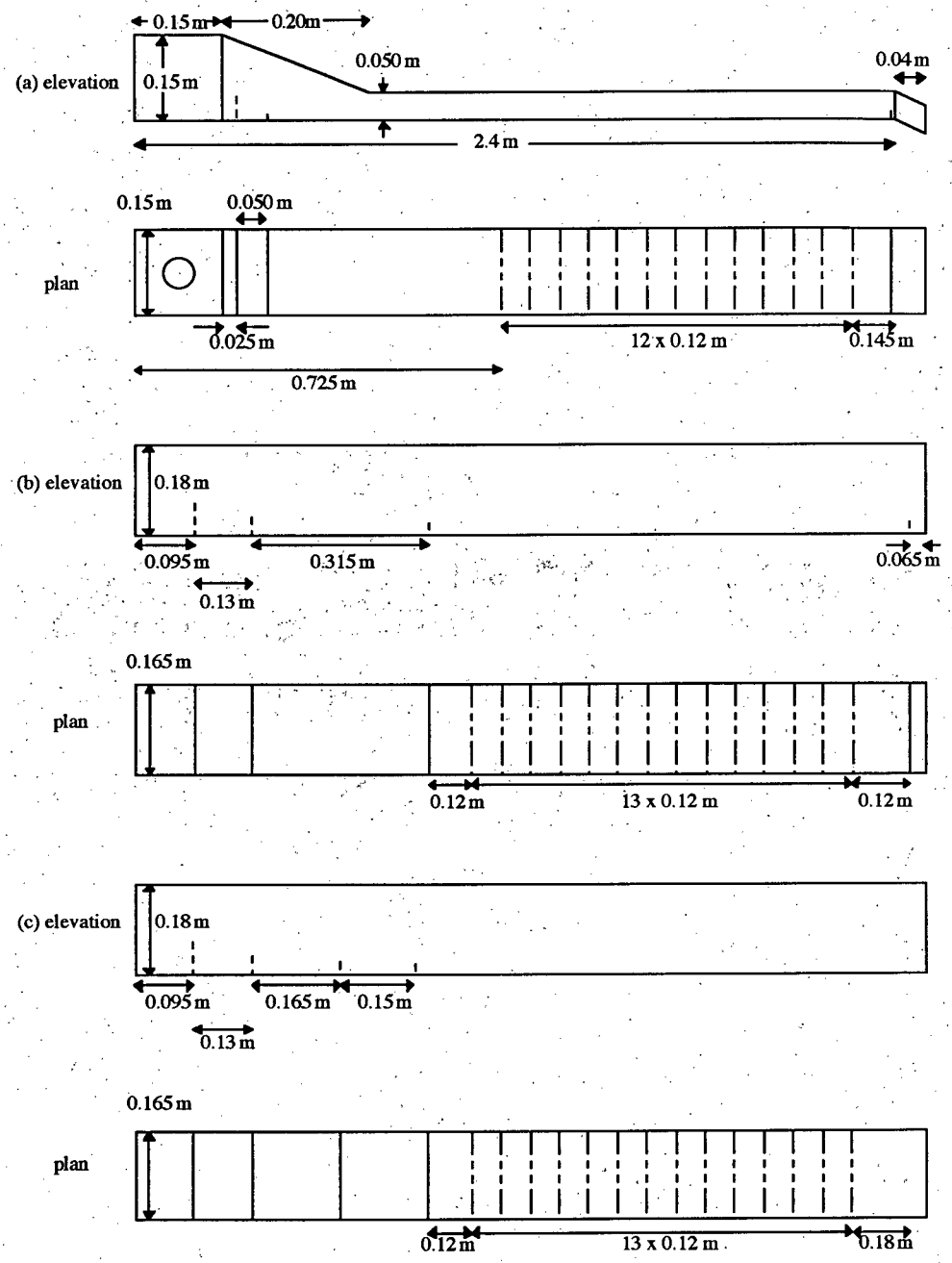


Figure 3.6 Dimensions of plexiglass troughs for the three flow rates (a) 0.03 m/s; (b) 0.15 m/s; and (c) 0.30 m/s. The vertical dotted lines in the elevation views represent dams of heights (left to right) to give laminar flow through the troughs: (a) 0.025 m, 0.005 m, 0.015 m; (b) 0.06 m, 0.045 m, 0.015 m, 0.015 m; (c) 0.06 m, 0.045 m, 0.015 m, 0.015 m. There were no dams at the end of troughs for 0.30 m/s flows. Uneven dashed lines represent the rows of fertilizer pellets, and the water flows from left to right.

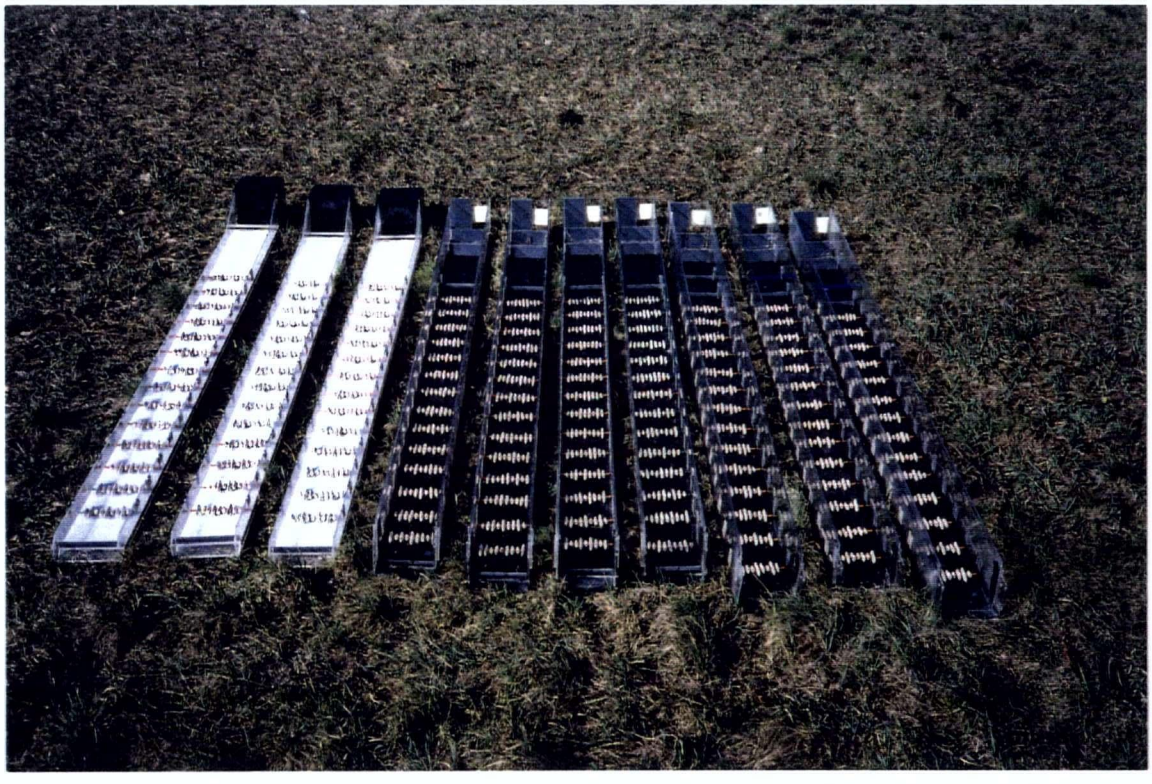


Figure 3.7 Completed troughs: From the left, the three white troughs were for 0.03 m/s velocities, the middle four were for 0.15 m/s velocities, and the last three were for 0.30 m/s velocities.

3.3 Outdoor Periphyton Growth Studies

Two troughs were made available at the Department of Fisheries and Oceans' Salmon Research Facility at Cultus Lake for periphyton accrual growth experiments. False bottoms, to eliminate shading from the trough walls, and 0.13 m dams at the ends were built, to give cross sectional trough dimensions of 0.30 m wide and 0.19 m deep. The troughs were lined with heavy plastic held in place by staples and glue.

Artificial periphyton substrates (0.2 m x 0.1 m x 0.4 m) consisted of 6 mm open-cell styrofoam sheet strapped to 7 mm plexiglass and bolted to a concrete block (Figure 3.8). The styrofoam was from the wholesale florist David L. Jones in Burnaby and the assembled blocks were borrowed from Fraser Valley Fish Hatchery. Three substrates were placed in each trough: for 0, 0.5, 1.0, 1.5, 3.0 and 5.0 μg P/L additions from the fertilizer pellets to Cultus Lake water.

Phosphorus was assumed to be the limiting nutrient for periphyton growth, as is usually the case for fresh water.

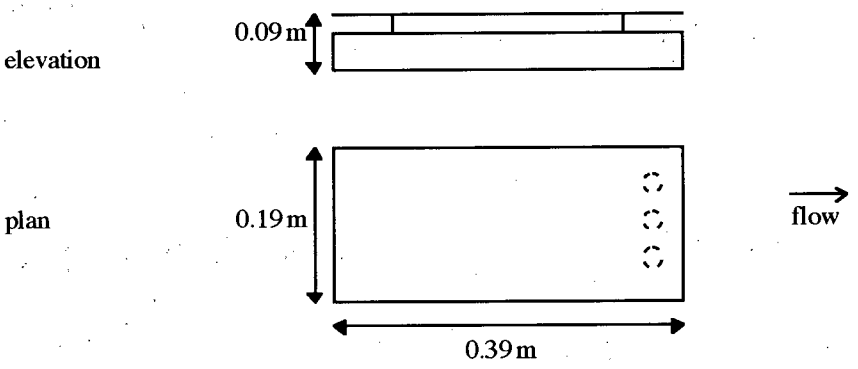


Figure 3.8 Periphyton blocks; styrofoam and plexiglass were bolted to the concrete blocks. Circles represent initial sampling locations for water flowing from left to right.

Water was pumped from 4.5 m below the surface of Cultus Lake directly to the troughs, and was adjusted to a velocity of 0.15 m/s at approximately 0.10 m above the periphyton blocks. At the head of the troughs water flowed into 20 L buckets, with holes and rocks in the bottom, to minimize the turbulence caused by inflowing water.

The amount of pellets needed to obtain the desired phosphorus concentrations were calculated from the previous trough experiments based on the 14 °C and 0.15 m/s test data: over the course of six weeks (42 days) approximately 20 % of the 9 g pellet dissolved releasing 0.3 g of phosphorus. The calculations were based on 7.4 L/s flowing through each trough using 9 g pellets. A linear dissolution rate and additive releases were assumed over the time frame of the experiments. In the first trough 43 pellets (390 g) were needed in two places to provide 0.5 and 1 μg P/L; The second trough needed 130 pellets (1169 g) in two places to provide 1.5 and 3 μg P/L as well as an additional 173 pellets (1559 g) to provide 5 μg P/L. The total amount of fertilizer used was 519 pellets or 4677 g.

The pellets were drilled and strung on 18 gauge galvanized wire with 5 mm diameter plastic beads separating them, and were attached to the troughs at various depths in order to

evenly distribute the nutrients in the flowing water. They were placed in a series of groups containing one or two wires, depending on the amount of pellets, so as to not "shade" the pellets downstream (Figure 3.9). Staples and duct tape were used to attach the wires to the top sides of the troughs. Shading by plywood sheets placed above the pellets was used to discourage algal growth.

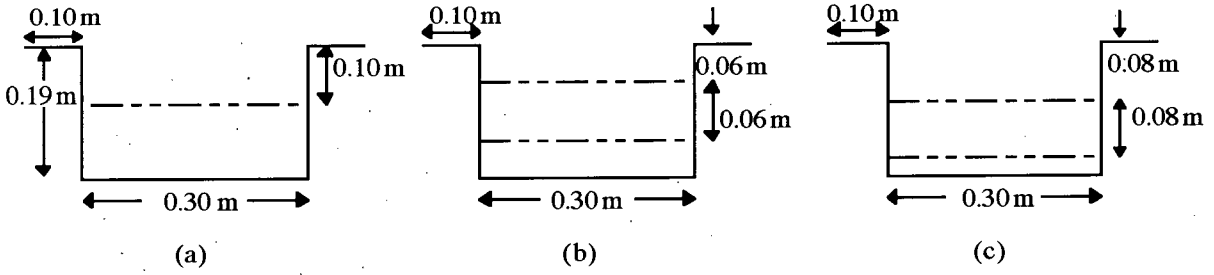


Figure 3.9 Cross section of wires and lengths required in troughs: (a) one wire per site, 0.70 m each, (b) two wires per site, 0.62 and 0.74 m each, (c) two wires per site, 0.66 and 0.82 m each.

The periphyton blocks were placed close to the north side of the troughs to eliminate shading from the walls (Figure 3.10). Four days after the blocks were put in the troughs the styrofoam was brushed horizontally and vertically with a soft brush to remove excess filamentous algae and distribute the algal cells evenly across the styrofoam sheets. The same brush was also used on the strings of fertilizer pellets to remove excess algae. Each sampling date the strands of pellets were brushed and the water velocities (0.15 m/s) were monitored (Figure 3.11).

The water temperature was recorded hourly by an Optic StowAway Temperature monitor (Onset WTA08, from Hoskin Scientific) anchored to one of the buckets. Twice a week the periphyton was sampled, and once a week light intensity was measured (by a LiCor Quantum Meter Model 185 a) and cloud cover noted.

Weekly water samples were taken during initial experiments to check calculated additions of phosphorus. Because of the limited sensitivity of the analytical method for dissolved phosphorus, the additions could not be accurately verified. However, average results from

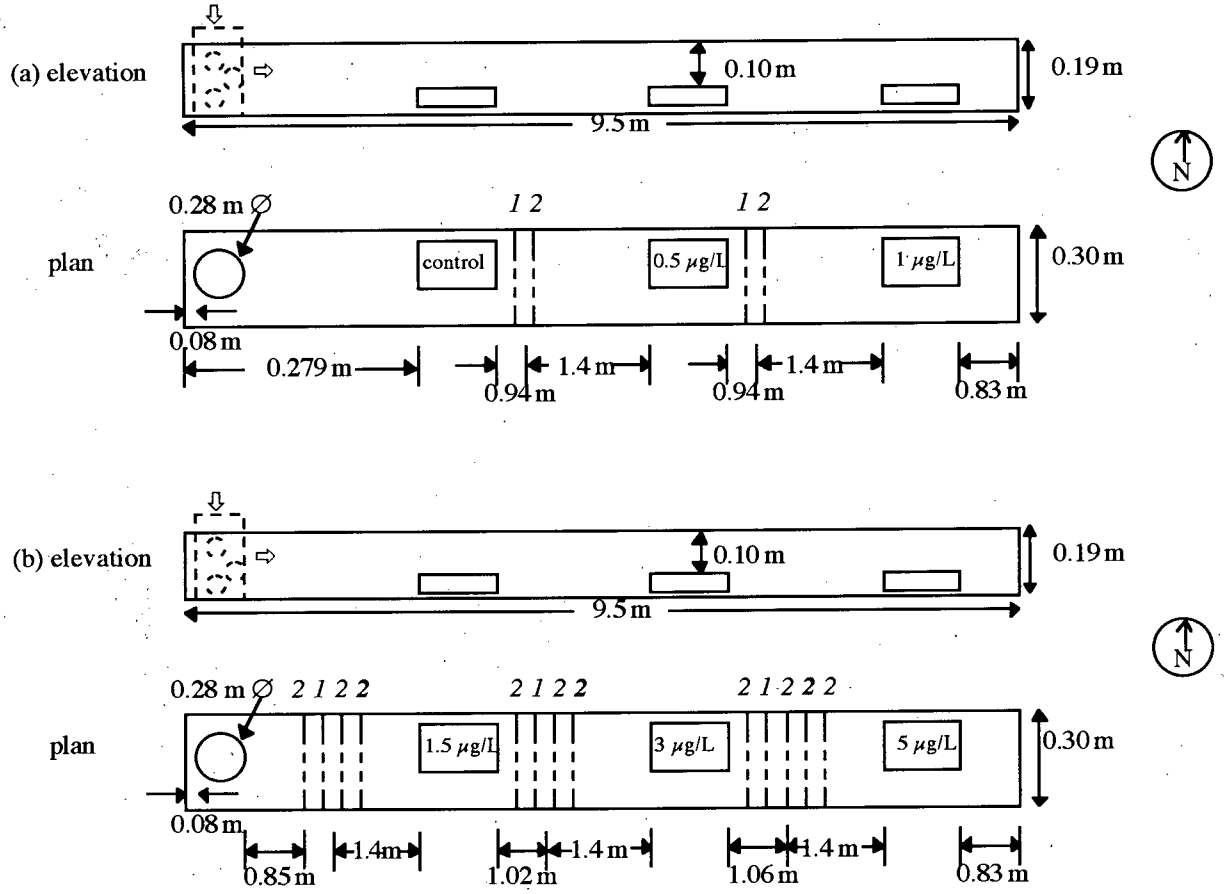


Figure 3.10 Outdoor trough dimensions with water flowing from the west at 0.15 m/s. Buckets (0.28 m diameter) to capture inflowing water are represented by circles in the plan view. Trough (a) contained periphyton blocks for 0, 0.5 and 1.0 μg P/L from fertilizer pellets and trough (b) contained blocks for 1.5, 3.0 and 5.0 μg P/L fertilizer addition. Groups of pellets were ~ 8 cm apart. The 1.4 m distances were measured from the centre of the groups of pellets to the blocks. Italic numbers above pellets rows indicate number of wires per site; bold-italic numbers represent wires of lengths 0.66 and 0.82 m.

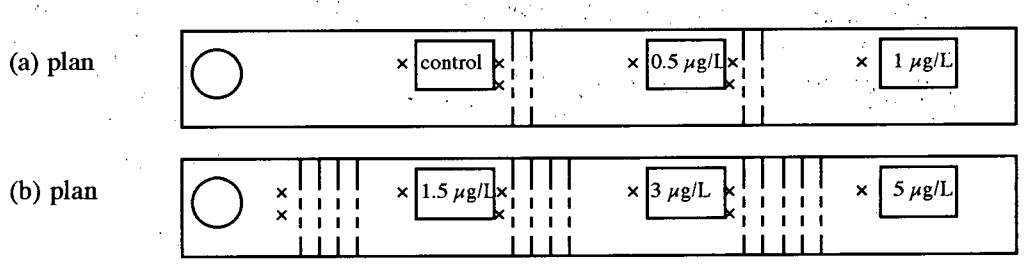


Figure 3.11 Locations (×) of weekly flow monitoring measurements in both troughs. All measurements were taken approximately 8-10 cm in front of objects and 10 cm under water.

unfertilized samples taken May 29 to July 17, 1995 were: orthophosphate = 0.004 mg/L, total phosphorus = 0.007 mg/L, nitrate ≤ 0.005 mg/L and ammonia ≅ 0.005 mg/L.

Quadruplicate cores (6.2 cm^2) of styrofoam were removed with a 7 dram (2.8 cm diameter) size pill bottle from each periphyton block at 3- to 4-day intervals, and then analyzed for chlorophyll *a*. Qualitative samples were taken from four of six periphyton blocks (0.0, 0.5, 1.5 and 3.0 μg P/L) on three occasions (June 19, July 10, and July 17, 1995). They were preserved in Lugol's solution and analyzed for algal species identification by Dr. Frances Pick, University of Ottawa. The two 1 month experiments ended when noticeable sloughing of algae from the periphyton substrates occurred.

3.4 Analytical Techniques

3.4.1 Algal Species Identification

The methodology for cell counts is outlined in the report by Yang et al. (1997) to B.C. Environment:

> "Enumerations were made using the Utermöhl method on a Wild M40 inverted microscope. Two millilitre aliquots were settled overnight (16 hours) in 26 mm diameter sedimentation chambers. For each sample, a minimum of 300 - 350 cells [were] counted along randomly selected transects to ensure an 85 - 90 % counting accuracy. The length of each transect equaled the diameter of the chamber. Cell counts and dimensions were recorded on a computerized counter."

Species of periphyton as a function of nutrient loading were identified as: *rare*, whereby species occurred < 3 cells in one transect; *common*, whereby species occurred 3 - 10 cells in one transect; *abundant*, whereby species occurred 10 - 30 cells in one transect; and *dominant*, whereby species occurred > 30 cells in one transect.

3.4.2 Alkalinity

All measurements were made during solution preparation or immediately after the solutions were changed. Alkalinity was determined using the titration method as given by

Standard Methods (APHA, 18th edition). The burette was filled with N/50 standard H_2SO_4 and 25 mL of sample were pipetted into a 125 mL flask. A stir bar and 2 drops bromcresol green indicator were added before titrating the solution to a yellow colour. The titration was repeated until volumes of acid added were within ± 0.02 mL.

3.4.3 Chlorophyll *a*

The chlorophyll *a* samples were kept frozen in black plastic bags until analysis under low light levels. The algae were removed from the styrofoam bottoms and the disks were cut into thirds so they would fit into the glass extraction vials. Excess water was poured out of the pill bottles (if not significant amounts of suspended algae). The foam was placed, using forceps, into 15 mL graduated glass vials, and chlorophyll *a* was extracted by the Standard Methods procedure (APHA, 18th edition). Five mL of 90 % acetone with 10 % $MgCO_3$ saturated distilled water was pipetted and used to rinse algae from lid and pill bottle into the glass vial. The volume was made up to 10 or 15 mL with solvent, depending on the dilution required, and the samples were capped and shaken by hand. They were then sonicated in cold water for 15 minutes, shaken and stored overnight at 4 °C. In the morning the samples were shaken, and if the chlorophyll *a* levels were very high the samples were sonicated again for 10-15 minutes. After centrifuging for 5 minutes at 2000 rpm in a refrigerated centrifuge, the extracts were read on a calibrated 10-AU Fluorometer by Turner Designs, Sunnyvale, California. For phaeophytin analysis, 2-3 drops of 10 % HCl were added. Addition of acid to chlorophyll *a* results in the loss of the magnesium atom, converting it to phaeophytin *a*. If necessary, the samples were diluted with 90 % acetone, 10 % distilled water. The following calibrated equation was used for calculating chlorophyll *a*:

$$\text{Chl } a \ (\mu g/L) = 1.899 \ (F_o - F_a) \ (1/0.9609) \ (v/V)$$

where F_o = chlorophyll *a* absorbance

F_a = phaeophytin *a* absorbance

v = volume of extract (mL)

V = volume of sample (mL).

3.4.4 Colour

The platinum/cobalt method was used to measure colour in samples of humic water against standard colour plates using the Hellige Aqua Tester (APHA, 18th edition). One unit of colour is produced by 1 mg platinum/L in the form of the chloroplatinate ion. One of two matched 50 mL nessler tubes was filled with distilled water while the other was filled with sample. If the humic water colour, compared to the distilled water and colour disks, was greater than 70 units the sample was diluted. Apparent colour was determined on the original sample without filtration or centrifugation. The colour value of water is extremely pH dependent and usually increases as pH increases.

3.4.5 Iron

Unfiltered samples were shaken and 100 mL poured into acid washed 250 mL plastic bottles. One mL concentrated HNO_3 was added and samples were stored at room temperature. Upon analysis the samples were acidified to pH 2 and analyzed on a Thermo Jarrell Ash Video 22 Atomic Absorption / Atomic Emission Spectrometer using Standard Method's Direct Air-Acetylene Flame Atomic Absorption Spectrometric Method (APHA, 18th edition).

3.4.6 Nitrogen

Ammonia concentrations were analyzed on a flow injection Lachat QuickChem Automated Ion Analyzer using QuickChem method #10-107-06-1-Z. The samples were preserved with concentrated sulfuric acid to lower the pH to 3 and then stored at 4 °C. The samples were heated with salicylate and hypochlorite in an alkaline phosphate buffer for analysis. The presence of tartrate in the buffer prevents precipitation of calcium and magnesium. An emerald green colour, proportional to the ammonia concentration, resulted and was intensified by adding sodium nitroprusside. Interfering compounds include colour, turbidity and certain organic species.

3.4.7 pH

The pH values were determined immediately with a Beckman Φ44 pH meter containing a Fisher polymer body combination electrode with an Ag/AgCl reference element pH electrode. The meter was standardized against Fisher pH 4 and pH 7 buffer solutions. Standard solutions were kept in the cold room (11 °C) to maintain temperature consistency between standards and samples.

3.4.8 Phosphorus

3.4.8.1 Sampling and Storage

All containers used for samples, storage and analyses were acid washed with 10 % HCl and rinsed 3 times with distilled water. Total phosphorus (TP) samples were acidified and digested immediately, then neutralized (within 2-3 days) and frozen in 7 mL plastic vials for later analysis. Orthophosphate (SRP) samples were immediately decanted into 7 mL plastic vials and frozen until analysis. Duplicates and blanks were poured for all TP and SRP samples.

3.4.8.2 Total Phosphorus

Calibration standards ranged from 0 to 10 mg/L and were made up in 50 mL volumetric flasks. Samples and standards (50 mL) were transferred to 100 mL glass tubes for conversion of total phosphorus to orthophosphate. One drop of phenolphthalein was added to each tube and concentrated H_2SO_4 was added dropwise until the pink colour vanished. One half mL of H_2SO_4 was added to the tubes before covering loosely with aluminum foil and autoclaving 30 minutes at approximately 120 °C. Liquid levels in the tubes needed to be checked after autoclaving to verify the tubes had not boiled over and possibly contaminated other samples.

After the samples had cooled completely they were neutralized to a pH of 7 with 6 N NaOH. A 100 mL acid washed beaker containing a stir bar was used for neutralization of the standards and samples. NaOH was added dropwise until the solution just turned pink and then 10 % HCl was added dropwise until it was clear again. Standards and blanks were poured into 25

mL plastic bottles (no duplicates) and the samples were poured into duplicate plastic vials, capped and frozen until analysis.

3.4.8.3 Orthophosphate

The samples were decanted and not filtered because of contamination from the filtration apparatus.

3.4.8.4 Autoanalyzer

Phosphorus concentrations were measured by the Lachat QuickChem Automated Ion Analyzer via flow injection using the methods outlined by QuickChem #10-115-01-1-Z for SRP and #10-115-01-1-C for TP. The orthophosphate ion reacted with ammonium molybdate and antimony potassium tartrate under acidic conditions. The resulting complex was reduced with ascorbic acid to form a blue complex. The concentration of orthophosphate in the sample was proportional to absorbance of light by the blue complex at 880 nm. Interfering iron and silica compounds were not present at high enough concentrations (50 mg/L and 4000 mg/L respectively) to alter results.

One blank, duplicate and standard were run with each set of 10 phosphorus samples to ensure quality control. Duplicates and standard values were checked to ensure that the difference between duplicate values and known standard values did not exceed 5 %. Less than 2 % difference was usually found, otherwise the batch of samples were re-run.

Table 3.4 Detection limits for parameters analyzed.

Parameter	Units	Detection Limit
Alkalinity	mg/L as $CaCO_3$	5
Chlorophyll *a*	μg/L	1
Colour	units	10
Iron	mg/L	0.2
Nitrogen	mg/L	0.05
Phosphorus	mg/L	0.05

3.5 Statistical Analyses

3.5.1 Laboratory Tests

Cumulative phosphorus (TP and SRP) release values over time were calculated for each sample. The average phosphorus value was used for duplicates. These values were statistically analyzed to determine the water chemistry variables which act as major predictors for phosphorus availability using Systat's version 6.0 Stepwise (step-up / forward addition) Linear Regression model. A minimum tolerance for entry into the model of 0.01 was used. Regression equations were derived to express phosphorus availability in terms of pH, alkalinity, calcium, colour and iron. The equations were derived for fertilizer granules (pellets were not available at this point) releasing nutrients over two week experimental periods in 11 °C water and simulated flow conditions, in water of chemistry: pH = 7.8 - 8.5, alkalinity = 20 - 160 mg/L as $CaCO_3$, calcium (hardness) = 25 - 175 mg/L as $CaCO_3$, colour = 50 - 200 units, and iron = 0 - 1.0 mg/L .

3.5.2 Indoor Trough Studies

A ratio of average weight lost over average initial weight was used as the dependent variable during statistical analysis in order to simplify calculations. As with the laboratory experiments, the major predictors for average weight lost / average initial weight were determined using Systat's version 6.0 Stepwise Linear Regression model. A regression equation was derived to express average weight lost / average initial weight in terms of time, temperature, velocity and pellet size. The equation was derived for an 88 day experimental period for pellets of 2 - 9 g in water of temperatures 8 - 14.5 °C and velocities 0.03 - 0.30 m/s.

3.5.3 Outdoor Periphyton Growth Studies

Systat's version 6.0 Stepwise Linear Regression model was used to determine the role of phosphorus concentration in influencing periphyton accumulation, measured as chlorophyll *a*, and to investigate the general tendencies of the data. Regression equations were derived to express chlorophyll *a* in terms of time and average orthophosphate-phosphorus concentration. The equations

were derived for month long experiments (late May to beginning of August) in water having temperature 14 - 23 °C and velocity of 0.15 m/s.

4. Results and Discussion

4.1 Introduction

The project was divided into three phases. Phase one investigated the release of phosphorus in jar tests from fertilizer granules in water of varying pH, alkalinity, hardness and colour. The reproducibility of phosphorus release was also determined. Phase two documented the dissolution rate of the fertilizer pellets in indoor hatchery troughs when subjected to various water temperatures and velocities. The third and final phase assessed the growth rate of periphyton using different amounts of fertilizer in outdoor flow-through troughs.

4.2 Phosphorus Availability for Various Water Chemistry Types

4.2.1 Introduction

A knowledge of how stream waters chemically interact with fertilizer components is essential for determining the correct amount of fertilizer to be added to provincial streams. Phosphorus and nitrogen present in the fertilizer pellets as $MgNH_4PO_4 H_2O$ enrich the stream water and stimulate algal growth. Once dissolved in the stream water, nitrogen is present as ammonium (NH_4^+) and remains biologically available to aquatic organisms. On the other hand, phosphorus, present as orthophosphate (PO_4^{3-}) in solution, can be precipitated, adsorbed, or changed to a biologically unavailable form in the presence of calcium, iron and humic material. Other water chemistry factors such as alkalinity and pH may also affect the dissolution of phosphorus from the fertilizer pellets.

Experiments at selected pH's, alkalinities and hardness (as Ca^{2+}) were conducted at slightly undersaturated conditions for the formation of precipitates. The presence of precipitates in solution could remove solubilized phosphorus from solution or prevent the initial solubilization from the fertilizer. Research was also conducted to determine the effects humic

substances could have on phosphate availability; for example, whether or not they adsorbed onto the pellets and impeded nutrient solubilization, or formed complexes with orthophosphate.

4.2.2 Phosphorus Release in the Presence of Varying pH, Alkalinity and Hardness

4.2.2.1 Results

Total phosphorus, soluble reactive phosphorus and pH values obtained from three experiments were summed for the two week analyses to give cumulative values presented in Table 4.1. Also present in Table 4.1 is the amount of ammonia released from the fertilizer over two weeks. The temperature of the cold room was checked each sampling event and was set at a constant 11 °C.

4.2.2.1.1 pH Change

pH change from addition of the fertilizer pellets to the water solutions was measured in the first experiment to determine if fertilizer additions altered the water chemistry. Systat's stepwise linear regression model was used to analyze the cumulative change in pH values over the course of the experiment (N = 105). Order of entry by the variables into the stepwise analysis (Table 4.2) gave an indication of their relative importance as predictors to the change in pH values.

The stepwise linear regression analysis of pH change yielded a main effect of alkalinity. This result was expected because of the buffering capacity contributed by alkalinity. Initial pH also had some effect because it relates to the amount of buffering achieved from alkalinity: maximum buffering is achieved when pH = pK in the carbonate system. There were no interactions between the variables. Thus, each variable had in independent effect in determining the pH level.

Table 4.1 Cumulative values of three two week experiments for change in pH and final pH, SRP, TP and NH_3 released in water of various pH, hardness (Ca^{2+}) and alkalinity. A "-" indicates the parameter was not measured. Bottles #1-11, 2-6, 3-6 and 3-12 contained no fertilizer. Bottle # 2-12 contained humic water for a preliminary experiment; [Ca^{2+}] was not analyzed.

Expt. # - Bottle #	pH (units)	[Ca^{2+}] (mg/L as $CaCO_3$)	Alkalinity (mg/L as $CaCO_3$)	Δ pH (units)	pH (units)	SRP (mg/L)	TP (mg/L)	NH_3 (mg/L)
1-1	7.8	25	160	2.18	9.98	11.00	13.61	-
1-2	7.8	25	160	1.98	9.78	10.84	12.61	-
1-3	7.8	100	160	1.10	8.90	4.15	9.75	-
1-4	7.8	100	160	0.95	8.75	5.81	9.11	-
1-5	7.8	175	160	0.62	8.42	5.21	8.88	-
1-6	7.8	175	160	0.62	8.42	4.26	8.43	-
1-7	8.5	25	160	0.60	9.10	8.34	8.83	-
1-8	8.5	25	160	0.33	8.83	7.74	9.59	-
1-9	8.5	175	160	-0.27	8.23	4.48	7.31	-
1-10	8.5	175	160	-0.24	8.26	3.71	7.61	-
1-11	7.8	25	160	0.82	8.62	0	0	-
1-12	7.8	25	160	-	-	-	-	5.11
2-1	7.8	25	20	-1.34	6.46	10.2	10.9	-
2-2	7.8	100	20	-1.93	5.87	8.35	9.22	-
2-3	7.8	175	20	-1.53	6.27	7.8	8.96	-
2-4	7.8	25	95	0.48	8.28	9.13	11.2	-
2-5	7.8	175	95	-0.13	7.67	5.29	8.51	-
2-6	7.8	25	20	-1.43	6.37	0	0	-
2-7	8.5	25	20	-1.56	6.94	10.2	10.7	-
2-8	8.5	100	20	-3.03	5.47	7.4	8.68	-
2-9	8.5	175	20	-2.99	5.51	6.97	8.12	-
2-10	8.5	25	95	-0.52	7.98	11.2	12.0	-
2-11	8.5	175	95	-0.19	8.31	4.9	7.89	-
2-12	8.5	-	115	0.72	9.22	9.76	12.15	-
3-1	7.8	25	20	-	-	9.40	10.2	-
3-2	7.8	25	20	-	-	9.74	10.5	-
3-3	7.8	25	20	-	-	9.91	10.1	-
3-4	7.8	25	20	-	-	9.97	10.5	-
3-5	7.8	25	20	-	-	9.18	10.1	-
3-6	7.8	25	20	-	-	0	0	-
3-7	8.5	175	160	-	-	3.62	5.17	-
3-8	8.5	175	160	-	-	6.07	7.51	-
3-9	8.5	175	160	-	-	4.21	5.50	-
3-10	8.5	175	160	-	-	5.30	7.53	-
3-11	8.5	175	160	-	-	5.17	4.21	-
3-12	8.5	175	160	-	-	0	0	-

Values for pH, SRP and TP for each sampling event are listed in Appendix III.

Table 4.2 Order of entry of alkalinity, pH, calcium and hours variables into stepwise regression for pH change with initial F-to-enter values.

Order of Entry	Variables	F-to-enter
1	Constant	-
2	Alkalinity	124.145
3	pH	75.909
4	Calcium	40.172
5	Hours	2.147

Changes in pH were tabulated as cumulative values; pH change in bottle # 1-12 which contained the same water for the duration of the two week experiment, was not analyzed. In future experiments the pH, SRP and TP could be measured for water containing fertilizer over 1 - 2 weeks; however, the purpose of this experiment was to determine changes over time. The maximum and minimum cumulative pH changes for two water types is shown in Table 4.3 with the variables related, in brackets, in terms of the highest or lowest in the range analyzed.

Table 4.3 Maximum and minimum cumulative pH change over the two week experiment.

	pH (units)	Alkalinity (mg/L as $CaCO_3$)	Calcium (mg/L as $CaCO_3$)	pH Change (units)
Minimum Change	8.5 (high)	20 (low)	175 (high)	-3.0
Maximum Change	7.8 (low)	160 (high)	25 (low)	+2.0

The relation of the variables to the cumulative change in pH is given by the following equation:

$$\text{pH Change} = 0.011[\text{Alkalinity}] - 1.214[\text{pH}] - 0.004[\text{Calcium}] - 0.001[\text{Time}] + 8.897 \quad [4\text{-}1]$$

where $r^2 = 0.818$; and standard error = 0.420.

The blank, containing Nitex mesh but no fertilizer, had a total pH change of 0.82 units for water of pH = 7.8, $[Ca^{2+}]$ = 25 mg/L as $CaCO_3$ and alkalinity = 160 mg/L as $CaCO_3$. The positive pH change over time was likely due to an equilibrium forming between the water solution, the Nitex mesh and air space in the bottle during mixing on the tumbler apparatus.

4.2.2.1.2 Alkalinity Change

Alkalinity values were measured in water containing fertilizer granules throughout a 24 hour period. They were found to change very little (10 - 20 mg/L as $CaCO_3$) from the calculated original values (Table 4.4) so measurements for this parameter were not continued in further experiments.

Table 4.4 Alkalinity of water exposed to fertilizer granules for 24 hours.

Bottle #	pH (units) / $[Ca^{2+}]$ (mg/L as $CaCO_3$) in bottles	Alkalinity (mg/L as $CaCO_3$) calculated original	Alkalinity (mg/L as $CaCO_3$) after 24 hours
1	7.8 / 25	158	171
2	"	158	170
3	7.8 / 100	158	173
4	"	158	169
5	7.8 / 175	158	175
6	"	158	167
7	8.5 / 25	167	177
8	"	167	174
9	8.5 / 175	167	189
10	"	167	182
11	7.8 / 25	158	158

4.2.2.1.3 Total Ammonia Released

Ammonia released over the 286 hour (2 week) period was found to be 5.11 mg/L from a bundle of fertilizer weighing 0.1003 g. Pons (1994) reported that the nitrogen content in the fertilizer was 8 %, so the total ammonia in the fertilizer bundle, assuming 100 % ammonia as nitrogen, was 8 mg. Therefore, the % N released after 286 hours in 1 L of water was 64 % as NH_3, or 0.0178 mg/hr assuming a linear release rate.

4.2.2.1.4 Standard Deviations of Phosphorus Release

The third experiment (Table 4.1) determined the standard deviations of TP and SRP releases under two water chemistry conditions. Bottles # 3-1 to # 3-5 contained water of pH = 7.8 units, alkalinity = 20 mg/L as $CaCO_3$, and calcium = 25 mg/L as $CaCO_3$ and bottles # 3-7 to # 3-11 contained water of pH = 8.5 units, alkalinity = 160 mg/L as $CaCO_3$, and calcium = 175

mg/L as $CaCO_3$. Bottles # 3-6 and # 3-12 were blanks for each water type. The calculated values for phosphorus release from fertilizer pellets normalized to one gram did not alter the results of TP and SRP released.

On several occasions the TP data had been less than the SRP data, and reruns were not able to correct for discrepancies in the results. These difficulties were due to some unexplained fluctuations in the autoanalyzer, and were only evident in this portion of the experiments.

The standard deviations (Figure 4.1) for phosphorus availability (SRP and TP respectively) in water of type pH = 7.8 units, alkalinity = 20 mg/L as $CaCO_3$, and calcium = 25 mg/L as $CaCO_3$ (bottles # 3-1 to # 3-5) were 0.276 (3.28 % of average value) and 0.311 (3.44 %), and were 0.890 (19.9 %) and 1.41 (26.2 %) in water of type pH = 8.5 units, alkalinity = 160 mg/L as $CaCO_3$, and calcium = 175 mg/L as $CaCO_3$ (bottles # 3-7 to # 3-11).

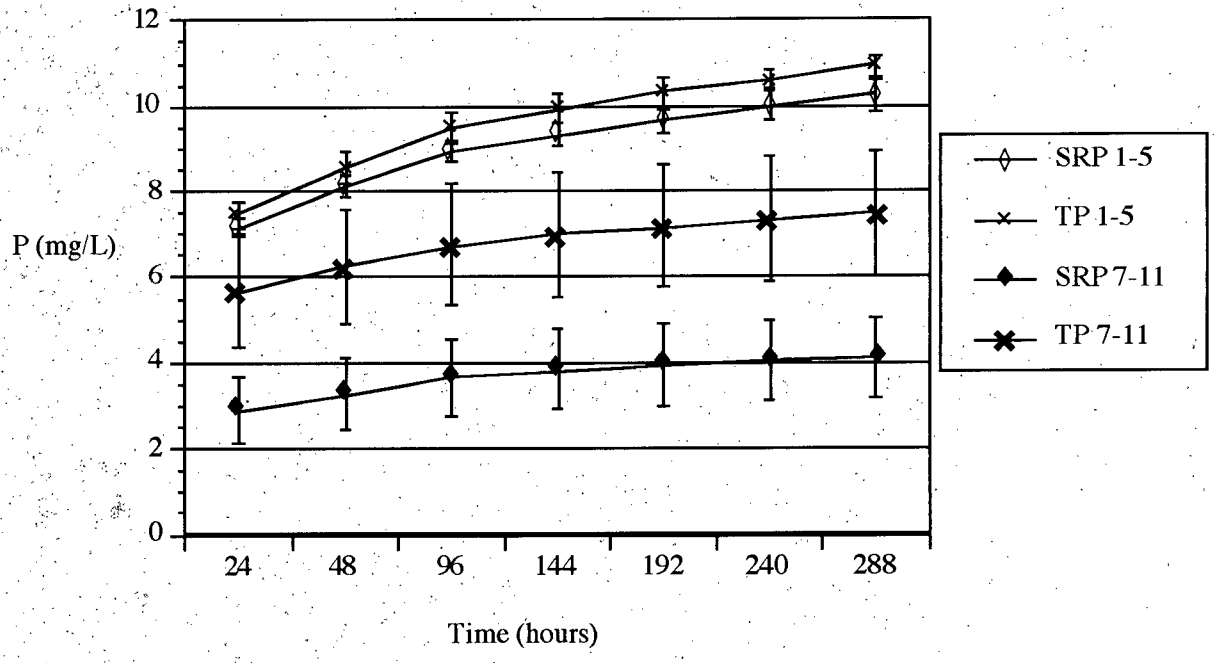


Figure 4.1 Standard deviations for two TP and SRP water chemistry types (N=5). Cumulative phosphorus release was plotted over time.

The phosphorus releases were very similar for bottles # 3-1 to # 3-5 while the releases in bottles # 3-7 to # 3-11 exhibited much greater variation. This variation was probably due to the very small sample size (100 mg) and the reaction chemistry causing precipitation on the granules etc.

at the higher pH, alkalinity and calcium levels. Most of the phosphorus released in the first 24 hours was from the powdery fragmentation from the fertilizer granules solubilizing quickly.

The release rates or slopes of the curves (Table 4.5) for 0.1 g fertilizer in 1 L bottles were similar for each group of SRP and TP releases, with SRP having a slightly higher slope than TP.

Table 4.5 Average slopes and r^2 values for two water chemistry types.

Bottle #'s	Slope (mg P/0.1 g·hr)	r^2
SRP 3-1 to 3-5	0.010	0.95
SRP 3-7 to 3-11	0.0035	0.93
TP 3-1 to 3-5	0.011	0.91
TP 3-7 to 3-11	0.0052	0.96

The phosphorus release rates for the fertilizer bundles, indicated by the parallel slopes, were very consistent.

4.2.2.1.5 Stepwise Linear Regression

The presence of phosphorus in the various water solutions was evaluated to determine which water chemistry parameters affected orthophosphate availability, whether through the dissolution of the fertilizer pellets or a reduction of solubility once in solution. The cumulative TP and SRP values for experiments 1 and 2 (total bottles = 24) were analyzed using Systat's stepwise linear regression model (N = 105). Order of entry by the variables into the stepwise analysis (Table 4.6) indicated their relative importance as predictors to the SRP and TP values.

Table 4.6 Order of entry of calcium, alkalinity, hours and pH variables into stepwise regression for SRP and TP with initial F-to-enter values.

Order of Entry	SRP Variables	SRP, F-to-enter	TP Variables	TP, F-to-enter
1	Constant	-	Constant	-
2	Calcium	94.675	Hours	50.954
3	Alkalinity	27.924	Calcium	49.934
4	Hours	13.647	pH	6.156
5	pH (not entered)	0.040	Alkalinity	1.589

pH was not entered into the SRP stepwise regression; its addition did not significantly change the r-value.

The stepwise linear regression analysis did not yield any main effects for both TP and SRP. Calcium was a main effect for SRP, but could also be regarded as a main effect for TP because of its similar F-to-enter values as hours, and independence (r^2 = 0.000, Table 4.7). The longer the pellets were in solution, the more phosphate was released. This resulted in hours having a main effect on TP availability. Calcium was a main effect for SRP availability, and removed phosphorus (SRP and TP) from solution through precipitation or adsorption to the pellets, Nitex mesh or Nalgene bottles. Removal of TP from solution was affected by pH, but it did not affect SRP solubility. Alkalinity had a minor effect on TP but had a larger (inverse) effect on SRP.

There were no interactions between the pH, calcium, alkalinity and hours variables as indicated by a correlation matrix (r^2) of regression coefficients (Table 4.7).

Table 4.7 Correlation matrix of regression coefficients of the regression equation for (a) SRP and (b) TP.

(a) SRP	Constant	Calcium	Alkalinity	Hours
Constant	1.000			
Calcium	- 0.59	1.000		
Alkalinity	- 0.513	- 0.000	1.000	
Hours	- 0.576	0.000	- 0.000	1.000

(b) TP	Constant	pH	Calcium	Alkalinity	Hours
Constant	1.000				
pH	- 0.993	1.000			
Calcium	- 0.063	0.000	1.000		
Alkalinity	- 0.142	0.082	0.000	1.000	
Hours	- 0.069	0.000	0.000	0.000	1.000

Coefficients and their standard error calculated in the regression are presented in Table 4.8.

Table 4.8 Regression results for SRP and TP.

Variable	SRP Coefficient	SRP Std. Error	TP Coefficient	TP Std. Error
Constant	9.111	0.259	17.139	1.799
pH	n/a	n/a	- 1.037	0.219
Calcium	- 0.022	0.001	- 0.012	0.001
Alkalinity	- 0.016	0.002	- 0.003	0.001
Hours	0.008	0.001	0.009	0.001

Equations for SRP and TP using regression coefficients for standardized variables take the general form:

$$SRP \text{ or } TP = a_1[Ca^{2+}] + a_2[\text{Alkalinity}] + a_3[\text{Time}] + \text{Constant.}$$

The phosphorus released was measured from 1 L solutions containing 0.1 g fertilizer granules giving units of mg/0.1 g fertilizer.

The equations derived are as follows:

$$\text{SRP (mg/0.1 g fertilizer)} = -0.022[Ca^{2+} \text{ (mg/L as } CaCO_3)] - 0.016[\text{Alkalinity (mg/L } CaCO_3)] + 0.008[\text{Time (hours)}] + 9.111 \quad [4\text{-}2]$$

where $r^2 = 0.809$, standard error = 0.941; and

$$\text{TP (mg/0.1 g fertilizer)} = -0.012[Ca^{2+} \text{ (mg/L as } CaCO_3)] - 0.003[\text{Alkalinity (mg/L } CaCO_3)] + 0.009[\text{Time (hours)}] - 1.037[\text{pH (units)}] + 17.139 \quad [4\text{-}3]$$

where $r^2 = 0.725$, standard error = 0.780.

These equations give cumulative SRP and TP levels released over the exposure time of the fertilizer pellets to the water.

4.2.2.1.6 Graphs of Phosphorus Release

Soluble reactive phosphorus and total phosphorus released for the various water types over the two week period was calculated as a percent based on a fertilizer content of 17.464 % phosphate by weight (I.M.C. Vigoro Inc.). Examples of SRP and TP levels in varying water conditions are shown in Figures 4.2 a - d, with more figures in Appendix IV.

4.2.2.1.7 Phosphorus Release Rates

Calculation of the slopes from the first two experiments with the deletion of the (0, 0) point gave an indication of the phosphorus release rate under varying water chemistry conditions. Table 4.9 a & b gives the release rates in decreasing order for each of the water chemistry conditions. Bottle # 2-6 was a blank and contained no fertilizer, and bottle # 2-12 contained humic water as a test for the next experiment.

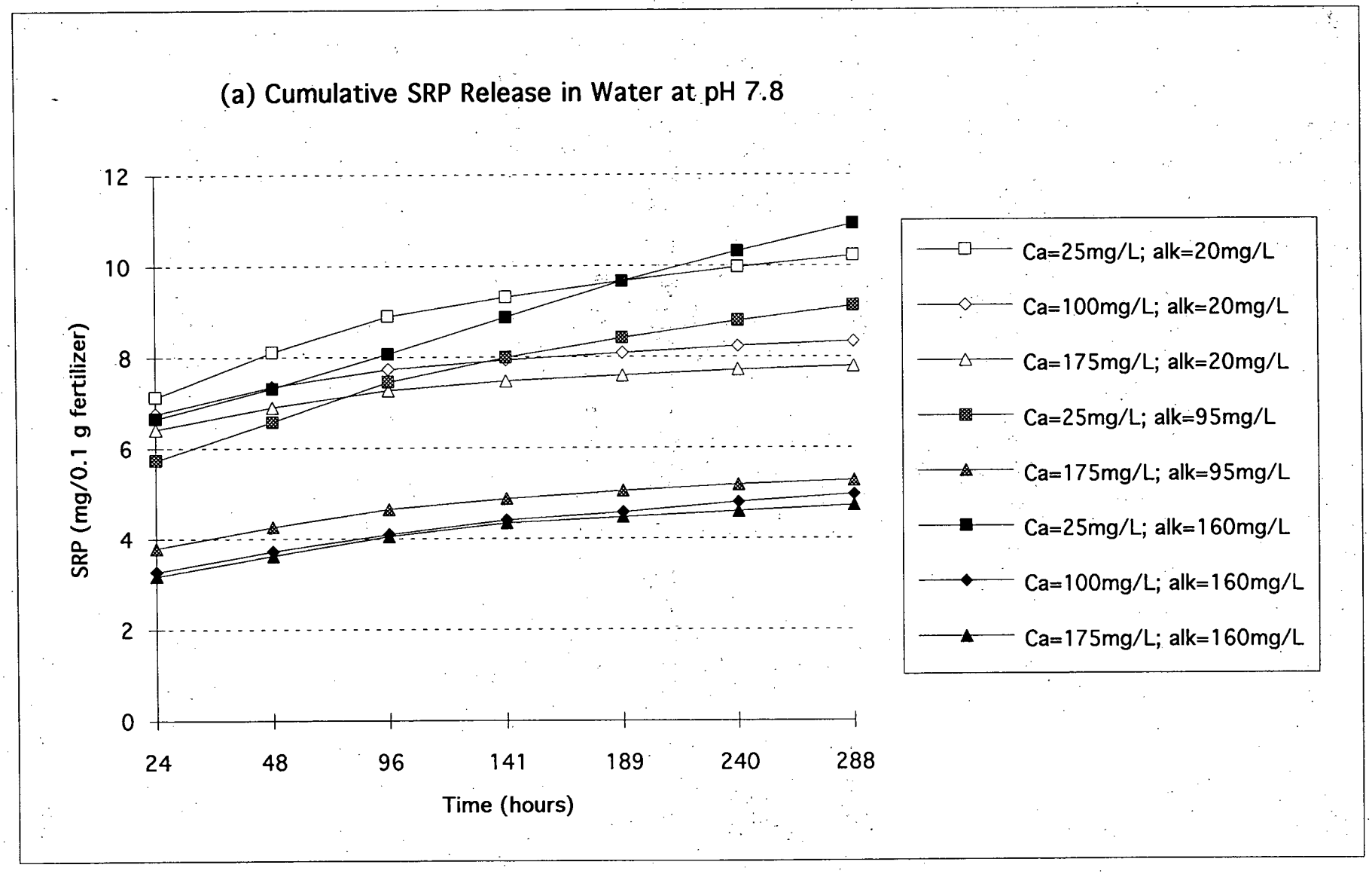
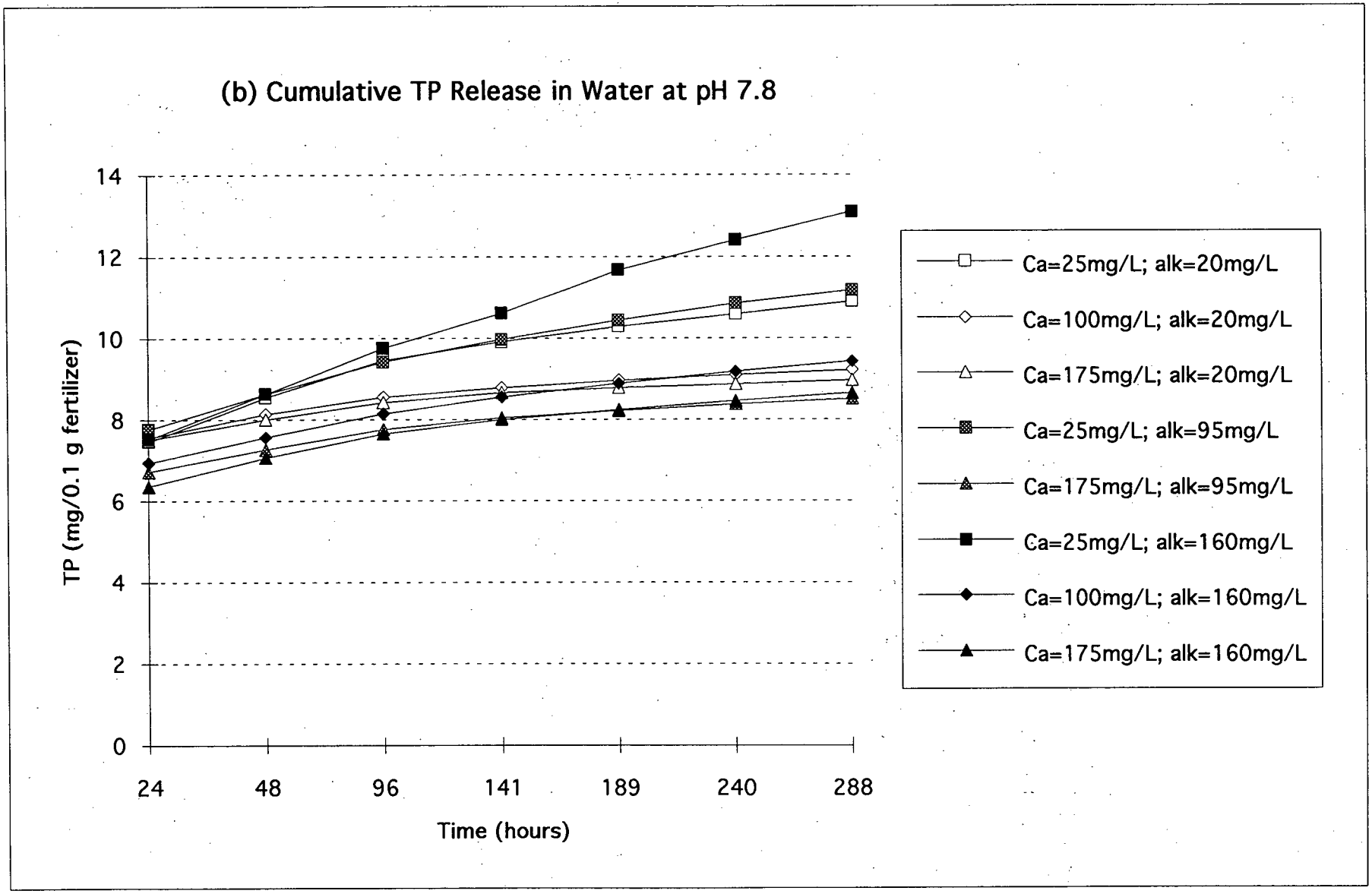
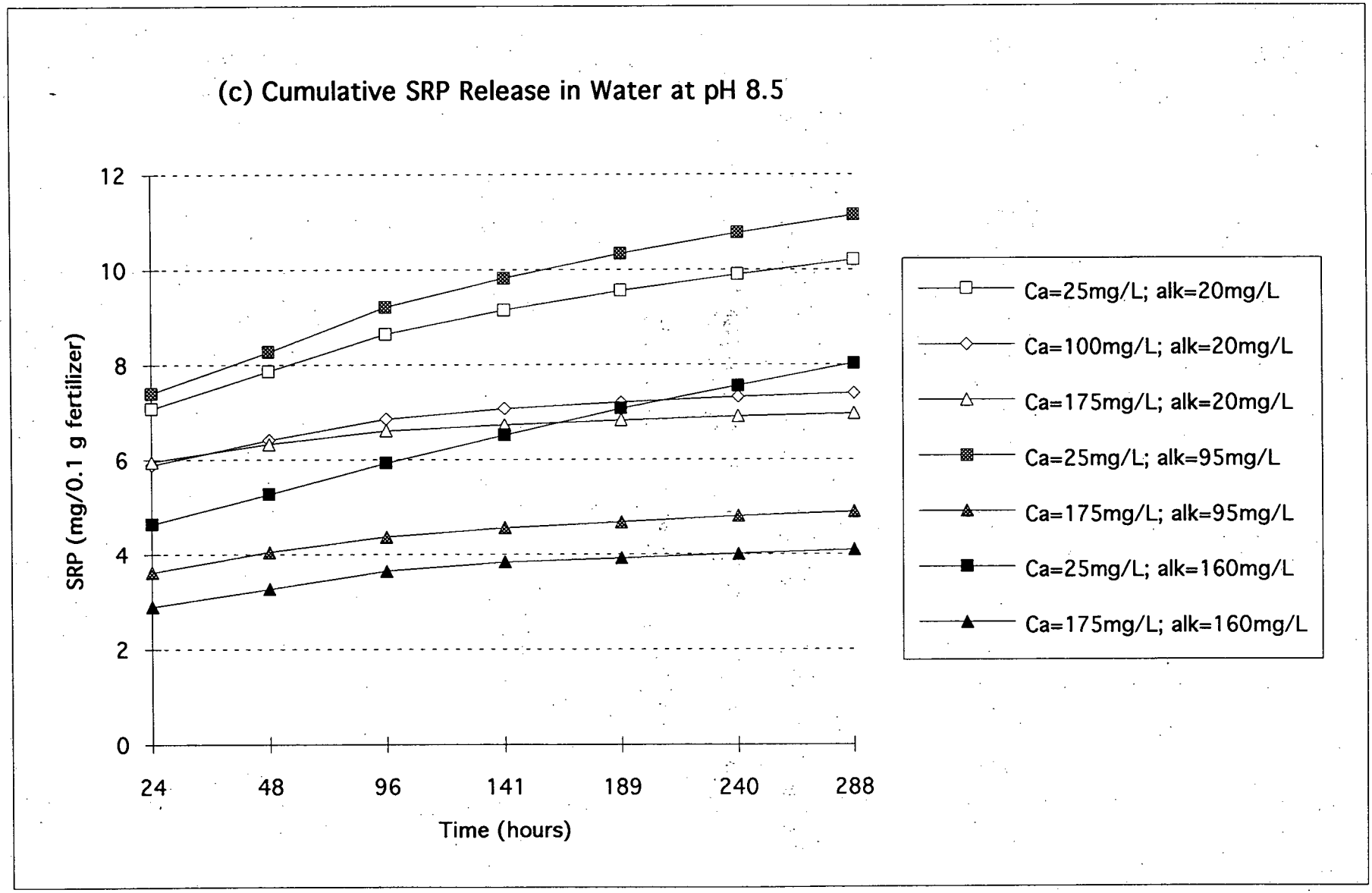


Figure 4.2 Cumulative phosphorus releases from 0.1 g fertilizer bundles: (a) SRP in water of pH 7.8, (b) TP in water of pH 7.8, (c) SRP in water of pH 8.5, and (d) TP in water of pH 8.5.


(b) Cumulative TP Release in Water at pH 7.8
TP (mg/0.1 g fertilizer)
0
2
4
6
8
10
12
14
24
48
96
141
189
240
288
Time (hours)
Ca=25mg/L; alk=20mg/L
Ca=100mg/L; alk=20mg/L
Ca=175mg/L; alk=20mg/L
Ca=25mg/L; alk=95mg/L
Ca=175mg/L; alk=95mg/L
Ca=25mg/L; alk=160mg/L
Ca=100mg/L; alk=160mg/L
Ca=175mg/L; alk=160mg/L


(c) Cumulative SRP Release in Water at pH 8.5
SRP (mg/0.1 g fertilizer)
12
10
8
6
4
2
0
24
48
96
141
189
240
288
Time (hours)
Ca=25mg/L; alk=20mg/L
Ca=100mg/L; alk=20mg/L
Ca=175mg/L; alk=20mg/L
Ca=25mg/L; alk=95mg/L
Ca=175mg/L; alk=95mg/L
Ca=25mg/L; alk=160mg/L
Ca=175mg/L; alk=160mg/L

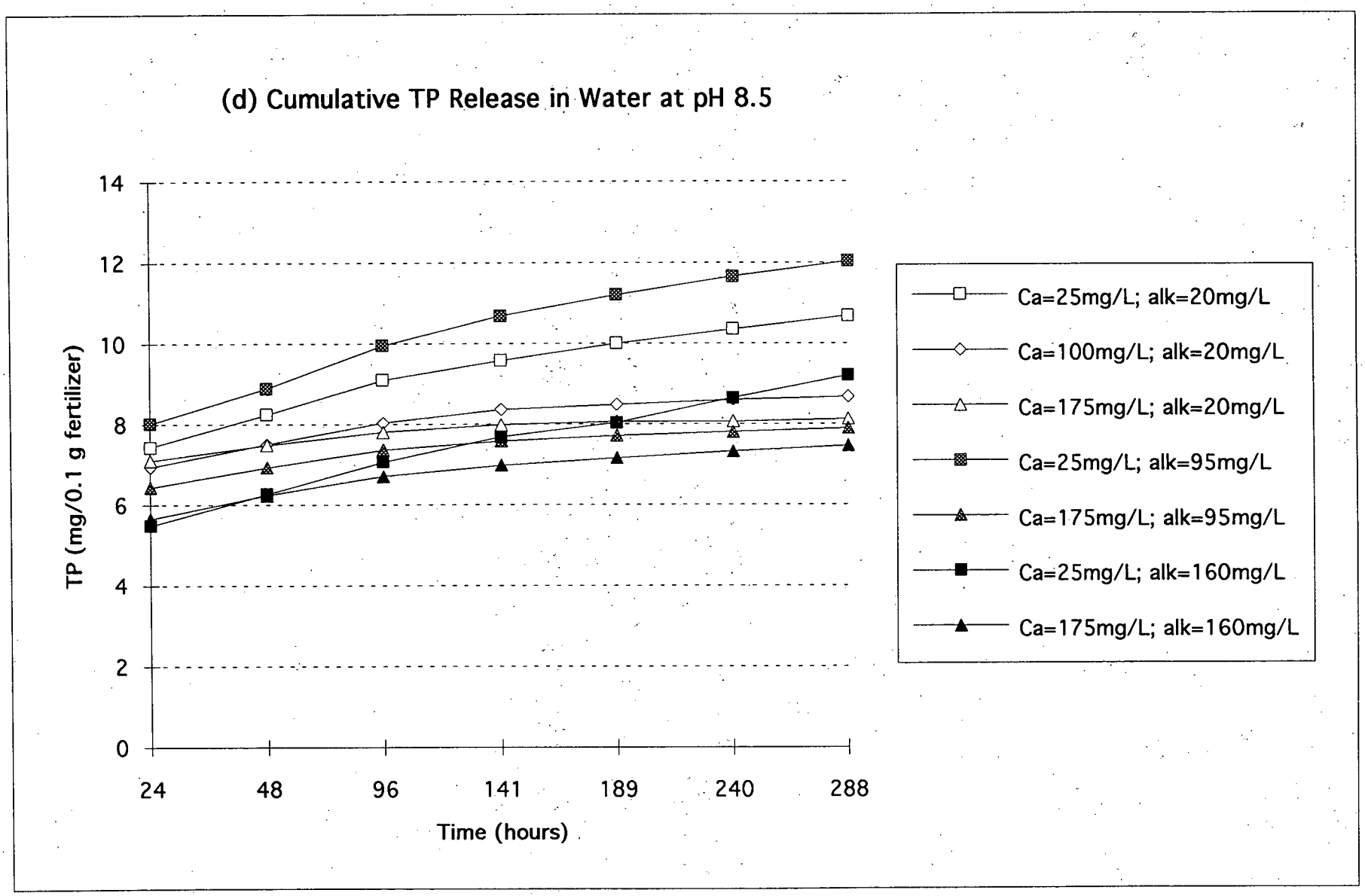

(d) Cumulative TP Release in Water at pH 8.5
TP (mg/0.1 g fertilizer)
0
2
4
6
8
10
12
14
24
48
96
141
189
240
288
Time (hours)
Ca=25mg/L; alk=20mg/L
Ca=100mg/L; alk=20mg/L
Ca=175mg/L; alk=20mg/L
Ca=25mg/L; alk=95mg/L
Ca=175mg/L; alk=95mg/L
Ca=25mg/L; alk=160mg/L
Ca=175mg/L; alk=160mg/L

Table 4.9 (a) Linear regression of SRP release from fertilizer bundles.

Bottle #'s	pH (units)	Ca^{2+} (mg/L as $CaCO_3$)	alkalinity (mg/L as $CaCO_3$)	slope (mg/0.1 g·hr)	r^2
1-1&2	7.8	25	160	0.016	0.99
2-12	7.6	-	115	0.014	0.98
2-10	8.5	25	95	0.014	0.95
2-4	7.8	25	95	0.012	0.94
1-7&8	8.5	25	160	0.012	0.99
2-7	8.5	25	20	0.011	0.94
2-1	7.8	25	20	0.011	0.90
1-3&4	7.8	100	160	0.0060	0.94
1-5&6	7.8	175	160	0.0055	0.89
2-2	7.8	100	20	0.0053	0.86
2-5	7.8	175	95	0.0052	0.89
2-8	8.5	100	20	0.0051	0.84
2-3	7.8	175	20	0.0047	0.86
2-11	8.5	175	95	0.0044	0.88
1-9&10	8.5	175	160	0.0041	0.85
2-9	8.5	175	20	0.0034	0.84

Table 4.9 (b) Linear regression of TP release from fertilizer bundles.

Bottle #'s	pH (units)	Ca^{2+} (mg/L as $CaCO_3$)	alkalinity (mg/L as $CaCO_3$)	slope (mg/0.1 g·hr)	r^2
1-1&2	7.8	25	160	0.022	0.97
2-12	7.6	-	115	0.016	0.98
2-10	8.5	25	95	0.015	0.95
1-7&8	8.5	25	160	0.013	0.97
2-4	7.8	25	95	0.012	0.95
2-1	7.8	25	20	0.012	0.89
2-7	8.5	25	20	0.012	0.94
1-3&4	7.8	100	160	0.0089	0.95
1-5&6	7.8	175	160	0.0080	0.90
2-5	7.8	175	95	0.0062	0.89
1-9&10	8.5	175	160	0.0062	0.88
2-8	8.5	100	20	0.0061	0.84
2-2	7.8	100	20	0.0056	0.87
2-11	8.5	175	95	0.0050	0.85
2-3	7.8	175	20	0.0050	0.84
2-9	8.5	175	20	0.0034	0.78

The high r^2 values indicate that the phosphorus release rates from the fertilizer were approximately linear for time > 24 hours. This long-term analysis of release rate is of interest because of the nature of the slow-release fertilizer. Higher release rates and initial concentrations of phosphorus released from the pellets were found for TP rather than SRP, which were expected because of precipitation and complexation of orthophosphate molecules.

Release rates of TP and SRP over the two week experiment varied from 0.0034 - 0.022 mg/0.1 g·hr. The lowest rate achieved for both TP and SRP was in bottle # 2-9 and resulted from the low amount of phosphorus released due to chemical inhibition, complexation, or precipitation. This gave rise to the early plateau for the solution Ca^{2+} = 175 mg/L as $CaCO_3$ and alkalinity = 20 mg/L as $CaCO_3$ in Figures 4.2 b & d.

Comparisons of the average release rates from the third experiment (to determine standard deviations) to the release rates in water of the same chemistry from the first two experiments are shown in Table 4.10.

Table 4.10 Comparison of average SRP and TP release rates (Tables 4.9 a & b) with results from Table 4.5.

Bottle #'s	Table	SRP or TP	pH (units)	Ca^{2+} (mg/L as $CaCO_3$)	alkalinity (mg/L as $CaCO_3$)	Slope (mg P/0.1 g·hr)
3-1 to 3-5	4.5	SRP	7.8	25	20	0.010
2-1	4.9 a	"	"	"	"	0.011
3-7 to 3-11	4.5	"	8.5	175	160	0.0035
1-9&10	4.9 a	"	"	"	"	0.0041
3-1 to 3-5	4.5	TP	7.8	25	20	0.011
2-1	4.9 b	"	"	"	"	0.012
3-7 to 3-11	4.5	"	8.5	175	160	0.0052
1-9&10	4.9 b	"	"	"	"	0.0062

4.2.2.1.8 Percent of Phosphorus Present as Orthophosphate

Calculation of SRP divided by TP was done to give an indication of the amount of phosphorus that existed in the water as orthophosphate under varying water chemistry conditions. It also determined the cause for lower phosphorus values: whether orthophosphate was complexed in solution or dissolution of the fertilizer was inhibited. Table 4.11 gives the SRP / TP percent in increasing order of calcium concentration, since calcium was the major predictor for phosphorus availability.

Table 4.11 Orthophosphate as a fraction of total phosphorus, in solution after 2 weeks.

Bottle #'s	pH (units)	Ca^{2+} (mg/L as $CaCO_3$)	alkalinity (mg/L as $CaCO_3$)	(SRP / TP) x 100
2-1	7.8	25	20	95.6
2-7	8.5	25	20	93.9
2-10	8.5	25	95	92.7
1-7&8	8.5	25	160	87.3
1-1&2	7.8	25	160	83.3
2-4	7.8	25	95	81.7
2-2	7.8	100	20	85.3
2-8	8.5	100	20	62.1
1-3&4	7.8	100	160	52.8
2-5	7.8	175	95	90.6
2-11	8.5	175	95	87.1
2-9	8.5	175	20	85.8
2-3	7.8	175	20	62.1
1-9&10	8.5	175	160	54.9
1-5&6	7.8	175	160	54.7

The highest SRP released in terms of TP existed independent of pH levels, but was strongly influenced by $[Ca^{2+}]$ with a higher %SRP at lower Ca^{2+} levels. The effect of alkalinity was inconclusive, but trends for higher amounts of orthophosphate were evident in water of lower alkalinity. These results correlated with statistical results in Table 4.6. The difference between $[Ca^{2+}]$ of 100 and 175 mg/L as $CaCO_3$ on %SRP was negligible. A limiting $[Ca^{2+}]$ value existed above 100 mg/L as $CaCO_3$ which impeded the release or solubility of orthophosphate.

4.2.2.2 Discussion

The fact that the fertilizer pellet release rates were very reproducible ensures the desired amount of nutrients will be released when a calculated amount of fertilizer is added to a provincial stream. Once the water chemistry of the stream is known, the desired nutrient addition should be easy to calculate from equations [4-2] and [4-3].

4.2.2.2.1 Alkalinity and pH Change

The change in water pH due to fertilizer addition, also found by Pons (1994), was of little concern since the concentrations of fertilizer used were significantly higher than those that are

used in field testing (mg vs. μg). The actual change of pH in field conditions is likely to be negligible but more thorough research in this area would be useful. The direction of pH change was directly related to alkalinity levels and inversely related to pH and calcium levels with minimal dependence on the amount of time the fertilizer remained in solution. Minimum pH change, or maximum buffering, is achieved when the pH of the water is close to the pK of the carbonate (i.e. alkalinity) system.

Alkalinity and pH levels had smaller effects than calcium on phosphorus availability in all three experiments but were not consistent for both TP and SRP. Pons (1994) also could not draw a conclusion for pH and alkalinity effects on phosphorus because of large standard deviations in data. These findings indicated that the initial pH of the water solutions do not affect phosphorus availability, and there were no interactive effects between the variables (from statistical analyses). However, pH does play an indirect role by influencing the abundance of potential phosphorus-complexing molecules (e.g. apatite, calcium carbonate and clays) through a shifting of the equilibruim.

Elevation of pH in water containing typical calcium concentrations increases apatite formation (Figure 2.5); further elevation (> pH 9.5) leads to formation of calcium carbonate which coprecipitates phosphate (Wetzel, 1975). Lowering of pH (around 5 to 6) favours high phosphate adsorption by clays, whereby phosphate anions are bonded to the positively charged edges of the clays, substituting silicate in the clay structure (Wetzel, 1975).

4.2.2.2.2 Ammonia Release

Ammonia release, measured as 64 % over the two week period, was in the same range as phosphorus release. Thus the even release of nutrients from the newly developed binder Daratak® XB-3631 was verified. Pons (1994) found similar results for ammonia release using the same water chemistry and fertilizer type: 62 % and 65 % of the nitrogen was released from the pellets over 2 weeks in water of pH 7.8, alkalinity = 160 mg/L as $CaCO_3$ and temperature = 11 °C.

4.2.2.2.3 Calcium, Alkalinity and pH Effects

The statistical analysis with the variables calcium, alkalinity and pH entered revealed that calcium had the largest effect on phosphorus availability. Calculations of SRP as a fraction of TP (Table 4.11) suggested that there was a saturation concentration of calcium which caused precipitation of phosphorus. For the purpose of the developed regression equations, the effect of calcium on phosphorus availability was assumed to be linear over the concentrations examined.

Table 4.11 also revealed that SRP (< 62.1 % of TP) was complexed at higher calcium and alkalinity levels, and that the release of phosphorus from the pellets was also inhibited (TP ≅ 4-7 mg/L) at these levels (Table 4.1). Therefore both the complexation of orthophosphate and inhibition of fertilizer dissolution are mechanisms which will influence phosphorus availability in natural streams and rivers under certain water quality conditions.

4.2.2.2.4 Calcium Complexes

Calcium hydroxyapatite, vs. other compounds in Tables 2.2 and 2.3, was regarded as the compound causing the largest removal of phosphate in typical natural water conditions based on its stability (pK_{sp} = 56; Snoeyink and Jenkins, 1980). Limiting pH to 7.8, calcium to 175 mg/L as $CaCO_3$, alkalinity to 160 mg/L as $CaCO_3$, and taking into account ionic strengths (using the extended Debye-Hückel relationship for solutions whose ionic strengths do not exceed 0.1 M) the equilibrium solubility of calcium and phosphate at 11 °C in the presence of calcium hydroxyapatite was calculated to be 0.0396 mg/L as $CaCO_3$ and 0.0470 mg/L respectively. These concentrations are much lower than those in the experimental solutions suggesting, as expected, that there are factors other than calcium hydroxyapatite which may cause the 'threshold' concentration of calcium described above.

Wetzel (1975) stated that in a solution system without other compounds, a calcium concentration of 40 mg/L (100 mg/L as $CaCO_3$; moderately soft water) at a pH of 7 limits the solubility of phosphate to about 10 μg/L; a calcium level of 100 mg/L (250 mg/L as $CaCO_3$; hard water) lowers the maximum equilibrium concentration of phosphate to 1 μg/L. These values are

within range of the phosphate concentration calculated above verifying the large effect calcium has on the solubility of phosphorus in natural waters. However the regression equations, developed earlier for phosphorus availability, cannot be compared with values from Wetzel (1975). The equations were developed for phosphorus release from the pellets over time, and not just for phosphorus cycling in the water column.

4.2.3 Experiment on the Effects of Humic Material and Soluble Iron

4.2.3.1 Results

Solutions removed from the tumbler were analyzed for TP, SRP, iron and colour. The values for TP, SRP and iron over the two week experiment were summed to give cumulative values presented in Table 4.12. Values for pH, SRP and TP for each sampling event are listed in Appendix III. Alkalinity and pH remained constant at 5.85 units and 7.6 mg/L as $CaCO_3$ respectively which are both lower than the parameters set in the previous experiments, thus the results could not be compared. The previous parameters were set for naturally occurring stream water chemistry levels in B.C. and not natural bog water which is higher in colour and iron, poorly buffered, and tends to be slightly acidic (lower pH and alkalinity; Thurman, 1985). The temperature of the cold room remained at 11 °C for the duration of the experiment.

Since iron was added to the solutions the 'minimum' level of cumulative iron was also tabulated in the third column of Table 4.12. These iron values were expressed as a minimum to account for the small concentrations present below the detection level of 0.2 mg/L in the humic water. In bottles 1-3 the iron 'present' in solution came from the coloured bog water.

Table 4.12 Final cumulative values for phosphorus release and iron levels (cumulative amounts added to bottles and measured) in varying humic water concentrations (as colour).

Bottle #	Colour (units)	Minimum Fe^{3+} (mg/L)	Fe^{3+} Present (mg/L)	SRP (mg/L)	TP (mg/L)	SRP / TP x 100
1	200	0	1.2 (blank)	9.77	11.17	87.5
2	100	0	0.3 (blank)	10.48	11.33	92.5
3	50	0	0.3 (blank)	13.72	14.8	92.7
4	0	0	< 0.2	11.83	13.13	90.1
5	0	1.4	< 0.2	10.72	11.44	93.7
6	0	7.0	0.8	10.83	11.47	94.4
7	200	1.4	2.4	9.1	10.48	86.8
8	100	1.4	0.9	10.77	11.95	90.1
9	50	1.4	< 0.2	11.52	13	88.6
10	200	7.0	5.0	9.31	11.07	84.1
11	100	7.0	3.1	12.48	13.22	94.4
12	50	7.0	3.3	10.99	12.58	87.4

Values for iron added = (blank + Fe added) x 7 for additions of solution to the bottles. Iron added was either 0, 0.2 or 1.0 mg/L.

Dissolved organic carbon (DOC) was measured and remained at a level proportionate to the amount of colour or humic material in the solutions (Figure 4.3). These initial values were slightly higher than those measured in water exposed to fertilizer for two days (Table 4.13); DOC levels after two days exposure to fertilizer remained constant or increased slightly thereafter.

Table 4.13 Average dissolved organic carbon levels at the start of fertilizer introduction and after two days of exposure.

Colour (units)	Initial DOC (mg/L)	DOC after 2 days (mg/L)
200	24	18
100	12	9.0
50	7.0	6.5

The primary concern in evaluating phosphorus availability in the presence of humic material and iron was to determine if iron and humic material (colour) reduced the dissolution of phosphorus from the fertilizer or decreased the orthophosphate levels in solution. The cumulative TP and SRP values for this experiment (total bottles = 12) were analyzed using Systat's stepwise linear regression model (N = 84). Order of entry by the variables into the stepwise analysis (Table 4.14) indicates their relative importance as predictors to the SRP and TP values.

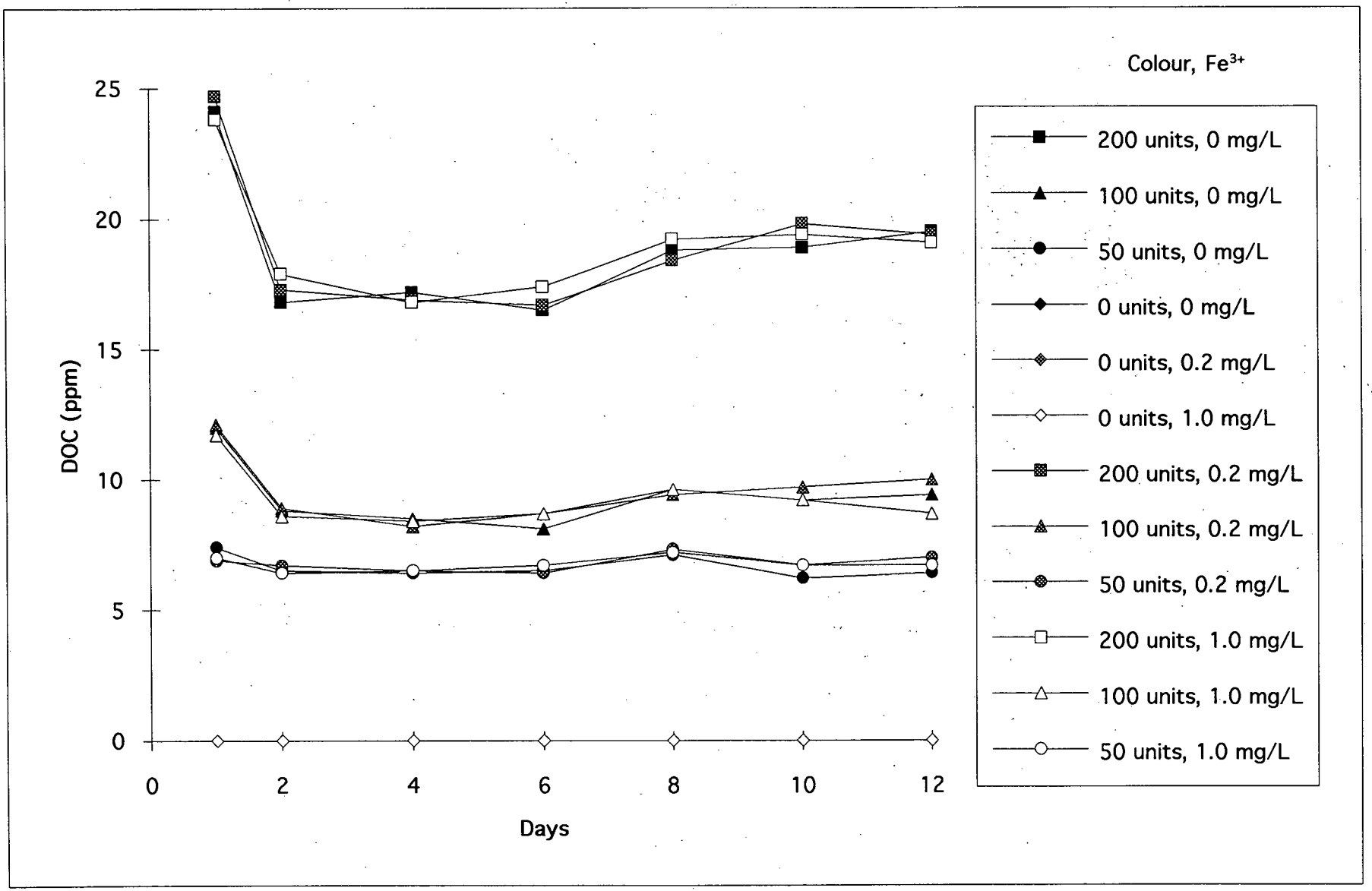


Figure 4.3 Dissolved organic carbon remaining in solutions containing colour (units) and iron (mg/L).

Table 4.14 Order of entry of time, colour and iron variables into stepwise regression for SRP and TP with initial F-to-enter values.

Order of Entry	SRP	SRP, F-to-enter	TP	TP, F-to-enter
1	Constant	-	Constant	-
2	Time	119.727	Time	191.263
3	Colour	15.126	Colour	6.953
4	Iron (not entered)	0.048	Iron (not entered)	0.006

The statistical analysis determined that iron was not a good predictor of SRP or TP release; time was the best predictor of SRP and TP release followed by colour. Higher colour levels resulted in less SRP and TP release, while longer time in solution resulted in more phosphorus release from the pellets.

As expected, there were no interactions found between colour and time variables (Table 4.15); they affected SRP and TP release independently.

Table 4.15 Correlation matrix of regression coefficients of the regression equations for both SRP and TP.

	Constant	Colour	Time
Constant	1.000		
Colour	- 0.528	1.000	
Time	- 0.722	- 0.000	1.000

Coefficients and their standard errors calculated in the regression are presented in Table 4.16.

Table 4.16 Regression results for SRP and TP.

Variable	SRP Coefficient	SRP Std. Error	TP Coefficient	TP Std. Error
Constant	7.947	0.204	8.393	0.203
Colour	- 0.009	0.001	- 0.007	0.001
Time	0.014	0.001	0.016	0.001

Equations for cumulative SRP and TP values using regression coefficients for standardized variables are as follows, with a plot of phosphorus release vs. colour in Figure 4.4:

SRP (mg/0.1 g fertilizer) = - 0.009[Colour (units)] + 0.014[Time (hours)] + 7.947 [4-4]

where $r^2 = 0.749$, standard error = 0.835; and

TP (mg/0.1 g fertilizer) = - 0.007[Colour (units)] + 0.016[Time (hours)] + 8.393 [4-5]

where $r^2 = 0.778$, standard error = 0.830.

The release rates for any day can be determined by dividing the above equations by time:

SRP release rate = - 0.009[Colour] / [Time] + 0.014 + 7.947 / [Time]; and [4-6]

TP release rate = - 0.007[Colour] / [Time] + 0.016 + 8.393 / [Time]. [4-7]

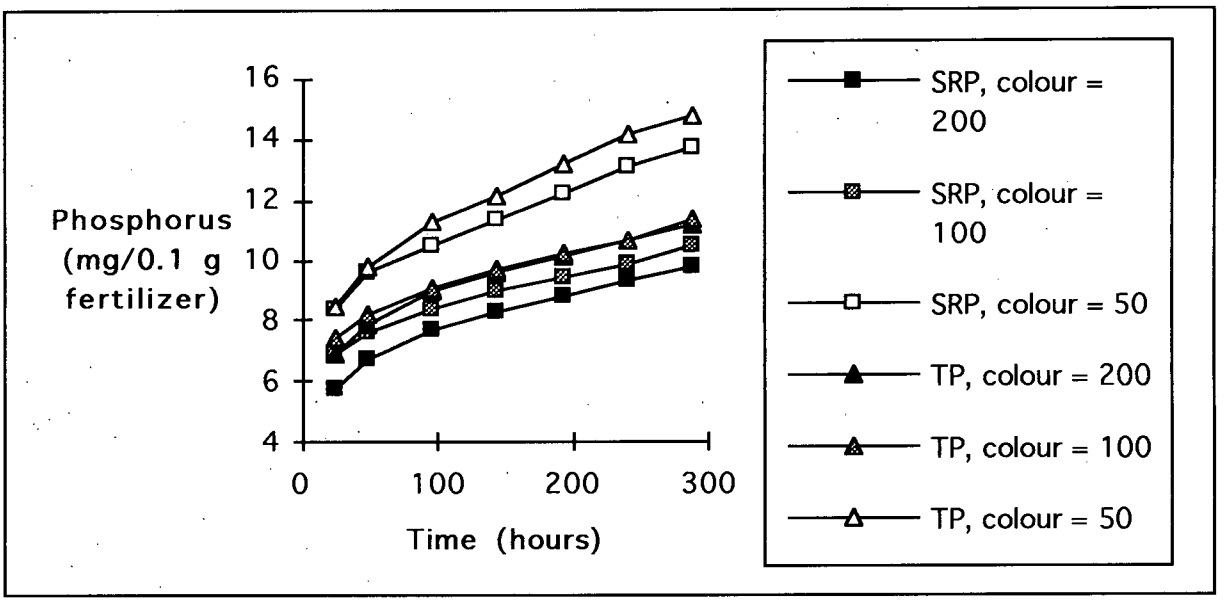


Figure 4.4 Phosphorus release vs. colour for SRP and TP.

4.2.3.2 Discussion

4.2.3.2.1 Humic Material Effects

For this experiment, statistical analysis of the iron and humic material variables revealed that humic material had the largest effect on phosphorus availability. As in the previous experiments, phosphorus levels appeared to reach a 'threshold' in the presence of humic material (50 - 100 colour units), above which the availability of phosphorus changed minimally (Figure 4.4). This level could not be calculated due to the unknown and varied nature of the humic material. However, the regression equations developed for coloured water having water chemistry

within experimental ranges allow for easy calculation of cumulative phosphorus levels, or phosphorus release rates. The effect of humic material on phosphorus availability was assumed to be linear over the concentrations examined. These calculations are only possible if the duration of fertilizer application and water colour levels are known.

Table 4.12 also revealed that SRP / TP did not change with higher iron and humic material levels, indicating that the limiting factor for phosphorus availability in humic water was dissolution of the pellets and not complexation of SRP. Therefore the humic material would have bound to orthophosphate molecules in the fertilizer and effectively 'coated' the pellets.

4.2.3.2.2 Iron

Surprisingly iron did not affect phosphorus release from the pellets, but opportunity for removal from solution existed in the experiments. Iron removal without the influence of humic material was evident in bottles 5 and 6 (Table 4.12); Fe^{3+} was removed but SRP and TP were not significantly affected. Potential sources of removal include:

(1) adsorption to the sides of the Nalgene containers during the experiment (they were acid washed after each water change which removed adsorbed iron and provided more binding 'sites');

(2) adsorption to fertilizer granules and Nitex mesh (colour change apparent at end of two week experiment);

(3) precipitation as iron hydroxides; and

(4) complexation with humic material.

Gerke and Hermann (1992) found that the main difference between P-adsorption by humic-Fe-surfaces and by amorphous Fe-oxide was the approximate tenfold higher adsorption capacity of the humic-Fe-surfaces.

The interaction between humic substances and iron involves the weakly acidic carboxylic and phenolic functional groups contained within the humic substances resulting in stability

constants that change proportional to pH and inversely proportional to ionic strength (Schnitzer and Khan, 1972).

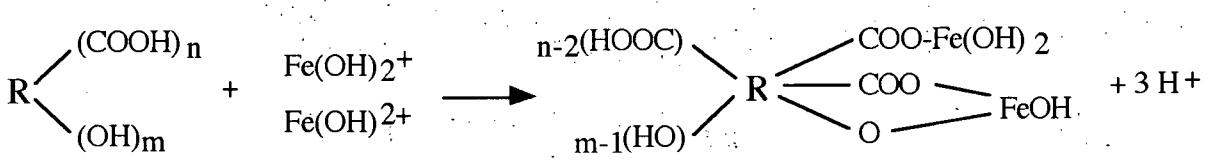


Figure 4.5 Interaction of humic acid and iron hydroxides (adapted from Schnitzer and Khan, 1972). Iron is bound as $Fe(OH)_2^+$ in the pH range of 3-8 units.

These iron-humic material complexes are then able to bind phosphate, shown in Figure 2.6. Schnitzer and Khan (1972) also found that in the absence of Fe^{3+} (and Al^{3+}), fulvic acid (a small humic acid molecule) did not react with phosphate. This observation demonstrated an interaction between humic material and phosphate, with the presence of iron enhancing the bonding of phosphate. Therefore, the presence of iron could be indirectly related to phosphate removal by humic materials.

Steinberg and Baltes (1984) recognized that in conditions of low pH, orthophosphate associates with humic material in the presence of iron (Figure 2.6) making it inaccessible to algae, yet providing a pool of potentially available dissolved organic orthophosphate (Jones et al., 1993).

4.2.3.2.3 pH

Future experiments should more specifically investigate pH levels: the pH and/or ionic composition of humic waters may affect the speciation and cycling of iron and phosphate (Jones et al., 1993), and displacement of hydrogen ions from the ligand occurs during the formation of a metal chelate or complex (Figure 4.5).

4.2.3.2.4 Dissolved Organic Carbon

The dissolved organic carbon values in the various levels of coloured water were replicates since DOC is not present in iron. DOC levels decreased initially due to complexation with the fertilizer pellets and then retained a fairly constant level (Figure 4.3). Mouldey & Ashley (1996) determined that the pellets dissolved at a slower rate after the first couple of weeks than when originally placed in water. The slight increase in DOC levels after the first week is consistent with their findings since less fertilizer compound would be available for complexation with DOC.

4.3 Fertilizer Solubility Tests with Varying Water Temperature and Flow Conditions

4.3.1 Introduction

To achieve the desired amounts of nutrients in streams requires a fertilizer which releases at a predictable rate. The dissolution rate of the fertilizer pellets plays a vital role in determining the loading rate of the fertilizer and when it should be applied to the streams. Three factors that could affect the dissolution rate of the fertilizer pellets are temperature, stream velocity, and size of the pellets (surface area to weight ratio). The even simultaneous dissolution of the nitrogen and phosphorus nutrients had been verified by Mouldey and Ashley (1996), and in section 4.2.2.1.3. A convenient application rate would be once yearly in springtime. The ideal lifespan of the pellets would be between three and six months, depending on the specific nutrient requirements of the streams.

The three factors, water temperature (8, 10, 14.5 °C), velocity (0.03, 0.15, 0.30 m/s) and pellet size (2, 6, 9 g), were compared in the following experiment to see which had the largest effect on the dissolution of the fertilizer pellets. The rate of dissolution was determined by comparing the initial and final dry weights of the pellets.

4.3.2 Results

The water quality at the Abbotsford Hatchery was in the range of the water chemistry used in the laboratory jar tests (see Methodology, Table 3.2). Any changes in the dissolution rates of the pellets due to water chemistry were assumed to be equal for all runs.

Weight lost from the fertilizer pellets (as a ratio of initial weight) was analyzed using Systat's stepwise linear regression model (N = 390). The order of entry by the variables into the statistical linear regression analysis with their initial F-to-enter values were: time (1100), velocity (12.167), size (6.491) and temperature (0.769). Order of entry indicated the variables' relative importance as predictors to the weight loss of the fertilizer pellets.

Time of exposure had the largest effect on weight loss; the longer the pellets were left in the simulated stream conditions, the more they dissolved. Regression coefficients for the variables time (0.863), velocity (0.174), size (-0.128) and temperature (0.044) indicated that velocity, size and temperature had a very small effect on pellet weight loss for the range of values studied.

No interactions were found between any of the variables (Table 4.17).

Table 4.17 Correlation matrix (r^2) of regression coefficients of the regression equation for pellet weight loss.

	Constant	Time	Velocity	Size	Temperature
Constant	1.000				
Time	- 0.205	1.000			
Velocity	- 0.294	- 0.000	1.000		
Size	- 0.478	- 0.000	0.000	1.000	
Temperature	- 0.777	0.000	- 0.003	0.000	1.000

Coefficients and their standard error calculated in the regression are presented in Table 4.18.

Table 4.18 Regression results for pellet weight loss.

Variable	Coefficient	Standard Error
Constant	0.074	0.009
Time	0.002	< 0.001
Velocity	0.132	0.018
Size	- 0.004	0.008
Temperature	0.001	0.007

The equation for weight loss (ratio = weight lost / initial weight) using regression coefficients for standardized variables takes the general form:

$$\text{ratio} = a_1[\text{Time}] + a_2[\text{Velocity}] + a_3[\text{Size}] + a_4[\text{Temperature}] + \text{Constant}$$

The equation derived is as follows:

$$\text{ratio} = 0.002[\text{Time (days)}] + 0.132[\text{Velocity (m/s)}] - 0.004[\text{Size (g)}] + 0.001[\text{Temperature (°C)}] + 0.074 \quad [4\text{-}8]$$

where $r^2 = 0.793$, and standard error = 0.036.

Since size and temperature did not have a large effect in weight loss, the 9 g pellet size and 9.7 °C water temperature were chosen to demonstrate pellet weight loss exposed to varying water velocities (Figure 4.6). There was no difference between 0.15 and 0.30 m/s velocities, and the very slow flow of 0.03 m/s is not indicative of many streams. Therefore, weight loss of the fertilizer pellets in streams depends only on time, and indicates the pellets have a constant dissolution rate.

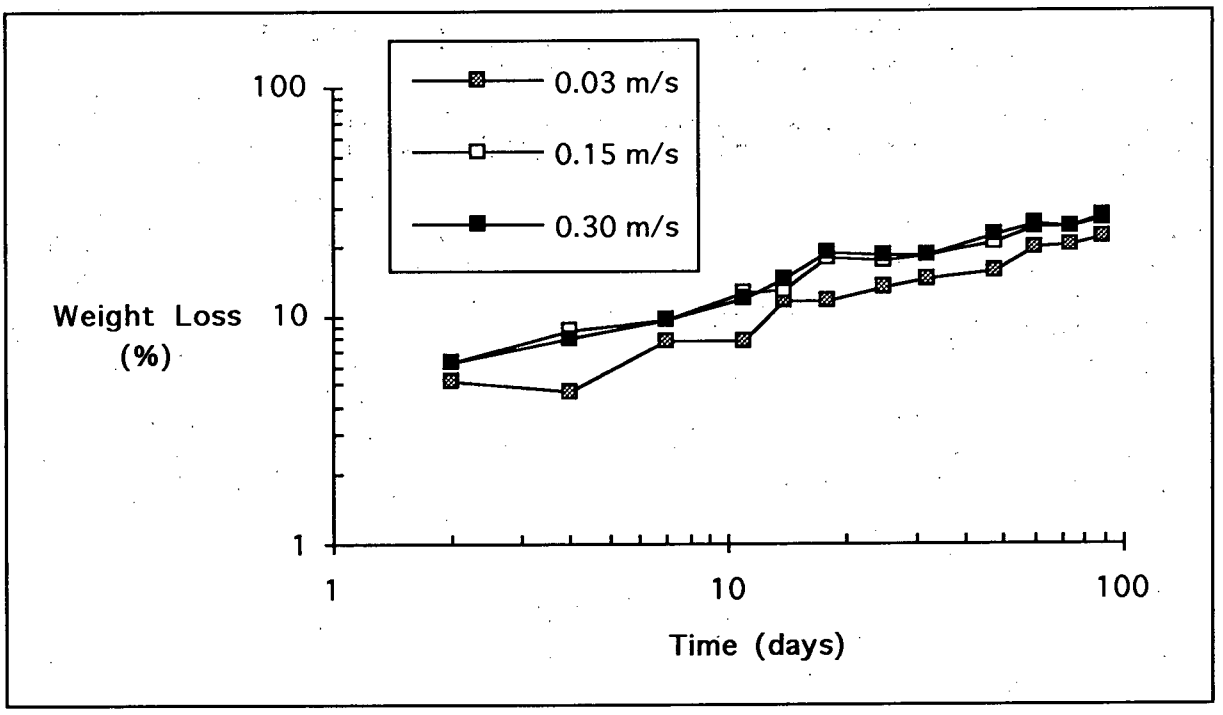


Figure 4.6 Log plot of average percent weight loss for 9 g pellet exposed to three velocities in 9.7 °C water over an 88-day period.

A linear regression of log average weight loss vs. log time for velocities 0.15 and 0.30 m/s gave r^2 values of 0.983 and 0.969 respectively. An average of regression coefficients for the two velocities resulted in the equation:

$$\log \% \text{ Weight lost} = 0.392 \, [\log \text{Time (days)}] + 0.688 \qquad [4\text{-}9]$$

and is true for velocities > 0.15 m/s.

4.3.3 Discussion

The results indicate that it is possible to have a reliable stream fertilizer application through the use of the slow release pellets. Maximum weight losses were measured due to the complete exposure of the pellets to flowing water. In field conditions, parts of the pellets are wedged between rocks and substrate which limits water flow over their surfaces. Whole pellets can be washed to slower flowing pools depending on the size of the pellet and the velocity of the stream, and some pellets may have algae and microbial growths on the surface depending on amount of sunlight exposure and water temperature (Section 3.3). All these field conditions would contribute to a slower release of nutrients from the fertilizer pellets compared to rates measured in this experiment.

The observation that temperature did not affect the pellet fertilizer's dissolution rates was supported by Dr. Bob Rehberg (I.M.C. Vigoro Inc.) and Pons (1994). I.M.C. Vigoro Inc. found that dissolution rates between 20 - 40 °C were not related to pellet dissolution due to the chemistry of the fertilizer (Rehberg, 1997, pers. comm.).

Dissolution of the fertilizer independent of stream temperature and velocity is important because in the spring and summer, when nutrients are needed, these stream conditions change significantly. Further experiments should include a wider temperature and velocity range present in B.C. streams during spring and summer months (6 - 25 °C; 0.1 - 2 m/s). Since temperature and velocity of the stream did not play a large role in fertilizer dissolution, the amount of slow release pellet fertilizer required for a stream is a function of nutrient concentration needed.

Size does not play a large factor in the dissolution rate of the pellets which allows for convenient calculations of amounts of fertilizer needed. One practical aspect is that size can be used to determine the length of time the stream is to be fertilized: the larger the pellets, the longer the residence time in the water. Theoretically, size was expected to affect the dissolution of the pellets since surface area is related to dissolution rate, however, the small range of sizes tested and available for practical application in streams ensures a minimal effect of pellet size on dissolution rate.

To achieve optimal fertilization, different pellets could be manufactured having different release rates (depending on binder type and its quantity in the pellets) and sizes, so the length of nutrient release could be customized for specific streams, based on the constant dissolution rate of the fertilizer pellets.

4.4 Periphyton Growth Tests with Various Amounts of Fertilizer Added

4.4.1 Introduction

A correct concentration of nutrients must be added to streams in order to avoid ineffective fertilization or undesirable algal growth. Upon nutrient addition, increases in algal abundance occurs as well as possible changes in species composition, depending on the amount of fertilizer added. These effects were determined in this last set of experiments through additions of various phosphorus concentrations in fertilizer pellets to outdoor troughs.

Four factors which affect periphyton growth rate include temperature, stream velocity, light levels and amount of fertilizer. Water temperature, velocity and light exposure were consistent for all periphyton blocks and troughs; temperature and light levels underwent natural seasonal fluctuations.

Verification of the optimal fertilizer concentration to be added and extent of species composition alteration in the streams was examined over approximately one month. Outdoor troughs exposed to five levels of fertilizer concentration and one blank (0, 0.5, 1.0, 1.5, 3.0 and

5.0 μg P/L) were used. The extent of periphyton growth was measured in terms of chlorophyll *a* content per unit area of styrofoam substrate during two experimental periods: May 23 - June 23 and June 26 - July 31, 1995.

4.4.2 Results

The water samples for nutrient chemistry were analyzed by Zenon Environmental Laboratories at upstream and downstream locations of fertilizer addition. The levels were all very close to the detection limits of the tests so no trends could be determined. Six sets of samples were taken from May - July 1995 and average upstream results were as follows: organic nitrogen, < 0.04 mg/L; total nitrogen, < 0.05 mg/L; NH_3, 0.005 mg/L; NO_2, < 0.001 mg/L; NO_3 + NO_2, < 0.005 mg/L; SRP, 0.004 mg/L; and TP, 0.007 mg/L. Water temperature averaged from 14 to 19 °C from May 23 to June 27, and 18 to 23 °C from June 27 to August 1, 1995 (Figures 4.7 a & b), and velocities remained constant at 0.15 m/s. Silt accumulated on the bottom of the troughs over the course of both experiments, but none was observed on the raised periphyton blocks.

4.4.2.1 Periphyton Biomass and Growth Rates

The linear and semi-log trends of chlorophyll *a* accrual in response to the various fertilizer amounts are shown in Figures 4.8 a & b and Figures 4.9 a & b. For both experiments the periphyton accumulation, measured as chlorophyll *a*, increased exponentially after the first week for all fertilizer treatments, followed by a period of slower increase. Figures 4.8 a and 4.9 a illustrate that periphyton accumulation was higher in the first experiment (May 23 - June 23) for the 3 μg P/L fertilizer addition than the other fertilizer levels over the first 27 days; then the growth rate for the 5.0 μg P/L fertilizer addition increased.

However, periphyton growth in mid-summer (June 26 - July 31) behaved differently from nutrient enrichment than earlier in the season (Figures 4.8 b and 4.9 b). Periphyton accrual was proportional to fertilizer added for the first 25 days, and then sloughing occurred after 28 days for 1.0, 3.0 and 5.0 μg/L phosphorus additions. The growth rates were generally slower for this experiment than the previous one.

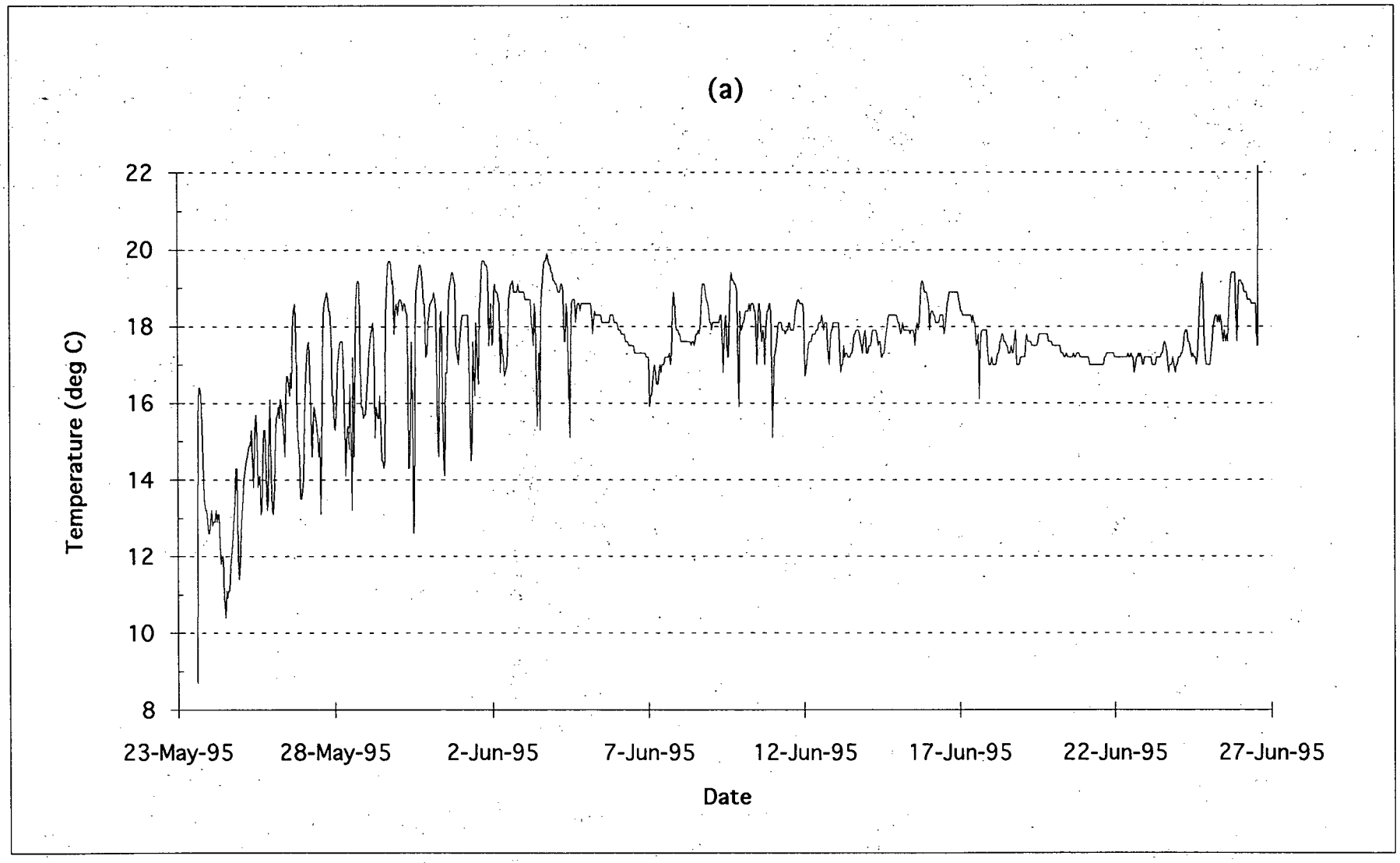
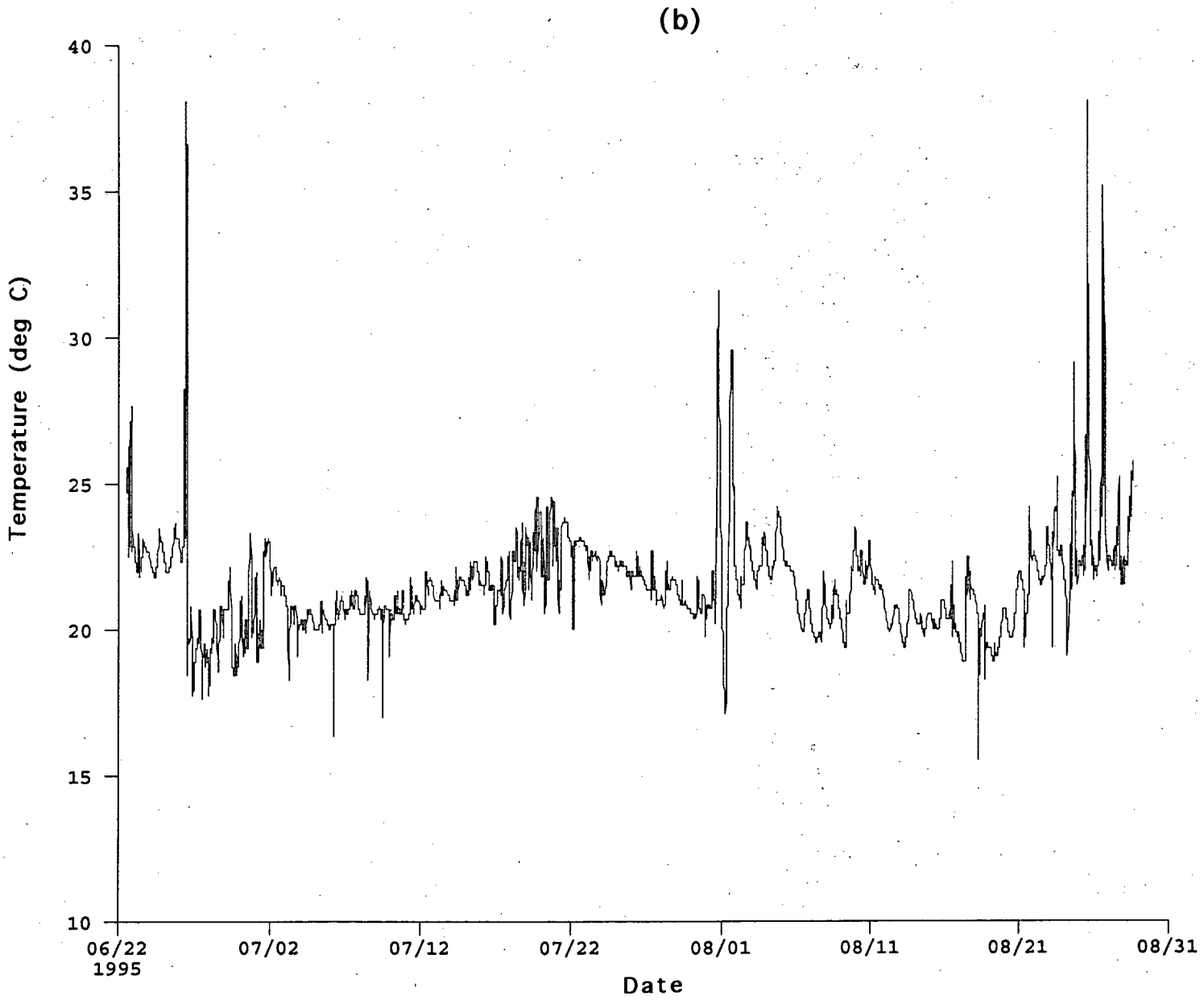


Figure 4.7 Temperature of water in troughs: (a) May 23 to June 27, 1995, and (b) June 22 to August 31, 1995. Completion of the second experiment and subsequent removal of the temperature probe from the water resulted in peaks at August 1.


(b)
Temperature (deg C)
40
35
30
25
20
15
10
06/22
1995
07/02
07/12
07/22
08/01
08/11
08/21
08/31
Date

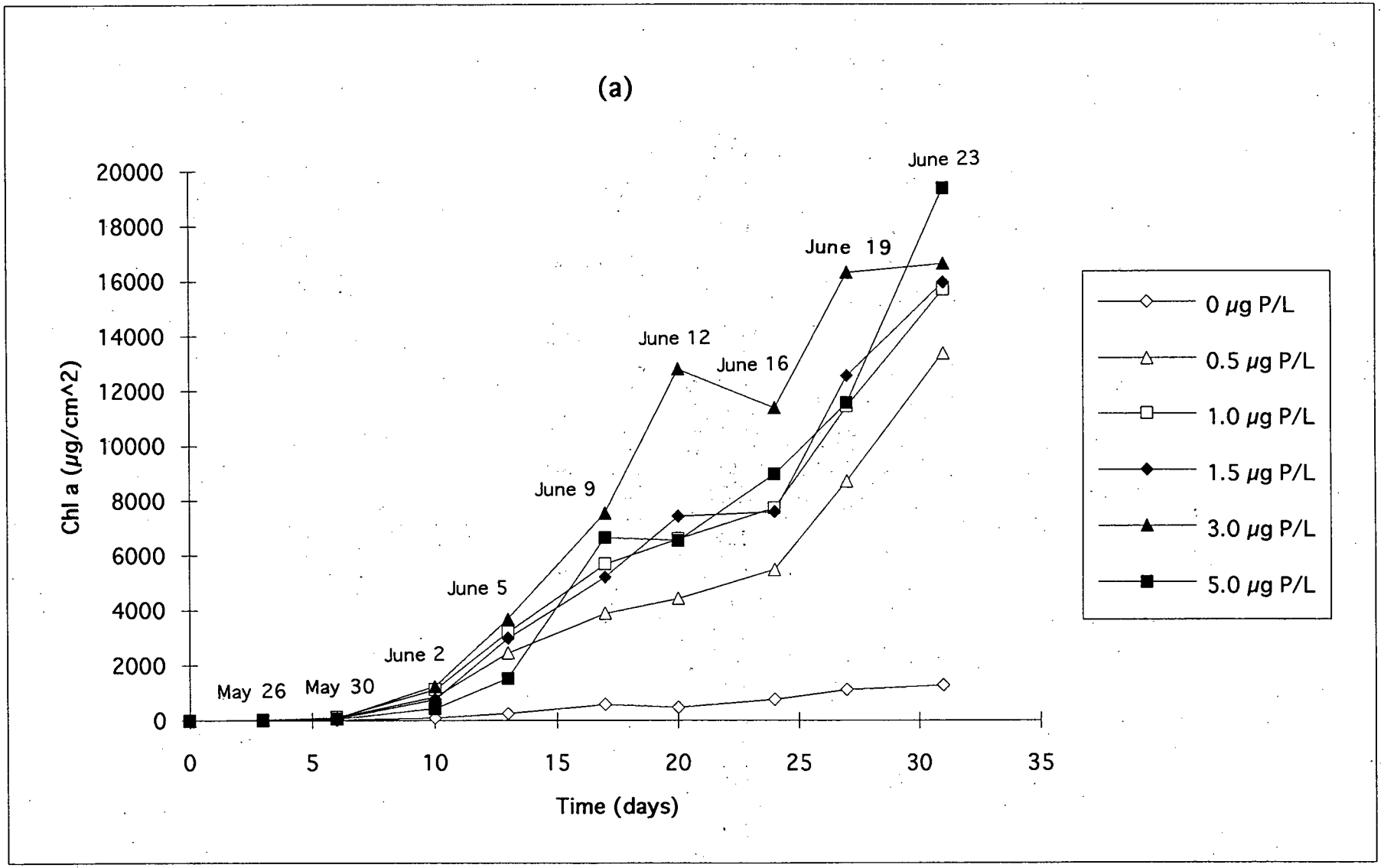
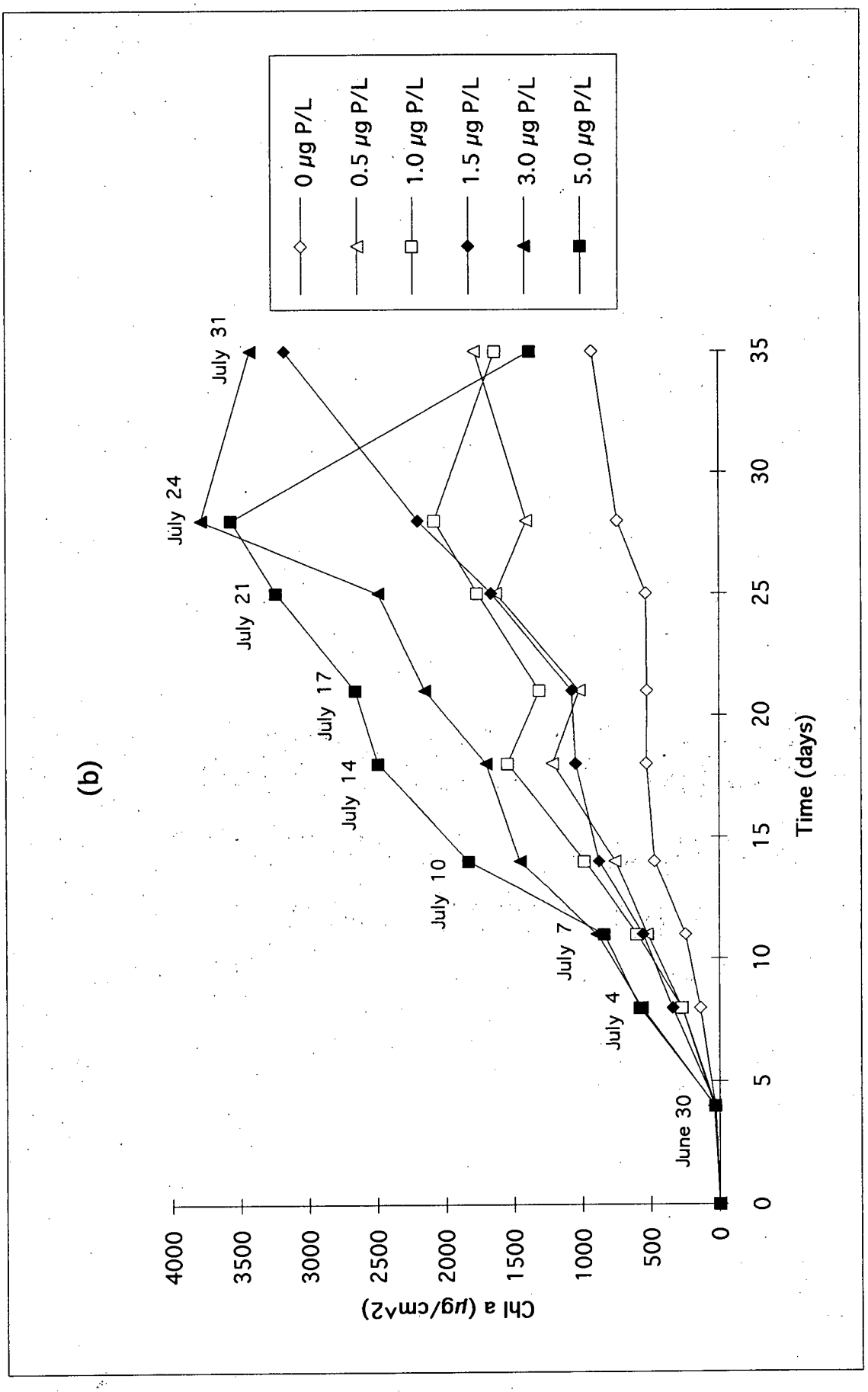


Figure 4.8 Chlorophyll a accumulation over time for various phosphorus concentrations in experiments (a) May 23 - June 23, 1995; and (b) June 26 - July 31, 1995.


(b)
0 µg P/L
0.5 µg P/L
1.0 µg P/L
1.5 µg P/L
3.0 µg P/L
5.0 µg P/L
July 31
July 24
July 21
July 17
July 14
July 10
July 7
July 4
June 30
Chl a (µg/cm^2)
Time (days)
0
500
1000
1500
2000
2500
3000
3500
4000
0
5
10
15
20
25
30
35

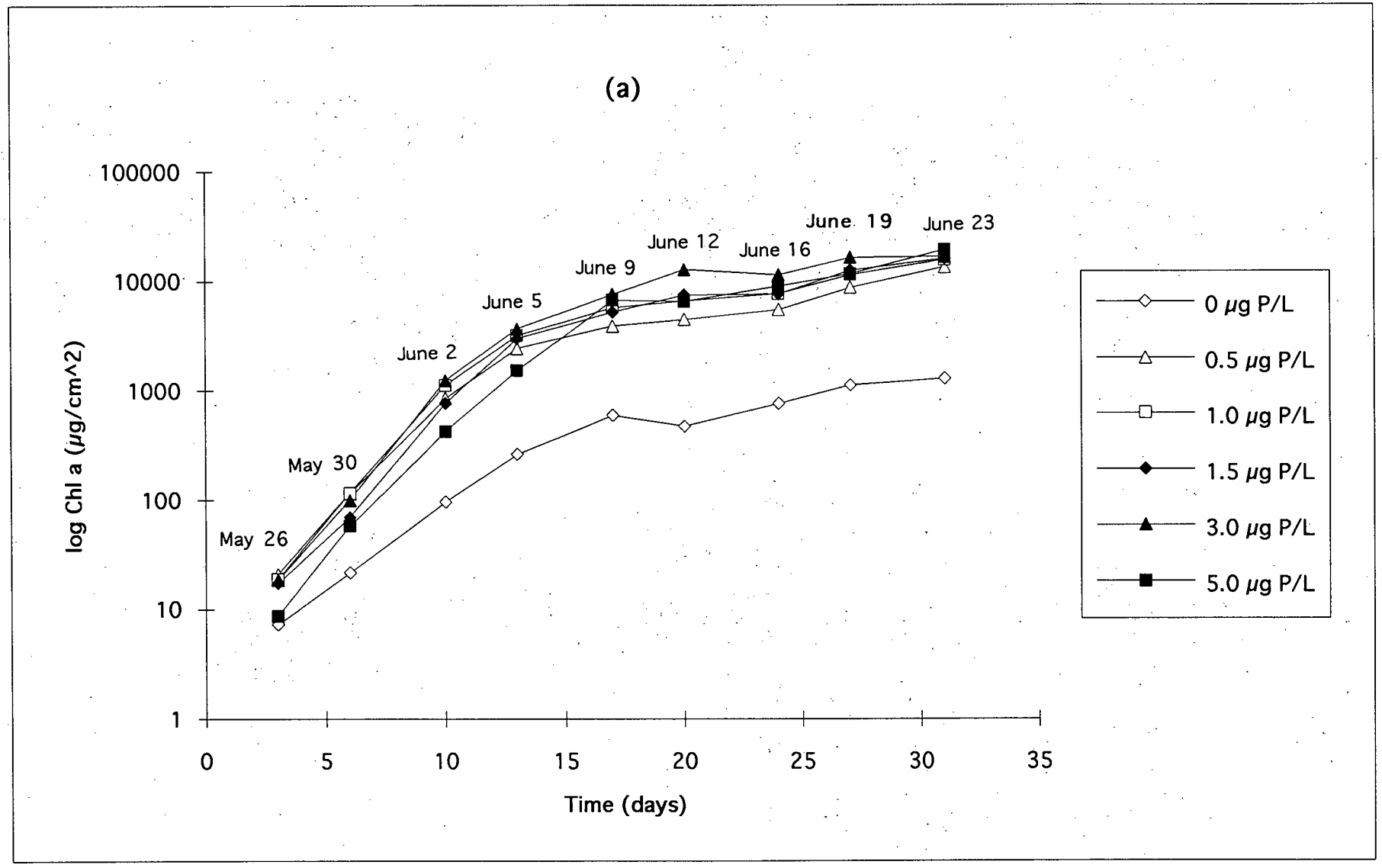
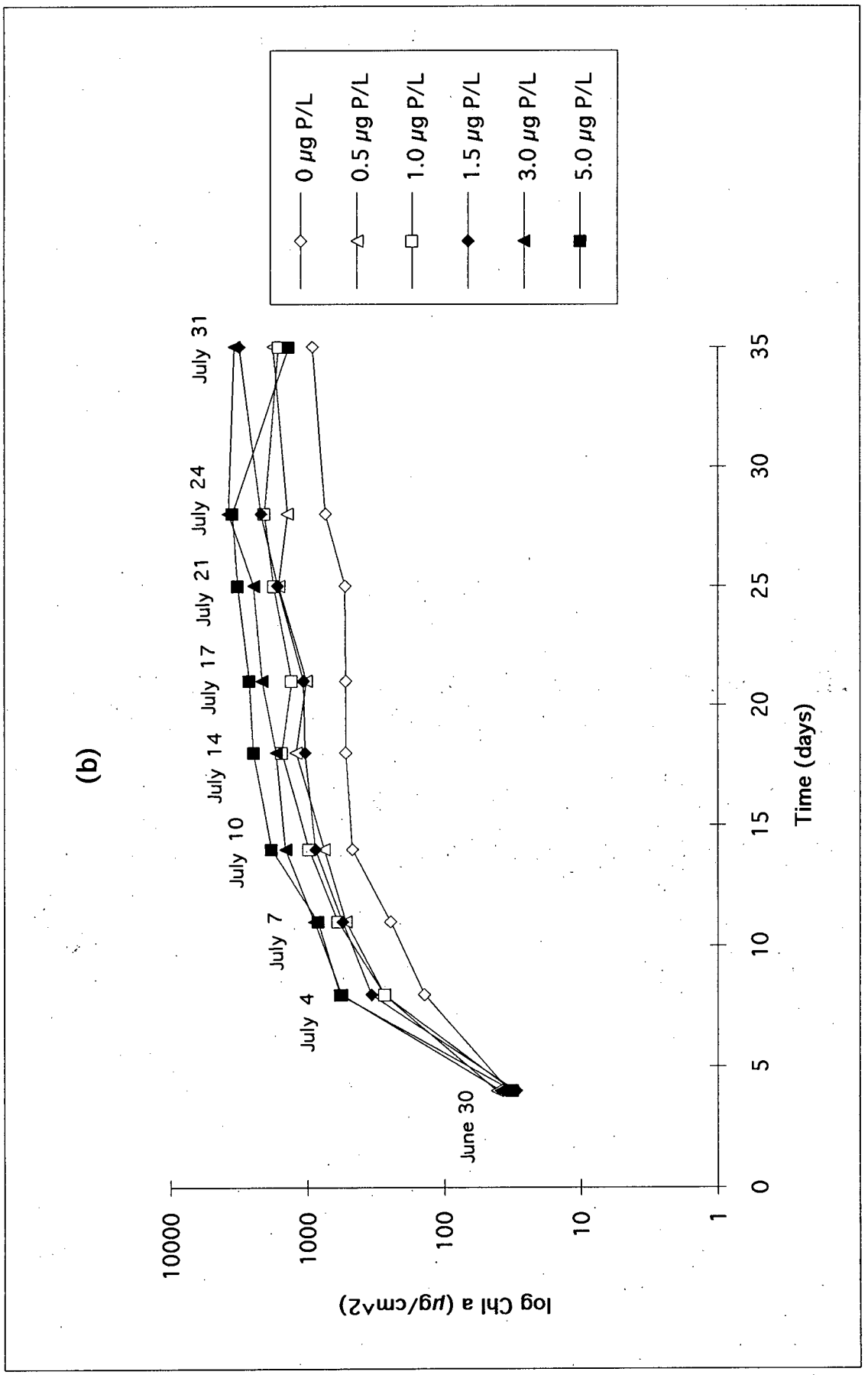


Figure 4.9 Semi-log plot of chlorophyll a accumulation over time for various phosphorus concentrations in experiments (a) May 23 - June 23, 1995; and (b) June 26 - July 31, 1995.


(b)
0 µg P/L
0.5 µg P/L
1.0 µg P/L
1.5 µg P/L
3.0 µg P/L
5.0 µg P/L
log Chl a (µg/cm^2)
10000
1000
100
10
1
June 30
July 4
July 7
July 10
July 14
July 17
July 21
July 24
July 31
0
5
10
15
20
25
30
35
Time (days)

Four different methods of data analysis were used to compute periphyton growth rates for the two experiments (Table 4.19 a & b), where y = [chl *a*], a = initial [chl *a*], and t = time:

1) linear regression over all the data, using chlorophyll *a* as the dependent variable ($y = a + kt$);

2) same as (1) but using log chlorophyll *a* as the dependent variable ($y = a10^{kt}$);

3) linear regression over 10-27 or 11-28 days to eliminate colonization time and sloughing, using chlorophyll *a* as the dependent variable; and

4) same as (3) but using log chlorophyll *a* as the dependent variable.

For methods 3 and 4 the periphyton growth rates, measured as μg Chl $a \cdot m^{-2} \cdot day^{-1}$, were calculated starting at 10 or 11 days, with the starting day chosen by visual examination to allow for colonization time (Bothwell, 1997, pers. comm.), and ending at 27 or 28 days before sloughing occurred.

Table 4.19 a Growth rates, 'k' as μg Chl $a \cdot m^{-2} \cdot day^{-1}$, of periphyton for the May 23 - June 23 experiment.

Fertilizer Amount (μg P/L)	**Days** 3-24 **y=**Chl *a*	3-24 Chl *a*	3-24 log Chl *a*	3-24 log Chl *a*	10-27 Chl *a*	10-27 Chl *a*	10-27 log Chl *a*	10-27 log Chl *a*
	k	r^2	k	r^2	k	r^2	**k**	**r^2**
0	37.5	0.912	0.0970	0.894	54.0	0.910	0.0549	0.998
0.5	286	0.969	0.113	0.845	403	0.932	0.0506	0.999
1.0	415	0.961	0.123	0.842	544	0.959	0.0515	0.999
1.5	427	0.937	0.130	0.866	615	0.937	0.0610	0.998
3.0	669	0.893	0.136	0.866	851	0.926	0.0597	0.998
5.0	473	0.887	0.146	0.905	647	0.956	0.0783	0.997

Table 4.19 b Growth rates, 'k' as μg Chl $a \cdot m^{-2} \cdot day^{-1}$, of periphyton for the June 26 - July 31 experiment.

Fertilizer Amount (μg P/L)	**Days** 4-25 **y=**Chl *a*	4-25 Chl *a*	4-25 log Chl *a*	4-25 log Chl *a*	11-28 Chl *a*	11-28 Chl *a*	11-28 log Chl *a*	11-28 log Chl *a*
	k	r^2	k	r^2	k	r^2	**k**	**r^2**
0	25.9	0.855	0.0526	0.753	21.6	0.806	0.0207	0.999
0.5	71.2	0.936	0.0658	0.797	57.1	0.838	0.0254	0.999
1.0	85.1	0.933	0.0730	0.766	78.9	0.934	0.0280	0.9995
1.5	70.0	0.949	0.0680	0.734	87.4	0.935	0.0315	0.9998
3.0	115	0.975	0.0717	0.718	148	0.937	0.0324	0.9998
5.0	157	0.962	0.0816	0.739	148	0.975	0.0321	0.999

The best method, judged by high r^2 values, of computing periphyton accrual rates for a specific phosphorus concentration after colonization (~10 days) was by a least squares (log-linear regression) fit of the chlorophyll *a* levels over time to the equation:

$$y = a \cdot 10^{kt}$$

where *y* is the Chl *a* concentration ($\mu g/m^2$) at day *t*, *a* is the initial chlorophyll *a* concentration, and *k* is the specific net growth rate, measured as μg Chl $a \cdot m^{-2} \cdot day^{-1}$ (Bothwell, 1988). Horner and Welch (1981) also found orthophosphate concentrations to demonstrate a highly significant positive association with chlorophyll *a*.

The growth rates, k, were expressed as a proportion of the maximum rate, k_{max}, from each experiment (k/k_{max}) to account for variation in temperature, light and other physical factors (Bothwell, 1985). Only data from the early part of the experiments were used to characterize exponential growth. A plot of k/k_{max} vs. added phosphate levels (Figure 4.10) shows periphytic algal growth saturated at phosphate additions ~ 1.0 $\mu g/L$ for May 26 - June 5 in the first experiment.

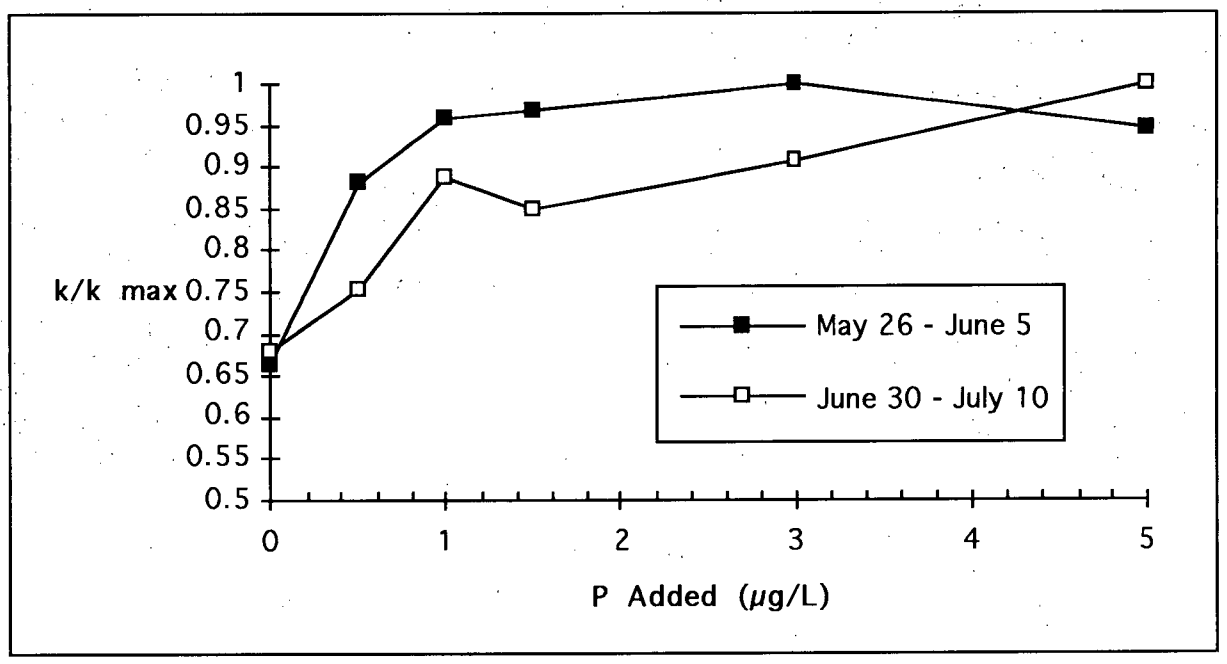


Figure 4.10 Normalized periphyton growth rates in response to phosphate addition.

A saturation level and optimal P addition could not be determined for the June 26 - July 31 experiment because colonization occurred very quickly and not enough samples were taken.

Models of chlorophyll *a* content per unit area of substrate for the different fertilizer treatments (Table 4.20) were calculated using Systat's linear regression model (N = 54) for both experiments to give equations of the form:

Chl *a* or log Chl *a* = a_1[Time] + a_2[P].

Table 4.20 Regression results for chlorophyll *a*.

Experiment	Method	Regression Equation	r^2	Standard Error of Estimate
May 23 - June 23	1	Chl *a* = 0.801[Time] + 0.267[P]	0.713	3025.499
"	2	log Chl *a* = 0.851[Time] + 0.153[P]	0.747	0.523
"	3	Chl *a* = 0.712[Time] + 0.351[P]	0.630	2732.666
"	4	log Chl *a* = 0.638[Time] + 0.351[P]	0.530	0.393
June 26 - July 31	1	Chl *a* = 0.715[Time] + 0.446[P]	0.710	549.231
"	2	log Chl *a* = 0.763[Time] + 0.259[P]	0.650	0.345
"	3	Chl *a* = 0.597[Time] + 0.681[P]	0.820	395.753
"	4	log Chl *a* = 0.599[Time] + 0.657[P]	0.790	0.134

Chlorophyll *a* accrual in terms of phosphorus levels and fertilization period could not be represented by a single equation. For the May to June experiment the regression model (method 2), developed over all the data (3 - 27 days), had the best fit based on r^2 values. However, for the June to July experiment the shortened linear model (11 to 28 days) had the highest r^2 value. These disparities likely arise from different environmental conditions and periphyton algal species over the course of the two experiments. The equations can also be used based on water temperatures: from May 23 - June 23 the temperature averaged 14 - 19 °C, and from June 26 - July 31 they averaged 18 - 23 °C.

4.4.2.2 Periphyton Community Composition

Periphyton was sampled on three occasions for species composition: June 19, water temperature = 17.5 °C; July 10, T = 20.5 °C; and July 17, 1995, T = 21 °C. Some distinct shifts of algal species abundance in relation to different fertilizer concentrations were apparent (Table

4.21). Abundant species included chrysophyta and cyanophyta divisions (Figure 4.11) with the majority of the communities comprised of diatoms. The blue-green *Oscillatoria* sp. remained at low numbers for all treatments but increased with phosphorus levels for only the June 19 sampling.

The most abundant diatoms included:

- *Diatoma sp.*, and *Melosira varians* which increased with phosphorus levels for June 19 and July 10 samples, and *Tabellaria fenestrata* which decreased with P levels over the same time frame;
- *Gomphoneis sp.*, *Synedra ulna* and *Tabellaria flocculosa* which increased with P levels for all samples, and *Fragilaria virescens* which decreased with P levels over the same time frame;
- *Fragilaria capucina* which increased significantly with P for June 19 and July 17 samples; and
- *Navicula cryptocephala* and *Synedra nana* which increased with initial P additon of 0.5 μg/L but decreased as P levels increased.

It should be noted that the periphyton was not sampled quantitatively and instead a representative sample of the different types of algae were collected.

Table 4.21 Periphyton species abundance for three sampling periods. R = rare (< 3 cells per transect); C = common (3-10 cells); A = abundant (10-30 cells); D = dominant (> 30 cells); and - = no observation.

Algal species	June 19/95				July 10/95				July 17/95			
	P+0 µg P/L	P+0.5 µg P/L	P+1.5 µg P/L	P+3.0 µg P/L	P+0 µg P/L	P+0.5 µg P/L	P+1.5 µg P/L	P+3.0 µg P/L	P+0 µg P/L	P+0.5 µg P/L	P+1.5 µg P/L	P+3.0 µg P/L
Achnanthes minutissima	R	C	R	-	R	C	R	-	R	R	R	-
Amphora ovalis	R	R	R	-	R	R	-	-	-	R	-	R
Cyclotella bodanica	C	A	C	C	C	C	R	C	A	C	R	C
Cymbella sp.	R	R	R	R	R	R	R	R	R	R	R	R
Diatoma elongatum	C	D	D	A	-	D	D	A	R	A	A	C
Diatoma vulgare	R	A	D	R	-	C	C	-	R	R	C	-
Eunotia exigua	R	C	R	R	C	C	R	R	R	R	R	R
Fragilaria capucina	-	-	-	D	-	-	-	-	-	-	D	-
Fragilaria construens	C	C	C	C	-	R	R	R	-	-	R	R
Fragilaria construens var.venter	R	C	C	C	-	R	R	R	R	R	R	R
Fragilaria crotonensis	-	-	C	C	R	R	A	C	R	C	C	C
Fragilaria virescens	A	A	C	R	D	A	C	C	D	C	C	R
Gomphoneis sp.	-	A	A	A	-	-	R	A	-	-	C	D
Gomphonema accuminatum	R	-	R	R	-	R	R	R	R	-	-	R
Melosira varians	R	-	R	D	-	-	R	A	-	-	C	-
Navicula cryptocephala	-	A	C	R	R	C	R	R	A	C	R	R
Oscillatoria sp.	-	-	R	C	-	-	R	-	-	-	R	-
Rhopalodia gibba	-	-	R	R	-	R	R	R	R	R	-	-
Surirella robusta	C	C	C	-	C	A	C	-	A	A	C	-
Synedra acus	R	R	-	-	R	R	-	-	R	R	-	C
Synedra nana	C	R	C	R	R	D	C	-	R	D	C	R
Synedra tabulata	C	R	R	-	R	-	-	-	-	R	-	-
Synedra ulna	-	A	D	A	A	A	A	D	A	D	D	A
Tabellaria fenestrata	D	A	R	-	-	-	-	R	-	A	R	-
Tabellaria flocculosa	A	R	-	D	R	-	D	D	-	-	D	A

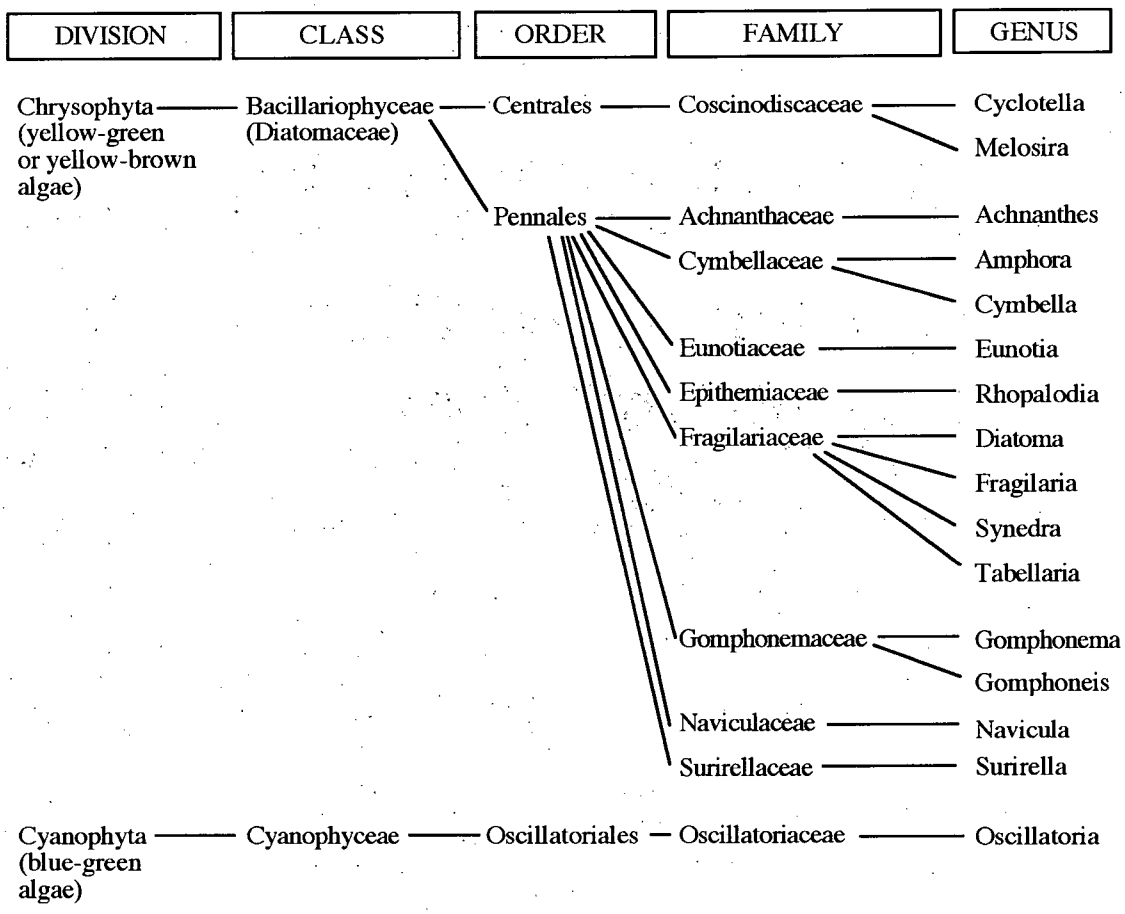


Figure 4.11 Classification scheme of abundant species of algae (adapted from Prescott, 1970) on periphyton blocks, according to the International Code of Botanical Nomenclature.

4.4.3 Discussion

4.4.3.1 Periphyton Biomass and Growth Rates

This controlled field experiment demonstrated the potential for enhancing periphyton growth through introduction of various fertilizer concentrations (Figure 4.8 a & b). Large differences in periphyton accrual were apparent in the two experiments, with maximum values reaching 19.5 mg/cm^2 for May 23 - June 23 and 3.8 mg/cm^2 for the June 26 - July 31 study. Research by Bothwell (1989) found chlorophyll *a* of diatom communities on styrofoam substrates to reach 75-200 mg/m^2 with similar 0.1-5 μg P/L additions January 29 to April 2, 1985, but at 50 cm/s water velocity. Stockner and Shortreed (1978) found results similar to Bothwell's (1989) of 80.0 mg/m^2 for 0.27 μg/L phosphorus levels (N:P = 13) and 133.6 mg/m^2 for 0.29 μg P/L and nitrogen additions (11.37 μg/L NO_3, N:P = 39), using 40 cm/s water velocity.

Addition of the fertilizer pellets (0.5 - 5 μg/L) clearly increased the periphyton biomass. Over 27 days, the May 23 - June 23 experiment resulted in a 7.8 - 14.5 times increase in chlorophyll a biomass, and 1.9 - 5.1 times increase over 28 days for the June 26 - July 31 experiment. Other experiments had similar results: Mundie et al. (1991) observed an increase of 10 μg/L phosphorus resulted in a 3.5 x increase of chlorophyll *a* biomass; Slaney and Ward (1993) observed 2.9 - 24.2 mg/m^2 chlorophyll *a* accrual on artificial substrata (June 9 - August 5, 1992) during 5 μg P/L additions to the Salmon River, Vancouver Island.

Maximum increases were found for additions of 3 μg P/L in the trough experiments, due to significant sloughing at the 5 μg P/L level. Sloughing of large quantities of accumulated biomass can be attributed to space limitation and self-shading phenomena, whereby cells closest to the substrate are weakened because of poor light or intolerable chemical conditions (Stockner and Shortreed, 1978; Jasper and Bothwell, 1986).

Several environmental factors such as light, temperature and nutrient levels could be responsible for biomass variations between the two outdoor trough experiments. Although

Bothwell (1988) found seasonal variations in light levels did not influence algal growth or biomass, the observations by Perrin and Johnston (1986) were more relevant for the outdoor trough experiments; phototoxicity by the ultraviolet spectra reduced periphyton growth at unshaded sites during very low flow.

Vymazal (1995) noted many planktonic diatoms have regular annual growth fluctuations with a maximum mostly in spring. This is mainly a result of temperature, but also other environmental conditions. Conversely, Moss (1973) found maximum growth rate temperatures for oligotrophic and eutrophic algal species to be between 15 and 32 °C, with the majority in the range 20-25 °C, indicating summer growth maxima. Thus another factor such as nutrient levels could be important in biomass variations, especially if the stream headwater is from a productive lake, such as Cultus Lake. Productivity reduces bioavailable nutrients, such as nitrogen and phosphorus, and dissolved silica (SiO_2) which is important for diatoms as well. Once the concentration of dissolved silica (SiO_2) drops to approximately 0.5 mg/L most planktonic diatoms cease to grow because of silica limitation (Vymazal, 1995). The combination of phototoxicity, increased temperature and decreased nutrient levels can explain the decrease in periphyton biomass and growth rates for the June 26 - July 31 experimental period.

Saturation of the relative specific growth rates of the diatom community in the Thompson River, B.C. was determined by Bothwell (1988) at ambient phosphorus levels of ~ 0.3 - 0.6 μg/L. Perrin et al., (1995) found saturation in the Athabasca River, Alberta to occur between 0.2 and 1.0 μg P/L. Saturation concentrations were similar in the outdoor trough experiments at Cultus Lake and were 1.0 μg/L in early summer. Mid-summer saturation concentrations could not be calculated but were expected to be similar for diatom communities throughout the summer season. Perrin et al., (1995) explained these site-specific responses by suggesting that "there are functional differences in the way the respective periphyton communities respond to phosphorus enrichment". Vymazal (1995) also observed that the saturating concentration varies with algal species.

It should be noted that although saturation of diatom growth rates occurs at low SRP concentrations, the biomass continues to increase with SRP additions up to 50 μg/L (Bothwell,

1989). The continued increase in chlorophyll *a* levels above the 'saturation' phosphate concentrations is explained by changes in cellular to community controlled growth rates. Higher phosphorus concentrations are needed to saturate and maintain growth of the denser algal community (Bothwell, 1989).

Periphyton growth increased exponentially in response to phosphate additions. This can be described by Monod's cellular growth rate kinetics: an initial cellular immigration or colonization lag period is followed by exponential growth and finally by a plateau signifying physical (e.g. light) and / or chemical (e.g. nutrient) limitations (Bothwell, 1989; Perrin et al., 1995; Vymazal, 1995). Wetzel (1975) stated that a lag phase is often not seen before the dominants reach exponential growth phases, but it can be observed in the first (May 23 - June 23) experiment due to frequent sampling. However, a biomass plateau and decline, as Bothwell (1989) observed in his first experiment, was not present here due to the short time frame of this experiment (1 vs. 2 months).

Algal growth rates, most accurately represented by a post-colonization log model of chlorophyll *a* over time (Table 4.19), ranged from 0.0506 - 0.0783 μg Chl $a \cdot m^{-2} \cdot day^{-1}$ for May 23 - June 23 and 0.0207 - 0.0324 μg Chl $a \cdot m^{-2} \cdot day^{-1}$ for June 26 - July 31. However, these equations were only valid over an approximate 10 - 28 day time frame while the algae were in exponential growth phase. Experiments over a longer time frame should be performed to include Monod's plateau phase of cellular growth kinetics to determine the long-term periphyton crop resulting from nutrient addition.

An optimal regression equation (Table 4.20) modeling chlorophyll *a* abundances in terms of phosphorus levels and fertilizer pellet exposure time in streams cannot be determined from these experiments due to varying environmental conditions between the experiments, as discussed earlier. However, orthophosphate concentrations demonstrated a highly significant ($P < 0.001$) positive association with ln chl *a* (Horner & Welch, 1981). The equations reported here give an upper limit for diatom-dominated, phosphate limited streams under similar physical and chemical conditions because of the low grazing pressure (Bothwell, 1989) and stability of the periphyton

substrate (Aloi, 1990). Also, the maximum amount of fertilizer was dissolved under the specified conditions was due to exposure of the entire pellet surface area to the flowing water. The pellets were also covered in both outdoor experiments to reduce the amount of sunlight which enhanced algal growth on the pellets and could inhibit nutrient release.

Perrin et al. (1995) showed that extrapolation of periphyton growth or biomass and the concentration of added phosphorus between rivers can be misleading. Effects of *in situ* interactions on periphyton biomass need to be determined before extrapolating phosphorus concentrations from trough to river systems. Periphyton accrual and growth rates can be affected by invertebrate grazers, current velocity, and rock size or substratum stability, light levels, nutrient concentration, nutrient ratios, and immigration of algal species from upstream. Peterson et al. (1993) observed a 2-year lag in the control of epilithic algae by grazers in the Kuparuk River, Alaska, and attribute it to the long life cycle of from 1-3 years for the dominant insects.

Calculation of fertilizer addition for optimum periphyton growth cannot be concluded from this experiment: lower fertilizer additions in potential stream sites are needed over a longer time frame (months to years). Nutrient amounts should be calculated for maximum periphyton growth in mid-to late summer months when most enrichment is needed, but sloughing or excess algal growth in less oligotrophic seasons should not occur.

4.4.3.2 Periphyton Community Composition

Results from the qualitative analyses confirmed that an increase in dissolved nutrients altered the algal species present in the stream community, and also caused denser growth in the more dominant species (Peterson et al., 1985; Keithan et al., 1988; Miller et al., 1992). Nutrient addition did not alter species succession from diatoms toward blue-green *Oscillatoria*, which is not consumed by invertebrate grazers and would inhibit fertilization efforts.

Wetzel (1975) stated that the spring maximum is usually dominated by one species and is often a diatom. This dominance of diatoms was observed in the periphyton samples (Table 4.22) as well as in other experiments; for example, Horner and Welch (1981) found algae growing on

flattened rock substrates consisted almost entirely of diatoms; Keithan et al. (1988) observed benthic algae for all nutrient treatments at two Pennsylvanian sites to be 96 % diatoms; and Johnston et al. (1990) found diatoms and green algae (chlorophytes) to dominate the algal periphyton on artificial substrata at fertilized sites.

Phosphorus addition to a tundra river simplified the diatom community through increased dominance by common species while the rare species became more scarce; after six weeks of phosphorus enrichment, the periphytic diatoms immediately downstream of the addition site showed a reduction in a density of oligotrophic indicator species, *Tabellaria flocculosa* (Peterson et al., 1985). Results from this experiment showed similar behaviour for *Tabellaria flocculosa* in the June 19 and July 10 data at low P loadings but its density significantly increased for loadings of 1.5 and 3.0 μg P/L. One explanation could be a reduction in numbers of other competitive species such as *Diatoma sp.* and *Synedra sp.* Peterson et al. (1985) also observed a reduction in numbers of species per unit area after phosphorus enrichment.

Although the diversity of diatoms has been shown to be lower in eutrophic than mesotrophic conditions, some species thrive in the eutrophic conditions (van Raalte et al., 1976). For example, Keithan et al. (1988) found *Eunotia exigua* to be the most abundant diatom in their Pennsylvania study site after phosphorus enrichment; they also found *Melosira varians* and *Diatoma vulgare* to be nutrient limited. *Eunotia exigua* did not behave in the same fashion in the outdoor troughs studied here, likely because of the different physical and chemical conditions; species that reacted favourably to nutrient addition in Cultus Lake troughs included *Diatoma sp., Fragilaria capucina, Fragilaria crotonensis, Gomphoneis sp., Melosira varians, Oscillatoria sp., Synedra nana* (at low concentrations), *Synedra ulna,* and *Tabellaria flocculosa.*

In situ river experiments over several years at the Kuparuk River, Alaska (Miller et al., 1992), resulted in the diatom community immediately switching from one dominated by *Hannaea arcus* to one dominated by species of *Achnanthes* and *Cymbella* upon nutrient addition; these changes occurred in Cultus Lake troughs but with other species than those named above due to different experimental conditions. After three years the Kuparuk River community

became dominated by the fast growing and more responsive *Eunotia, Cymbella* and *Achnanthes* species while the numbers of established species of *Hannaea, Diatoma* and *Fragilaria* declined. Some of the dominant species noted with a 'slow' positive response to P-fertilization, *Tabellaria flocculosa, T. fenestrata*, and *Synedra ulna*, were also observed in this experiment.

However, Miller et al. (1992) determined that the largest variation in community was between years and less variation was associated with river fertilization. Additionally, they found that the largest change in the diatom community, in both the river and bioassay tubes, occurred between 15 and 25 day samples. Therefore, in order to accurately determine the effects of nutrient additions on algal communities, it is apparent that observations must be made over longer time frames than was done in this experiment. Algal growth in streams must be observed over several months to years to determine equilibrium or 'plateau' growth rates, and the range of annual variations.

5. Conclusions and Recommendations

This study has shown that calcium (25 - 175 mg/L as $CaCO_3$) had a larger effect than pH (7.8 - 8.5 units) and alkalinity (20 - 160 mg/L as $CaCO_3$) on phosphorus release from fertilizer pellets. Humic material (50 - 200 colour units) was a greater predictor for phosphorus release compared to iron (0 - 1.0 mg/L) for fertilizer granules in 1 L containers on a tumbler (simulated stream conditions) at 11 °C. Thus calcium levels, taken as equivalent to hardness levels, can be measured and dosages can be calculated for streams eligible for fertilization. Further studies on phosphorus release should include lower pH values (down to about 5 units) in order broaden the information available on effects of bog waters, and higher calcium levels (to about 200 - 300 mg/L as $CaCO_3$ for hard water; Murphy et al., 1983) so fertilizer amounts for Provincial interior streams can be calculated. Effects of other divalent metals present in fresh waters, such as aluminum and magnesium, on phosphorus release would also be of interest. Further research with humic materials should include pH measurements to determine extent of interactions because hydrogen ions are displaced from phosphate when a metal chelate or complex is formed.

Experiments observing fertilizer dissolution in terms of weight loss in indoor troughs with water of 8 - 14.5 °C flowing at 0.03 - 0.30 m/s over 2 - 9 g pellets determined that size, temperature, and velocity (for > 0.15 m/s) did not affect fertilizer dissolution within the ranges analyzed. Dissolution in the field was less (Mouldey and Ashley, 1996) than the controlled trough studies due to variable flows and 'shading' from bottom substrate. Rather than increase dissolution rates, large increases in velocity are likely to carry the pellets downstream to calmer river reaches unless sheltered by bottom substrate. Smaller experiments which could incorporate a larger temperature range of 6 - 25 °C, and velocity range of 0.1 - 2 m/s as experienced by Mouldey and Ashley (1996) in B.C. streams, would be beneficial. Also of benefit would be a study of bottom substrate effects (e.g. sand, cobbles and small rocks) on the dissolution rate of the slow-release fertilizer.

Periphyton growth in experimental troughs at Cultus Lake, B.C. was found to be enhanced by phosphorus additions. A saturation level for periphyton growth was achieved at ~ 1.0 μg/L orthophosphate from May - June. In June - July growth and biomass increased proportionately to fertilizer additions. Fertilizer treatments also altered the dominant diatom species. A minimum level of nutrients needed to enhance algal biomass and subsequent fisheries production could not be determined because more information is needed over longer time frames. Site specific experimentation is still needed to determine algal responses to phosphorus loading through slow-release pellet fertilization. Further studies should include effects of various nitrogen and phosphorus ratios, substrate types, and water velocities on algal biomass and species composition.

With the new slow-release fertilizer pellet, productive stream nutrient levels can be maintained through annual fertilization applications in early summer, following the freshet but before nutrients become limited by periphyton growth. An example calculation for stream enrichment is in Appendix 5. The following equations are recommended as a basis for estimating stream fertilization requirements.

[4-2] SRP (mg/g fertilizer) = - 0.22[Ca^{2+} (mg/L as $CaCO_3$)] - 0.16[Alkalinity (mg/L $CaCO_3$)] + 0.08[Time (hours)] + 91.11

[4-3] TP (mg/g fertilizer) = - 0.12[Ca^{2+} (mg/L as $CaCO_3$)] - 0.03[Alkalinity (mg/L $CaCO_3$)] + 0.09[Time (hours)] - 10.37[pH (units)] + 171.39

[4-4] SRP (mg/g fertilizer) = - 0.09[Colour (units)] + 0.14[Time (hours)] + 79.47

[4-5] TP (mg/g fertilizer) = - 0.07[Colour (units)] + 0.16[Time (hours)] + 83.93

[4-9] log % Weight lost = 0.392 [log Time (days)] + 0.688, based on a 9 g pellet.

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7. Appendix I - Pellet Weights (g) Used In Laboratory Experiments

A-1.1 Pellet weights used in each sample bottle.

Experiment #	1	2	3	4
pH (units)	7.8, 8.5	7.8, 8.5	7.8, 8.5	pH 5.85;
Alkalinity (mg/L as $CaCO_3$)	160	20, 95	20, 160	Alkalinity = 7.6 (mg/L as $CaCO_3$);
Calcium (mg/L as $CaCO_3$)	25, 100, 175	25, 100, 175	25, 175	[Fe] = 0.2, 1.0 mg/L; Colour=200, 100, & 50 units
Bottle # 1	0.1009	0.0999	0.1000	0.1000
2	0.1003	0.0999	0.1007	0.1001
3	0.1001	0.0999	0.1000	0.1003
4	0.1004	0.1005	0.1001	0.1004
5	0.1005	0.1007	0.1005	0.1004
6	0.1000	0	0	0.0999
7	0.1006	0.1002	0.1000	0.1001
8	0.1002	0.1003	0.1003	0.1005
9	0.1007	0.1003	0.1001	0.1005
10	0.1002	0.1003	0.1000	0.1001
11	0	0.1002	0.1001	0.1004
12	0.1003	0.1006*	0	0.1002

A-1.2 Pellet weights converted to phosphorus weight, based on 17.46 % P in the fertilizer.

Experiment #	1	2	3	4
pH (units)	7.8, 8.5	7.8, 8.5	7.8, 8.5	pH 5.85;
Alkalinity (mg/L as $CaCO_3$)	160	20, 95	20, 160	Alkalinity = 7.6 (mg/L as $CaCO_3$);
Calcium (mg/L as $CaCO_3$)	25, 100, 175	25, 100, 175	25, 175	[Fe] = 0.2, 1.0 mg/L; Colour=200, 100, & 50 units
Bottle # 1	0.01762	0.01744	0.01746	0.01746
2	0.01751	0.01744	0.01758	0.01748
3	.01748	0.01744	0.01746	.001752
4	0.01753	0.01755	0.01748	0.01753
5	0.01755	0.01758	0.01755	0.01753
6	0.01746	0	0	0.01745
7	0.01756	0.01749	0.01746	0.01748
8	0.01749	0.01751	0.01751	0.01755
9	0.01758	0.01751	0.01748	0.01755
10	0.01749	0.01751	0.01746	0.01748
11	0	0.01749	0.01748	0.01753
12	0.01751	0.01756*	0	0.01750

* Humic water containing pH 6 and alkalinity = 115 mg/L as $CaCO_3$.

8. Appendix II - Data for Pellet Drying Time

Large (~ 9 g) pellets in 105 °C oven

A-2.1 **TEST 1**

Dry Weight (A)	Oven Dry Weight (B)	A - B	Time in Oven (hours)	% Weight Lost
9.7	9.66	0.04	0	0.41
9.67	9.64	0.03	0	0.31
9.87	9.83	0.04	0	0.41
9.36	9.04	0.32	2	3.42
9.22	8.95	0.27	2	2.93
9.47	9.19	0.28	2	2.96
9.72	9.33	0.39	3	4.01
9.47	9.09	0.38	3	4.01
10.1	9.69	0.41	3	4.06
9.88	9.19	0.69	12.6	6.98
9	8.33	0.67	12.6	7.44
8.76	8.15	0.61	12.6	6.96

A-2.2 **TEST 2 (additional drying times)**

Dry Weight (A)	Oven Dry Weight (B)	A - B	Time in Oven (hours)	% Weight Lost
8.85	8.38	0.47	2	5.31
9.64	9.25	0.39	2	4.05
9.77	9.36	0.41	2	4.20
10.11	9.7	0.41	3	4.06
9.23	8.85	0.38	3	4.12
8.66	8.26	0.4	3	4.62
9.39	8.94	0.45	4	4.79
9.2	8.69	0.51	4	5.54
9.93	9.47	0.46	4	4.63
8.82	8.3	0.52	6	5.90
9.52	8.97	0.55	6	5.78
9.64	9.09	0.55	6	5.71
9.48	8.85	0.63	8	6.65
9.69	9	0.69	8	7.12

NOTE: Pellets were soaked for 12 hours before drying in oven.

A-2.3 **Averages**

Time in Oven (hours)	% Weight Lost
0	0.375959158
2	3.809470478
3	4.145960219
4	4.989412506
6	5.792798908
8	6.883156327
12.6	7.130573477

Small (~ 2 g), medium (~ 6 g) and large (~ 9 g) pellets in 70 °C oven

TEST 3

A-2.4 **Large Pellets**

Dry Weight (A)	Oven Dry Weight (B)	A - B	Time in Oven (hours)	% Weight Lost
9.07	9.04	0.03	0	0.33
9.83	9.8	0.03	0	0.31
9.49	9.47	0.02	0	0.21
9.84	9.74	0.1	1	1.02
9.24	9.16	0.08	1	0.87
8.94	8.86	0.08	1	0.89
9.79	9.67	0.12	2	1.23
9.31	9.19	0.12	2	1.29
9.49	9.34	0.15	4	1.58
9.47	9.34	0.13	4	1.37
9.63	9.51	0.12	4	1.25
9.66	9.54	0.12	4	1.24
8.84	8.72	0.12	5	1.36
10.03	9.89	0.14	5	1.40
9.44	9.28	0.16	5	1.69
9.35	9.18	0.17	8	1.82
9.41	9.24	0.17	8	1.81
9.66	9.49	0.17	8	1.76
9.77	9.57	0.2	12	2.05
9.22	8.97	0.25	12	2.71
10.15	9.94	0.21	12	2.07
9.41	9.19	0.22	24	2.34
8.91	8.72	0.19	24	2.13
9.08	8.84	0.24	24	2.64

A-2.5 **Medium Pellets**

Dry Weight (A)	Oven Dry Weight (B)	A - B	Time in Oven (hours)	% Weight Lost
4.31	4.29	0.02	0	0.46
4.69	4.67	0.02	0	0.43
4.52	4.5	0.02	0	0.44
4.34	4.3	0.04	1	0.92
5.01	**3.98**	1.03	1	20.56
5.61	5.55	0.06	2	1.07
4.55	4.49	0.06	2	1.32
5.9	5.66	0.24	5	4.07
5.48	5.23	0.25	5	4.56
6.39	6.12	0.27	8	4.23
6.28	5.98	0.3	8	4.78
5.77	5.51	0.26	12	4.51
6.63	6.32	0.31	12	4.68
6.34	6.01	0.33	24	5.21
5.13	4.87	0.26	24	5.07

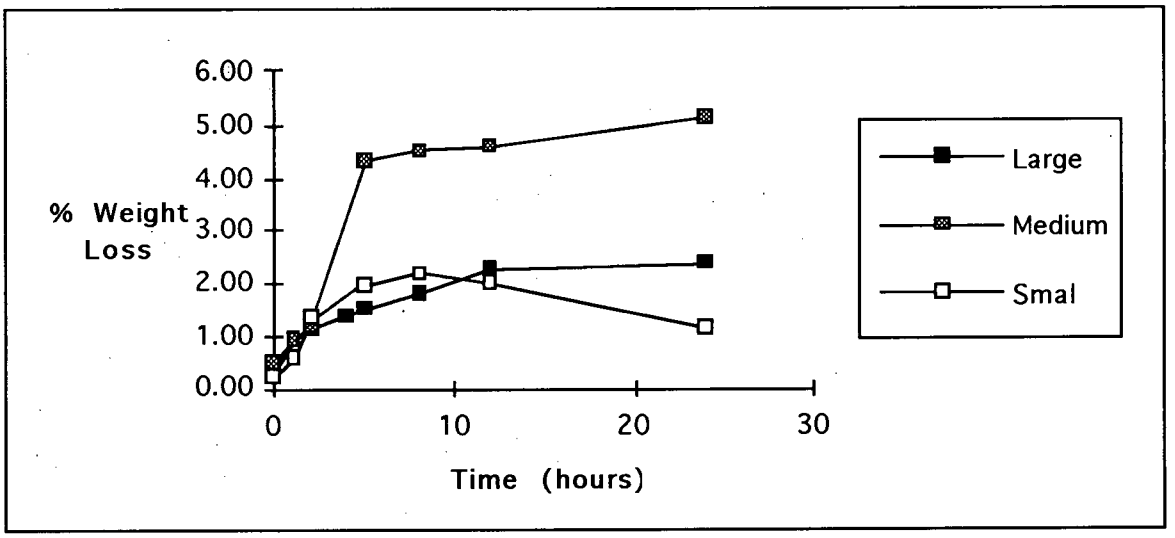
A-2.6 **Small Pellets**

Dry Weight (A)	Oven Dry Weight (B)	A - B	Time in Oven (hours)	% Weight Lost
2.74	2.74	0	0	0.00
3.02	3.01	0.01	0	0.33
3.12	3.11	0.01	0	0.32
3.01	3.01	0	1	0.00
2.73	2.7	0.03	1	1.10
3.19	3.14	0.05	2	1.57
2.79	2.76	0.03	2	1.08
2.76	2.7	0.06	5	2.17
2.94	2.89	0.05	5	1.70
3.11	3.04	0.07	8	2.25
2.93	2.87	0.06	8	2.05
2.42	2.36	0.06	12	2.48
2.74	2.7	0.04	12	1.46
3.12	3.08	0.04	24	1.28
3.2	3.17	0.03	24	0.94

A-2.7 **Average Weight Lost**

Hours in Oven	Large	Medium	Small
0	0.28	0.44	0.22
1	0.93	0.92	0.55
2	1.14	1.19	1.32
4	1.36		
5	1.48	4.31	1.94
8	1.79	4.50	2.15
12	2.28	4.59	1.97
24	2.37	5.14	1.11

A-2.8 Average percent weight lost vs. drying time in 70 deg C oven.



9. Appendix III - pH , SRP and TP Values for Each Experiment

EXPERIMENT 1 (Figure 3.2)

pH Values

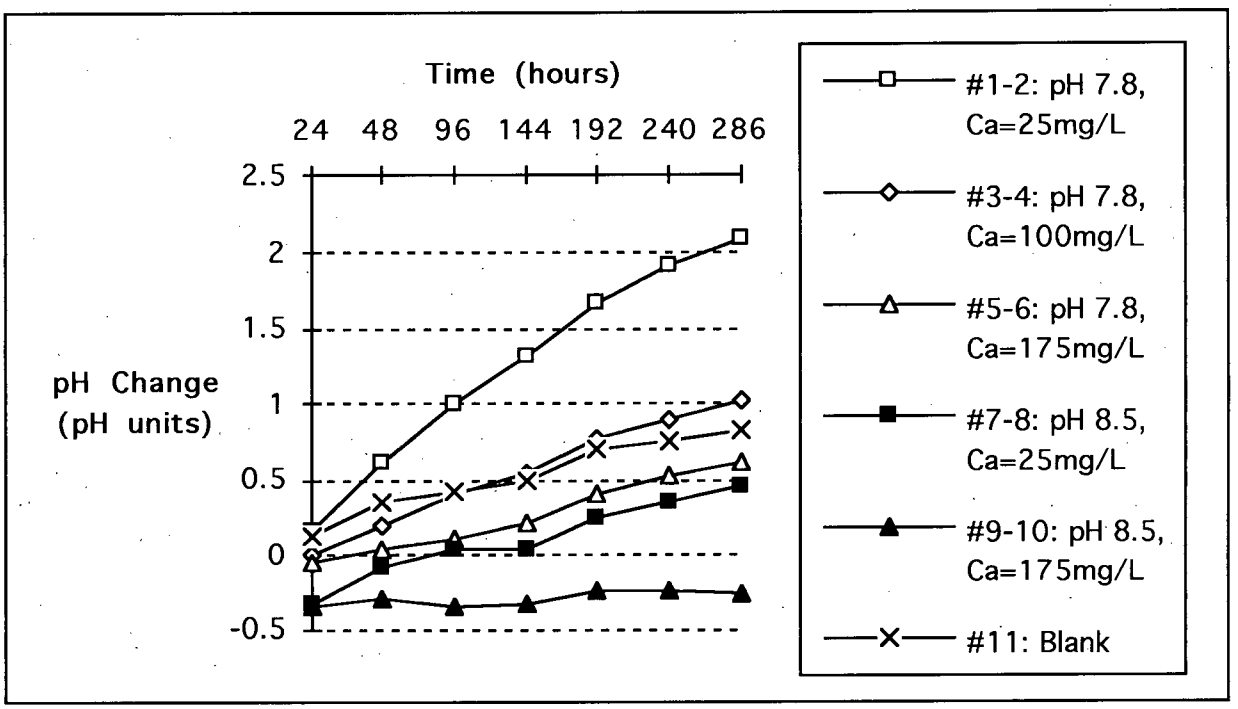
A-3.1 Cumulative change in pH (pH units) from addition of fertilizer (June 17-28, 1994)

Batch #	1	2	3	4	5	6	7
Cumul. Hrs.	24	48	96	144	192	240	286
Bottle # 1	0.22	0.73	1.13	1.39	1.75	2.06	2.18
2	0.1	0.5	0.89	1.23	1.57	1.77	1.98
3	0.01	0.21	0.44	0.63	0.89	0.99	1.1
4	-0.01	0.17	0.36	0.47	0.67	0.82	0.95
5	-0.03	0.08	0.13	0.24	0.42	0.53	0.62
6	-0.07	-0.01	0.09	0.19	0.38	0.52	0.62
7	-0.33	-0.08	0.06	0.06	0.32	0.46	0.6
8	-0.33	-0.1	0.02	0.02	0.18	0.26	0.33
9	-0.33	-0.3	-0.34	-0.32	-0.26	-0.24	-0.27
10	-0.36	-0.29	-0.35	-0.33	-0.24	-0.23	-0.24
11	0.12	0.35	0.42	0.49	0.7	0.76	0.82

A-3.2 Average of duplicates

Batch #	1	2	3	4	5	6	7
Cumul. Hrs.	24	48	96	144	192	240	286
Bottle # 1-2	0.16	0.615	1.01	1.31	1.66	1.915	2.08
#3-4	0	0.19	0.4	0.55	0.78	0.905	1.025
#5-6	-0.05	0.035	0.11	0.215	0.4	0.525	0.62
#7-8	-0.33	-0.09	0.04	0.04	0.25	0.36	0.465
#9-10	-0.345	-0.295	-0.345	-0.325	-0.25	-0.235	-0.255
#11	0.12	0.35	0.42	0.49	0.7	0.76	0.82

A-3.3 Cumulative pH change for water having alkalinity = 160 mg/L as $CaCO_3$.



SRP Values

A-3.4 Individual batch change in SRP (mg/L) from addition of fertilizer (June 17-28, 1994) (* = filtered)

Batch # Indiv. Hrs.	1* 24	2* 24	3* 48	4* 48	5 48	6 48	7 48
Bottle # 1	6.42	0.57	0.73	0.89	1.02	0.74	0.63
2	6.9	0.74	0.79	0.71	0.57	0.56	0.57
3	2.46	0.44	0.32	0.31	0.19	0.24	0.19
4	4.09	0.46	0.43	0.3	0.17	0.19	0.17
5	3.41	0.55	0.54	0.31	0.13	0.14	0.13
6	2.94	0.35	0.33	0.27	0.11	0.13	0.13
7	4.62	0.68	0.7	0.67	0.68	0.53	0.46
8	4.67	0.58	0.62	0.49	0.44	0.43	0.51
9	3.13	0.45	0.43	0.21	0.08	0.09	0.09
10	2.66	0.3	0.33	0.17	0.09	0.09	0.07
11	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

A-3.5 Cumulative change in SRP (mg/L)

Cumul. Hrs.	0	24	48	96	144	192	240	286
Bottle # 1	0	6.42	6.99	7.72	8.61	9.63	10.37	11
2	0	6.9	7.64	8.43	9.14	9.71	10.27	10.84
3	0	2.46	2.9	3.22	3.53	3.72	3.96	4.15
4	0	4.09	4.55	4.98	5.28	5.45	5.64	5.81
5	0	3.41	3.96	4.5	4.81	4.94	5.08	5.21
6	0	2.94	3.29	3.62	3.89	4	4.13	4.26
7	0	4.62	5.3	6	6.67	7.35	7.88	8.34
8	0	4.67	5.25	5.87	6.36	6.8	7.23	7.74
9	0	3.13	3.58	4.01	4.22	4.3	4.39	4.48
10	0	2.66	2.96	3.29	3.46	3.55	3.64	3.71

A-3.6 Average of duplicates

Batch #	1	2	3	4	5	6	7
Cumul. Hrs.	24	48	96	144	192	240	286
Bottle # 1-2	6.66	7.315	8.075	8.875	9.67	10.32	10.92
#3-4	3.275	3.725	4.1	4.405	4.585	4.8	4.98
#5-6	3.175	3.625	4.06	4.35	4.47	4.605	4.735
#7-8	4.645	5.275	5.935	6.515	7.075	7.555	8.04
#9-10	2.895	3.27	3.65	3.84	3.925	4.015	4.095

A-3.7 Standard deviation of 0.1 g releases

Batch #	1	2	3	4	5	6	7	
Cumul. Hrs.	24	48	96	144	192	240	286	Average
Bottle # 1-2	0.3394	0.4596	0.502	0.3748	0.0566	0.0707	0.1131	0.27
#3-4	1.1526	1.1667	1.2445	1.2374	1.2233	1.1879	1.1738	1.20
#5-6	0.3323	0.4738	0.6223	0.6505	0.6647	0.6718	0.6718	0.58
#7-8	0.0354	0.0354	0.0919	0.2192	0.3889	0.4596	0.4243	0.24
#9-10	0.3323	0.4384	0.5091	0.5374	0.5303	0.5303	0.5445	0.49

A-3.8 Cumulative SRP releases normalized to 1 g of fertilizer in bundles

Cumul. Hrs.	0	24	48	96	144	192	240	286
Bottle # 1	0	63.627	69.277	76.511	85.332	95.441	102.78	109.02
2	0	68.794	76.171	84.048	91.127	96.81	102.39	108.08
3	0	24.575	28.971	32.168	35.265	37.163	39.56	41.459
4	0	40.737	45.319	49.602	52.59	54.283	56.175	57.869
5	0	33.93	39.403	44.776	47.861	49.154	50.547	51.841
6	0	29.4	32.9	36.2	38.9	40	41.3	42.6
7	0	45.924	52.684	59.642	66.302	73.062	78.33	82.903
8	0	46.607	52.395	58.583	63.473	67.864	72.156	77.246
9	0	31.082	35.551	39.821	41.907	42.701	43.595	44.489
10	0	26.547	29.541	32.834	34.531	35.429	36.327	37.026

A-3.9 Average of normalized releases

Batch #	0	1	2	3	4	5	6	7
Cumul. Hrs.	0	24	48	96	144	192	240	286
Bottle # 1-2	0	66.21	72.724	80.28	88.229	96.125	102.58	108.55
#3-4	0	32.656	37.145	40.885	43.927	45.723	47.868	49.664
#5-6	0	31.665	36.151	40.488	43.38	44.577	45.924	47.22
#7-8	0	46.266	52.54	59.112	64.888	70.463	75.243	80.074
#9-10	0	28.815	32.546	36.328	38.219	39.065	39.961	40.757

A-3.10 Standard deviation of normalized releases

Batch #	1	2	3	4	5	6	7	
Cumul. Hrs.	24	48	96	144	192	240	286	Average
Bottle # 1-2	3.6531	4.8755	5.3291	4.0974	0.9677	0.2703	0.6668	2.84
#3-4	11.428	11.56	12.328	12.251	12.106	11.748	11.604	11.86
#5-6	3.2034	4.5983	6.0642	6.3362	6.473	6.5388	6.5342	5.68
#7-8	0.4825	0.2041	0.749	2.0005	3.6751	4.3659	4.0002	2.21
#9-10	3.2071	4.2499	4.9405	5.2154	5.142	5.1389	5.2769	4.74

TP Values

A-3.11 Individual batch change in TP (mg/L) from addition of fertilizer (June 17-28, 1994)

Batch #	1	2	3	4	5	6	7
Indiv. Hrs.	24	24	48	48	48	48	48
Bottle # 1	7.57	1.11	1.24	0.92	1.31	0.74	0.72
2	7.48	1.1	1.03	0.77	0.81	0.74	0.68
3	7.3	0.59	0.55	0.4	0.34	0.31	0.26
4	6.58	0.68	0.59	0.43	0.33	0.26	0.24
5	6.32	0.8	0.75	0.38	0.25	0.21	0.17
6	6.4	0.6	0.45	0.3	0.24	0.23	0.21
7	5.29	0.77	0.77	0.66	0.83	0.67	0.5
8	5.69	0.79	0.81	0.59	0.54	0.56	0.61
9	5.34	0.65	0.54	0.28	0.2	0.16	0.14
10	5.98	0.51	0.42	0.24	0.17	0.16	0.13
11	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

A-3.12 Cumulative change in TP (mg/L) from addition of fertilizer (June 17-28, 1994)

Cumul. Hrs.	0	24	48	96	144	192	240	286
Bottle # 1	0	7.57	8.68	9.92	10.84	12.15	12.89	13.61
2	0	7.48	8.58	9.61	10.38	11.19	11.93	12.61
3	0	7.3	7.89	8.44	8.84	9.18	9.49	9.75
4	0	6.58	7.26	7.85	8.28	8.61	8.87	9.11
5	0	6.32	7.12	7.87	8.25	8.5	8.71	8.88
6	0	6.4	7	7.45	7.75	7.99	8.22	8.43
7	0	5.29	6.06	6.83	7.49	7.66	8.33	8.83
8	0	5.69	6.48	7.29	7.88	8.42	8.98	9.59
9	0	5.34	5.99	6.53	6.81	7.01	7.17	7.31
10	0	5.98	6.49	6.91	7.15	7.32	7.48	7.61

Cumulative change in TP (mg/L) from addition of fertilizer (June 17-28, 1994)
A-3.13 Average of duplicates

Batch #	1	2	3	4	5	6	7
Cumul. Hrs.	24	48	96	144	192	240	286
Bottle # 1-2	7.525	8.63	9.765	10.61	11.67	12.41	13.11
#3-4	6.94	7.575	8.145	8.56	8.895	9.18	9.43
#5-6	6.36	7.06	7.66	8	8.245	8.465	8.655
#7-8	5.49	6.27	7.06	7.685	8.04	8.655	9.21
#9-10	5.66	6.24	6.72	6.98	7.165	7.325	7.46

A-3.14 Standard deviation of 0.1 g releases

Batch #	1	2	3	4	5	6	7	
Cumul. Hrs.	24	48	96	144	192	240	286	Average
Bottle # 1-2	0.0636	0.0707	0.2192	0.3253	0.6788	0.6788	0.7071	0.39
#3-4	0.5091	0.4455	0.4172	0.396	0.4031	0.4384	0.4525	0.44
#5-6	0.0566	0.0849	0.297	0.3536	0.3606	0.3465	0.3182	0.26
#7-8	0.2828	0.297	0.3253	0.2758	0.5374	0.4596	0.5374	0.39
#9-10	0.4525	0.3536	0.2687	0.2404	0.2192	0.2192	0.2121	0.28

A-3.15 Cumulative TP releases normalized to 1 g of fertilizer in bundles

Cumul. Hrs.	0	24	48	96	144	192	240	286
Bottle # 1	0	75.025	86.026	98.315	107.43	120.42	127.75	134.89
2	0	74.576	85.543	95.813	103.49	111.57	118.94	125.72
3	0	72.927	78.821	84.316	88.312	91.708	94.805	97.403
4	0	65.538	72.311	78.187	82.47	85.757	88.347	90.737
5	0	62.886	70.846	78.308	82.09	84.577	86.667	88.358
6	0	64	70	74.5	77.5	79.9	82.2	84.3
7	0	52.584	60.239	67.893	74.453	76.143	82.803	87.773
8	0	56.786	64.671	72.754	78.643	84.032	89.621	95.709
9	0	53.029	59.484	64.846	67.627	69.613	71.202	72.592
10	0	59.681	64.77	68.962	71.357	73.054	74.651	75.948

A-3.16 Average of normalized releases

Batch #	0	1	2	3	4	5	6	7
Cumul. Hrs.	0	24	48	96	144	192	240	286
Bottle # 1-2	0	74.801	85.785	97.064	105.46	115.99	123.35	130.3
#3-4	0	69.232	75.566	81.251	85.391	88.733	91.576	94.07
#5-6	0	63.443	70.423	76.404	79.795	82.239	84.433	86.329
#7-8	0	54.685	62.455	70.324	76.548	80.088	86.212	91.741
#9-10	0	56.355	62.127	66.904	69.492	71.333	72.926	74.27

A-3.17 Standard deviation of normalized releases

Batch #	1	2	3	4	5	6	7	
Cumul. Hrs.	24	48	96	144	192	240	286	Average
Bottle # 1-2	0.3171	0.3411	1.7696	2.7885	6.2586	6.2275	6.4794	3.45
#3-4	5.225	4.6036	4.3335	4.1306	4.2082	4.5669	4.7133	4.54
#5-6	0.788	0.5981	2.693	3.2453	3.3072	3.1584	2.8696	2.38
#7-8	2.9712	3.134	3.4378	2.9624	5.5782	4.8208	5.611	4.07
#9-10	4.7036	3.7384	2.9105	2.638	2.4333	2.4389	2.3732	3.03

EXPERIMENT 2 (Figure 3.3)

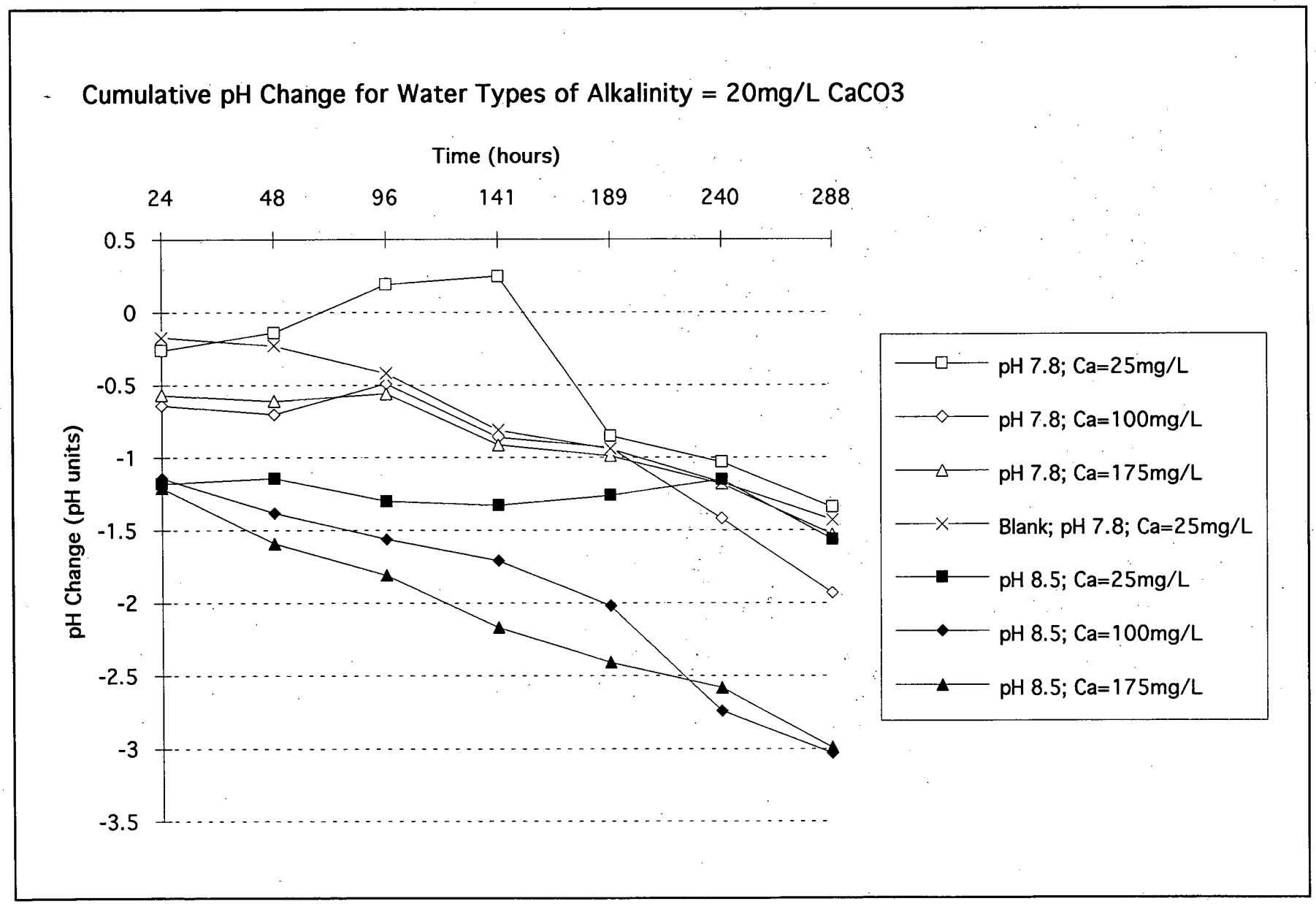
pH Values

A-3.18 Cumulative change in pH (pH units) from addition of fertilizer (July 14-26, 1994)

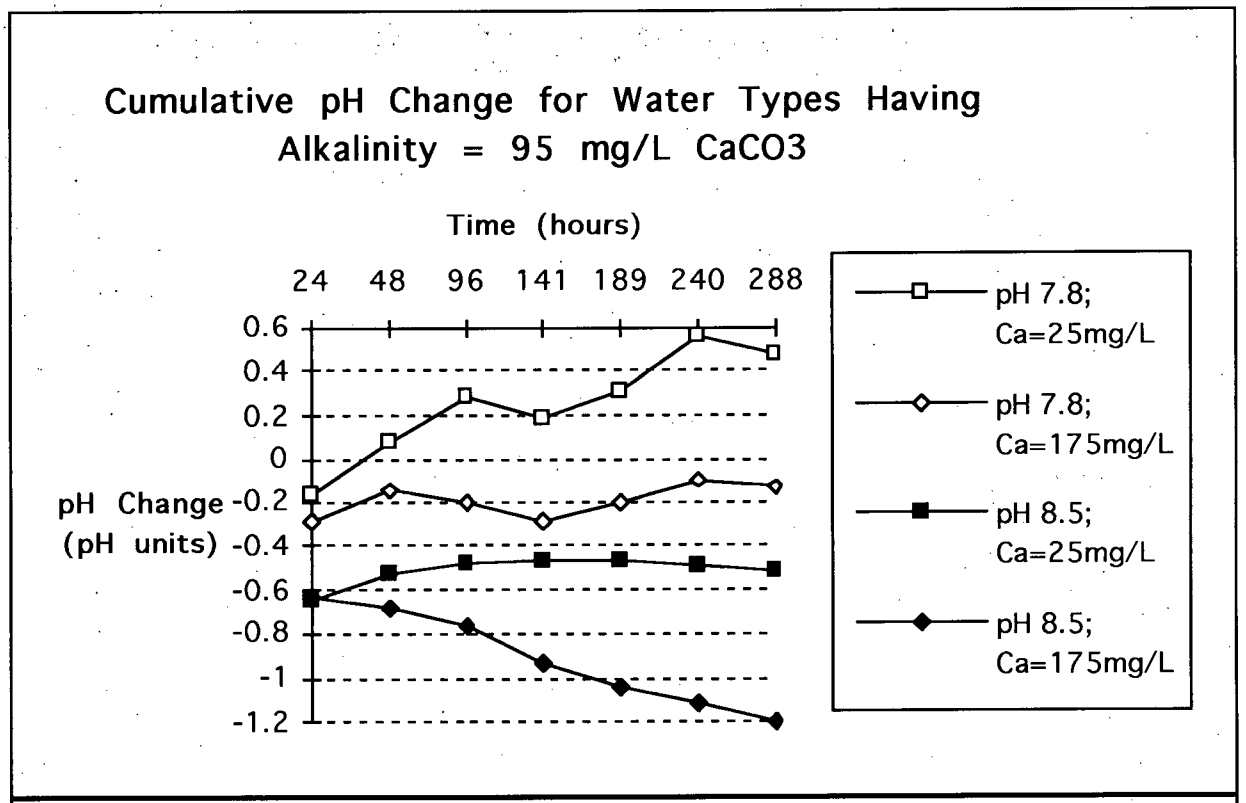
Batch #	1	2	3	4	5	6	7	Alkalinity
Cumul. Hrs.	24	48	96	141	189	240	288	(mg/L as $CaCO_3$)
Bottle # 1	-0.26	-0.14	0.19	0.25	-0.85	-1.03	-1.34	alk=20
2	-0.64	-0.7	-0.49	-0.86	-0.93	-1.42	-1.93	"
3	-0.57	-0.61	-0.56	-0.91	-0.99	-1.18	-1.53	"
7	-1.18	-1.14	-1.3	-1.33	-1.26	-1.15	-1.56	"
8	-1.14	-1.38	-1.56	-1.71	-2.02	-2.74	-3.03	"
9	-1.21	-1.59	-1.81	-2.17	-2.41	-2.58	-2.99	"
6 (blank)	-0.17	-0.23	-0.42	-0.81	-0.94	-1.17	-1.43	"

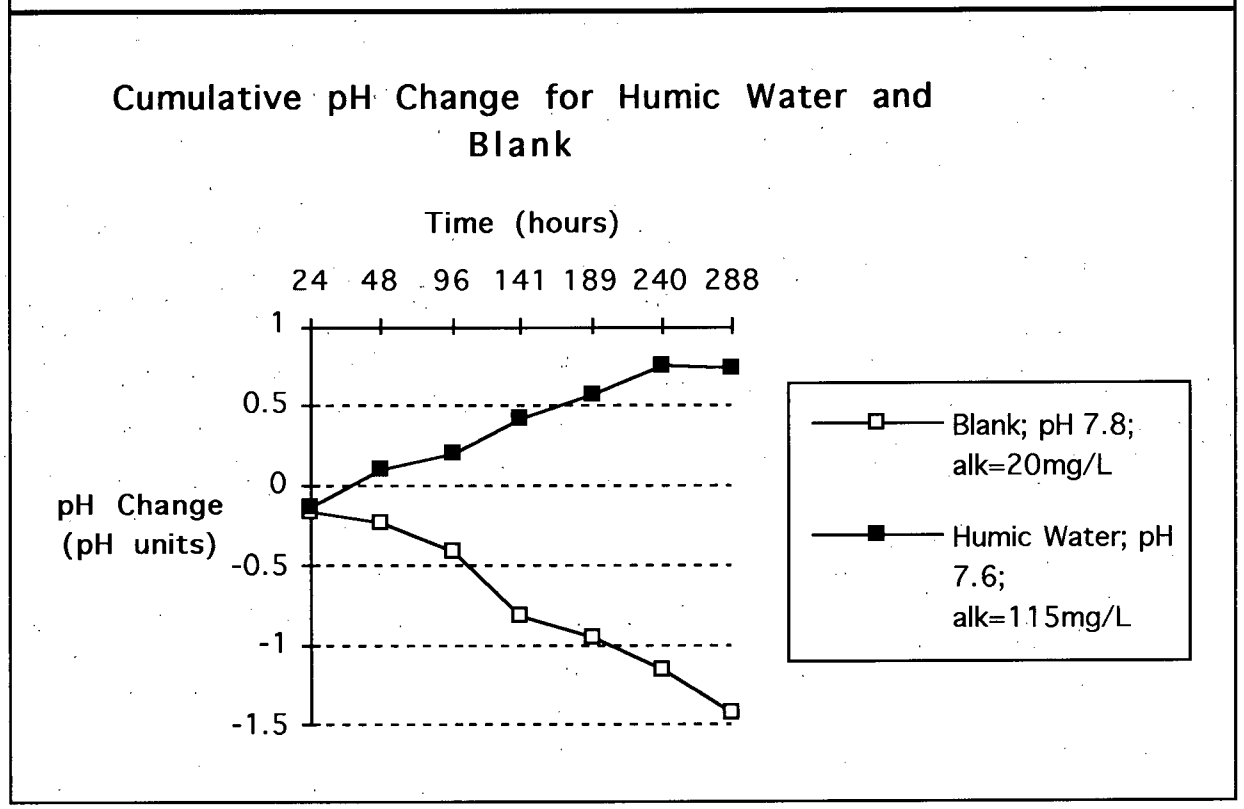
Cumul. Hrs.	24	48	96	141	189	240	288	
4	-0.17	0.08	0.28	0.19	0.31	0.56	0.48	alk=95
5	-0.29	-0.15	-0.21	-0.29	-0.2	-0.1	-0.13	"
10	-0.65	-0.53	-0.48	-0.47	-0.47	-0.49	-0.52	"
11	-0.64	-0.68	-0.77	-0.93	-1.04	-1.11	-1.19	"

Cumul. Hrs.	24	48	96	141	189	240	288	
6	-0.17	-0.23	-0.42	-0.81	-0.94	-1.17	-1.43	alk=20
12	-0.13	0.1	0.19	0.42	0.56	0.74	0.72	humic water


Cumulative pH Change for Water Types of Alkalinity = 20mg/L CaCO3
Time (hours)
24
48
96
141
189
240
288
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
pH Change (pH units)
pH 7.8; Ca=25mg/L
pH 7.8; Ca=100mg/L
pH 7.8; Ca=175mg/L
Blank; pH 7.8; Ca=25mg/L
pH 8.5; Ca=25mg/L
pH 8.5; Ca=100mg/L
pH 8.5; Ca=175mg/L

A-3.20


Cumulative pH Change for Water Types Having Alkalinity = 95 mg/L CaCO3
Time (hours)
24 48 96 141 189 240 288
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
pH Change (pH units)
pH 7.8; Ca=25mg/L
pH 7.8; Ca=175mg/L
pH 8.5; Ca=25mg/L
pH 8.5; Ca=175mg/L


Cumulative pH Change for Humic Water and Blank
Time (hours)
24 48 96 141 189 240 288
1
0.5
0
-0.5
-1
-1.5
pH Change (pH units)
Blank; pH 7.8; alk=20mg/L
Humic Water; pH 7.6; alk=115mg/L

A-3.21

SRP Values

A-3.22 Individual batch change in SRP (mg/L) from addition of fertilizer (July 14-26, 1994) (unfiltered)

Batch #	1	2	3	4	5	6	7
Indiv. Hrs.	24	24	48	45	48	51	48
Bottle # 1	7.13	0.98	0.79	0.42	0.35	0.3	0.26
2	6.76	0.59	0.39	0.2	0.15	0.15	0.11
3	6.42	0.48	0.38	0.2	0.12	0.11	0.09
4	5.74	0.84	0.88	0.53	0.43	0.38	0.33
5	3.8	0.46	0.4	0.22	0.17	0.14	0.1
6	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
7	7.08	0.79	0.78	0.51	0.4	0.34	0.31
8	5.89	0.53	0.44	0.22	0.13	0.11	0.08
9	5.96	0.37	0.28	0.13	0.09	0.08	0.06
10	7.41	0.86	0.95	0.61	0.51	0.44	0.37
11	3.62	0.43	0.32	0.19	0.12	0.13	0.09
12	5.95	0.85	0.67	0.6	0.6	0.56	0.53

A-3.23 Cumulative change in SRP (mg/L) from addition of fertilizer (July 14-26, 1994)

Cumul. Hrs.	24	48	96	141	189	240	288
Bottle # 1	7.13	8.11	8.9	9.32	9.67	9.97	10.23
2	6.76	7.35	7.74	7.94	8.09	8.24	8.35
3	6.42	6.9	7.28	7.48	7.6	7.71	7.8
4	5.74	6.58	7.46	7.99	8.42	8.8	9.13
5	3.8	4.26	4.66	4.88	5.05	5.19	5.29
6	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
7	7.08	7.87	8.65	9.16	9.56	9.9	10.21
8	5.89	6.42	6.86	7.08	7.21	7.32	7.4
9	5.96	6.33	6.61	6.74	6.83	6.91	6.97
10	7.41	8.27	9.22	9.83	10.34	10.78	11.15
11	3.62	4.05	4.37	4.56	4.68	4.81	4.9
12	5.95	6.8	7.47	8.07	8.67	9.23	9.76

TP Values

A-3.24 Individual batch change in TP (mg/L) from addition of fertilizer (July 14-26, 1994)

Batch #	1	2	3	4	5	6	7
Indiv. Hrs.	24	24	48	45	48	51	48
Bottle # 1	7.46	1.08	0.92	0.46	0.37	0.3	0.31
2	7.56	0.57	0.43	0.22	0.18	0.14	0.12
3	7.51	0.49	0.43	0.24	0.12	0.08	0.09
4	7.76	0.87	0.79	0.56	0.46	0.41	0.33
5	6.73	0.54	0.49	0.29	0.17	0.15	0.14
6	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
7	7.44	0.8	0.86	0.48	0.42	0.35	0.33
8	6.94	0.57	0.53	0.32	0.13	0.12	0.07
9	7.1	0.39	0.32	0.18	0.07	<0.05	0.06
10	8.02	0.87	1.06	0.74	0.51	0.46	0.37
11	6.44	0.49	0.43	0.22	0.14	0.09	0.08
12	7.78	0.94	0.79	0.71	0.69	0.64	0.6

A-3.25 Cumulative change in TP (mg/L) from addition of fertilizer (July 14-26, 1994)

Cumul. Hrs.	24	48	96	141	189	240	288
Bottle # 1	7.46	8.54	9.46	9.92	10.29	10.59	10.9
2	7.56	8.13	8.56	8.78	8.96	9.1	9.22
3	7.51	8	8.43	8.67	8.79	8.87	8.96
4	7.76	8.63	9.42	9.98	10.44	10.85	11.18
5	6.73	7.27	7.76	8.05	8.22	8.37	8.51
6	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
7	7.44	8.24	9.1	9.58	10	10.35	10.68
8	6.94	7.51	8.04	8.36	8.49	8.61	8.68
9	7.1	7.49	7.81	7.99	8.06	8.06	8.12
10	8.02	8.89	9.95	10.69	11.2	11.66	12.03
11	6.44	6.93	7.36	7.58	7.72	7.81	7.89
12	7.78	8.72	9.51	10.22	10.91	11.55	12.15

EXPERIMENT 3 (Figure 3.4)

SRP Values

A-3.26 Individual batch change in SRP (mg/L) from addition of fertilizer (July 20-31, 1995)

Date Time Scale (days)	20-Jul 1	21-Jul 2	23-Jul 4	25-Jul 6	27-Jul 8	29-Jul 10	31-Jul 12
Bottle#1	6.44	0.85	0.64	0.42	0.41	0.33	0.31
2	6.99	0.7	0.53	0.44	0.42	0.31	0.35
3	6.83	0.73	0.66	0.48	0.46	0.4	0.35
4	6.96	0.86	0.65	0.4	0.45	0.35	0.3
5	6.62	0.68	0.58	0.35	0.36	0.32	0.27
6	0	0	0	0	0	0	0
7	2.95	0.15	0.13	0.15	0.09	0.08	0.07
8	4.68	0.43	0.3	0.24	0.15	0.15	0.12
9	3.24	0.26	0.2	0.18	0.11	0.13	0.09
10	4.34	0.32	0.19	0.16	0.1	0.1	0.09
11	4.19	0.33	0.17	0.18	0.09	0.11	0.1
12	0	0	0	0	0	0	0

A-3.27 Cumulative change in SRP (mg/L) from addition of fertilizer (July 20-31, 1995)

Cumul. Hrs.	0	24	48	96	144	192	240	288
Bottle#1	0	6.44	7.29	7.93	8.35	8.76	9.09	9.4
2	0	6.99	7.69	8.22	8.66	9.08	9.39	9.74
3	0	6.83	7.56	8.22	8.7	9.16	9.56	9.91
4	0	6.96	7.82	8.47	8.87	9.32	9.67	9.97
5	0	6.62	7.3	7.88	8.23	8.59	8.91	9.18
6	0	0	0	0	0	0	0	0
7	0	2.95	3.1	3.23	3.38	3.47	3.55	3.62
8	0	4.68	5.11	5.41	5.65	5.8	5.95	6.07
9	0	3.24	3.5	3.7	3.88	3.99	4.12	4.21
10	0	4.34	4.66	4.85	5.01	5.11	5.21	5.3
11	0	4.19	4.52	4.69	4.87	4.96	5.07	5.17
12	0	0	0	0	0	0	0	0

A-3.28 Normalized SRP (SRP / pellet wt.) for individual batch change

Date	20-Jul	21-Jul	23-Jul	25-Jul	27-Jul	29-Jul	31-Jul
Time Scale (days)	1	2	4	6	8	10	12
Bottle#1	64.40	8.50	6.40	4.20	4.10	3.30	3.10
2	69.41	6.95	5.26	4.37	4.17	3.08	3.48
3	68.30	7.30	6.60	4.80	4.60	4.00	3.50
4	69.53	8.59	6.49	4.00	4.50	3.50	3.00
5	65.87	6.77	5.77	3.48	3.58	3.18	2.69
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	29.50	1.50	1.30	1.50	0.90	0.80	0.70
8	46.66	4.29	2.99	2.39	1.50	1.50	1.20
9	32.37	2.60	2.00	1.80	1.10	1.30	0.90
10	43.40	3.20	1.90	1.60	1.00	1.00	0.90
11	41.86	3.30	1.70	1.80	0.90	1.10	1.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00

A-3.29 Cumulative normalized change in SRP (mg/L) from addition of fertilizer

Cumul. Hrs.	0	24	48	96	144	192	240	288
Bottle#1	0	64.40	72.90	79.30	83.50	87.60	90.90	94.00
2	0	69.41	76.36	81.62	85.99	90.16	93.24	96.72
3	0	68.30	75.60	82.20	87.00	91.60	95.60	99.10
4	0	69.53	78.12	84.61	88.61	93.11	96.60	99.60
5	0	65.87	72.64	78.41	81.89	85.47	88.66	91.34
6	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0	29.50	31.00	32.30	33.80	34.70	35.50	36.20
8	0	46.66	50.95	53.94	56.33	57.83	59.32	60.52
9	0	32.37	34.97	36.97	38.76	39.86	41.16	42.06
10	0	43.40	46.60	48.50	50.10	51.10	52.10	53.00
11	0	41.86	45.16	46.86	48.65	49.55	50.65	51.65
12	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TP Values

A-3.30 Individual batch change in TP (mg/L) from addition of fertilizer (July 20-31, 1995)

Date	20-Jul	21-Jul	23-Jul	25-Jul	27-Jul	29-Jul	31-Jul
Time Scale (days)	1	2	4	6	8	10	12
Bottle#1	6.9	0.98	0.85	0.49	0.39	0.31	0.26
2	7.32	0.86	0.72	0.55	0.42	0.35	0.27
3	6.64	0.85	0.83	0.58	0.47	0.34	0.34
4	7.3	1.18	0.88	0.46	0.42	-	0.3
5	6.97	0.94	0.79	0.47	0.4	0.27	0.27
6	0	0	0	0	0	0	0
7	3.99	0.26	0.27	0.19	0.18	0.14	0.14
8	5.7	0.36	0.47	0.29	0.26	0.24	0.19
9	4.03	0.31	0.34	0.24	0.2	0.2	0.18
10	6.04	0.44	0.31	0.23	0.17	0.19	0.15
11	2.92	0.43	0.15	0.21	0.22	0.15	0.13
12	0	0	0	0	0	0	0

A-3.31 Cumulative change in TP (mg/L) from addition of fertilizer (July 20-31, 1995)

Cumul. Hrs.	0	24	48	96	144	192	240	288
Bottle#1	0	6.9	7.88	8.73	9.22	9.61	9.92	10.18
2	0	7.32	8.18	8.9	9.45	9.87	10.22	10.49
3	0	6.64	7.49	8.32	8.9	9.37	9.71	10.05
4	0	7.3	8.48	9.36	9.82	10.24	10.24	10.54
5	0	6.97	7.91	8.7	9.17	9.57	9.84	10.11
6	0	0	0	0	0	0	0	0
7	0	3.99	4.25	4.52	4.71	4.89	5.03	5.17
8	0	5.7	6.06	6.53	6.82	7.08	7.32	7.51
9	0	4.03	4.34	4.68	4.92	5.12	5.32	5.5
10	0	6.04	6.48	6.79	7.02	7.19	7.38	7.53
11	0	2.92	3.35	3.5	3.71	3.93	4.08	4.21
12	0	0	0	0	0	0	0	0

A-3.32 Normalized TP (TP / pellet wt.) for individual batch change

Date Time Scale (days)	20-Jul 1	21-Jul 2	23-Jul 4	25-Jul 6	27-Jul 8	29-Jul 10	31-Jul 12
Bottle#1	69.00	9.80	8.50	4.90	3.90	3.10	2.60
2	72.69	8.54	7.15	5.46	4.17	3.48	2.68
3	66.40	8.50	8.30	5.80	4.70	3.40	3.40
4	72.93	11.79	8.79	4.60	4.20	0.00	3.00
5	69.35	9.35	7.86	4.68	3.98	2.69	2.69
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	39.90	2.60	2.70	1.90	1.80	1.40	1.40
8	56.83	3.59	4.69	2.89	2.59	2.39	1.89
9	40.26	3.10	3.40	2.40	2.00	2.00	1.80
10	60.40	4.40	3.10	2.30	1.70	1.90	1.50
11	29.17	4.30	1.50	2.10	2.20	1.50	1.30
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00

A-3.33 Cumulative normalized change in TP (mg/L) from addition of fertilizer

Cumul. Hrs.	0	24	48	96	144	192	240	288
Bottle#1	0	69.00	78.80	87.30	92.20	96.10	99.20	101.80
2	0	72.69	81.23	88.38	93.84	98.01	101.49	104.17
3	0	66.40	74.90	83.20	89.00	93.70	97.10	100.50
4	0	72.93	84.72	93.51	98.10	102.30	102.30	105.30
5	0	69.35	78.70	86.56	91.24	95.22	97.91	100.59
6	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0	39.90	42.50	45.20	47.10	48.90	50.30	51.70
8	0	56.83	60.42	65.11	68.00	70.59	72.98	74.88
9	0	40.26	43.36	46.75	49.15	51.15	53.15	54.95
10	0	60.40	64.80	67.90	70.20	71.90	73.80	75.30
11	0	29.17	33.47	34.96	37.06	39.26	40.76	42.06
12	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00

EXPERIMENT 4 (Figure 3.5)

SRP Values

A-3.34 Individual batch change in SRP (mg/L) from addition of fertilizer (August 14-25, 1995)

Date Time Scale (days)	14-Aug 1	15-Aug 2	17-Aug 4	19-Aug 6	21-Aug 8	23-Aug 10	25-Aug 12
Bottle#1	5.76	0.93	0.98	0.64	0.49	0.52	0.45
2	6.9	0.74	0.78	0.54	0.46	0.42	0.64
3	8.38	1.24	0.87	0.85	0.88	0.89	0.61
4	7.32	0.97	0.99	0.7	0.56	0.65	0.64
5	6.57	0.93	0.92	0.63	0.54	0.52	0.61
6	7.82	0.75	0.76	0.49	0.39	0.32	0.3
7	6.19	0.72	0.47	0.41	0.46	0.38	0.47
8	7.41	0.79	0.6	0.52	0.58	0.45	0.42
9	7.13	0.87	1.01	0.72	0.63	0.58	0.58
10	6.1	0.74	0.81	0.55	0.43	0.34	0.34
11	7.96	0.98	1.03	0.66	0.59	0.67	0.59
12	7.34	0.78	1	0.5	0.52	0.43	0.42

A-3.35 Cumulative change in SRP (mg/L) from addition of fertilizer (Aug 14-25, 1995)

Cumul. Hrs.	0	24	48	96	144	192	240	288
Bottle#1	0	5.76	6.69	7.67	8.31	8.8	9.32	9.77
2	0	6.9	7.64	8.42	8.96	9.42	9.84	10.48
3	0	8.38	9.62	10.49	11.34	12.22	13.11	13.72
4	0	7.32	8.29	9.28	9.98	10.54	11.19	11.83
5	0	6.57	7.5	8.42	9.05	9.59	10.11	10.72
6	0	7.82	8.57	9.33	9.82	10.21	10.53	10.83
7	0	6.19	6.91	7.38	7.79	8.25	8.63	9.1
8	0	7.41	8.2	8.8	9.32	9.9	10.35	10.77
9	0	7.13	8	9.01	9.73	10.36	10.94	11.52
10	0	6.1	6.84	7.65	8.2	8.63	8.97	9.31
11	0	7.96	8.94	9.97	10.63	11.22	11.89	12.48
12	0	7.34	8.12	9.12	9.62	10.14	10.57	10.99

TP Values

A-3.36 Individual batch change in TP (mg/L) from addition of fertilizer (August 14-25, 1995)

Date Time Scale (days)	14-Aug 1	15-Aug 2	17-Aug 4	19-Aug 6	21-Aug 8	23-Aug 10	25-Aug 12
Bottle#1	6.89	0.96	1.11	0.67	0.49	0.54	0.51
2	7.44	0.78	0.84	0.62	0.51	0.43	0.71
3	8.51	1.29	1.45	0.93	1	0.97	0.65
4	8.14	1.06	1.1	0.8	0.64	0.7	0.69
5	7.05	0.93	0.95	0.68	0.56	0.63	0.64
6	8.17	0.76	0.79	0.56	0.43	0.43	0.33
7	6.69	0.86	0.94	0.54	0.5	0.41	0.54
8	8.01	0.88	0.87	0.54	0.67	0.5	0.48
9	8.22	0.94	1.1	0.79	0.71	0.63	0.61
10	7.11	0.91	1.01	0.76	0.49	0.38	0.41
11	8.11	0.98	1.13	0.81	0.66	0.83	0.7
12	8.17	0.93	1.09	0.84	0.56	0.51	0.48

A-3.37 Cumulative change in TP (mg/L) from addition of fertilizer (Aug 14-25, 1995)

Cumul. Hrs.	0	24	48	96	144	192	240	288
Bottle#1	0	6.89	7.85	8.96	9.63	10.12	10.66	11.17
2	0	7.44	8.22	9.06	9.68	10.19	10.62	11.33
3	0	8.51	9.8	11.25	12.18	13.18	14.15	14.8
4	0	8.14	9.2	10.3	11.1	11.74	12.44	13.13
5	0	7.05	7.98	8.93	9.61	10.17	10.8	11.44
6	0	8.17	8.93	9.72	10.28	10.71	11.14	11.47
7	0	6.69	7.55	8.49	9.03	9.53	9.94	10.48
8	0	8.01	8.89	9.76	10.3	10.97	11.47	11.95
9	0	8.22	9.16	10.26	11.05	11.76	12.39	13
10	0	7.11	8.02	9.03	9.79	10.28	10.66	11.07
11	0	8.11	9.09	10.22	11.03	11.69	12.52	13.22
12	0	8.17	9.1	10.19	11.03	11.59	12.1	12.58

DOC Values

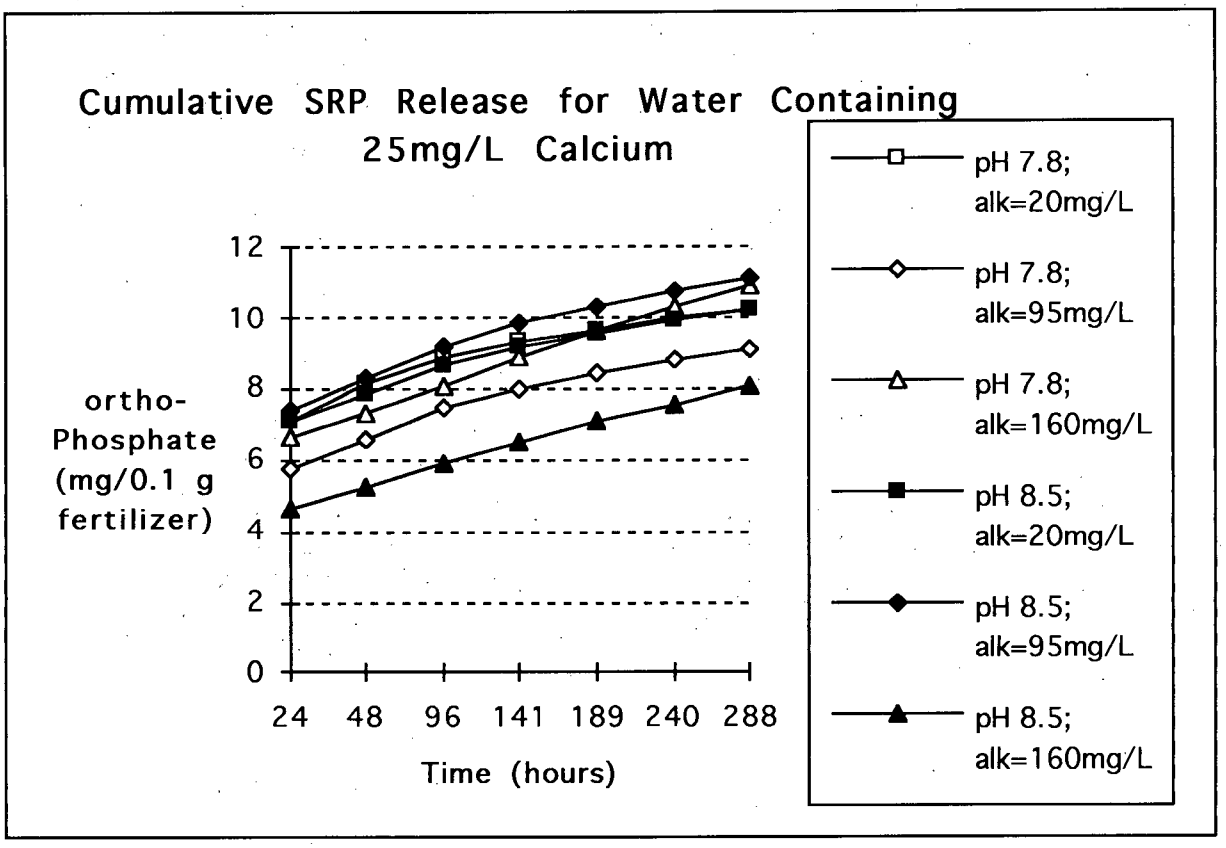
A-3.38 Individual batch change in DOC (mg/L) from addition of fertilizer (August 14-25, 1995)

Date Time Scale (days)	14-Aug 1	15-Aug 2	17-Aug 4	19-Aug 6	21-Aug 8	23-Aug 10	25-Aug 12
Bottle#1	24.1	16.8	17.2	16.5	18.8	18.9	19.5
2	12	8.8	8.5	8.1	9.6	9.2	9.4
3	7.4	6.5	6.4	6.5	7.1	6.2	6.4
4	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0
7	24.7	17.3	16.9	16.7	18.4	19.8	19.4
8	12.1	8.9	8.2	8.7	9.4	9.7	10
9	6.9	6.7	6.5	6.4	7.3	6.7	7
10	23.8	17.9	16.8	17.4	19.2	19.4	19.1
11	11.7	8.6	8.4	8.7	9.6	9.2	8.7
12	7	6.4	6.5	6.7	7.2	6.7	6.7

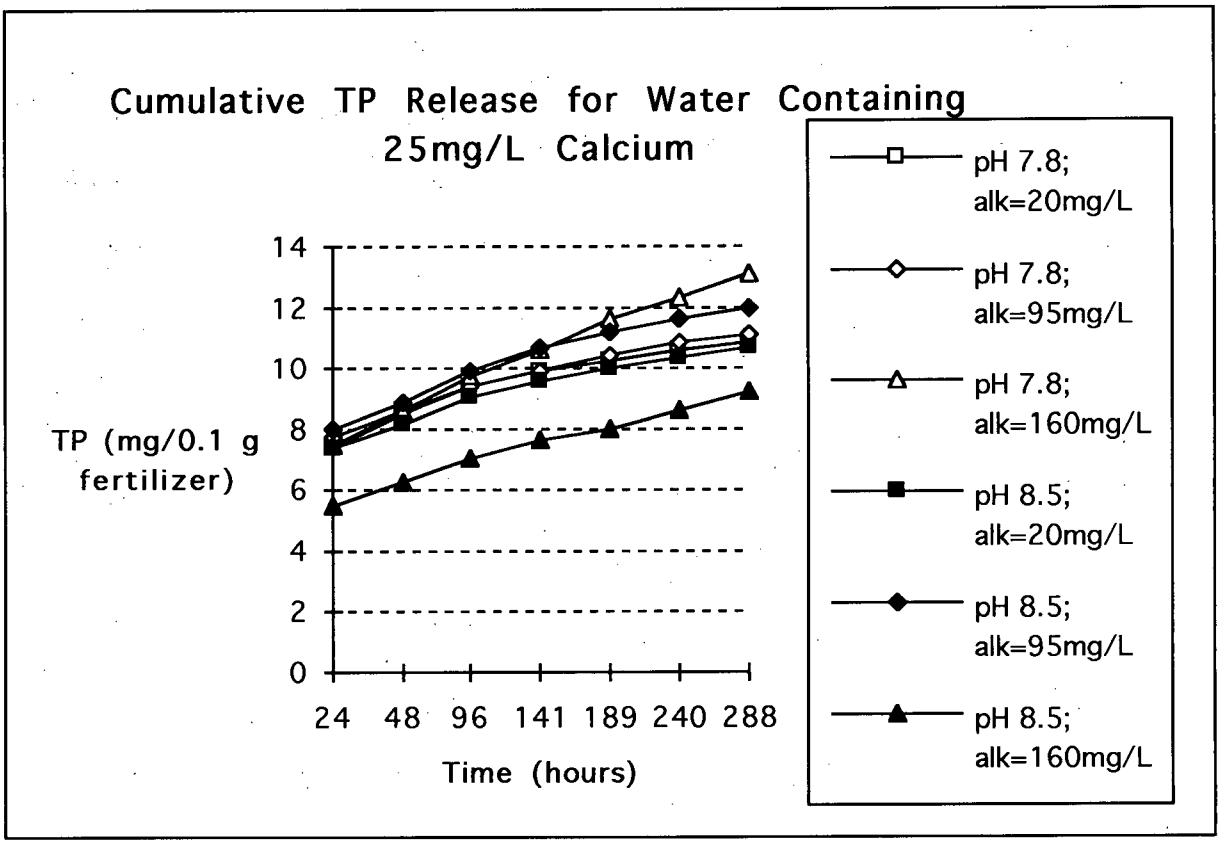
10. Appendix IV - Plots of SRP and TP in Various Solutions at 11 °C

Note: All calcium and alkalinity values are mg/L as $CaCO_3$.

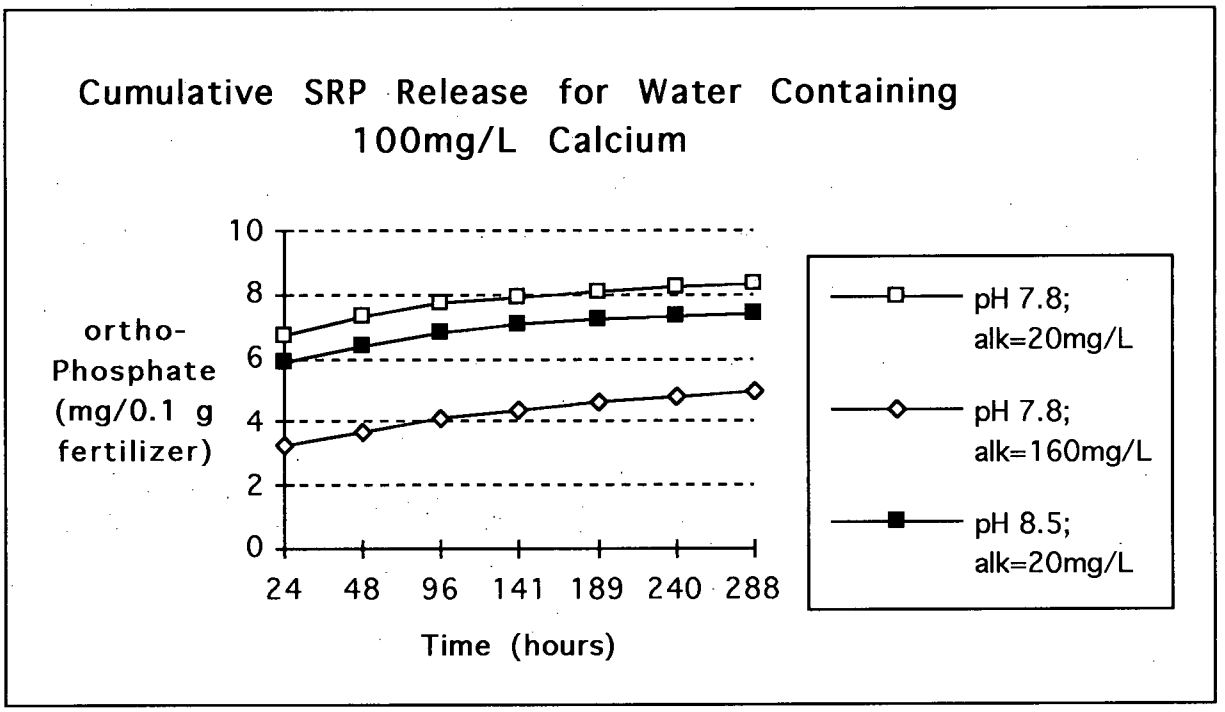
A-4.1



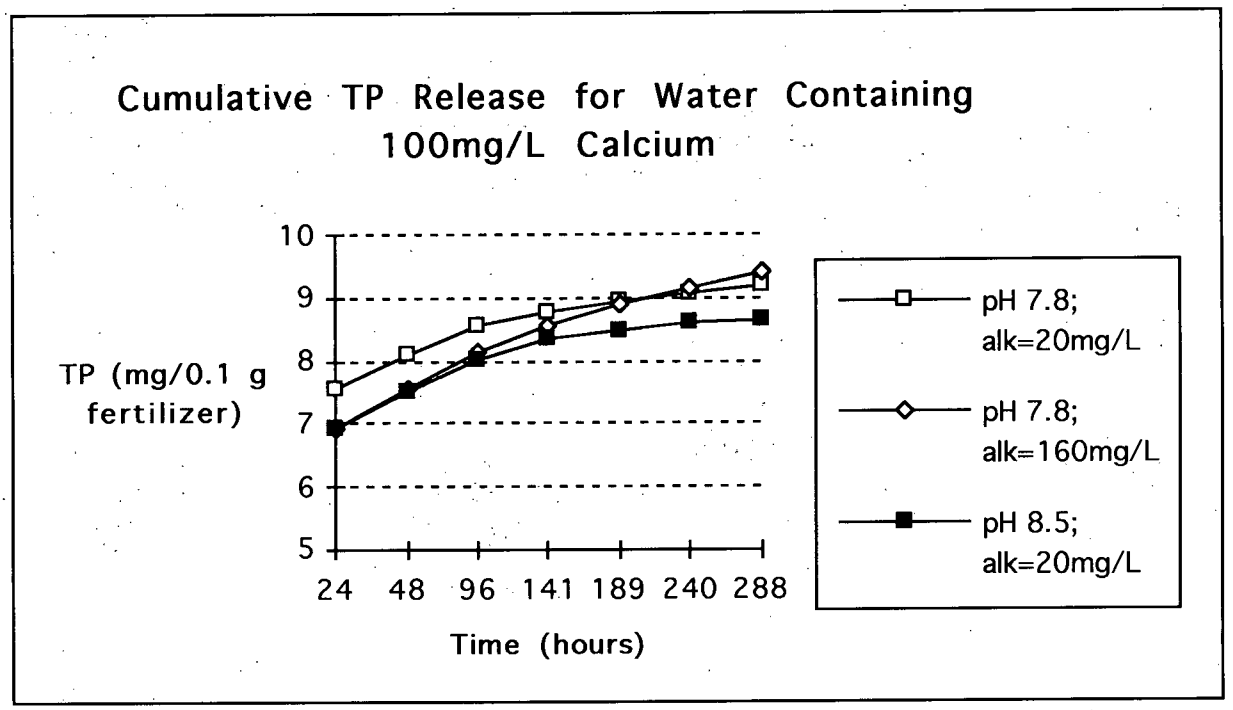
A-4.2


Cumulative TP Release for Water Containing 25mg/L Calcium
TP (mg/0.1 g fertilizer)
14
12
10
8
6
4
2
0
24 48 96 141 189 240 288
Time (hours)
pH 7.8; alk=20mg/L
pH 7.8; alk=95mg/L
pH 7.8; alk=160mg/L
pH 8.5; alk=20mg/L
pH 8.5; alk=95mg/L
pH 8.5; alk=160mg/L

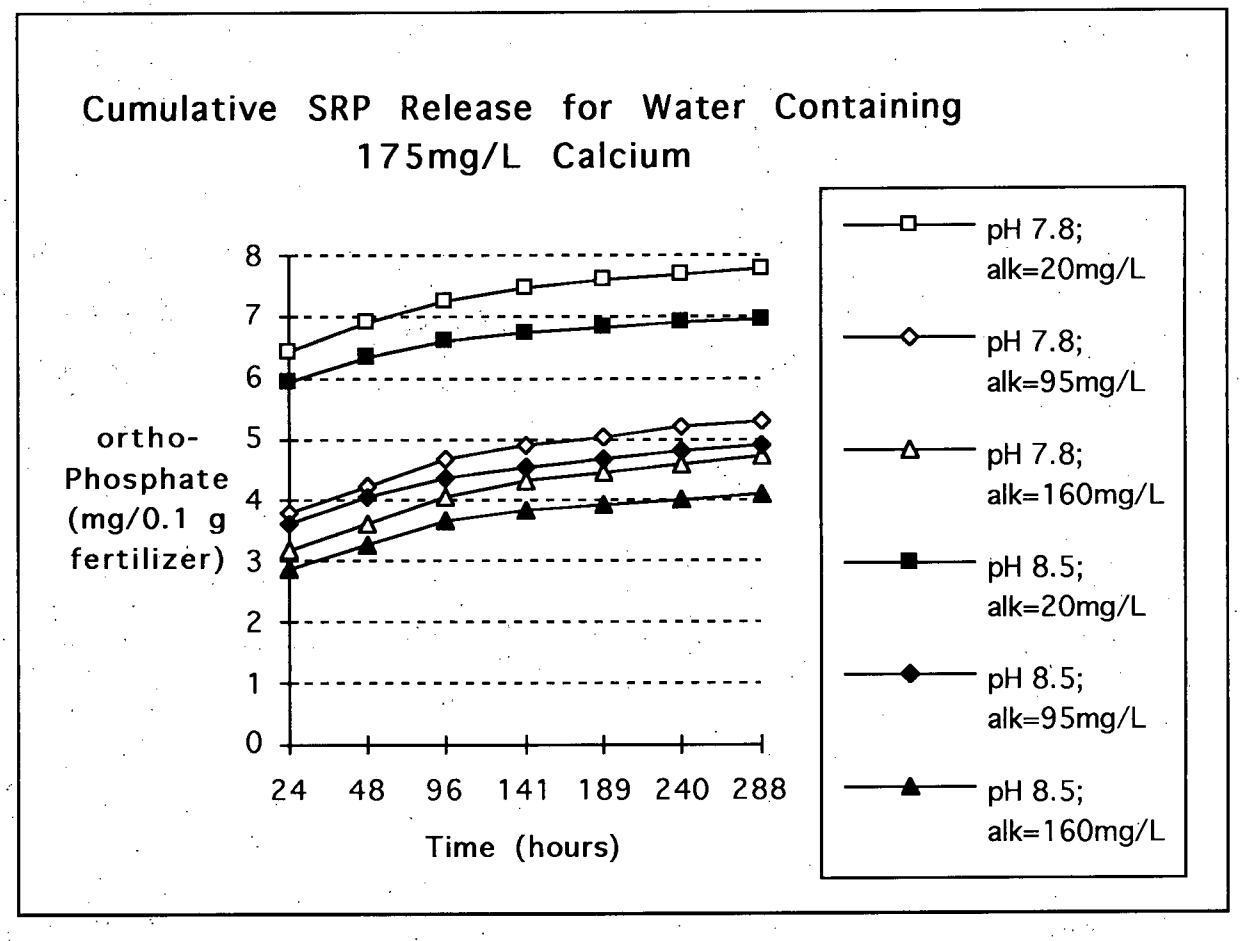
A-4.3


Cumulative SRP Release for Water Containing 100mg/L Calcium
ortho-Phosphate (mg/0.1 g fertilizer)
10
8
6
4
2
0
24 48 96 141 189 240 288
Time (hours)
pH 7.8; alk=20mg/L
pH 7.8; alk=160mg/L
pH 8.5; alk=20mg/L

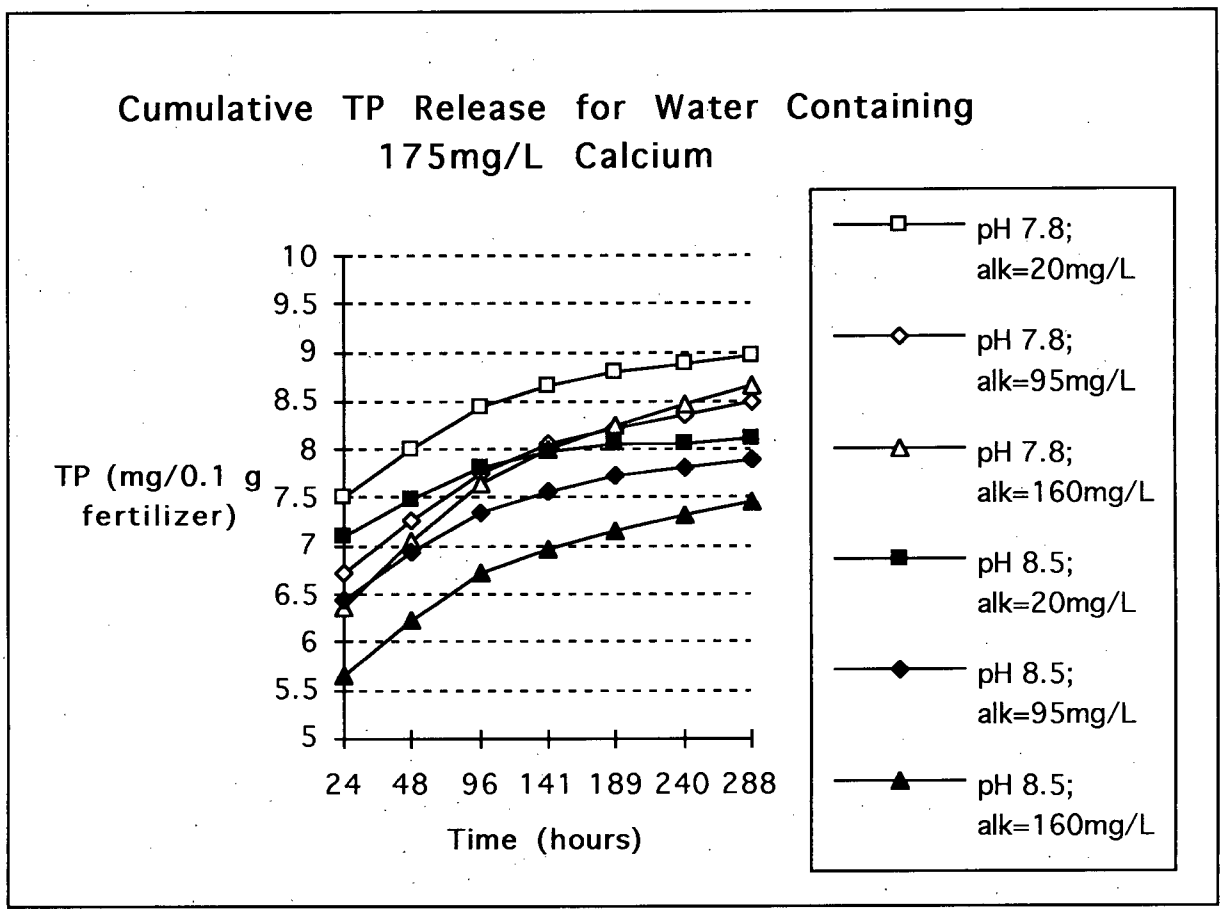
A-4.4

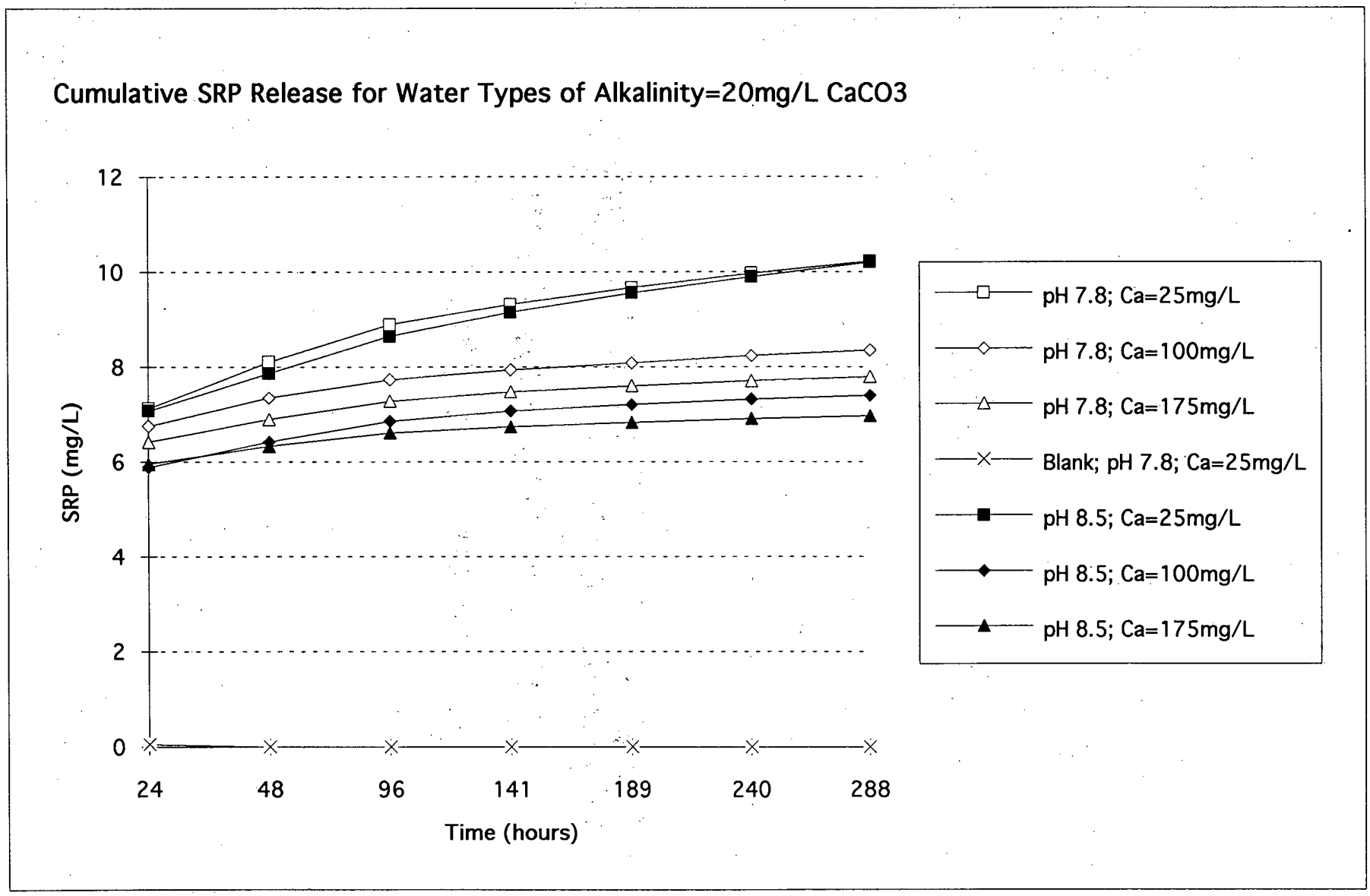

Cumulative TP Release for Water Containing 100mg/L Calcium
TP (mg/0.1 g fertilizer)
10
9
8
7
6
5
24 48 96 141 189 240 288
Time (hours)
pH 7.8; alk=20mg/L
pH 7.8; alk=160mg/L
pH 8.5; alk=20mg/L

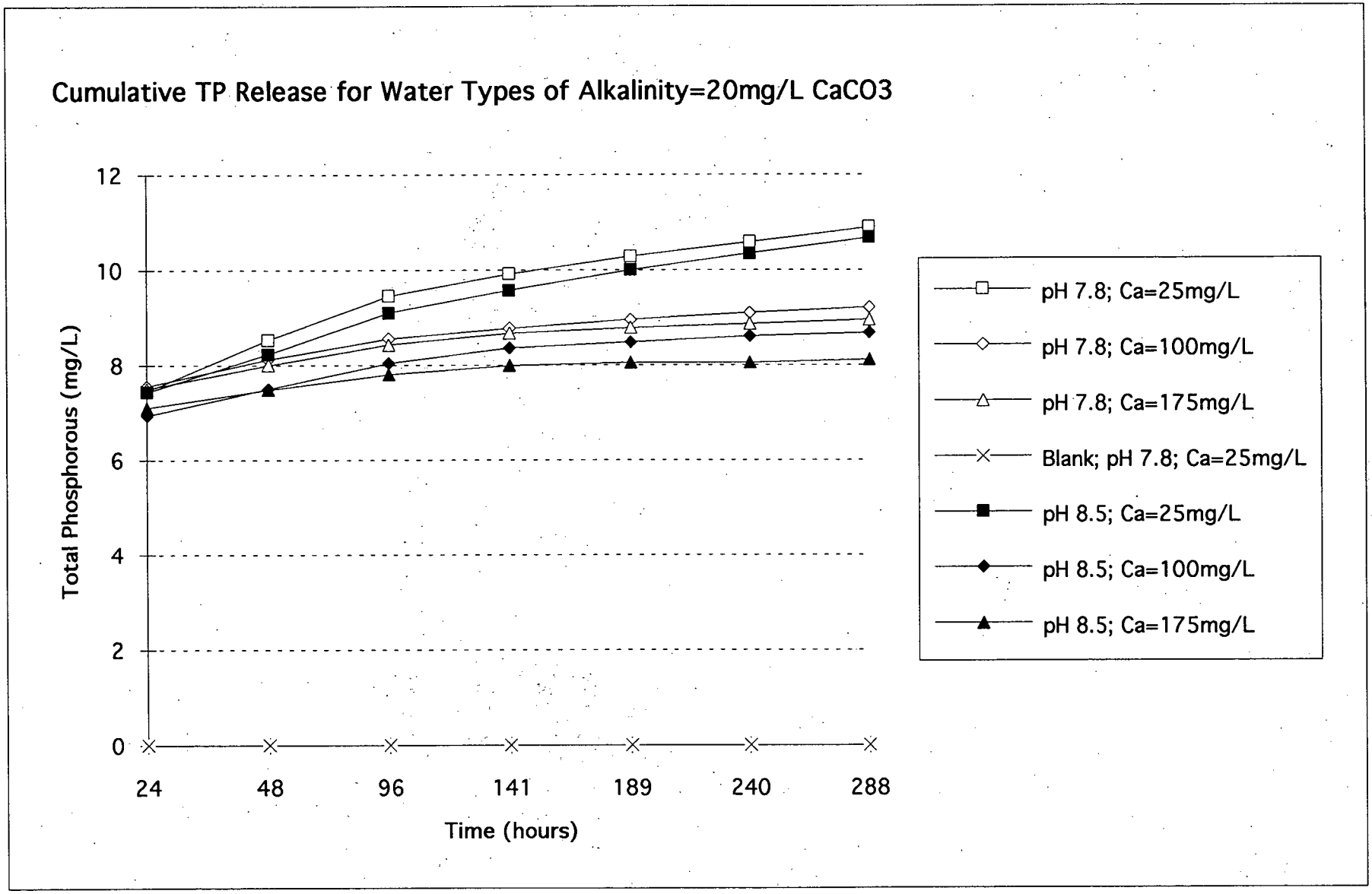
A-4.5


Cumulative SRP Release for Water Containing 175mg/L Calcium
ortho-Phosphate (mg/0.1 g fertilizer)
8
7
6
5
4
3
2
1
0
24 48 96 141 189 240 288
Time (hours)
pH 7.8; alk=20mg/L
pH 7.8; alk=95mg/L
pH 7.8; alk=160mg/L
pH 8.5; alk=20mg/L
pH 8.5; alk=95mg/L
pH 8.5; alk=160mg/L

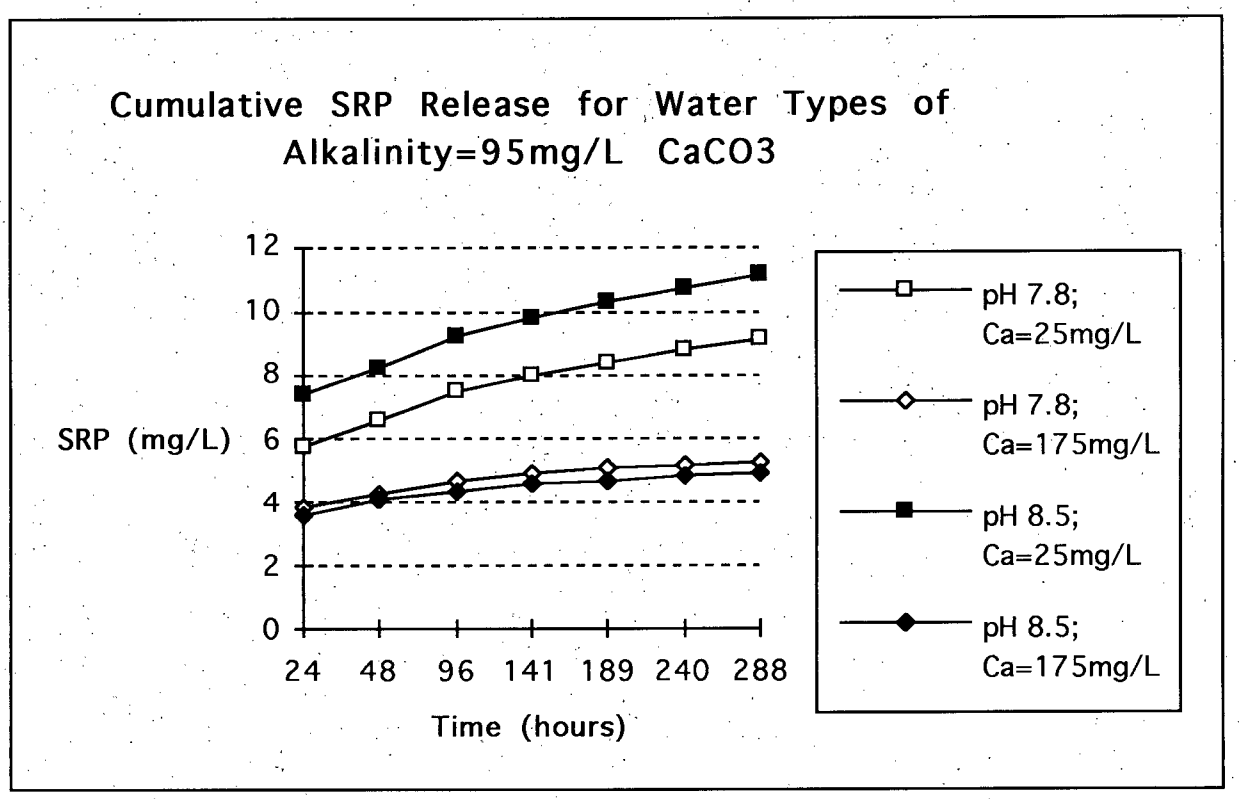
A-4.6


Cumulative TP Release for Water Containing 175mg/L Calcium
TP (mg/0.1 g fertilizer)
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
24 48 96 141 189 240 288
Time (hours)
pH 7.8; alk=20mg/L
pH 7.8; alk=95mg/L
pH 7.8; alk=160mg/L
pH 8.5; alk=20mg/L
pH 8.5; alk=95mg/L
pH 8.5; alk=160mg/L

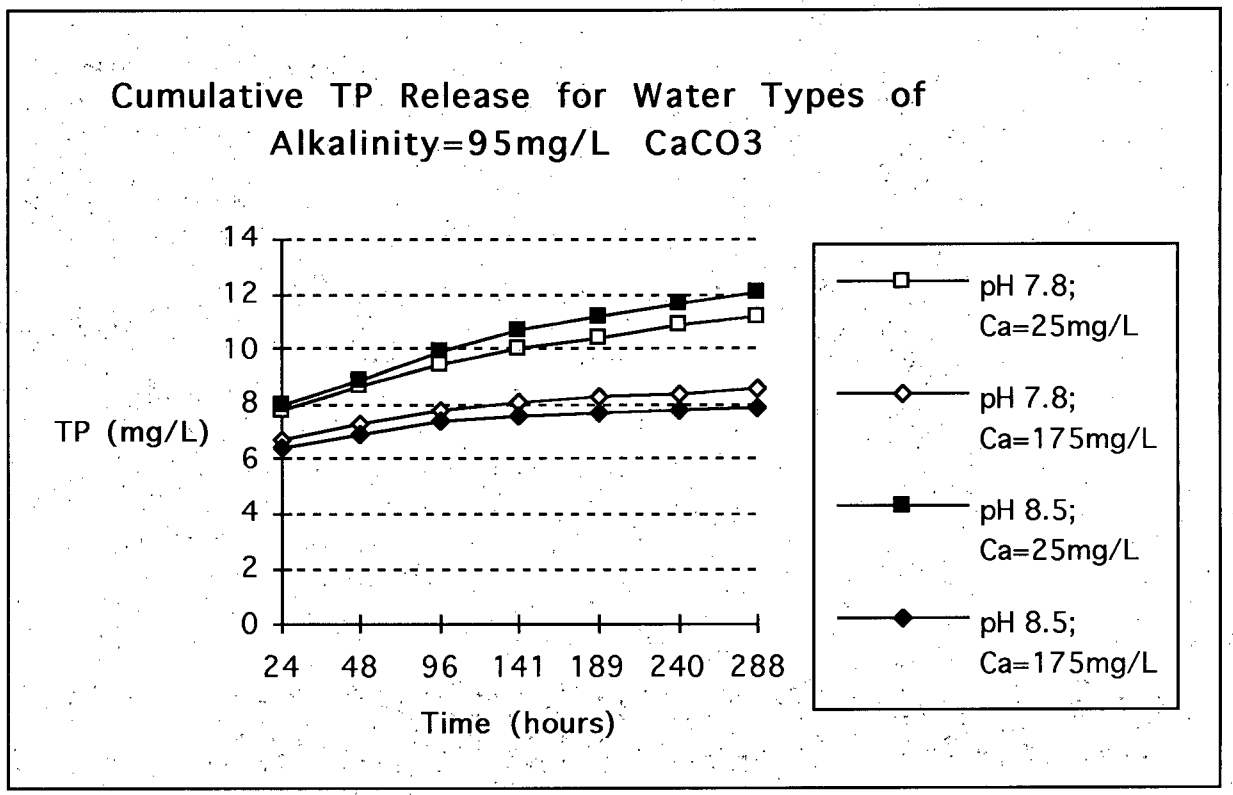

Cumulative SRP Release for Water Types of Alkalinity=20mg/L CaCO3
SRP (mg/L)
12
10
8
6
4
2
0
24
48
96
141
189
240
288
Time (hours)
pH 7.8; Ca=25mg/L
pH 7.8; Ca=100mg/L
pH 7.8; Ca=175mg/L
Blank; pH 7.8; Ca=25mg/L
pH 8.5; Ca=25mg/L
pH 8.5; Ca=100mg/L
pH 8.5; Ca=175mg/L


Cumulative TP Release for Water Types of Alkalinity=20mg/L CaCO3
Total Phosphorous (mg/L)
12
10
8
6
4
2
0
24
48
96
141
189
240
288
Time (hours)
pH 7.8; Ca=25mg/L
pH 7.8; Ca=100mg/L
pH 7.8; Ca=175mg/L
Blank; pH 7.8; Ca=25mg/L
pH 8.5; Ca=25mg/L
pH 8.5; Ca=100mg/L
pH 8.5; Ca=175mg/L

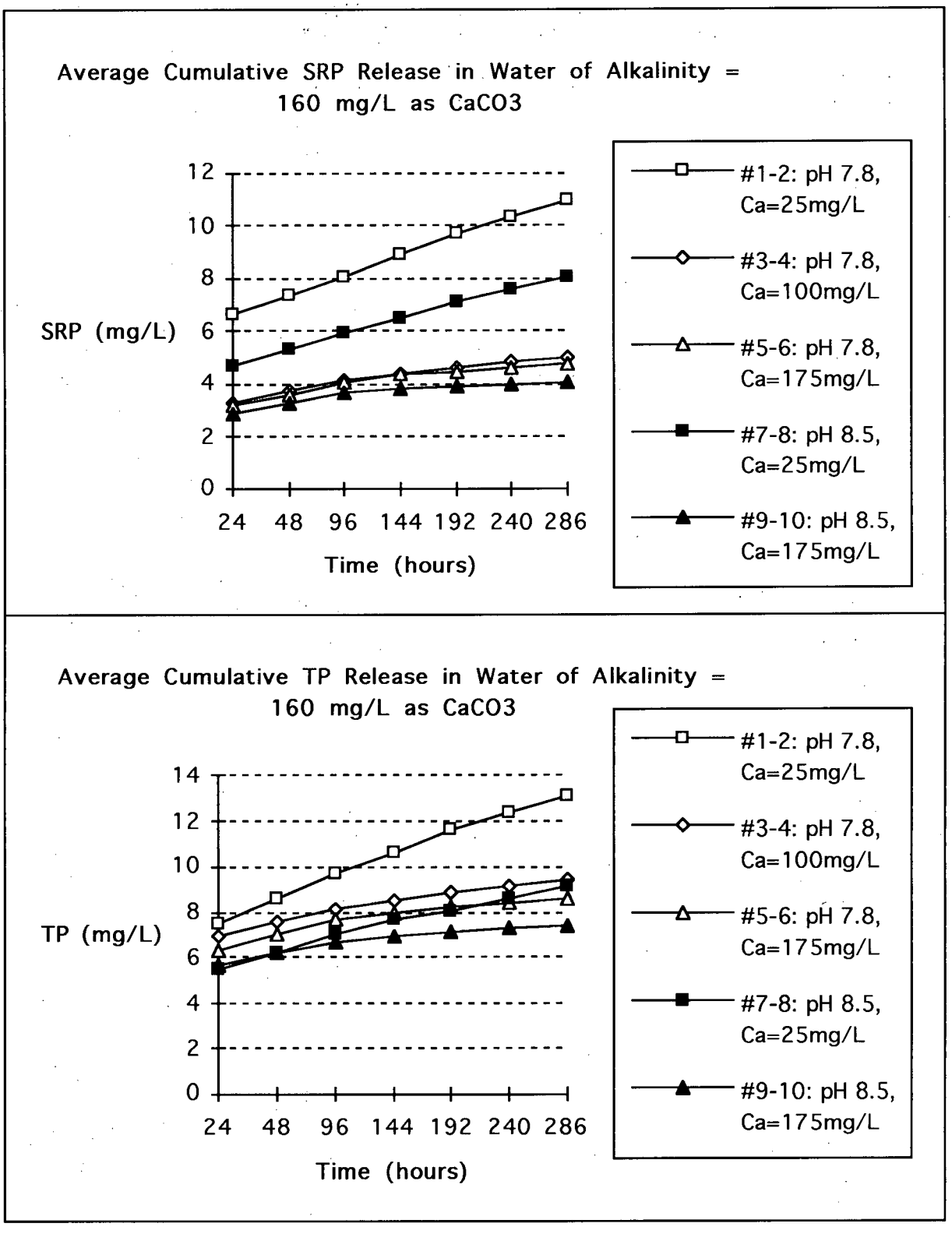
A-4.9


Cumulative SRP Release for Water Types of Alkalinity=95mg/L CaCO3
SRP (mg/L)
0
2
4
6
8
10
12
24
48
96
141
189
240
288
Time (hours)
pH 7.8; Ca=25mg/L
pH 7.8; Ca=175mg/L
pH 8.5; Ca=25mg/L
pH 8.5; Ca=175mg/L

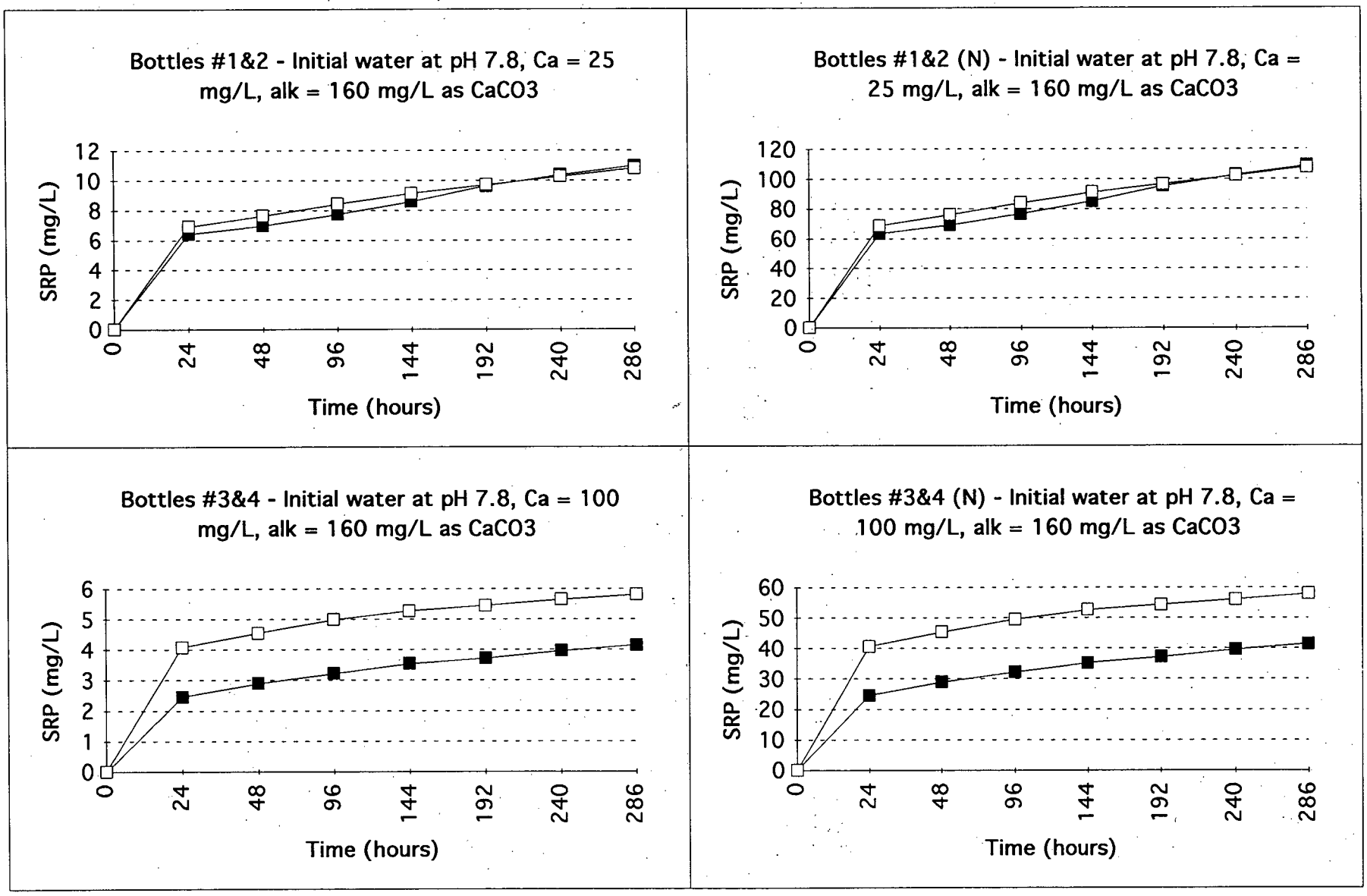
A-4.10


Cumulative TP Release for Water Types of Alkalinity=95mg/L CaCO3
TP (mg/L)
0
2
4
6
8
10
12
14
24
48
96
141
189
240
288
Time (hours)
pH 7.8; Ca=25mg/L
pH 7.8; Ca=175mg/L
pH 8.5; Ca=25mg/L
pH 8.5; Ca=175mg/L

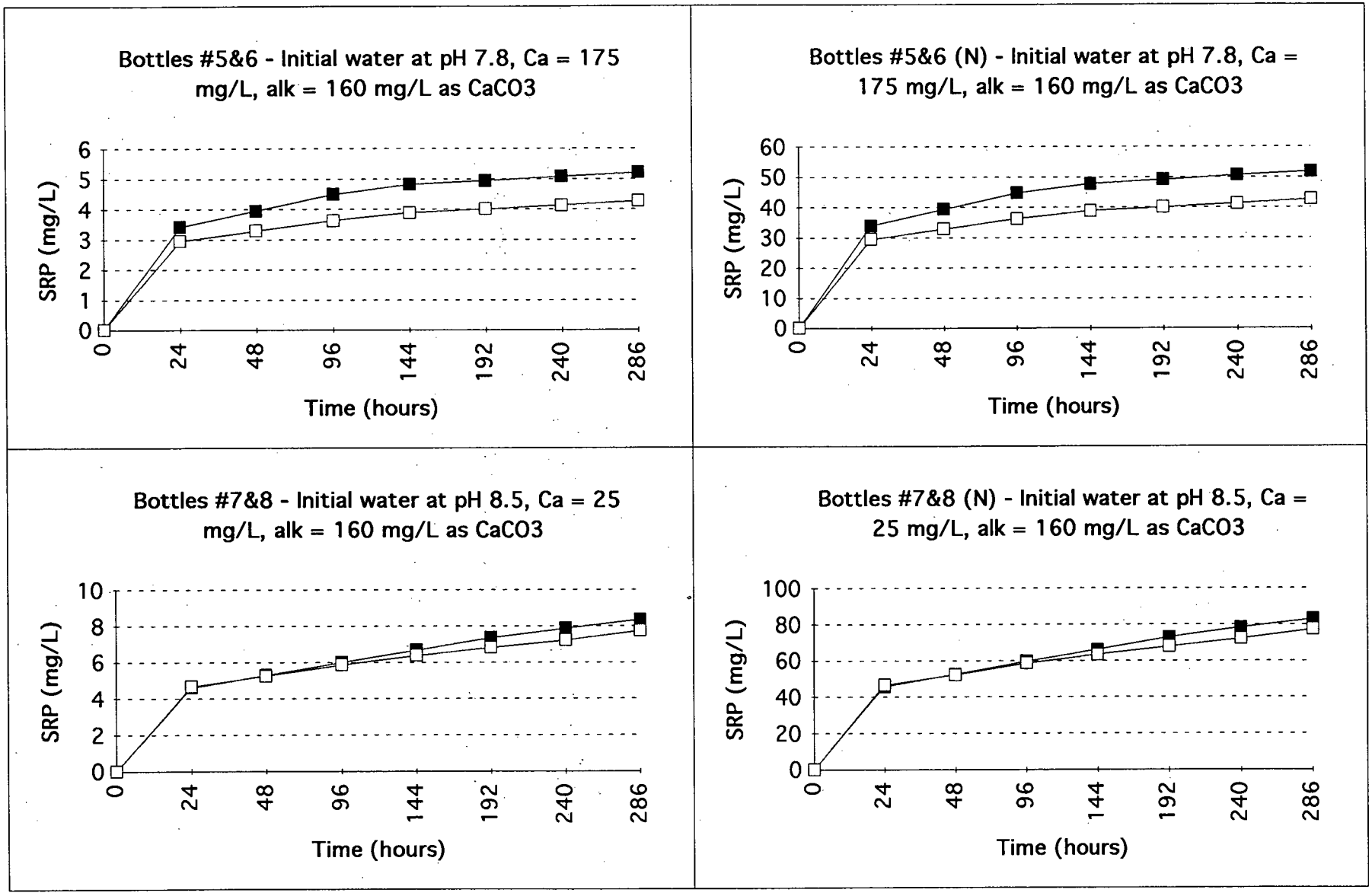
A-4.11


Average Cumulative SRP Release in Water of Alkalinity = 160 mg/L as CaCO3
SRP (mg/L)
0
2
4
6
8
10
12
24 48 96 144 192 240 286
Time (hours)
#1-2: pH 7.8, Ca=25mg/L
#3-4: pH 7.8, Ca=100mg/L
#5-6: pH 7.8, Ca=175mg/L
#7-8: pH 8.5, Ca=25mg/L
#9-10: pH 8.5, Ca=175mg/L
Average Cumulative TP Release in Water of Alkalinity = 160 mg/L as CaCO3
TP (mg/L)
0
2
4
6
8
10
12
14
24 48 96 144 192 240 286
Time (hours)
#1-2: pH 7.8, Ca=25mg/L
#3-4: pH 7.8, Ca=100mg/L
#5-6: pH 7.8, Ca=175mg/L
#7-8: pH 8.5, Ca=25mg/L
#9-10: pH 8.5, Ca=175mg/L

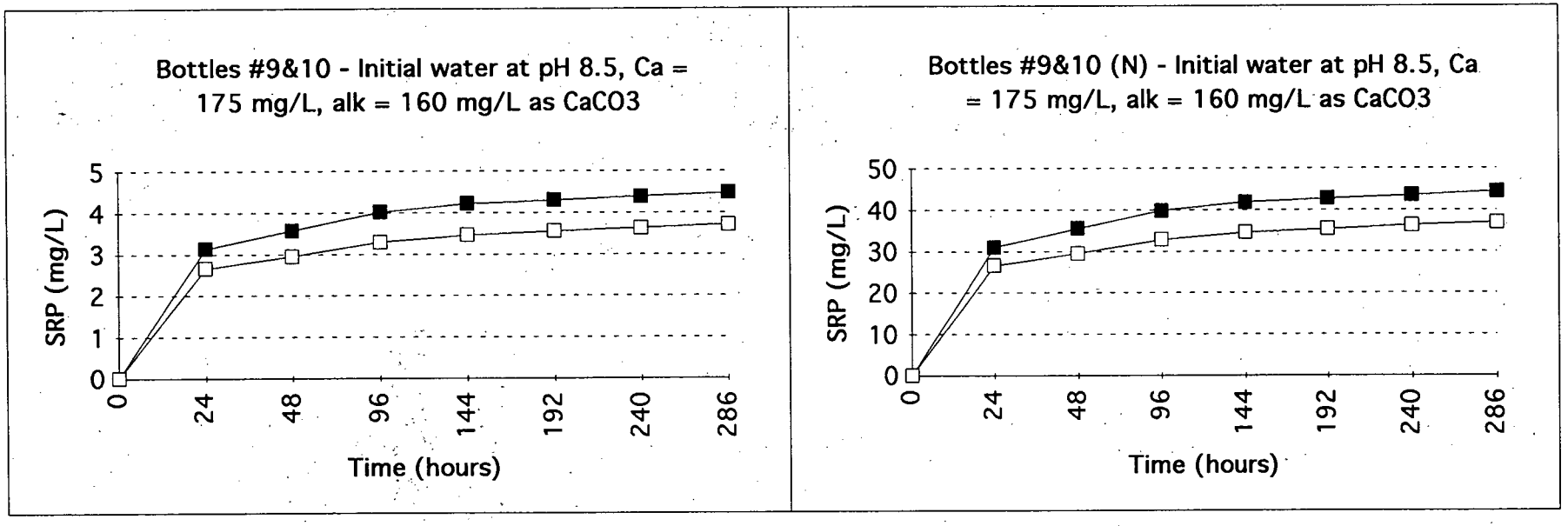
A-4.12



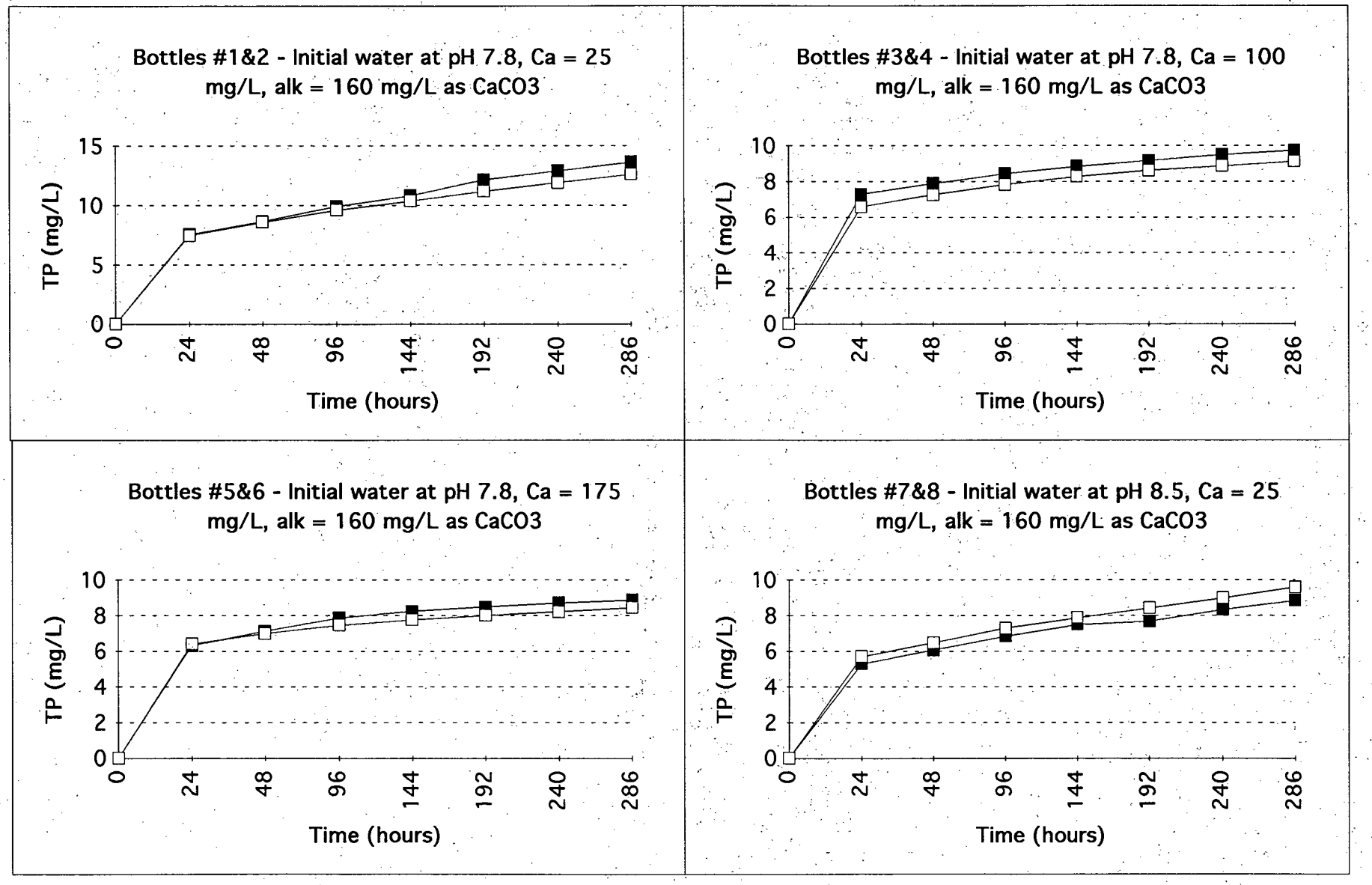
Cumulative duplicate SRP releases for: i) 0.1 g bundles (left column); and ii) normalized bundles to 1 g (right column).



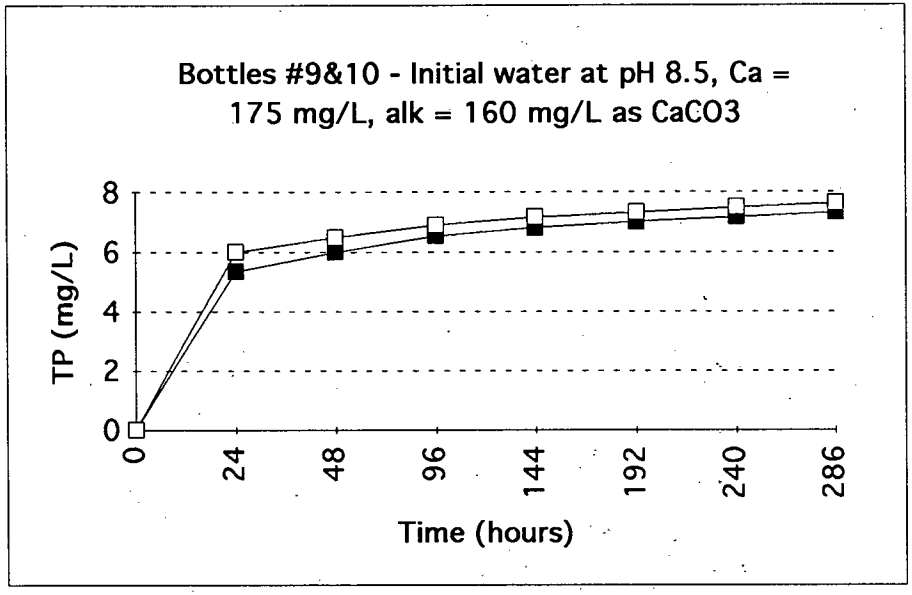
Cumulative duplicate SRP releases for: i) 0.1 g bundles (left column); and ii) normalized bundles to 1 g (right column).



Cumulative duplicate SRP releases for: i) 0.1 g bundles (left column); and ii) normalized bundles to 1 g (right column).



Cumulative duplicate TP releases for 0.1 g bundles.



Cumulative duplicate TP releases for 0.1 g bundles.

11. Appendix V - Sample Calculation for Stream Fertilization

Given a stream (1000 L/s; Ca^{2+} = 100 mg/L as $CaCO_3$; alkalinity = 50 mg/L as $CaCO_3$; pH = 7.8) needs fertilizer added to increase SRP by 1 μg/L over a duration of 2 weeks, the calculations required to determine the amount of fertilizer and size of pellets are as follows:

Determine SRP needed for 1 μg/L in 1 m^3/s flow for 14 days

SRP (kg) = (1000 L/s)(86400 s/d)(14 days)(1 μg/L)(10^{-9} kg/μg)
= 1.21

SRP released in water chemistry over 14 days, equation [4-2]

SRP (mg/g fertilizer) = - 0.22[Ca^{2+} (mg/L as $CaCO_3$)] - 0.16[Alkalinity (mg/L $CaCO_3$)] + 0.08[Time (hours)] + 91.11

SRP (mg/g fertilizer) = - 0.22(100 mg/L as $CaCO_3$) - 0.16[50 mg/L $CaCO_3$] + 0.08[336 hours] + 91.11

= 88.0

Weight fertilizer needed (W)

88.0 mg / g = 1.21 x 10^6 mg / W

W = 13.8 kg

Size of pellets for complete dissolution after 14 days

log % Weight lost = 0.392 [log Time (days)] + 0.688

% Weight lost = 13.7

13.7 % of a 9 g pellet = 1.23 g

Add a safety factor to pellet size, and ensure velocity of river will not carry fertilizer downstream. Otherwise, may need to have fertilizer made with a larger proportion of binder to make the pellets heavier.

12. Appendix VI - Honorariums for Thesis Assistance

Chocolate Nut Granola Cookies

1 cup margarine
3/4 cup granulated sugar
3/4 cup brown sugar
2 eggs
2 tsp. grated orange rind
1 tsp. vanilla
1 3/4 cup flour
1 tsp. salt
1 tsp. baking soda
3 cups granola
1 6-oz. package chocolate chips
1 cup chopped walnuts or almonds

1. In large bowl combine butter and sugars; beat until creamy.

2. Add eggs, orange peel, and vanilla; beat until fluffy.

3. Combine flour, salt, and soda; add to creamed mixture and stir until blended.

4. Stir in granola, chocolate chips and nuts.

5. Drop by heaping teaspoon onto greased cookie sheet.

6. Bake at 350 °F for 10-12 minutes.

Makes ~ 6 dozen cookies. ☺