A RIVER NUTRIENT PROCESSING MODEL FOR POINT SOURCE INPUTS

by

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ABSTRACT

Phosphorus, in its bioavailable forms, is one of the primary nutrients associated with the stimulation of primary productivity. In excess and in consort with other conditions, it is known to contribute toward environmental maladies such as algal blooms which lead to an overall degradation in water quality. Point source derived phosphorus remains one of the major regulatory concerns for discharge to surface water bodies. Evidence in the literature suggests that construction of tertiary wastewater treatment plants for the purpose of reducing phosphorus loadings below that provided by secondary treatment may be unwarranted because of large non-point phosphorus loading. A study was performed on the Neuse River, North Carolina, to determine the processing of point source phosphorus by rivers to which municipal treatment plants are discharged. The study included slope sampling for phosphorus and nitrogen species, major cations and anions, and other standard parameters. Data were then used to evaluate the "Stream Nutrient Processing Simulation" (SNUPS), a mathematical model which simulated the processing of point source phosphorus by rivers. The model included equations from the current EPA Qual-IIe model with enhancements to the phosphorus and nitrogen compartments and the use of a "slug" oriented, slope sampling modeling philosophy.

Data were collected downstream of the Raleigh, N.C. wastewater treatment plant effluent discharge during the months of April and September of 1986. Phosphorus loadings in the river decreased as flow progressed downstream in April but remained constant in September. Two hypothesis were proposed to account for the observations: a.) Reactive phosphorus may have been rendered biologically unavailable by complexing with metal colloids in September, or b.) April phosphorus processing may have been mediated by microbial mass discharged in the treatment plant effluent. Both hypothesis were evaluated using the current version of the SNUPS Model which did not satisfactorily simulate the data. Further development of the model is underway.

PART 1

INRODUCTION

Dissolved phosphorus, and nitrogen species are widely accepted as the principal causative agents for the stimulation of primary production in natural surface waters. Cycling and transport of these nutrients are dependent not only upon hydraulic characteristics of the system but also upon interactions with the indigenous biota. Nitrogen and phosphorus are generally taken up by algae in relatively constant proportions and released back to the environment through decomposition. The extent of primary production is generally governed by the demand for either nitrogen or phosphorus and its availability.

Dissolved phosphorus from point source discharges is often a closely regulated constituent because of its role in stimulating primary production. This regulation may take the form of treatment facility permits which require the installation of more advanced treatment methods or bans on the use of phosphorus-containing materials, such as household detergents. Evidence in the literature indicates that further regulation imposed upon point sources for phosphorus discharge seldom results in appreciable change in the downstream productivity levels and that overall dissolved phosphorus levels may not be significantly altered (Baker 1984). It is suggested that this is due to the overabundance of dissolved phosphorus from non-point sources such as agricultural runoff containing fertilizers or animal excrement.

Previous studies on the processing of phosphorus in the aquatic environment have relied upon the use of grab samples collected at random time sequences or, at best, some form of synoptic sampling where grabs or composites were gathered at regular intervals. Random samples tend to provide the least reliable data for interpretation since it is difficult to correlate non-connected events. For example, an isolated flow measurement cannot be realistically correlated with a grab sample for a chemical species collected a week later. Use of synoptic sampling is far more organized and some correlations are possible. Use of composited synoptic samples provides a good indication of what is happening on an average, but results are still difficult to interpret relative to the processing of specific discharges. This may be partially eliminated by using automated samplers taking discrete samples. Difficulties are reintroduced by the inability to determine which samples correlate to specific incidents at the point source discharge.

The study to be presented herein is designed to circumvent many of these problems. Samples were collected using slope sampling methods in which sample collection times at downstream locations were dictated by the time of travel in the river. In this way the same slug of water was sampled at each location as it was transported downstream so that processing of the constituents of interest could be studied as though they were dynamically acted upon in a fixed reactor.

In addition to analysis for nutrient species, a sampling set of other constituents which might affect phosphorus processing was constructed. This set was to be as complete as practical including analyses for suspended solids, major cation and anion species, chlorophyll-a, and traditional in-situ parameters such as pH, secchi depth, temperature and dissolved oxygen.

With the completion of sampling, data were entered into a mathematical model. Basic equations as used in the Qual-IIe have been modified using the results of the data analysis. In addition, the model philosophy has been modified to reflect the types of results that are to be expected using a slope sampling regime.

PART 2

HISTORICAL REVIEW

2.1 CLASSIFICATION OF PHOSPHORUS COMPOUNDS

Phosphorus compounds in the aqueous environment are classified as either particulate or dissolved (Figure 2.1). The total of these two fractions constitutes what is termed total phosphorus. Particulate phosphorus is that fraction which is adsorbed or bound to particles of matter, or "absorbed" as would be the case with biological assimilation. Dissolved phosphorus can be further classified and orthophosphate or complex phosphate.

2.2 ANALYTICAL METHODS FOR PHOSPHORUS COMPOUNDS

The classical analytical techniques for phosphorus compounds can be found in Standard Methods for the Examination of Water and Wastewater (American Public Health Association., 1985). Most analyses are performed for total phosphorus because the procedure does not require preservation of samples. However, orthophosphate is the fraction that is most readily assimilable by organisms. The orthophosphate fraction must be analyzed within 24 hours because there are no preservation techniques universally acceptable to prevent loss due to bioassimilation. This requirement makes the analysis inconvenient, especially when conducting long term field investigations. In addition to orthophosphate, a fraction of phosphorus in particulate form is also bioavailable. This fraction can be analyzed using algal bioassays or various physical or chemical extraction techniques.

The most popular laboratory technique for the analysis of phosphorus has been the molybdenum blue ascorbic acid method (Murphy and Riley, 1962). Using this method, orthophosphate reacts in an acid medium with reagents to form phosphomolybdic acid that is reduced to the molybdenum blue complex by ascorbic acid. The intensity of the color follows Beer's law for dilute solutions of phosphorus. This method is used for final measurement for all forms of phosphorus that can be solubilized.

Historic phosphorus analytical chemical classification include total phosphorus and dissolved phosphorus. Techniques for both of these measurements are reasonably simple and are easily adapted to field and laboratory studies, the major difference between them being in sample preparation. For both assays, acidification of the water immediately after collection has been recommended to reduce degradation of complex phosphorus compounds to orthophosphate. Because most inorganic particulate matter, bacteria and algae cannot pass through a 0.45 micron filter, dissolved phosphorus has often been defined as that fraction which passes through such a filter prior to acidification. Total phosphorus is acidified in its "as-collected" state. It has often been assumed that assaying for dissolved phosphorus is a good measure of bioavailable phosphorus. This fraction, when analyzed using the molybdenum- blue technique, is often referred to as Filterable Reactive Phosphorus (FRP). The arithmetic difference between total phosphorus and dissolved phosphorus (or FRP) has been interpreted as the non-bioavailable phosphorus.

2.3 PHOSPHORUS FRACTIONS AND BIOAVAILABILITY

The above assumptions relative to the bioavailability of filtered phosphorus are not entirely correct as it is now felt that all bioavailable phosphorus may not be represented by the dissolved phosphorus fraction. Indirect techniques have been developed to circumvent the difficulties of directly assaying for this fraction. These include bioassays (Logan et al., 1979; Logan, 1980; Cowan and Lee, 1976; Dorich and Nelson, 1977) and physical and chemical extraction methods of which the most popular is analysis by NaOH extraction methods (Verhoff, 1979).

The modified bottle test bioassay method is performed by incubating suspended sediment in a microorganism and algae suspension. Controls containing the organisms and known concentrations of nutrients are also incubated. From comparisons of starting and ending concentrations in the controls and test bottles, the amount of phosphorus biologically extracted from the sediment may be calculated. The technique may be used to assess the rate of biological availability of particulate-bound phosphates. In the river environment, if the rate of phosphorus release from the particulates is sufficiently rapid, the quantity of bioavailable phosphorus transported is determined by the rate of incorporation into biomass. If, however, the release rate is slow, then all of the potentially bioavailable particulate phosphorus will be transported as non-living particulate matter (Verhoff, 1979).

The NaOH-extractable phosphorus is that portion of the particulate-bound phosphorus which may be removed by contact with sodium hydroxide. This has been termed the soluble reactive phosphorus component of the NaOH-extract (NaOH-SRP) and has been found to correspond closely to the algal available particulate phosphorus (Sonzogni et al., 1981). Further evidence of this correlation was obtained in studies of Sandusky River water (Baker, 1984). Algae were observed to extract 20.7 percent of particulate phosphorus. A close correlation was seen with the NaOH-SRP fraction which was found to be 22.4 percent of the particulate phosphorus (DePinto et al. 1981). Similarly, algal available phosphorus was determined in bioassays of both suspended and bottom sediments by Young (1985). During the bioassays, changes in the NaOH-SRP were nearly equal to the phosphorus used by the algae in the bioassays (Young, 1985).

Much of the above work is responsible for considerable debate over the kinetics of phosphorus cycling in freshwater environments, especially relative to those fractions which are considered to be bioavailable. Evidence indicates that the assumption that the molybdenum blue ascorbic acid method is an accurate measure of bioavailable dissolved phosphorus may not be entirely correct and that errors as high as 100 percent may be induced in orthophosphate estimation (Rigler 1964).

Early work by Rigler (1964 and 1968) postulated that errors in the molybdenum blue method were attributed to the conversion of low molecular weight organic phosphorus compounds to a color producing compound during the acidification phase of analysis. These errors were demonstrated by comparing results obtained by applying the molybdenum blue ascorbic acid method directly to lake water filtrate and to lake water filtrate from which all organic phosphorus had been removed using an HZO column which retains inorganic phosphorus but not organic phosphorus. Rinsing the HZO column with NaOH would produce an eluent to which the dissolved P fraction would be released for subsequent analysis. In most cases, the HZO column:NaOH eluent contained lower concentrations of orthophosphate than did the direct analysis of the untreated lake water filtrate.

The hypothesis that more than one form of phosphorus was sensitive to the molybdenum blue ascorbic acid technique (Rigler, 1968) led to the postulation that cycling of phosphorus within the water column of a lake required more than two compartments (Figure 2.2). Furthermore, an assessment of the bioavailability of the phosphorus in each of these compartments was required. A diphasic model was proposed by Lean (1973) after applying gel separation techniques to radioactive 32-P labeled natural water. Lean demonstrated that particulate phosphorus that incorporated in living organisms was released as a high molecular weight substance (termed XP) which was then adsorbed to a colloidal material (Figure 2.2). This colloidal material acted as an intermediate for the majority of the XP phosphorus prior to its conversion to dissolved inorganic phosphorus. Although a small amount of XP was converted directly to dissolved inorganic phosphorus, the colloidal intermediate step was necessary to convert the majority of the XP to the dissolved, bioavailable form. These colloidal phosphate complexes were discovered to be negatively charged. It was hypothesized that if they became bound to positive ions, such as Ca^{++} or Fe^{+++}, they would be biologically unavailable. This would be due to the inability for further XP to be passed through the colloidal phosphorus intermediate to the dissolved phosphorus pool. In a flowing river environment, such a process could be responsible for the blockage of bioavailable phosphorus until the "bound" colloidal material was removed. The possible existence of a second dissolved compartment, which could by-pass this problem, was dismissed by Lean (1974). Chemical analysis for FRP using the molybdenum blue ascorbic acid method could lead to high estimation of bioavailable phosphorus since the relatively unavailable colloidal phosphorus could be observed as part of the dissolved bioavailable fraction.

Further work performed by Downes and Pearl (1978a) separated the filterable reactive phosphorus into two distinct fractions: reactive high molecular weight phosphorus (RHMW-P) with molecular weights > 5000 and orthophosphate (PO4-P). The acid in the molybdenum blue-ascorbic acid method was found to hydrolyze RHMW-P to orthophosphate, thereby creating an error in orthophosphate measurements. RHMW-P was bioavailable (Downes and Pearl 1978b), although at a slower rate than orthophosphate; RHMW-P compounds might take several days to be utilized by algae in bioassays. It was postulated that a majority of the RHMW-P was organically bound because it could be converted to orthophosphate using UV radiation. However, the possibility of FeP and CaP polymers and organic-inorganic complexes could not be dismissed. The existence of these cation-phosphorus complexes could limit further bioavailability.

The existence of some fraction other than orthophosphate was further supported by Peters (1978), however, it was observed to be a low molecular weight fraction which existed in a size range between 0.1 and 0.45 microns. This fraction was seen as involved in short term dynamics (Peters, 1979).

2.4 TRANSPORT DYNAMICS OF STREAM PHOSPHORUS.

2.4.1 General.

Much of the total phosphorus in streams can be non-point source in origin. Non-point sources of phosphorus include agricultural runoff and phosphorus adsorbed to eroded 10 soil. Sharpley (et al., 1979) found that stream bank erosion and the resuspension of stream sediments contributed 86 percent of the particulate phosphorous and 77 percent of the total phosphorus transported annually by streams in an experimental watershed in New Zealand. Estimation of the relative contribution of phosphorous from surface runoff must be approached with caution due to variations of the amounts of the various phosphorous forms transported from different types of catchments.

2.4.2 Factors Affecting Transport.

The factors influencing phosphorus transport in flowing waters include time (i.e. velocity), temperature, rainfall, land use, suspended solids concentration, factors affecting biological assimilation, and others (Cahill 1974). In rivers, two calculations are of primary interest: the concentration (important in assessing the algal phosphorus assimilation rate) and the flux (mass/unit time, input/output rates on loads) (Cahill 1974).

2.4.3 Types of Transport.

Two types of transport dynamics may be observed, each dependent upon the response of river stage (or depth) to runoff. Transport dynamics may be classified as either steady stage or unsteady stage as follows:

1.) Steady Stage transport occurs in stable response rivers. A stable response river is one in which increases in runoff result in only minor increases in river stage or depth. Steady stage transport exists for many substances, including total phosphorus, where the concentration is a function of the flow rate. For steady stage transport, the stage of the river is dominant over other factors such as land use, rainfall and temperature in its effect on the concentration of a substance. During steady stage transport, total phosphorus will tend to increase with increasing flow rate. In contrast, orthophosphate concentration shows an inverse relationship to flow (Wang and Evans, 1977). The inverse relationship, as exhibited by orthophosphate, is often referred to as the dilution effect.

2.) Unsteady Stage transport occurs in an event response river (Yaksich, et al., 1980). An event response river is one in which river stage or depth increases greatly with increase in runoff. Concentrations of substances such as total phosphorus become a function of the amount of sediment resuspension and non-point source runoff. During a runoff event, stream velocity becomes a primary factor affecting concentrations through stream bed scouring and resuspension of sediments (Yaksich et al., 1983). In Unsteady Stage transport there is generally a correlation between total phosphorous and total suspended solids during high flows; these correlations are useful modeling tools. However, during low flows, there is little, if any, correlation between TP and TSS making the modeling of phosphorus difficult (Yaksich et al., 1980).

During a storm, in an event response river (unsteady stage), the river flow increases due to runoff and the concentration of total phosphorus and total suspended solids also increase. Temporally, the peak concentration of total phosphorus precedes the peak flow. The concentration of NaOH-SRP parallels the total phosphorous concentration exhibiting a relatively constant NaOH-SRP:TP ratio (Baker, 1982). On the Sandusky River, Baker observed the mean NaOH-SRP:TP ratio to be between 20.8-24.8. The ratio of total phosphorus to sediment was found to decrease with increasing suspended sediment concentration. Baker states that this was probably due to an increase in the average distribution of particle size at the higher sediment concentration in which a higher concentration of smaller particles was observed. Smaller sediment particles appeared to be more involved in the phosphorus sorption process.

Most total phosphorus moves down-river via a series of resuspensions and settlings coinciding with high flow events. Phosphorus adsorbed to bed load is transported a finite distance with each event. Channel slope, as well as stream alterations, influence the distance of travel (Verhoff et al., 1978). Baker (1980) found that phosphorus deposited in Lake Erie from the Sandusky River was in the form of particulate phosphorus. Due to adsorption to suspended sediment, the original soluble reactive phosphorus fraction was transported only during storm events.

Phosphorus sorption to suspended matter may be, in part, influenced by the chemical makeup of the particulates and/or the water. Certain metallic substances associated with clays, especially iron, have a tendency to adsorb phosphates. In correlating esturarine pH versus iron, humic acid and phosphate concentrations, Carpenter and Smith (1985) demonstrated there was adsorption of phosphate onto colloidal iron phases in freshwater followed by subsequent colloidal aggregation. Phosphate desorption occurred upon mixing with seawater.

From the foregoing, it can be seen that the transport of phosphorus is dependent upon flow and an association with suspended matter. During low flow conditions, phosphorus associated with particulates and suspended matter settles. The dominant form of phosphorus likely to be found in the water column is in the dissolved state. With the increased velocity experienced during high runoff conditions, the phosphorus is resuspended and particulate adsorbed phosphorus becomes the dominant form.

2.5 POINT SOURCE PHOSPHORUS

It is generally accepted that total phosphorous concentrations in excess of 0.01 mg/l will contribute to eutrophication of a lake or reservoir (Vollenweider 1968, Randall 1978). In a survey of a variety of wastewater treatment plant discharges, the median concentration of total phosphorus was found to be 6.1 +/- 0.17 mg/l (Gakstatter et al., 1978). During a study on the Housatonic River in Connecticut, it was found that 89 percent of the total phosphorus from primary wastewater treatment plants was soluble (Connecticut EPA, 1983). In addition, algal assays performed on wastewater treatment discharges demonstrated an average of 72 percent of the total wastewater phosphorus was bioavailable during short term incubations of fourteen days (Young, 1982). From initial inspection it is easy to conclude that phosphorus loadings from wastewater treatment plants should be of concern with respect to increases in primary productivity rates downstream.

Other evidence in the literature suggests that concern for phosphorus of point source origin may be overemphasized and that non-point source phosphorus appears to contribute the majority of phosphorus load. Sharpley et al. (1979) found that 86 percent of total phosphorus found in a stream from an agricultural watershed was not of point source origin. Stream phosphorus was of non-point origin due to surface and subsurface runoff from agricultural, urban, and forested lands. Furthermore, several studies illustrate that it is reasonable for reservoir algal growths to continue to increase despite a decrease in WWTP discharge to them if a "non-eutrophic" concentration of phosphorus was never reached in the reservoir due to non-point phosphorus inputs. These are as follows:

- In a survey of southeastern reservoirs, Randall (1978) found that nutrient concentration (nitrogen and phosphorus) was not a strong function of tributary wastewater treatment plant discharges. Total point source discharges accounted for only

7 percent of the phosphorus received by the reservoir (Randall et al. 1979).

- Baker (1980) observed that phosphate reduction from point sources did not substantially reduce algal growth in Lake Erie. Assuming that all upstream phosphorus from wastewater treatment plants is exported, only 13 percent of the total phosphorus load may be accounted for at the Fremont Station at the mouth of the Sandusky River.
- A 49 percent decrease of total phosphorus discharges from wastewater treatment plants on the Housatonic River did not affect the water quality of Lake Lillinonah (Massachusetts Division of Water Pollution Control and Connecticut EPA, 1983). This was in part due to the large distances between discharges and the receiving body.
- On the Holston River and the Cherokee Reservoir in Tennessee, general water quality, as measured by a decrease in algal growth, increased with decreased waste discharges. Reductions also resulted in improved reservoir BOD, DO, TDS and total nitrogen. However, phosphorus concentrations remained relatively constant (Higgins, 1979). Phosphorus was clearly not the cause of increased primary productivity.

- In a study of the water quality of the Sangamon River and the east and west branches of the DuPage River, Illinois, such small quantities of phosphorus were added from point sources relative to non-point sources that further control on treatment plants would have little effect (Wilkin et al. 1980).

Point source phosphorus has been demonstrated to be more bioavailable than is non-point source phosphorus (Baker, 1982). In a study of four municipal treatment plant effluents, of the total phosphorus discharged, 82 percent of dissolved and 55 percent of particulate phosphorus was bioavailable (DePinto et al., 1980). This was in contrast to a study by Lee et al. (1980) in which 20 percent of non-point particulate was found to be bioavailable for both urban and agricultural runoff. In all cases, particulate phosphorus settled out before the bioavailable fraction was released and was lost from the bioavailable pool (Logan, 1978; Verhoff and Heffner, 1979; and DePinto et al., 1981). Thus, to assess the ultimate impact of tributary point source phosphorus on a downstream reservoir, it is necessary to first determine its tributary phosphorus kinetics.

Baker (1980) measured the mean of the total phosphorus and soluble reactive phosphorus concentrations along the length of the Sandusky River. It was noted that there was a decrease in concentration below each town rather than an expected increase. Removal appeared to be by biological uptake or chemical precipitation reactions rather than dilution. It was postulated that the bulk of point source total phosphorus was converted to particulate P and later incorporated into the sediments. Biological uptake, rather than physical adsorption, was important in processing point source phosphorus (Baker, 1982). In all cases, most of the dissolved phosphorus was removed from the water column within twenty-five miles of the outfall. Other examples available in the literature demonstrating the reduction of point source phosphorus in rivers include the Sangamon River and the east and west branches of the DuPage River, Illinois (Wilkin et al., 1980), the Occoquan Creek, Washington, D.C. (Randall, 1978), Rapid Creek (Harms, 1976) and the Potomac River, Maryland (Pritchard, 1972).

There are additional illustrations of the loss of point source phosphorus to the sediments within a short distance downstream of a wastewater treatment plant. Verhoff et al. (1978), demonstrated wastewater treatment plant orthophosphate accumulated in the sediments downstream of the outfall. Harms (1975) showed that sediments downstream from a point source always contained higher concentrations of phosphorus than those upstream. He postulated that a potential for release existed due to a concentration gradient between the interstitial water and the overlying waters; however, this was of little significance unless anoxic conditions were encountered. Yaksich et al. (1980) found that during low flows, 75 percent of the total phosphorus was lost after traveling 16 km. At high flows, only total phosphorus was resuspended. Orthophosphate was neither resuspended nor deposited. Carlson et al. (1978) demonstrated the ability of calcareous sediments to remove wastewater phosphorus from the water column. The reaction of calcium with phosphorus immobilized dissolved phosphorus and prevented its re-introduction into the water column.

It can be concluded that while point source discharges can be a source of bioavailable phosphorus, the distance upstream of a lake or reservoir is of considerable importance. Through normal biological activity and physical sedimentation, point source phosphorus may be removed from the water column within a relatively short distance from the source. Once in the sediments, the phosphorus does not appear to be resuspended in a bioavailable form, rather, it remains bound in an unavailable particulate form. Sediment bound phosphorus transported downstream provides a relatively unimportant contribution to lake and reservoir eutrophication.

2.6 PREVIOUS MODELS

Many references have been presented in the literature within the past ten years concerning various aspects of modeling river water quality. Two categories appear most frequently: (a) hydrodynamic models emphasizing sediment transport, especially during periods of runoff (e.g. Song and Yang 1979; Demetracopoulos, 1983; Decoursey, 1985; Grenney and Heyse, 1985; Nicholson and O'Connor, 1986) and (b) dissolved oxygen sag models with various degrees of interaction with select parameters (e.g. Demetracopoulos and Stephan, 1983; Bingham et al., 1984; Warwick and McDonnell, 1985; Bhargava, 1986; WIlliams and Lewis, 1986). None of the models cited above make specific reference to modeling phosphorus dynamics.

Most phosphorus models currently available concentrate on total watershed input of phosphorus rather than specific point source input. Although these have value for overall watershed management, they do not aid significantly in assessing the impact of wastewater treatment facilities and individual effluent discharge locations relative to a downstream lake or a reservoir. This is particularly evident in the work of Baker (1980, 1982) in studies conducted on the Sandusky River Basin in Ohio. The principal objection to the Sandusky Model concerned the data presented for the inorganic orthophosphate fraction. Because the collection methodology did not take into account the instability of the orthophosphate fraction, accuracy was improved by applying a correction factor derived from statistical methods. Using this technique, the degree of certainty was increased substantially for application to the entire river basin but remained low for application to individual discharges.

An extensive model was prepared for the U.S. Environmental Protection Agency (EPA) by the Northern Virginia Planning District Commission (1983) for use on the drainage basin of the Chesapeake Bay. The model was divided into three interrelated submodels covering three distinct areas. These were termed as the Basin Model, the Tidal Tributary Model and the Main Bay Model. Concern for the impact of point source discharges was covered primarily in the Basin Model, however, in an attempt to minimize computer time needed upon execution, the model used average concentrations and long time steps to simulate the basin interactions. The model design was primarily to assess the basin as a whole and the effect of basin quality upon bay quality, and was not amenable to use for evaluating the effects of individual point source discharges. In this model, input of phosphorus to the bay was associated primarily with runoff events and lacked the resolution to assess point sources adequately.

One of the more promising models demonstrating effects of point source inputs to flowing streams was the EPA Qual-IIe model. This model traces it origin to the early work of Streeter-Phelps (1962) and has appeared in several earlier, "Qual" Model versions (Texas Water Development Board, 1970; Water Resources Engineers, 1972; Meta Systems, 1979; Rosner et al., 1981). The classical Streeter-Phelps stream re-oxygenation equation was supplemented with modular subroutines permitting modeling of a broad range of oxygen sinks and sources. Modifications made by Walker (1980 and 1981) to the Meta Systems Qual-II version (1979) took into greater account water quality contributions due to nutrient cycling with the inclusion of algal self shading, algal uptake of ammonia and/or nitrate, and organic nitrogen and organic phosphorus components. Major ions were not included and phosphorus is simulated in only organic and dissolved compartments. Adsorption of phosphorus by suspended sediment was not considered to be required because steady-state equilibrium was assumed. The Walker model also did not simulate periphyton fluctuations. However, due to its modular design, it represents a good starting point for the present modeling effort.

Other models constructed for river basins have been primarily concerned with flow conditions or a dissolved oxygen sag curve. At the present time, no all-inclusive model exists dealing with point source discharges of phosphorus to a river, and its processing and transport therein.

2.7 Existing USGS Data for Study Site

A moderate amount of Neuse River water quality data has been collected by the United States Geological Survey (USGS) since 1971. Data exist for several sites on the Neuse River, including locations upstream (Falls station) and downstream (Clayton station) of Raleigh, N.C. These data were collected periodically with the purpose of providing a historical account of the improvement or deterioration of water quality as a result of water management activities. River discharge data were collected regularly at both stations, providing an unbroken daily record of discharge. An important determinant, not included in routine USGS data reporting, was stream velocity which regulates the suspension of particles.

While the USGS data were appropriate for assessing trends in water quality for the river as a whole, they were inadequate for the assessment of the actual impact upon the river due to current levels of phosphorus discharge from the wastewater treatment plant at Raleigh, or to support any point source modeling effort:

- Data, especially those for the downstream site at Clayton, were collected at irregular intervals making it difficult to perform meaningful data analysis on a seasonal basis.

- The lack of coordination in collection dates between the downstream Clayton site and the upstream Falls site made it impossible to develop significant upstream versus downstream relationships for a given sampling date.
- The paucity of data collected at both sites made it impossible to perform effective statistical analyses to investigate any correlations.

Additional problems arose with the USGS data set with the construction of the reservoir dam at the Falls site in 1980. Non-point source total phosphorus has been demonstrated in the literature to be a function of suspended solids loading, which in turn is a function of flow velocity (Baker, 1980). The data available from the USGS for the Falls site indicated an erratic correlation between flow rate, suspended solids and total phosphorus concentrations. This was probably caused by the operation of the spillway at the reservoir dam. When loads were considered, rather than concentrations, there appeared to be a moderate non-linear correlation of both total phosphorus and suspended sediment with flow rate. In contrast, at the Clayton station, total phosphorus load increased with increased sediment load.

At both sites there appeared to be a strong correlation between the total phosphorus concentration and the FRP concentration. The presence of these correlations indicated an interrelationship between FRP concentrations and particulate concentrations. This may have been due to a chemical or adsorption equilibrium whereby orthophosphate consumed in the system through various sink reactions (e.g. bioassimilation), was subsequently replenished from the particulate phosphorus pool. If particulate phosphorus was primarily of non-point origin (as postulated by Baker in the Sandusky River) then it could be inferred that much of the orthophosphate which remained in the river may be from non-point rather than point sources. This contradicts a North Carolina Department of Environmental Management (DEM) report (Linthurst et al., 1983) which stated that a small phosphorus contribution was made from sediment export from agricultural lands in the Neuse River, Falls basin. The report stressed that estimates of the sediment phosphorus may have been low due to assumptions made during calculations.

2.8 SUMMARY OF PHOSPHORUS SOURCES AND SINKS

The following is a listing of possible phosphorus sources and sinks which are to be addressed by this study and incorporated into the mathematical model.

1. Algal phosphorus uptake (sink). This occurs principally through the uptake of dissolved inorganic phosphorus, although there may be uptake of dissolved organic phosphorus during conditions of competition with planktonic bacteria (Currie and Kalff, 1984). This is a phosphorus sink with some loss to the system due to algal sedimentation.
2. Algal excretion of organic phosphorus (source/sink). This is an organic phosphorus source with subsequent conversion to dissolved phosphorus or loss to the system by certain complexing mechanisms (Nalewajko, Dunstall and Shear, 1976).
3. Bioflocculation (sink). Bioflocculation immediately downstream of a point source outfall with the uptake of phosphorus-containing compounds by bacterial biomass in the wastewater treatment plant discharge (Bhargava 1986). This would be a dissolved phosphorus sink with loss to the system through sedimentation.
4. Adsorption to suspended sediment particles (Baker, 1982) (sink).
5. Complexing with colloidal material (sink). This is an intermediate between dissolved organic phosphorus and bioavailable dissolved inorganic phosphorus under normal conditions. It may become a bioavailable sink if this material complexes with iron or calcium ions (Lean 1973,

Downes and Pearl 1978).

6. Reactive high molecular weight phosphorus (RHMW-P) compounds (source). These are bioavailable, but may require time to become bioavailable and subsequently may remain in the system for a long period of time (Pearl and Downes, 1978).
7. Relatively unavailable dissolved inorganic phosphorus (HCl-P) from apatite derived sources (Young et al. 1985) (source). This form has a low bioavailability.

PART 3

MATERIALS

3.1 FIELD PHASE

3.1.1 Time of Travel

- Fluorometer, Turner Instruments
- Rhodamine WT, Dow Chemical
- Rubber Gloves, Fisher Scientific
- Plastic Apron, Fisher Scientific
- 5 Gallon Pail

3.1.2 Water Sampling

- Milk Bottle Sampler
- Water Sampler, Van Dorn

3.1.3 Flow Measurement

- Price Meter with Bridge Board

3.1.4 Sample Preparation

- Liquid Nitrogen
- 5 liter Dewar Flasks with Fiberglass carrying shells
- Cryogenic Mittens
- Centrifuge tubes, clear polyepropylene, Fisher Scientific, with blue screw-caps
- Pressure Filtering Apparatus
- Air Pump, foot style.
- Filters, membrane, Millipore 0.45 micron
- Filter flasks, polypropylene
- Sample bottles, 2 liter polypropylene (for composites)

PART 4

METHODS

4.1 GENERAL

The study was divided into two phases: the field study and mathematical modeling. The field study was conducted on the Neuse River, North Carolina on a series of reaches upstream and downstream of the Raleigh, North Carolina wastewater treatment plant. The mathematical model was constructed from relationships inferred from the field data.

The field study consisted of six sampling runs, each under different seasonal or diurnal conditions. The thrust of the study was to collect as many types of data as was practical that could be related to phosphorus processing downstream of the wastewater treatment plant discharge; emphasis was placed on species of phosphorus. The slope sampling method was used wherein sampling times were dictated by the time of travel of river inputs. This method was chosen so as to follow a single discharge incident as it traveled downstream from the treatment plant. More definitive relationships between phosphorus and other water quality parameters could be established measuring the change in a single water mass moving downstream than using traditional sampling strategies which generally use average daily values at each station.

4.2 THE FIELD STUDY

4.2.1 The Sampling Site:

Sampling was conducted on a stretch of the Neuse River influenced by the discharge of the Raleigh, N.C. wastewater treatment plant. The area was well suited to the study requirements for several reasons:

- The wastewater treatment plant was a secondary treatment system with no special treatment for phosphorus.
- There was no phosphate detergent ban in force during the study period.
- A length of river existed for approximately 20 miles downstream of the treatment plant where no additional point sources discharged and there was only one minor tributary.
- The river flow was regulated by a dam upstream of the Raleigh plant thereby assuring relatively constant time of travel.
- There were no pooling areas such as lakes or ponds.

Six sampling stations were located on the river, each conveniently accessible from bridges. The first station was approximately two miles upstream of the treatment plant and was used to establish baseline and background water quality. Five other stations were located downstream of the treatment plant with the final station located just upstream of

Smithfield, N.C. Sampling stations were not located farther downstream due to potential influences from the treatment plant discharge at Smithfield.

4.2.2 Sampling Runs:

Runs were performed in pairs separated by two hours. Runs 1 and 2 were conducted in two days during April of 1986. Runs 3 and 4 and runs 5 and 6 were sampled in September of 1986 (Table 4.1). The three run pairs (i.e., 1 and 2, 3 and 4, 5 and 6) differed from each other in the time of day in which they commenced to permit observation of diurnal influences on phosphorus processing (Table 4.1).

Table 4.1
Sample Run Commencement Times

	Run Number					
	1	2	3	4	5	6
Date	4/86	4/86	9/86	9/86	9/86	9/86
Time	08:45	10:45	13:00	15:00	05:00	07:00

4.2.3 Time of Travel.

Time of travel of the river was used to determine the sampling time at each station. Time of travel measurements were performed on the first two days of the week in which runs were conducted (i.e. just prior to sampling, but allowing sufficient time for the dye to be flushed downstream). It was assumed that the time of travel remained relatively constant throughout the sampling periods because the U.S. Army Corp of Engineers controlled the discharge of flow to the river at the dam at Falls Reservoir. There were no incidents of runoff induced by precipitation during the study period.

Time of travel measurements were performed using rhodamine WT. Dye was introduced to the river in excess at a bridge site upstream of station 1. Samples of the river were taken at 15 minute intervals at each site downstream using ISCO automatic samplers with discrete sample bases. Water samples were analyzed for fluorescence using a Turner fluorometer. The time between peaks in fluorescence were used to determine the time of travel between stations.

4.2.4 Flow Measurement:

River flows were determined using a Price meter suspended by a cable from a bridge-board. Depth measurements were performed utilizing a gauge attached to the bridge-board cable and graduated in tenths of a foot. Flow measurements were made using the standard two-fifths/four-fifths rule at five foot intervals. Where practical, measurements were taken on the upstream side of the bridge to minimize inaccuracies imposed by bridge supports. At stations 5 and 6, this was not possible due to build-ups of debris on the upstream side of the bridges.

4.2.5 Sample Collection.

Samples were collected using a vertical, depth integrating sampler suspended from a bridge board by a cable. Samples were taken at the center of the bridge and points midway between the center of the bridge and the river banks. Each depth-integrated sample was taken in triplicate (A, B and C). All A, B and C samples were combined yielding three composite samples for each station. This provided samples which were representative of the entire cross-section of the river.

Table 4.2 lists all sampling analyses collected and performed. Temperature, pH, dissolved oxygen and Secchi depth were measured at each sampling site for each sampling run. Samples for pH measurement were collected using a Van Dorn sampler and were measured using a portable pH meter. Temperature and dissolved oxygen were measured instream using a Dissolved Oxygen/temperature probe which had been calibrated in air. Secchi depth was taken using a standard 10 inch Secchi disc from the sunny side of each bridge. These measurements were performed once per sample run pair.

Table 4.2 - Analyses Performed For Each Run

RUN Number	1	2	3	4	5	6
TSS	x		x		x	
TDS	x					
Temperature	x	x	x	x	x	x
Dissolved Oxygen	x	x	x	x	x	x
pH	x	x	x	x	x	x
Secchi Depth	x	x	x	x	x	x
Conductivity	x		x		x	
Alkalinity		x		x		x
Turbidity		x		x		x
FRP	x	x	x	x	x	x
TFP	x	x	x	x	x	x
Total-P	x	x	x	x	x	x
TKN			x	x	x	x
NO_2^-	x	x	x	x	x	x
NO_3^-	x	x	x	x	x	x
NH_4^+	x	x	x	x	x	x
Cl^-	x	x	x	x	x	x
$SO_4^=$	x	x	x	x	x	x
Ca^+	x	x	x	x	x	x
Mg^{++}	x	x	x	x	x	x
Na^+	x	x	x	x	x	x
K^+	x	x	x	x	x	x
Fe	x	x	x	x	x	x
Cu			x	x	x	x
Mn	x	x	x	x	x	x
Chlorophyll-a			x	x	x	x

4.2.6 Sample Processing:

Immediately following collection, samples were processed for shipping utilizing preservation techniques specific for the parameters to be analyzed (Table 4.3).

Table 4.3 - Sample Preservation

Sample Type	Field Preparation	Method of Analysis
FRP	Filtered, Frozen	molydenum blue-ascorbic acid
TP	Unfiltered, Frozen	digested, melydenum blue-ascorbic acid
NO_2^-, NO_3^-	Filtered, Acidified	cadmium reduction
NH_4^+	Unfiltered, Acidified	phenate method
TKN	Unfiltered, Acidified	Micro Kjeldahl
Anions (Metals)	Unfiltered, Acidified	ion chromatograph
Cations	Unfiltered	ion chromatograph
Chlorophyll-<u>a</u>	Filtered	acetone extraction on filters

All samples for phosphorous analysis were preserved by quick freezing using liquid nitrogen (Ottaviano, 1986). Approximately 45 ml of aliquots were placed into 50 ml plastic centrifuge tubes. Sample tubes were placed in a metal rack in groups of five and immediately placed for three minutes in a Dewars flask filled with liquid nitrogen. Completely frozen samples were transferred to an ice chest filled with crushed dry ice.

Samples for filterable reactive phosphorus and total filterable phosphorous were passed through a Gelman 0.45 micron filter prior to freezing. Field filtering was accomplished using a pressure filter and a hand pump. The pressure filter was constructed using a six inch long, three inch diameter length of PVC pipe with a gasketed, threaded cap on either end. The bottom end contained a plastic support screen held in place on the base by a plastic ring. The top and bottom caps had a hole drilled in them for introduction of air and discharge of filtered sample, respectively. Filter pressure was maintained at not greater than 15 psi. Filtered samples were frozen as described above.

Samples for nitrogen species and cations were acidified with two drops of sulfuric acid and placed in coolers filled with dry ice. Anion samples were stored in a separate chest. To prevent freezing, anion samples were separated from contact with the dry ice using a styrofoam baffle. Samples for nitrate and nitrite analyses were filtered as described above. Ammonia samples were filled to just below the total capacity of the 50 ml centrifuge tubes. The remainder of the composite sample was transferred to a one quart glass or plastic bottle and boxed with styrofoam padding; these were used for suspended solids analysis.

During the September sampling runs (runs 3-6) samples were collected for chlorophyll analysis. Chlorophyll-a samples were filtered on site with the air pressure filter using 0.45 micron filters. Samples were preserved prior to filtering. Two liters of sample were filtered for each sample. Filters were transferred to plastic centrifuge tubes, capped and placed in coolers on dry ice.

Samples were transported in coolers on dry ice to a laboratory at Rensselaer Polytechnic Institute in Troy, New York where they were transferred immediately to refrigerators and freezers as appropriate.

4.2.7 Sample Analysis:

All phosphorous analyses were performed on a Technicon Autoanalyser using the automated Ascorbic Acid Reduction Method as outlined in Standard Methods. Filterable reactive phosphorous was measured directly after sample thawing at ambient temperature. Total phosphorus and total filterable phosphorus samples were acidified and digested in an autoclave prior to analysis (Standard Methods, 1986).

Nitrate and nitrite were analyzed on a Technicon Autoanalyser. Analyses of nitrate/nitrite was by the automated Cadmium Reduction Method which converts all nitrate to nitrite with a Cu-Cd column. Analysis of nitrite alone was performed by removing the Cu-Cd column from the system.

Nitrate levels were obtained by calculating the difference between the above two values. Ammonia analyses were performed using the automated Phenate Method.

Other cations and anions were analyzed using an ion chromatograph. TSS were analyzed by standard gravimetric techniques. The chlorophyll-a analysis was performed after acetone extraction using spectrophotometric techniques.

PART 5

DATA ANALYSIS

5.1 GENERAL

The purpose of this study was to identify biological, chemical and physical processes which contribute to the reduction of point-source phosphorus discharged by wastewater treatment plants within river flow. The primary mechanisms of interest were those which relate to the processing and subsequent reduction of phosphorus loads in the river. Regression analyses were performed on constituents potentially influencing dissolved phosphorus loads versus FRP loads for the sites downstream of the treatment plant discharge to identify parameters which influenced river processing of phosphorus. FRP is the phosphorus species which is considered to be most readily biologically available.

5.2 RESULTS

5.2.1 River and Treatment Plant Flows:

Velocity and depth were measured at each of the six sites in five foot horizontal intervals using a Price meter. Where depths were greater than 1 foot, computed velocities were the average of measurements taken at one-fifth and four-fifths of the total depth from the water surface. Cross-sectional areas for each section were computed as the product of the lateral width of each section (5 feet) and the section's average depth. The measured velocities for each section were multiplied by the respective cross-sectional areas to produce a section flow value. Total flow for the site was obtained by summing the calculated flows for all sections.

Errors were introduced in velocity measurements at certain downstream sites due to collected debris and/or sand bars located at and around the bridge supports. These errors became evident upon integration of the velocity measurements and subsequent flow calculations. To minimize the effects of these errors on loading calculations, flows were re-computed using results of regressing the calculated flows against distance. The resulting regression formulae were utilized to produce normalized flow values that were used in loading calculations as described below.

The slope of the river downstream of the wastewater treatment plant was relatively uniform for the portion of the river sampled. Therefore, it was deemed appropriate to base flow values for sites with unreliable measurements on a regression slope calculated from the values which were more viable. For the April samplings (run #1 and run #2), flows from downstream sites 2, 4 and 6 were subjected to linear regression, yielding a flow slope of 2.07 with a correlation coefficient of 1.00. For the September runs, flow under the bridge at site #2 was also blocked with debris causing a flow measurement lower than found at the previous site. Thus for September, sites 3, 4 and 5 flows were used for regression yielding a flow slope of 3.66 with a correlation coefficient of 0.80 (Table 5.1).

Two observations support the confidence in the regression estimates for flows:

1) The correlation coefficients for the points regressed provided the best goodness of fit. (Table 5.1) ; and

2) The sum of the average wastewater treatment plant discharges (Table 5.2) and Site 1 flows were within the range of the values calculated for the Y intercepts in both regressions. This would be expected because the Y intercept values should be an estimate of the point zero flow for downstream sites.

Table 5.1: River Flow Adjustments, cfs

STA	miles	Measured	BestFit	Measured	BestFit
		APRIL 86		SEPTEMBER 86	
1	-1.8	229.75	229.75	237.2850	237.29
2	0.0	284.54*	284.54	210.7870	308.72
3	6.2	335.35	293.70	332.6748*	324.10
4	9	300.28*	300.28	321.3564*	334.36
5	14.4	391.11	310.73	358.5823*	358.58
6	19.4	320.78*	320.78	-	372.45

* Sampling Points used in regression estimates.

Downstream Flow Regression Equations:

Q[April], cfs = (2.0742 * miles) + 280.84, R = 1.00
Q[Sept], cfs = (3.6628 * miles) + 301.39, R = 0.80

Table 5.2: Wastewater Treatment Plant Flows

	MGD			cfs		
TIME	24-Apr	16-Sep	18-Sep	24-Apr	16-Sep	18-Sep
MID			26			40.25
2 AM			26			40.25
4 AM			23			35.60
6 AM			18			27.86
8 AM			15			23.22
10 AM	17.0		13	26.32		20.12
NOON	24.0	15.0	20	37.15	23.22	30.96
2 PM	35.0		36	54.18	54.18	55.73
4 PM	34.5	36.0	35	53.41	55.73	54.18
6 PM		31.0	30		47.99	46.44
8 PM		26.0	27		40.25	41.80
10 PM			25			38.70
MID						40.25

Final river flow estimates for each site and each run were calculated using the above observations. An assumption was made that the base flow of the river and the measured

FIG 5.1: pH APRIL RUNS 1 & 2

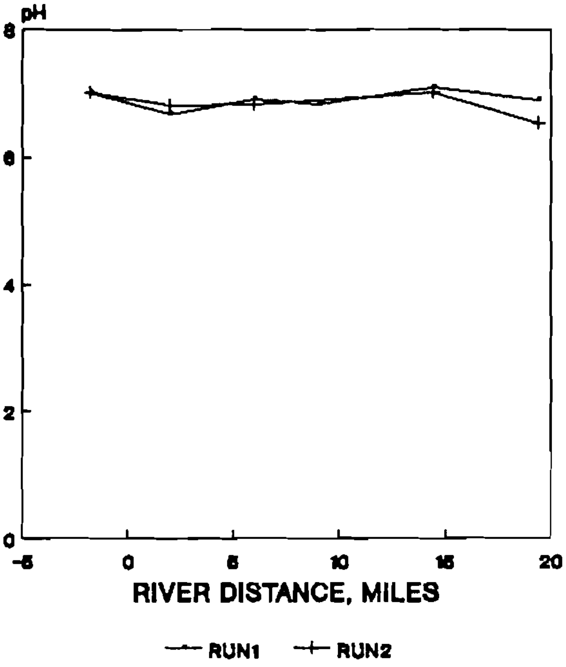
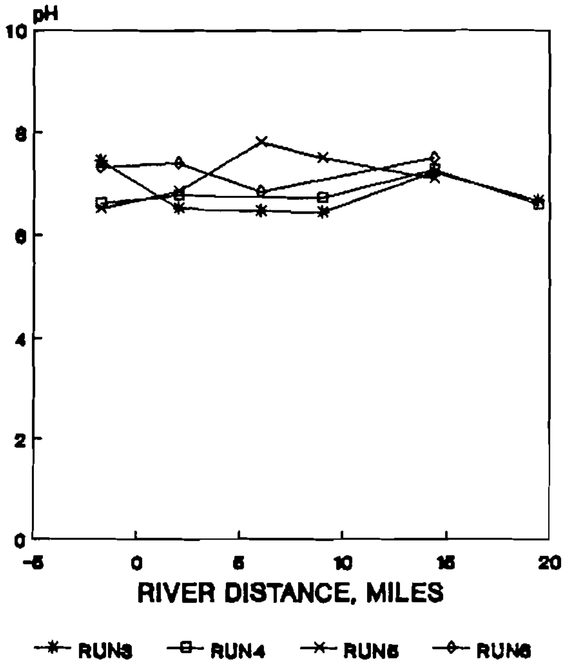


FIG 5.2: pH SEPTEMBER RUNS 3-6



upstream flow at Site 1 remained relatively constant for the entire sampling period. Flow slopes from the regression analyses for the sampling periods were used to estimate the interflow contribution for the length of the river. River flow downstream of the wastewater treatment plant discharge was adjusted by the quantity of water exiting the treatment plant on the sampling day and time (Table 5.2). Resultant estimated river flows used for loading computations are presented in Table 5.3.

Table 5.3: River Flow (cfs)
Adjusted for Treatment Plant Flow

STA	Run#1	Run#2	Run#3	Run#4	Run#5	Run#6
1	229.75	229.75	237.29	237.29	237.29	237.29
0	261.48	275.42	287.59	289.14	258.96	262.83
2	265.63	279.56	294.92	296.47	266.28	270.15
3	273.93	287.86	309.57	311.12	280.93	284.80
4	280.15	294.08	320.56	322.11	291.92	295.79
5	291.35	305.28	340.34	341.89	311.70	315.57
6	301.72	315.66	358.65	360.20	330.02	333.89

5.2.2 pH.

pH was measured on site for each sampling run using a portion of the composite samples collected for chemical analyses. Values for pH were approximately neutral with a minimum of 6.4 and a maximum of 7.5 (Table 5.4 and Figures 5.1 and 5.2). Measurements upstream of the treatment plant discharge were neutral to slightly alkaline (<7.5). After passing the treatment plant discharge point, the stream pH

FIG 5.3: DO AND TEMPERATURE, APRIL

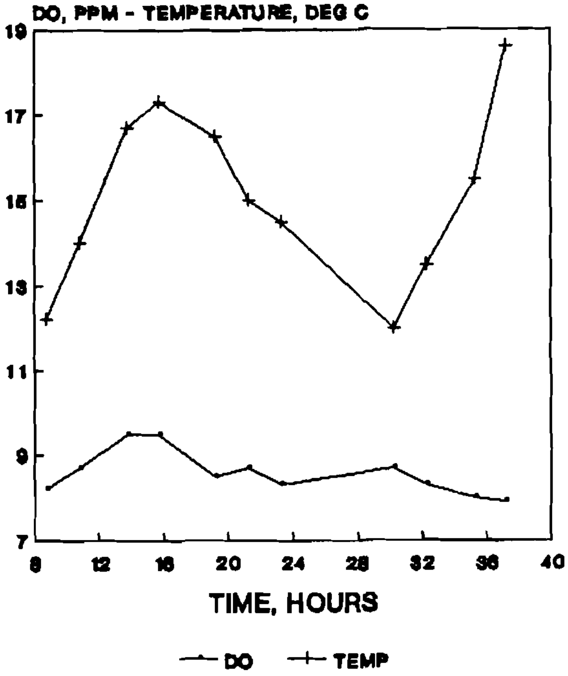
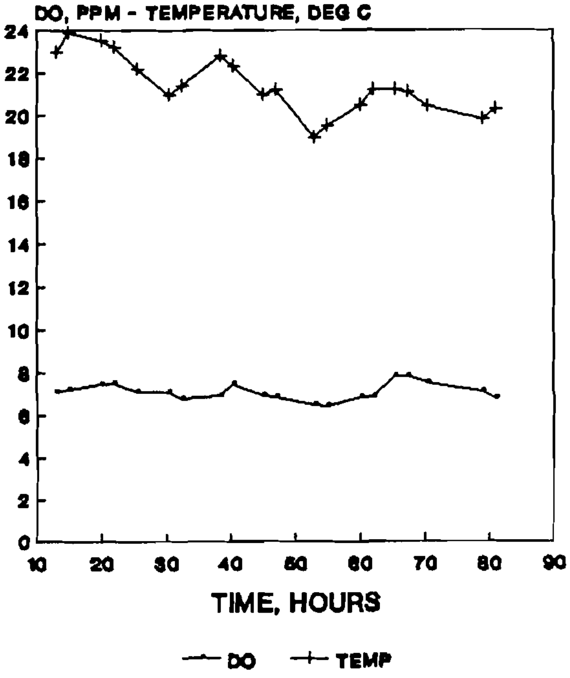


FIG 5.4: DO AND TEMPERATURE, SEPT



generally dropped below neutral. Slightly alkaline conditions were generally re-established by site 5 but the pH dropped again at site 6. Observation of pH was of particular importance in assessing the possible interaction of phosphates with other ions.

Table 5.4: pH

		Site					
	RUN	1	2	3	4	5	6
April 1986	1	7.0	6.7	6.9	6.8	7.1	6.8
	2	7.0	6.8	6.8	NA	7.0	6.5
Sept. 1986	3	7.5	6.5	6.5	6.4	7.2	6.7
	4	6.6	6.7	NA	6.7	7.3	6.6
	5	NA	6.6	6.9	6.6	6.8	NA
	6	7.3	7.4	6.9	NA	7.5	NA

5.2.3 Temperature, Dissolved Oxygen and Light Transmission.

Temperature plays an important role in the rates of all biological and chemical reactions and many physical processes. Although the flow measurements from both sampling periods were of similar magnitude, temperatures encountered in April were nearly 10 degrees Centigrade lower than in September (Table 5.5).

Dissolved oxygen concentrations remained aerobic throughout the study (Table 5.5). Both dissolved oxygen and temperature oscillated diurnally with the time of day and daylight (Figure 5.3). The dissolved oxygen oscillations tracked the daylight hours as might be expected in a system where active photosynthesis was taking place.

"Solar irradiance" was estimated using secchi depth as an index (Table 5.5). Sampling runs were conducted on sunny days only so that cloud cover would have no influence on photosynthesis by cloud cover. The range of data from secchi disk measurements was similar for April and September.

Table. 5.5: Time, Temperature, Dissolved Oxygen and Secchi Disc Measurements

	Site					
	1	2	3	4	5	6
Run 1 Time	08:45	13:45	19:15	23:15	06:15	11:15
Temp, Deg C	12.2	16.7	16.5	14.5	12.0	15.5
D.O., mg/L	8.2	9.5	8.5	8.3	8.7	8.0
Secchi, in.	26.0	29.0		21.0	25.0	
Run 2 Time	10:45	15:45	21:15	NA	08:15	13:15
Temp, Deg C	14.0	17.3	15.0	NA	13.5	18.6
D.O., mg/L	8.7	9.5	8.7	NA	8.3	7.9
Secchi, in	27.5	29.5	0	NA	28.0	27.0
Run 3 Time	13:00	20:00	01:30	NA	14:30	21:00
Temp, Deg C	23.0	23.5	22.2	21.0	22.8	21.0
D.O., mg/L	7.1	7.5	7.1	7.1	6.9	6.9
Secchi, in	30.0			37.5	0	
Run 4 Time	15:00	22:00	03:30	08:30	16:30	23:00
Temp, Deg C	23.9	23.2	NA	21.4	22.3	21.2
D.O., mg/L	7.2	7.5	NA	6.8	7.5	6.9
Secchi, in	NA	0	NA	25.5	29.0	0
Run 5 Time	05:00	12:00	17:30	22:30	07:00	13:00
Temp, Deg C	19.0	20.5	21.2	20.4	19.8	NA
D.O., mg/L	6.5	6.85	7.8	7.5	7.1	NA
Secchi, in	0	32.0	29.0	0	0	NA
Run 6 Time	07:00	14:00	19:30	00:30	09:00	15:00
Temp, Deg C	19.5	21.2	21.1	NA	20.3	NA
D.O., mg/L	6.5	6.9	7.8	NA	6.8	NA
Secchi, in	0	34.0	0	NA	32.0	NA

5.2.4 Phosphorus

5.2.4.1 Treatment Plant FRP

Treatment plant loads of Total Phosphorus and FRP were calculated from the concentrations in hourly composited samples made up from discrete samples collected every 15 minutes (Table 5.6). Measured treatment plant Total Phosphorous was almost completely FRP with consistent concentrations of approximately 6 mg/L throughout the measured periods. The calculated loads annotated with an "*" were used in estimating the combined loading of FRP in the river upon passage by the treatment plant between sites 1 and 2 at the time of stream sampling.

Table 5.6. Wastewater Treatment Plant FRP Loads, lbs/day

TIME	24-Apr	16-Sep	18-Sep
MID			1301
2 AM			1301
4 AM			1151
6 AM			901
8 AM			751
9 AM			701 *
10 AM	851		651
11 AM	1026 *		826 *
NOON	1201	751	1001
1 PM	1476 *	1251	1401
2 PM	1751	1751	1801
3 PM	1739	1776	1776
4 PM	1726	1801 *	1751
5 PM		1676	1626
6 PM		1551 *	1501
7 PM		1426	1426
8 PM		1301	1351
10 PM			1251

* WWTP, FRP Loading used in calculating combined WWTP/river loads.

FIG 5.5: FRP LOADS APRIL RUNS 1 & 2

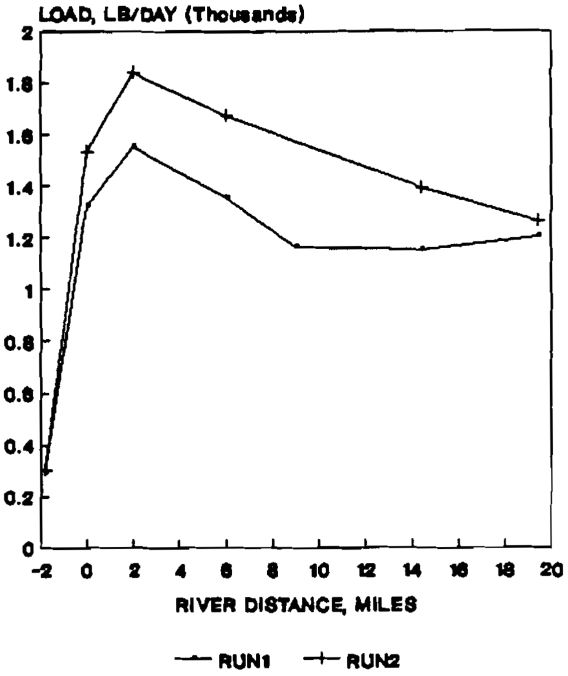
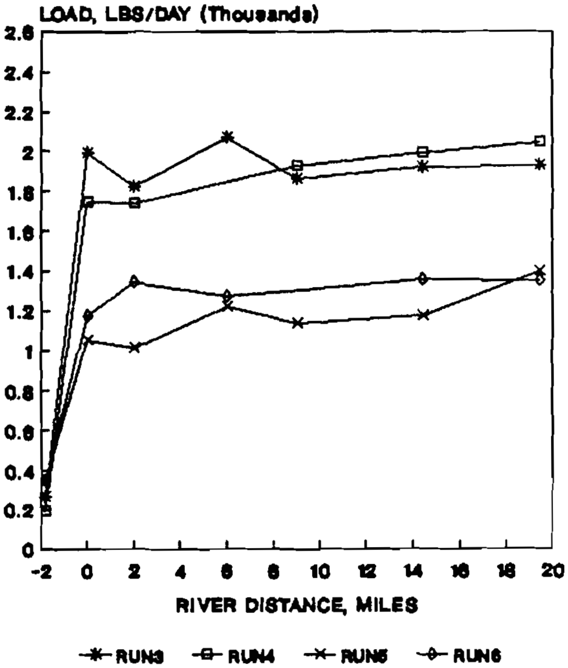


FIG 5.6: FRP LOAD SEPT RUNS 3-6



5.2.4.2 River Processing of FRP

The in-stream processing of FRP loads was exhibited to varying degrees during the six sampling runs (Table 5.7). Reductions of phosphorus downstream of the wastewater treatment plant discharge point were most evident in those samples collected in April 1986 (Runs 1 and 2, Figure 5.5). During these runs, river FRP loading increased from approximately 200 lbs/day (90 kg/day) upstream of the treatment plant input to 1500-1900 lbs/day (680-860 kg/day) immediately downstream; where upon the loading declined to 1200 lbs/day (545 kg/day) at site 6, the last site sampled. This represented a decrease of 20 to 35 percent of the FRP over the 20 miles studied. Reduction of FRP loading was less pronounced in the water samples collected in September, 1986. Little to no reduction was observed in samples collected during September (Figure 5.6).

The two April sampling runs were started at approximately 9:00 A.M. and 11:00 A.M., respectively, of the same day (Table 5.7). The loading of phosphorus in the river at the treatment plant discharge was calculated from the mixture of the measured treatment plant phosphorus loading and the river loading at the upstream site. The sampled flow passed by the treatment plant at approximately 11:30 A.M. and 1:30 P.M., respectively, with subsequent travel downstream to site 3 during daylight hours; sampling between sites 3 and

5 occurred during nighttime hours. Site 5 was sampled in the next followed by site 6, prior to and after noon. Measured FRP loads during these runs increased slightly from 300 lbs/day (135 kg/day) to approximately 1700 lbs/day (770 kg/day) at site 2, the first site downstream of the wastewater treatment plant discharge. Subsequent flow downstream was marked by gradual reduction of the FRP load to approximately 1230 lbs/day (560 kg/day), even during hours of darkness, particularly during run 2.

Table 5.7: FRP vs. TFP and TP Loads (lbs/day)

		Site NUMBER					
RUN		1	2	3	4	5	6
	Mile	-1.8	2.0	6.0	9.0	14.4	19.4
April							
1	Time	08:45	13:45	19:15	23:15	06:15	11:15
	FRP	293	1553	1353	1159	1150	1203
	TFP	363	1527	1399	1377	1237	1313
	TP	374	1627	1523	1346	1292	1382
2	Time	10:45	15:45	21:15	01:15	08:15	13:15
	FRP	303	1842	1671	NA	1390	1262
	TFP	349	1878	1752	NA	1444	1355
	TP	316	1901	1786	NA	1500	1468
September							
3	Time	13:00	20:00	01:30	06:30	14:30	21:00
	FRP	266	1822	2071	1862	1916	1923
	TFP	305	1841	2046	1983	1965	1981
	TP	322	1899	2146	2127	2145	2145

Table 5.7: FRP vs. TFP and TP Loads (continued)
lbs/day

Site NUMBER

RUN		1	2	3	4	5	6
	Mile	-1.8	2.0	6.0	9.0	14.4	19.4
4	Time	15:00	22:00	03:30	08:30	16:30	23:00
	FRP	194	1738	NA	1926	1989	2041
	TFP	262	1789	NA	1990	2005	2057
	TP	322	1895	NA	2192	2124	2206
5	Time	05:00	12:00	17:30	22:30	07:00	13:00
	FRP	347	1009	1218	1135	1173	1395
	TFP	354	1002	1168	1182	1290	1463
	TP	403	1057	1201	1229	1327	NA
6	Time	07:00	14:00	19:30	00:30	09:00	15:00
	FRP	347	1339	1271	NA	1352	1346
	TFP	354	1503	1440	NA	1530	1616
	TP	403	1363	1366	NA	1496	1583

Sampling runs 3 and 4 began at 1 and 3 P.M. respectively (Table 5.7). Flow of the sampled slug of water passed the treatment plant at approximately 4:30 and 6:30 P.M., respectively, with subsequent travel downstream during hours of darkness until site 4 was reached. Site 4 represented early next morning sampling, site 5 represented mid- to late-afternoon sampling and site 6 was sampled at night. River loading increased upon passage by the treatment plant from approximately 230 lbs/day (105 kg/day) to 1900 lbs (860 kg/day); however, no significant reduction of FRP occurred downstream during daylight and hours of darkness.

Sampling runs 5 and 6 were started in the early morning hours to observe an earlier part of the diurnal cycle (Table

5.7). Treatment plant passage occurred at approximately 8:30 and 10:30 A.M., respectively, with daylight travel through to site 3. Site 4 was sampled at night with sites 5 and 6 sampled the following morning and afternoon, respectively. FRP loads increased from 350 lbs/day (160 kg/day) at site #1 to approximately 1340 lbs/day (610 kg/day) at site #2 with little change for the remainder of the sample period.

5.2.4.3 FRP vs.TP and TFP

Total phosphorus is defined as the sum of all phosphorus, both dissolved and particulate, which is present in a water sample. Total filterable phosphorus (TFP) is that fraction of the total phosphorus which is filterable by a specific pore size filter. This is gernerally accepted to consist of the more reactive, dissolved inorganic components (principally orthophosphate) as well as less reactive dissolved inorganic and organic constituents. Filterable reactive phosphorus (FRP) is the most chemically reactive and bioavailable component and is generally accepted to be predominately orthophosphate. Loads of FRP, TP and TFP appeared to track each other as the slugs of water moved downstream from the wastewater treatment plant (Table 5.7).

5.2.5 Nitrogen Compounds

Nitrate loading followed transport trends similar to those of FRP (Table 5.8). Processing of nitrate was evident in the April runs 1 and 2, as it was for phosphorus. The treatment plant discharge increased nitrate-N loading from 580 lbs/day (260 kg/day) at site #1 to approximately 2700 lbs/day (1225 kg/day) at site #2. Nitrate loading decreased slightly downstream to approximately 1230 lbs/day (560 kg/day) at site #6. Similar to FRP, little to no reduction of nitrate loads by river processes were evident during the September runs #3, #4 and #5. Loads increased from 1000 lbs/day (455 kg/day) at site #1 to 2700-5800 lbs/day (12245-2630 kg/day) (depending upon the run) at site #2 following the treatment plant discharge and remained elevated throughout the remainder of the sampling periods. Nitrate loads decreased during run 6 in September. Values increase from 1070 lbs/day (485 kg/day) to 4500 lbs/day (2040 kg/day) with the input from the treatment plant followed by a reduction to 3300 lbs/day (1495 kg/day) at downstream site #6.

Incomplete ammonia data are available. Ammonia loads revealed no similarity with FRP with values ranging from a low of 11 lbs/day (5 kg/day) to a high of 140 lbs/day (64 kg/day) (Table 5.8). The trend of the loading followed no consistent pattern except that they tended to peak at site 3 and rapidly decrease at site 4.

Table 5.8: FRP vs. Nitrate, Ammonia and TKN Loads (lbs/day)

		Site NUMBER					
RUN		1	2	3	4	5	6
	Mile	-1.8	2.0	6.0	9.0	14.4	19.4
1	FRP	293	1553	1353	1159	1151	1203
	NO_3	594	2547	2214	2083	2119	2292
	NH_3	87	129	133	91	110	81
	TKN	NA	NA	NA	NA	NA	NA
2	FRP	303	1842	1672	NA	1390	1262
	NO_3	569	2967	2326	NA	2401	2466
	NH_3	87	120	140	NA	115	68
	TKN	NA	NA	NA	NA	NA	NA
3	FRP	266	1822	2071	1862	1916	1923
	NO_3	967	NA	5879	5924	NA	NA
	NH_3	NA	NA	33	NA	NA	26
	TKN	805	2050	2468	2919	2072	3575
4	FRP	194	1738	NA	1926	1989	2041
	NO_3	984	3075	NA	5154	5593	5835
	NH_3	26	NA	NA	17	NA	NA
	TKN	1330	2124	NA	2603	2505	2600
5	FRP	347	1009	1218	1135	1173	1396
	NO_3	1074	2683	3194	3481	2939	4866
	NH_3	NA	NA	20	16	NA	NA
	TKN	NA	1779	2028	2202	2301	2987
6	FRP	347	1339	1271	NA	1352	1346
	NO_3	1074	4493	3069	NA	3060	3298
	NH_3	NA	NA	NA	NA	11	18
	TKN	2007	1586	2271	NA	2278	2662

TKN analysis were performed on only the September samples. Loading of TKN upstream of the treatment plant ranged from 800-2000 lbs/day (360-910 kg/day) and tended to increase with distance downstream to values between 2600-3600 lbs/day (1180-1630 kg/day). Consistently, there was a peak in loading at site 4, after which either the slope of the loading increase decreased or there was a decrease in loading at the next site (Table 5.8).

5.2.6 Suspended Solids.

TSS loads were erratic with no apparent pattern. TSS data demonstrated an unexplained increase in solids loading at downstream sites during each run (Table 5.9). For runs 1 and 2, suspended solids decreased after the treatment plant discharge and increased by nearly 200 percent at site 3. For runs 3 and 4, suspended solids loads increased dramatically at site 4. For runs 5 and 6, suspended solids loading had smaller oscillations.

Table 5.9: FRP vs. TSS

		Site NUMBER					
RUN		1	2	3	4	5	6
	Mile	-1.8	2.0	6.0	9.0	14.4	19.4
1	FRP	293	1553	1353	1159	1151	1203
	TSS	21785	16172	38519	21584	18366	27147
2	FRP	303	1842	1672	NA	1390	1262
	TSS	21785	17020	40478	22657	19244	28401
3	FRP	266	1822	2071	1862	1916	1923
	TSS	43807	44167	56353	86081	52726	62509
4	FRP	194	1738	NA	1926	1989	2041
	TSS	43807	44399	56634	86496	52966	62779
5	FRP	347	1009	1218	1135	1173	1396
	TSS	52384	40566	47513	34673	NA	53683
6	FRP	347	1339	1271	NA	1352	1346
	TSS	52384	41155	48167	35132	NA	54313

5.2.7 Anions and Cations

Analyses were performed on nine anions and cations to determine correlations with phosphorus loading during river transport (Table 5.10). These included the cations sodium, potassium, magnesium, iron, calcium, copper and manganese. Anions included sulfate and chloride (in addition to the nitrogen compounds discussed above). All analyses were performed as total ions.

Table 5.10: FRP vs. Ion Loads

Site NUMBER

RUN		1	2	3	4	5	6
	Mile	-1.8	2.0	6.0	9.0	14.4	19.4
1	FRP	293	1553	1353	1159	1151	1203
	SO_4	16587	18276	21355	18761	20673	21409
	Na	30116	50562	49691	47092	48771	46053
	Cl	16092	28809	25827	21131	27470	30561
	Mg	3280	3936	3852	3955	4128	4226
	Fe	693	859	930	1147	1114	1203
	Ca	3342	3864	3793	4030	4128	4226
	K	3676	6297	5711	6188	6075	6502
	Cu	0	0	0	0	0	0
	Mn	210	258	221	272	251	195
2	FRP	303	1842	1672	NA	1390	1262
	SO_4	13245	21795	19588	NA	22254	22789
	Na	33012	43529	57895	NA	53290	51580
	Cl	8665	31931	28381	NA	27188	30152
	Mg	3317	4172	4280	NA	4441	4252
	Fe	706	723	822	NA	1086	1344
	Ca	3342	4323	4699	NA	4934	4303
	K	3676	7275	7181	NA	6908	8214
	Cu	0	0	0	0	0	0
	Mn	235	181	248	NA	230	238
3	FRP	266	1822	2071	1862	1916	1923
	SO_4	5493	10217	11353	11819	NA	13140
	Na	17898	43431	49480	49221	53175	57969
	Cl	16376	25518	26803	27754	NA	31052
	Mg	3661	4560	4898	5049	5330	5649
	Fe	648	794	823	1071	880	870
	Ca	10483	14936	16067	16350	16992	18164
	K	3920	8077	8840	9038	9413	10048
	Cu	196	164	128	121	79	71
	Mn	311	281	256	253	189	187

Table 5.10 cont'd: FRP vs. Ion Loads

Site NUMBER

	RUN	1	2	3	4	5	6
	Mile	-1.8	2.0	6.0	9.0	14.4	19.4
4	FRP	194	1738	NA	1926	1989	2041
	SO_4	4270	8785	NA	11141	11555	12989
	Na	16619	44191	NA	48013	54031	58219
	Cl	16159	21355	NA	32735	37484	38709
	Mg	3678	4707	NA	4923	5274	5563
	Fe	716	799	NA	1018	853	957
	Ca	10526	15121	NA	16371	17069	18048
	K	3942	8199	NA	8417	8811	9444
	Cu	119	75	NA	46	31	32
	Mn	307	272	NA	255	184	201
5	FRP	347	1009	1218	1135	1173	1396
	SO_4	12354	14557	15191	15633	17339	19031
	Na	33878	46387	49696	51377	54578	58674
	Cl	12017	21964	28511	26381	31630	42121
	Mg	3861	4194	4379	4587	4960	5245
	Fe	776	679	727	839	896	889
	Ca	11633	13725	14480	15099	16234	17128
	K	4261	6217	6685	7077	7445	8149
	Cu	47	43	45	31	45	71
	Mn	375	273	237	220	213	190
6	FRP	347	1339	1271	NA	1352	1346
	SO_4	12354	17252	NA	NA	NA	NA
	Na	33878	52883	53449	NA	58940	59362
	Cl	12017	36145	NA	NA	NA	NA
	Mg	3861	4425	4608	NA	5146	5313
	Fe	776	650	726	NA	878	851
	Ca	11633	14506	14884	NA	16548	17329
	K	4261	6986	6879	NA	7622	8095
	Cu	47	34	31	NA	45	72
	Mn	NA	272	246	NA	221	180

Individual ion behavior could be grouped as follows:

5.2.7.1 Sulfate.

A slight increase of sulfate was observed immediately after the treatment plant. Subsequent to the discharge, the

FIG 5.7: TOTAL IRON LOADS

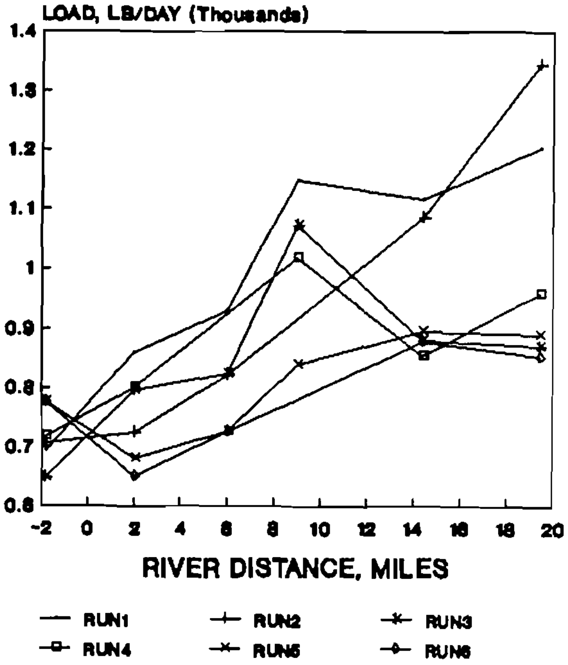


FIG 5.8: CHLORIDE LOADS

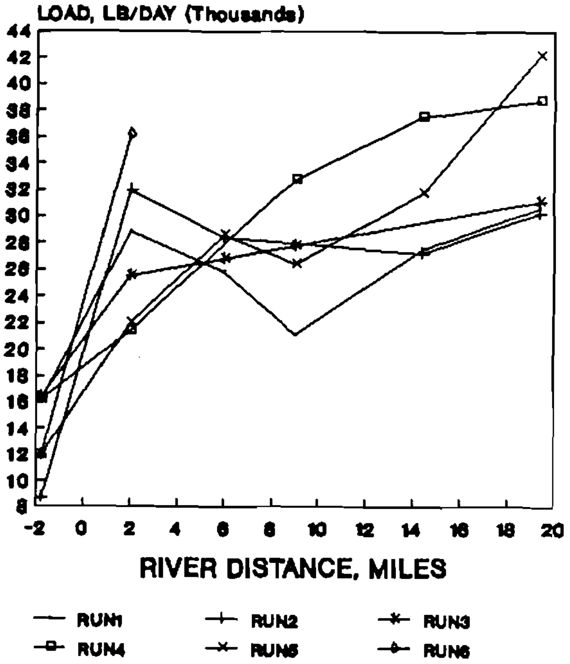
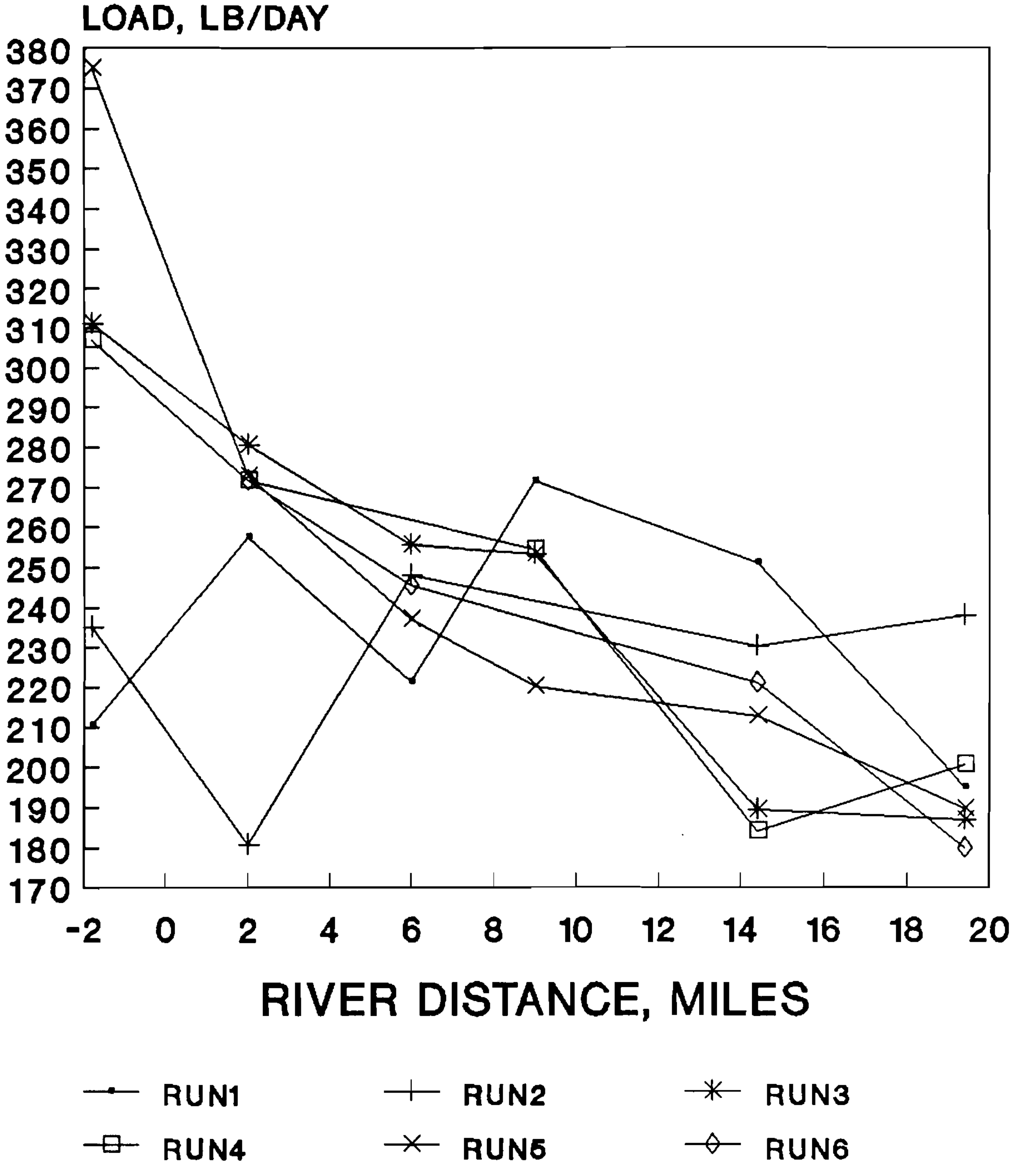


FIG 5.9: Mn LOADS



load remained somewhat constant with a moderate drop near sites 3 and 4 for runs 1 and 2, respectively. Curiously, loads continued to increase with distance downstream of the WWTP discharge. Runs #3 through #6 showed a gradual increase after the treatment plant contribution (Table 5.10).

5.2.7.2 Calcium, Magnesium, Potassium and Iron:

All of the September runs exhibited a gradual increase in concentration of these ions as the river proceeded downstream (Table 5.10, Figure 5.7).

5.7.7.3 Sodium and Chloride:

Both sodium and chloride are usually considered to be conservative elements which are not removed or added by biological processes (Table 5.10). There was a downward trend in loading of these elements during transport downstream for runs 1 and 2 (Figure 5.8). For runs 3 through 6 loading increased gradually, downstream. The impact of the treatment plant discharge was clearly shown.

5.2.7.4 Copper and Manganese:

Both Cu and Mn exhibited a trend opposite to the other ions with loading decreasing with distance downstream (Table 5.10 and Figure 5.9). Except for run 1, the treatment plant effluent contributed neither of these numbers.

5.3 DISCUSSION

5.3.1 Phosphorus

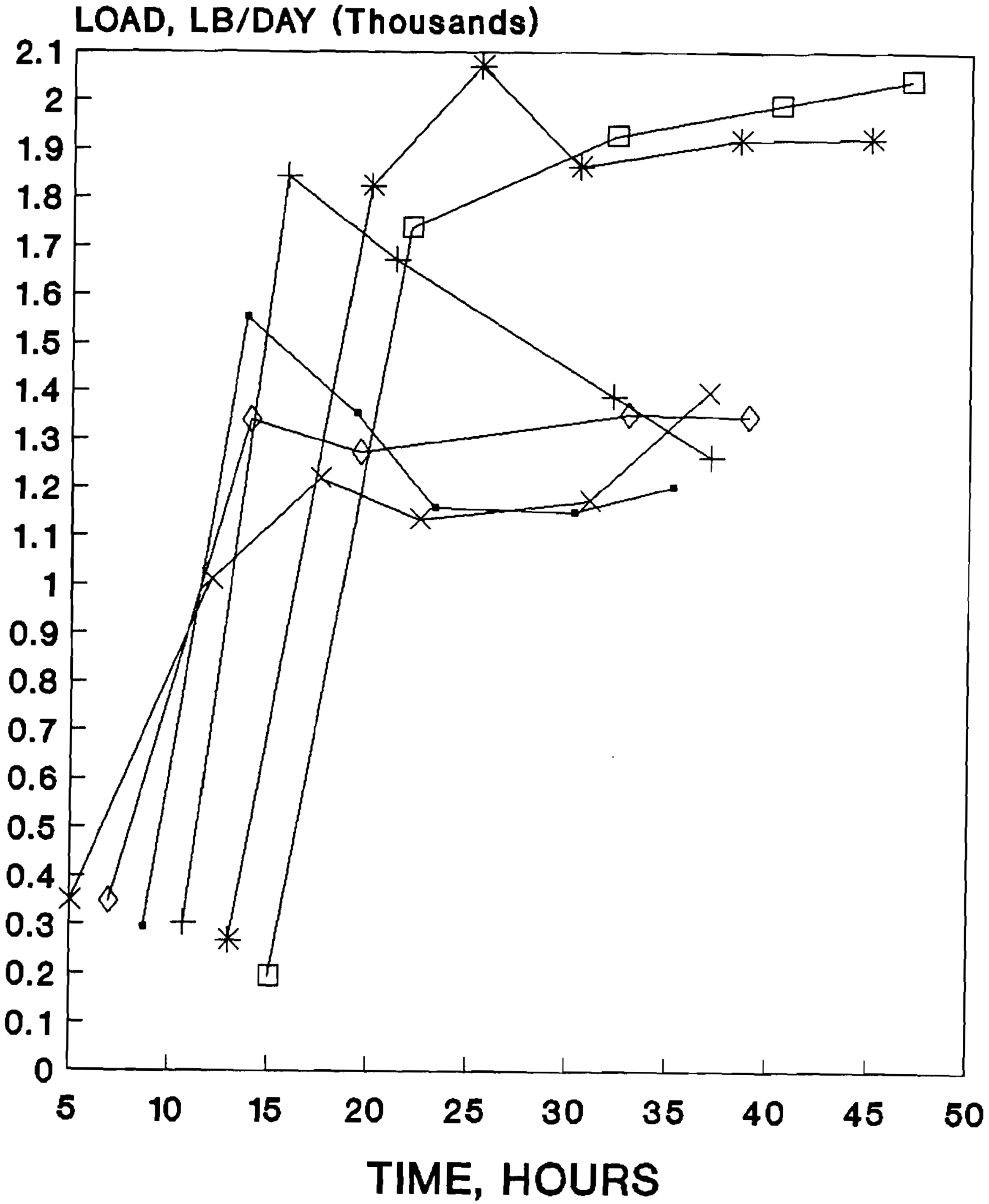
River processing of point source FRP was most evident in runs 1 and 2 performed in April. For both of these runs, FRP loads increased between sampling sites 1 and 2 as a result of point source addition from the treatment plant, and subsequently decreased by 20-35 percent as flow proceeded downstream. Similar FRP reduction was not as evident in September during runs 3 through 6. It would be convenient to ascribe this observed difference to a lack of biological processing in September. However, other factors do not support this hypothesis.

- Water Temperature: The water temperature was approximately 10 degrees warmer in September than it was in April. One would normally expect that this would encourage biological growth and commensurate phosphate uptake.
- Diurnal Light Cycle: The April runs 1 and 2 were initiated in mid-morning. The treatment plant contributed phosphate-loaded flow to the sampled water slug at mid-day. The sampled slug continued downstream to site 3 during daylight hours. September runs 3 and 4 were started at mid-day with treatment plant flow and phosphate load contributed in the evening. A lack of FRP reduction might be

expected as these combined flows were transported downstream to site 3 during hours of darkness. However, September runs 5 and 6 commenced in the early morning. In a fashion similar to the April runs 1 and 2, treatment plant addition and transport past site 2 and 3 were during daylight hours. If photoinduced biological assimilation were solely responsible for the FRP processing, it would be expected that FRP variation during runs 1, 2, 5 and 6 would be similar. The fact that they were not indicates that conditions other than diurnal light for biological activity were responsible for the discrepancy.

- Periphyton Growth: Flourishing growths of periphyton were observed on-site in September in the shallows adjoining the banks and on sand bars in the middle of the river. These were not evident in April. This would support the contention that a larger plant biomass was present in September. It would be reasonable to expect that the larger visible September biomass would foster higher rate of FRP processing than the April runs. However, the FRP data exhibit the opposite observation.

FIG 5.10: RELATIVE TIME OF FRP SAMPLING



These indicate that some mechanisms, other than purely biological, were responsible either for the reduction in April or suppression of reduction in September. Further analysis of the observations between each set of runs might provide a key to this mechanism. The following patterns are noted:

- Phosphorus loadings from the treatment plant discharge were approximately the same for runs 1, 2, 3 and 4 but were lower for runs 5 and 6 (Table 5.6). This resulted in a 25 percent lower overall loading to the river for runs 5 and 6.
- The FRP loading appeared to plateau at approximately the same level during all runs at site 4 regardless of the amount of FRP added. Also, for runs initiated before noon (runs 1, 2, 5 and 6), all FRP loadings at site 6, the last site sampled, were observed to be approximately the same (Figure 5.10).
- With the exception of FRP reduction that continued through the night for run 2, none of the remaining runs exhibited any decrease in FRP loading after the first daylight cycle following treatment plant discharge. (Note: Run 2 FRP loads were 20 percent higher than those of run 1). No decrease in FRP load was observed either during the night or during

daylight of the subsequent day for runs 1, 5 and 6. Runs 3 and 4, which experienced no daylight cycle immediately downstream of the treatment plant discharge, demonstrated no apparent decrease in FRP load at any of the downstream sites.

Two possible explanations for these observations are proposed: 1) The reduction of FRP in the Neuse River downstream of the Raleigh treatment plant may be related to the diurnal cycle with the existence of a low end limit, and/or 2). There may exist a limit to short term phosphorus processing under the conditions found in the Neuse during the sampled time periods. Some possible mechanisms for this might be:

- The processing agents (biological, chemical or physical) change as water flows downstream. There may have been different dominant mechanisms for FRP processing at the 5 mile point than are present at the 15 mile point. Only those upstream of the 5 mile point may have been capable of processing in daylight hours.
- Processing agents may have been discharged from the treatment plant, along with the FRP loading, which were viable in the new environment only for a limited time of travel downstream and only under daylight conditions.

- Processing agents downstream become acclimated to a new level of phosphorus and no longer continue to process below a certain level.
- Processing agents become more dilute downstream either through die-off or sedimentation and are not available in significant enough numbers to continue reduction. Conditions may exist downstream which may inhibit phosphorus processing.

These mechanisms will be discussed further in light of correlations performed on other parameters.

5.3.1.1 TP and TFP relationships.

Both total phosphorous and total filterable phosphorus loads demonstrated good correlations with FRP loads (Table 5.7). Correlation coefficients from linear regressions of FRP versus TP were in the high 90 percents for runs analyzed in pairs (1-2, 3-4 and 5-6) suggesting the processing of each is linked to the other.

Graphic analyses of the difference (delta) between each of these categories are illustrated in Figures 5.11 through 5.14 and tabulated in Table 5.11. These include the following deltas for each sampling site:

FIG 5.11: DELTA TFP-FRP LOADS

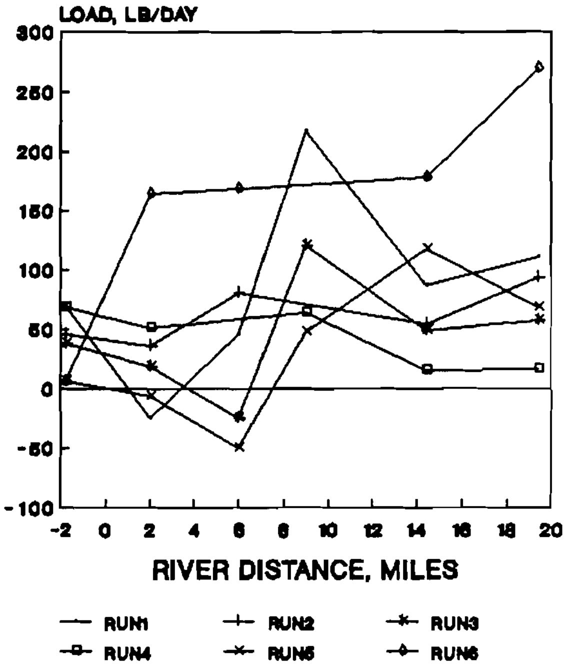


FIG 5.12: DELTA TP-TFP LOADS

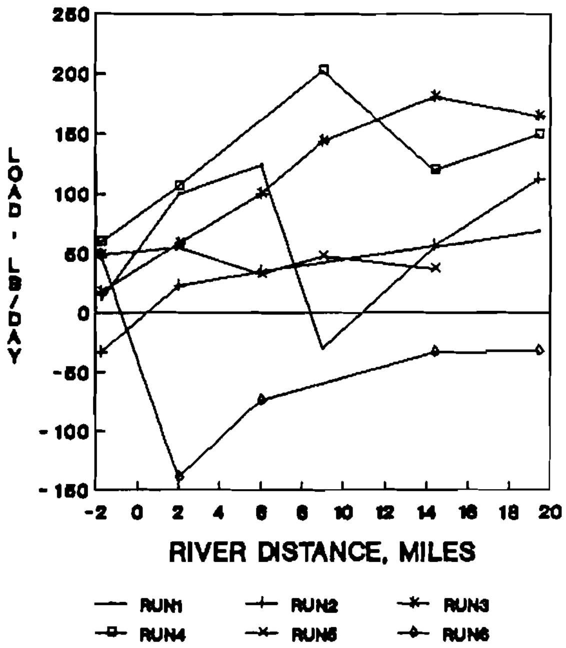
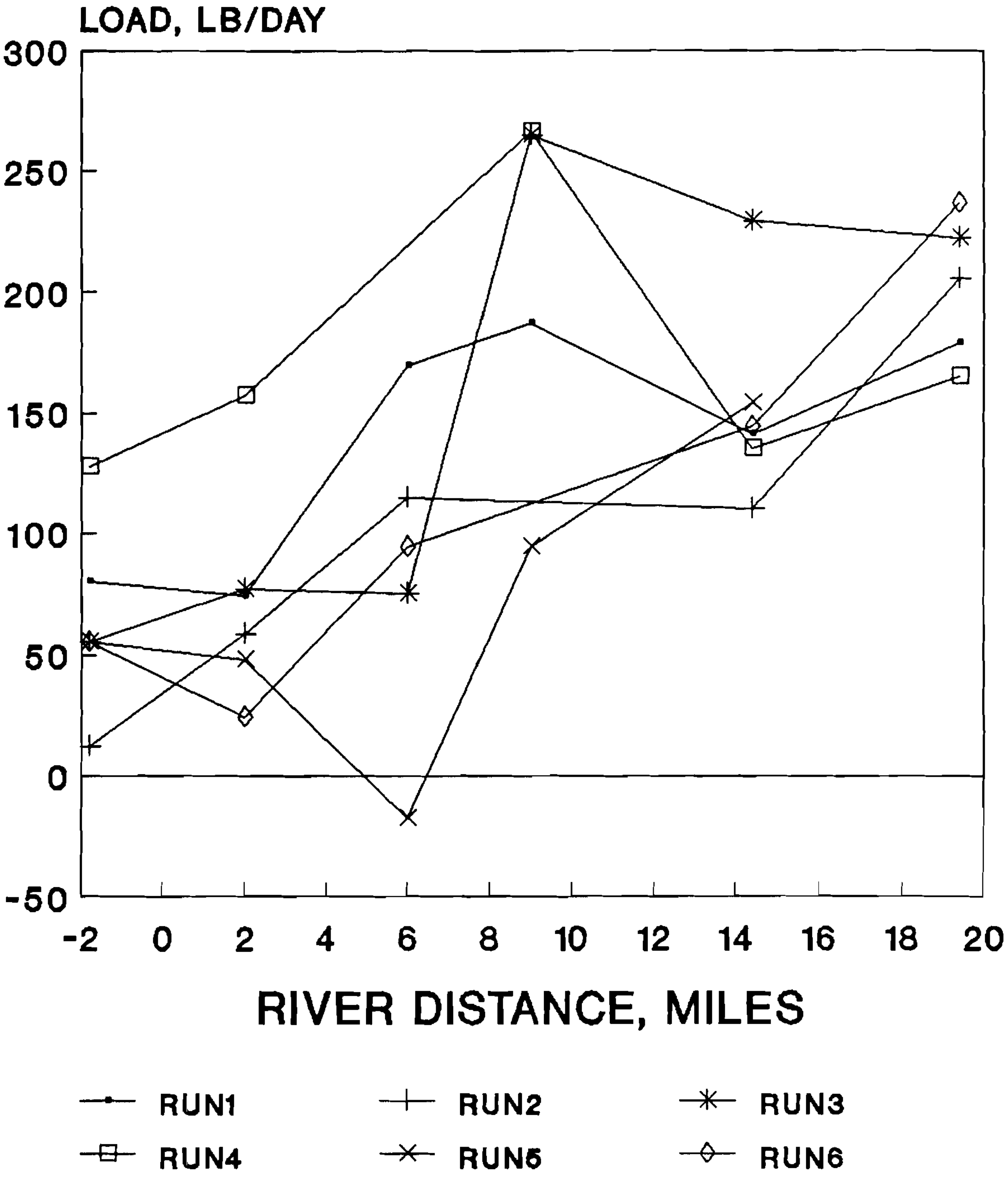


FIG 5.13: DELTA TP-FRP LOADS



- TFP minus FRP (Figures. 5.11) representing the filterable, unreactive (non-bioavailable) fraction which is accepted to be dissolved phosphorus. It may also include phosphorus adsorbed on colloidal material small enough to pass through a 0.45 micron filter, but unreactive in the FRP analysis.
- TP minus TFP (Figures 5.12) representing the particulate portion of the total phosphorus loadings.
- TP minus FRP (Figures 5.13) representing the total non-bioavailable portion of the total phosphorus loadings (assuming all particulate phosphorus is not available).

Table 5.11: Delta-P Ratios

Site NUMBER

RUN		1	2	3	4	5	6
	Miles	-1.8	2.0	6.0	9.0	14.4	19.4
dis 1	TFP-FRP:TP	.1854	-.0158	.0300	.1614	.0668	.0800
prt	TP-TFP:TP	.0298	.0616	.0814	-.0224	.0425	.0494
tot	TP-FRP:TP	.2152	.0457	.1114	.1390	.1094	.1294
dis 2	TFP-FRP:TP	.1451	.0190	.0451	NA	.0362	.0637
prt	TP-TFP:TP	-.1059	.0119	.0191	NA	.0373	.0765
tot	TP-FRP:TP	.0392	.0309	.0642	NA	.0735	.1402
dis 3	TFP-FRP:TP	.1192	.0098	-.0117	.0568	.0228	.0270
prt	TP-TFP:TP	.0530	.0307	.0466	.0677	.0840	.0766
tot	TP-FRP:TP	.1722	.0404	.0350	.1245	.1068	.1036
dis 4	TFP-FRP:TP	.2119	.0267	NA	.0290	.0072	.0073
prt	TP-TFP:TP	.1854	.0562	NA	.0923	.0564	.0674
tot	TP-FRP:TP	.3974	.0829	NA	.1214	.0636	.0748
dis 5	TFP-FRP:TP	.0159	-.0068	-.0420	.0384	.0886	NA
prt	TP-TFP:TP	.1217	.0520	.0273	.0384	.0274	NA
tot	TP-FRP:TP	.1376	.0452	-.0147	.0768	.1160	NA
dis 6	TFP-FRP:TP	.0159	.1201	.1236	NA	.1193	.1705
prt	TP-TFP:TP	.1217	-.1023	-.0543	NA	-.0227	-.0208
tot	TP-FRP:TP	.1376	.0178	.0693	NA	.0966	.1496

Analysis of these deltas as ratios of total phosphorus provided some insight into the mechanisms which were at work in transferring phosphorus between bioavailable and non-reactive forms. Similarities in curve patterns between runs indicated that the mechanisms were probably similar for the six runs. Interpreting negative ratios as equal to zero, the following observations can be made relative to these ratios:

- In all cases the TP-FRP:TP ratio upstream of the wastewater treatment discharge was appreciably higher than at most downstream sites, indicating a higher percentage of non-available phosphorus prior to the treatment plant discharge. Ratios ranged from 13 to 40 percent of total phosphorus. Of the unreactive phosphorus, 70-100 percent was filterable for runs 1, 2 and 3; 50 percent was filterable and 50 percent was particulate for run 4; and almost 90 percent was particulate for runs 5 and 6.
- At site 2, immediately downstream of the wastewater treatment plant, the TFP-FRP:TP ratios were much lower than they were at the upstream site. This indicated that almost all of the phosphorus present at site 2 was dissolved reactive phosphorus. With the exception of run 6, most of the unreactive phosphorus was particulate. It is possible that the treatment plant contributed a carryover of microbial culture and other nutrients. This would indicate that the primary mechanism may be biological. In most cases, these same conditions persist at site 3.
- At site 4, TFP-FRP:TP and TP-FRP:TP ratios increased from as low as 7 percent to as high as

16 percent over site 3. This indicated an increase in non-available phosphorus. None of this phosphorus appeared to be particulate during April (runs 1 and 2) because the TP-TFP:TP ratio approximated 0. This suggested that either there was a release of organically bound phosphorus or that there was physical adsorption to colloidal material sufficiently fine to pass through the 0.45 micron filter. For September (runs 3 through 6), the site 4 non-available phosphorus partitioned evenly between filterable and particulate forms.

- Downstream of site 4, the non-available phosphorus forms decreased again for runs 1 through 4 with the majority of it in the particulate phase. Runs 5 and 6 continue with the same level or a slight increase in the non-available P fraction of the total P.

It would appear from the foregoing that the character of the river changed somewhat with distance downstream of the wastewater treatment plant. Two particularly significant mile points were evident. The first was after the wastewater treatment plant discharge and the second was around site 4. As was to be expected, there was an increase in total phosphorus immediately downstream of the wastewater treatment plant and the majority of the phosphorus was dissolved and bioavailable. Also, because runs 1 and 2 demonstrated an appreciable decrease in river FRP loading, this particulate phosphorus may still be bound in a biological form suspended in the water column. Site 4, however, presented an interesting anomaly in that no significant phosphorus processing was evident beyond this point and the ratios of non-reactive to reactive phosphorus increased suddenly. In addition, there was a suggestion of a shift in form of the reactive phosphorus from particulate to filterable form. However, adsorption to filterable colloidal particles may have been the mechanism accounting for this, because there was nothing to indicate a massive source of dissolved organic phosphorus from biological excretions. There were no evident discharges at site 4, implying that there were no external sources of phosphorus.

5.3.2 Phosphorus and Nitrogen Species

Correlation coefficients of 80 to 88 percent from linear regressions indicated strong correlations between FRP and nitrate. Because nitrate acts as a co-nutrient with dissolved phosphorus in the stimulation of primary productivity, the hypothesis that processing in the Neuse is biologically mediated is supported.

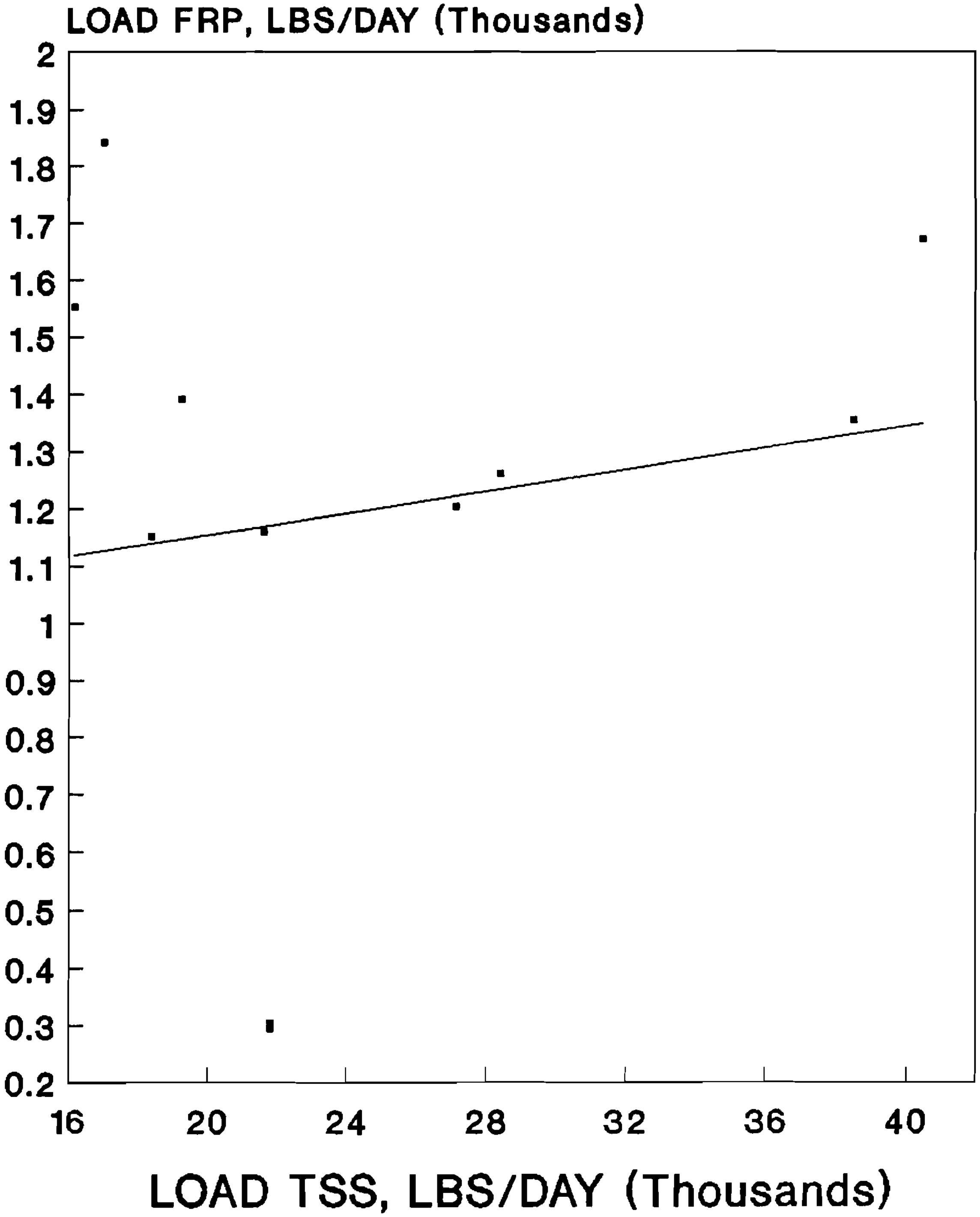
No correlation was seen between either ammonia or TKN with FRP. However, both ammonia and TKN appeared to exhibit an anomaly around site 4. In the case of ammonia, loads always decreased at site 4 to approximately 30 percent of what they were at site 3. TKN loads demonstrate a more rapid increase up to site 4 than those exhibited with flow to subsequent sites.

5.3.3 Total Suspended Solids

Baker (1980) demonstrated that total phosphorus loads tracked TSS loads in the Sandusky River Basin during moderate to high flows. It is reasonable to assume that the total phosphorus might have been associated with suspended solids as biological particulate (e.g. organic detritus, seston), or adsorbed to suspended particulate matter. Since total phosphorus tracked and correlated well with FRP in the Neuse River, the relationship between FRP and TSS may be used as an index to test this relationship between TP and TSS.

Linear regressions between TSS and FRP loads produced correlation coefficients of 2.5, 21 and 5.2 percent for run pairs 1-2, 3-4 and 5-6, respectively, which supported this conclusion. Observation of the way points position around the regression line do illustrate that approximately half of the data taken do fall on or very close to the regression line (Figure 5.14). This might indicate that under certain conditions, there may be some correlation between total suspended solids and FRP concentration, but this relationship

Fig. 5.14: TSS Vs. FRP LOADS - RUNS 1&2



is not consistent. Further study may be necessary to identify this relationship and the limits imposed upon it.

5.3.4 Phosphorus, Anions & Cations

Certain anions and cations were selected for their potential to affect the riverine processing of phosphorus. The following mechanisms were postulated:

- As a stimulator/inhibitor to biological growth. Algae and bacteria require micronutrients (trace elements including Fe, Mn, Cu, Zn, Si, Mo and Co) as well as macronutrients (Ca, Mg, N, P, K, S, Na, Cl) for their growth. Since these are generally not in short supply (growth limiting), direct stimulation of growth from their presence is not likely. In excess, many of these cations (especially copper and zinc) might be expected to act as a biological growth inhibitor.
- As media for chemical complexation. Metal ions, especially iron, calcium and magnesium are known to form colloidal complexes with phosphorus compounds in aquatic systems, under the proper conditions. These complexes will restrict the bioavailability of phosphorus.

Graphic analysis of the loadings of each ion species relative to the distance transported downstream provided visual insight into the fate of the individual ions over the length of river studied. Four patterns were evident from analysis of river load vs. distance traveled. Figures 5.10 trough 5.12 are referenced for illustration:

- o Gradual increase in loading as the slug of water is transported downstream. This might indicate constant contributions from sources other than the wastewater treatment plant over the length of the river (perhaps interflow inputs).
- o Gradual decrease in loading as the slug of water traveled downstream. This trend would be expected of elements that were removed from the water column, or were diluted by other sources of flow such as interflow.
- o Increase river loading at the wastewater treatment plant and the tracking with the FRP loads. An increase of loading immediately downstream of the wastewater treatment plant would indicate contribution of these elements to the river by the plant. Tracking a similar pattern as that of the phosphorus data would indicate that similar processes might act on these substances as were observed for phosphorus.
- o A seemingly random pattern of increases and decreases from site to site. This would indicate

some process or group of processes acting as a source at some sites and a sink at others for the specific element or could be due to analytical errors or sampling errors. These processes might also impact on phosphorus loads at groups of sampling sites but the effect may not be consistent for all sites.

Analysis of processing ion loads relative to phosphorus processing was made using the load vs. distance graphs in conjunction with linear regressions performed on individual ions and/or groups of ions relative to FRP. Correlations were calculated using data from downstream sites only, since these were the data influenced by the discharge from the treatment plant (Table 5.12). Interpretation was tempered with judgement relative to the periods when phosphorus was seen to exhibit processing (April runs 1 and 2) and periods when little processing was evident (September runs 5 through 6). Poor correlations during periods of processing followed by good correlations during periods of low processing probably indicate that there is no linkage and that both phosphorus and the comparative ion were, at best, being affected by the same advective, hydrodynamic forces. Particular interest was also focused on those elements which might help to explain the anomaly at site 4 as discussed in the section on phosphorus.

Table 5.12. Correlation Coefficients, Ions vs. FRP Loads

Ion	April Runs 1&2	September Runs 3&4	September Runs 5&6
Na	0.11	0.83	0.84
Cl	0.50	0.99	0.96
SO_4	-0.06	0.82	0.83
Ca	0.26	0.83	0.66
Mg	0.13	0.77	0.68
K	0.32	0.57	0.75
Fe	-0.86	0.36	0.31
Cu	NA	-0.64	0.46
Mn	-0.38	-0.76	-0.47

5.3.4.1 Sodium and Chloride:

Both sodium and chloride ion are accepted as being conservative elements whose concentration are affected by few mechanisms other than dilution. Barring other sources for these ions, sodium and chloride are reasonable indicators of pure advective transport wherein constituents are affected only by dilution and no apparent processing occurs.

Poor correlation was indicated with FRP during runs 1 & 2 in April when FRP load was observed to decrease in the river downstream of the wastewater treatment plant discharge. This would support the hypothesis that the decrease in FRP in April was due to processing rather than dilution. September runs 3 through 6, where little decrease in FRP load occurs downstream of the treatment plant, demonstrates excellent correlation between FRP and both sodium and chloride loads. This would indicate that FRP transport downstream of the wastewater treatment plant was primarily advective in September.

5.3.4.2 Sulfate:

Sulfate loads demonstrated poor correlation with the FRP loads for April Runs 1 and 2 (Table 5.12) with a negative linear correlation coefficient of -0.06. September runs 3 through 6 were observed to show good correlations with an average coefficient of 0.825. Visual observation of sulfate load data for September runs reveal trends toward a gradual increase in sulfate load as water is transported downstream in contrast to September FRP loads which remain relatively unchanged with downstream transport. Coupled with the lack of consistent correlation, it appeared that the sulfate load has little influence on FRP processing.

5.3.4.3 Calcium, Magnesium and Potassium:

River loads for calcium, magnesium and potassium exhibited similar patterns for all April and September run. This would indicate that they are influenced by the same mechanisms. Indications are that the quantity of FRP loading present was not influenced by calcium, magnesium or potassium individually. Similar correlations are seen relative to FRP as above with approximately 60 percent of the variance described as linear for April runs 1 and 2 and up to 80 percent for September runs 3 through 6. The similarity in the river load patterns indicate that these elements should be tested for combined influence on FRP loads. This is discussed below under the section on multiple regressions.

5.3.4.4 Iron.

Iron loads demonstrated good negative correlation with FRP loads in April. This indicated that there was a trend for FRP load to decrease as iron load increased. September runs indicated no correlation. However, it is interesting to note the rather consistent increase in iron load in nearly every run at site 4. The observation that the conservative constituent loads (sodium and chloride) tend to decrease at site 4 indicates that a mechanism other than advection in the river is responsible for the increase in iron loads at this location. This may be an indication of a change in the chemical character in the river at site 4 which may inhibit further FRP processing.

5.3.4.5 Copper and Manganese:

Since copper was not analyzed in April samples, it could not be compared with the erratic pattern exhibited by the river transport of manganese. However, both of these elements exhibited similar trends in September runs with a decrease in load as water was transported downstream. No correlation with FRP loads was observed in either April or September for these constituents.

5.3.6 Ions in Combination:

Multiple linear regressions were performed to determine if correlations of combinations of ion loads with FRP could be discerned. Iron was chosen as the primary element to test in unison with others because of the anomaly observed at site 4. Iron, as a positive metallic ion, has been shown to complex directly with phosphorus compounds under the proper conditions (Carpenter and Smith 1985). Additionally, iron, as well as other metal ions such as calcium and magnesium are capable of complexing with intermediate colloidal phosphorus, rendering it unable to complete it's transformation to dissolved inorganic phosphorus (Lean 1973). Linear regressions were performed on all data for these two elements taken in combination against FRP loading (Table 5.13).

Table 5.13: Correlations for Ions in Combination vs. FRP Loads

Runs	Fe|Mg	Fe|Ca	Ca|Mg	Fe|Ca|Mg
1 & 2	0.809	0.826	0.696	0.911
3 & 4	0.810	0.704	0.978	0.983
5 & 6	0.906	0.716	0.913	0.968

Multiple correlations tabulated in Table 5.13. indicate the Fe|Mg combination to manifest the best overall correlation for all six runs. However, the Ca|Mg combination is superior for the September runs. Correlations for Fe in combination with Ca were good for the April runs only.

Combinations of all three elements in multiple regression demonstrated improved correlation for all runs.

It is evident that there is improved correlation between ion loads in combination with FRP loads. Visual observation of correlations did not prove adequate to fully assess the impact of all ions analyzed. To determine statistically the ions which most significantly correlated with FRP loads, stepwise linear regressions were performed. Results indicate that iron was the most strongly correlated ion for runs 1 and 2 while calcium had superior correlations for September runs 3 through 6. These materials, may be linked to removal of phosphorus.

Metallic ions may often be associated with suspended sediment. To determine if suspended sediment served as a possible source of anions, multiple regressions were performed on Fe|Ca|Mg combination with TSS river loads. Correlations suggested Fe|Ca|Mg might have had somme association with suspended solids in the month of September (Table 5.14).

Table 5.14. Fe, Ca and Mg Correlations with TSS

Runs	1&2	3&4	5&6
R^2	0.031	0.876	0.691

The high correlations between combined ion loads and

FRP loads indicated that these elements taken in combination might have been involved in the processing of phosphorus in the river. Because there was little processing of FRP in September runs despite apparent favorable conditions, it was probable that much of the phosphorus, which was interpreted as reactive, was at least temporarily rendered non-reactive phosphorus.

Because of the good correlations found with anions in combination, it is postulated that these elements complex with phosphorus and form colloids in suspension which are not bioavailable over the short term but are capable of passing through the 0.45 micron filter (Lean, 1973). As a colloidal material, the complexes resist precipitation and persist in the water column for a greater distance downstream than they might otherwise. The high incidence of iron and calcium starting at site 4 appears to mediate this complexing at that point in the river flow and further phosphorus processing is reduced beyond this point.

5.3.6 Summation

More favorable physical and biological conditions for the processing of FRP downstream of the wastewater treatment plant were more apparent in September than they were in April. Despite this, FRP reduction occurred in April but not in September. This would indicate that some other mechanism might be at work.

Consistently, there appeared to be an anomaly at site 4 wherein loads of various chemical species would either increase rapidly or decrease rapidly. These were often inconsistent with effects of dilution as evidenced by the lack of parallel with loads of the conservative elements, sodium and chloride.

While poor consistent correlation was found between FRP and most species, good correlation was observed between FRP and anions taken in combination. Since there was little processing of FRP in September, it was postulated that the material being analysed may not have been immedialely available, even though it was not retained by an 0.45 micron filter (Downes and Pearl, 1978a and b). These phosphorus species are proposed to be colloidal forms from the complexing between phosphorus and cations such as iron and calcium. In this form they could pass through an 0.45 micron filter and not be available in the river for biological processing (Lean, 1973).

PART 6

MODEL DEVELOPMENT

6.1 GENERAL

The culmination of the study was the analysis of the data and the construction a mathematical model to demonstrate the processing of nutrients discharged by point sources such as wastewater treatment plants in rivers and streams. The "Stream Nutrient Processing Simulation " (SNUPS) model attempts to perform this simulation in a manner which mimics the slope sampling method. Time of travel information is provided or estimated by the user. This is utilized by the model as the primary index to determine residence time within subreaches for a series of discrete slugs of water as they are transported downstream. The model simulates one diurnal cycle by producing four individual runs commencing six hours apart. Treatment plant flow and solar radiation become the primary variables for comparison between runs.

Reaches are determined by the user to be discrete sections of a river for which similar conditions exist. Alternately, each reach might represent an area between two convenient sampling points. Ideally, reaches should be chosen as river sections for which similar hydraulic conditions exist. To increase resolution of calculations, the model automatically breaks reaches into several subreaches for the purpose of calculation, as specified by the user, in miles or fraction of a mile. Choice of subreach size should be dictated by a balance between the assumed mixing length for the river being modeled and the degree of calculation resolution desired.

6.2 CONSTITUENT TRANSPORT EQUATIONS

The constituent transport equations which govern the change in parameters as they are transported from reach to reach take into account all of the sources of a constituent minus all of the sinks for the constituent. The equation for the concentration within a given reach at a given point in time takes the general form:

Concentration = Advective Transported Concentration
+ Sources of the Component
- Sinks of the Component

where the source and sink terms are represented by the change in component concentration for the residence time within the reach, dC/dt.

The primary thrust of the model is to simulate point-source nutrient processing in a river with particular emphasis upon phosphorus. Those processes seen as being phosphorus releasing or consuming are the following:

- Algal productivity. Algae depend upon phosphorus in the carrying on of both photosynthesis and to a lesser degree respiration. They are responsible for incorporating a fraction of the dissolved, bioavailable phosphorus into their cell mass. As a result, algae serve as a source for particulate phosphorus and a sink for dissolved phosphorus.

- Bacterial activity. Bacteria are the primary processing medium in wastewater treatment plants. Many nutrient processing models ignore the processes of microbial activity and bioflocculation which persist in the river immediately after the treatment plant outfall (Bhargava 1986). Microbial activity due to carryover of microbial biomass to the river is shown to be a short term nutrient sink and particulate source downstream of the treatment plant outfall.
- Colloidal P. A phosphorus colloid complex is formed as an intermediate between biologically excreted dissolved organic P and bioavalable dissolved inorganic P (Kean 1973). The forming of cationic-colloid:P complexes may effectively block this conversion. This significantly reduces the rate of P cycling by decreasing the amount of bioavailable P which is resolubilized.
- Sediment adsorption. Suspended sediment, under the proper conditions of pH and temperature, will serve to adsorb phosphorus compounds. This is

demonstrated as a phosphorus sink.

- Settling. Particulate bound phosphorus, whether incorporated into cell mass or adsorbed to particles is subject to settling under diminished local velocity conditions.
- Benthic interchange. A portion of the phosphorus pool is released from the sediments back to the water column.
- Driving forces. Variable parameters to set the above processes in motion. These include, solar irradiation, temperature and local average velocity.

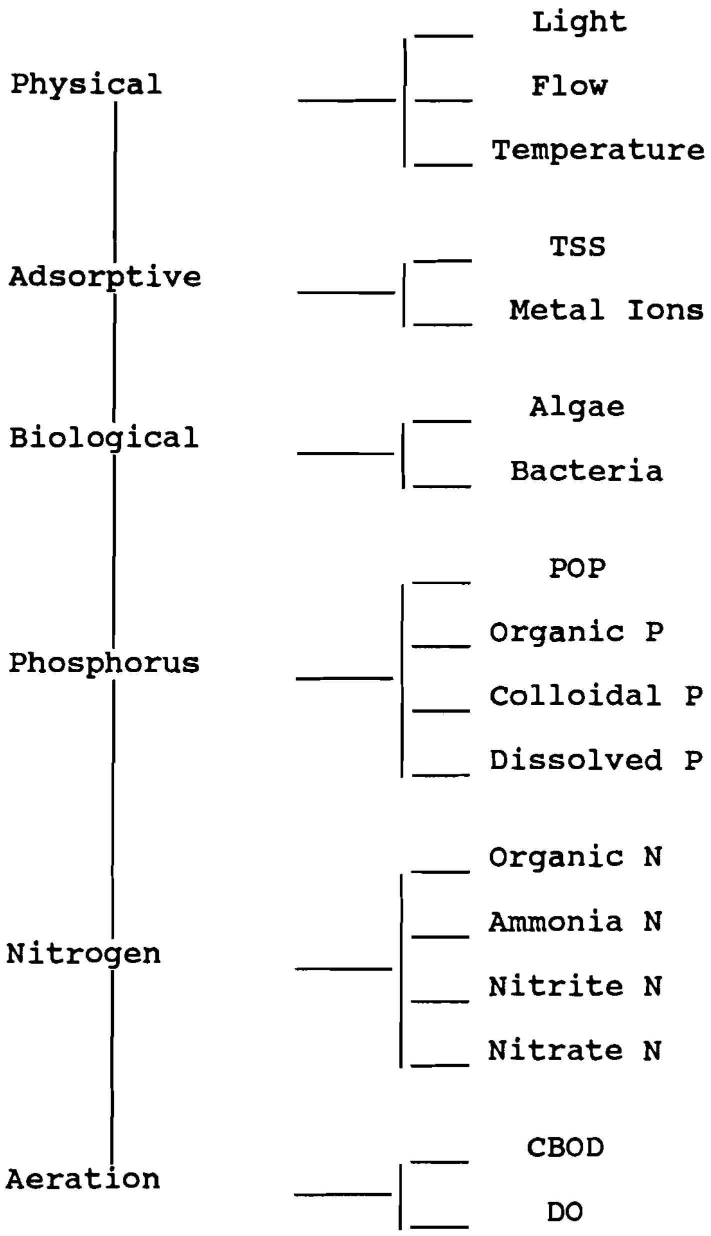
No nutrient model would be complete without at least allowing for the classic water quality parameters. In addition to nutrient processing (primarily phosphorus and secondarily nitrogen), dissolved oxygen and carbonaceous oxygen demand are simulated as indicators of model culpability. The general structure of the SNUPS Model is outlined in Figure 6.1.

6.3. SUPPORT VARIABLES

6.3.1 Algal Growth and Nutrient Uptake Variables

The uptake of nutrients by both algae and bacteria is responsible for two interrelated mechanisms: first, the stimulation of biological productivity and hence the increase in biomass and second, the commensurate reduction of nutrient concentration in the available nutrient pool. The primary factors used in the estimation of algal and bacterial growth are their respective specific growth rates, u_algae and u_micro. Both of these factors are estimated relative to maximum growth rates (u_algalmax and u_micromax respectively). The fraction of these maximum rates that are realized as specific growth rates is a function of the availability of necessary nutrients for algal and bacterial growth, the availability of light and the temperatire of the medium. Equations provided for the

FIGURE 6.1: STRUCTURE OF SNUPS MODEL



estimation of the specific growth rates for both algae and bacteria are essentially identical with the light term eliminated for the bacterial case. Three options are provided:

Option 1, Multiplicative. This option simulates the effects of nitrogen and phosphorus concentration in the same manner as they are seen in enzymatic processes (DeGroot, 1983). Each is given equal weight relative to the evaluation of the individual factor, FL, FN and FP.

```
     u_algae = u_algalmax * FL * FN * FP
     u_micro = u_micromax * FN * FP
```

where:
FL = Light factor
FN = Nitrogen Factor
FP = Phosphorus Factor

Option 2, Limiting Nutrient. This option simulates the effects of nitrogen and phosphorus relative to Liebig's Law of the Minimum. The nutrient factor which is in least supply is used in the calculation. The other nutrient is ignored (Park et al. 1979).

```
IF FP > FN THEN
     u_algae = u_algaemax * FL * FN
     u_micro = u_micromax * FN
  ELSE
     u_algae = u_algaemax * FL * FP
     u_micro = u_micromax * FP
```

Option 3, Inverse Additive. This option allows for the interaction between more than one limiting nutrient. The equation represents a combination of the above two options by treating the factors mathmatically analogous to the treatment of two resistors in series (Scavia and Park, 1976).

```
u_algae = u_algaemax * FL
          * ( 2 * FP /((1 / (FN +1))))

u_micro = u_micromax
           * ( 2 * FP /((1 / (FN +1))))
```

Some care must be exercised in the use of the latter option in that erroneous results will be encountered for high FN (FN approaches unity) or low FP (FP approaches zero). In both cases, the result approaches 2 * FP rather than FP as might be construed intuitively (Walker 1983).

6.3.2 Growth Limitation Factors, FN, FP and FL

The nutrient growth limitation factors for nitrogen (FN) and phosphorus (FP) as used in estimating the specific growth rates for algae (u_algae) and bacteria (u_micro) are calculated as follows:

```
FN = BioAssim_N / ( BioAssim_N + Kn )
```

where:
BioAssim_N = Ammonia_N + Nitrate_N, mg/l
Kn = Monod half-saturation constant for nitrogen, mg/l

$$FP = FRP / (FRP + Kp)$$

where:
FRP= concentration of Filterable Reactive Phosphorus, mg/l
Kp = Monod half-saturation constant for phosphorus, mg/l

The calculation of FL, used in the estimation of the algal specific growth rate (u_algal), may be performed using one of three methods. Each incorporates one of the three most popular options used to calculate the light attenuation factor integrated relative to water column depth.

Option 1, Half-Saturation Option. This is derived from the Monod expression.

$$FL = (1/(y * depth)) * \ln((KL + Light) /(KL + (Light * EXP(-y * depth))))$$

where:
KL = half saturation coefficient for light, BTU/sqft-hr
= 5.0 (default value)
Light= surface light intensity, BTU/sqft-hr
y = light extinction coefficient, 1/ft
depth= average depth, ft

Option 2, Smith's Function. This equation incorporates second order effects of light intensity (Smith, 1936).

$$varA = (Light / KL) + SQRT((1 + (Light/KL)))$$

$$varB = ((Light / KL) * EXP(-y * depth)) + SQRT(1 + SQR(Light / (KL * EXP(-y * depth))))$$

$$FL = (1/(y * depth)) * \ln(varA / varB)$$

where:

KL = Smith's coefficient for light, BTU/sqft-hr
= 8.66

Option 3, Steele's Function. Photoinhibition of algal growth is represented using an exponential function (Steele, 1962).

varA = EXP(-EXP((-y * depth) * (Light/KL)))

varB = EXP(- Light / KL)

FL = (2.718 / (y * depth)) * (varA - varB)

where:
KL = Steele's coefficient for light, BTU/sqft-hr
= 21.55

Option 4, MS CLEANER Combination. This option uses either the Smith function when the light intensity is below saturation and the Steele function when light intensity is greater than saturation (Park 1979). This combination is proposed since the use of the Steele function alone may predict response relative to conditions which are above light saturation. As a result, too low a factor might be realized under non-inhibiting light conditions (Groden 1977).

6.3.3 Light Extinction Coefficient, y.

Three components are provided to estimate the light extinction coefficient. Two of these components take into account effects of algal self-shading. These switches are used to evaluate variables y0, y1 and y2 in the following equation:

$$y = y0 + (y1 * Susp\_Sed) + (y3 * ChloroA) + (y4 * ChloroA^{0.6666})$$

where:

y0 = background shading component
y1 = linear particle:mass turbidity coefficient
y2 = linear algal self-shading coefficient
y3 = non-linear algal self-shading coefficient

and:

$$ChloroA = a0 * Algae$$

a0 = chlorophyll fraction of algal biomass
Algae= Algal Biomass, mg/l

In the use of this equation, any one component may be excluded by equating its y(n) factor to zero. The background shading component, y0, represents shading other than that imparted by the algal biomass or that due to suspended solids concentration, or turbidity. This represents that shading which is found in filtered water and is due primarily to color imparted by dissolved substances. A separate turbidity factor for suspended solids is incorporated to allow for shading due to fluctuation in solids concentration.

Values for the y2 and y3 are linear and non-linear algal self-shading coeficients, respectively. Values for the coefficients are selected with the following options:

Option 1: No algal self-shading

$$y1 = 0, y2 = 0$$

Option 2: Linear algal self-shading (Meta Systems)

$y1 = 0.011$, $y2 = 0$

Option 3: Nonlinear algal self-shading (Zison 1978)

$y1 = 0.00268$, $y2 = 0.0165$

6.4 PARAMETERS

6.4.1 Algae.

Algae act as a source for particulate nutrients and a sink for dissolved, bioavaliable nutrients through the incorporation of these nutrients into biomass during the photosynthetic process. The rate of photosynthesis and the associated nutrient uptake is light and temperature dependent. Algal biomass is used later in the model as both a source and a sink term for dissolved oxygen concentration, as well.

Change in Algal Biomass =
Algal growth - Loss of mass due to respiration
- Loss of mass due to settling

-OR-

$$dAlgae/dt = (u\_algae * Algae) - (p * Algae) - ((o1 / Depth) * Algae)$$

where:

Algae= Algal Biomass, mg/l
depth= average depth, feet
o1 = Algal Settling Rate, ft/day
p = Algal Respiration Rate, day^{-1}
u_algae= Specific Algal Growth Rate (light & temperature dependent), day^{-1}

The temperature, light and nutrient dependence of the change in algal biomass is reflected in the model evaluation of the algal growth rate. This was treated above in the discussion on the calculation of the specific growth rate, u_algae.

6.4.2 Bacteria.

Bacteria are treated similarly to algae with the omission of the light term in the calculation of the specific growth rate. Change in bacterial biomass is calculated as follows:

Change in Bacterial Biomass =
Bacterial growth
- Loss of mass due to respiration
- Loss of mass due to settling

-OR-

$$\text{dMicrob/dt} = (\text{u\_micro} * \text{Microb}) - (\text{pm} * \text{Microb}) - ((\text{o7} / \text{Depth}) * \text{Microb})$$

where:

Microb= Bacterial Biomass, mg/l
depth= average depth, feet
o7 = Bacterial Settling Rate, ft/day
P_m = Bacterial Respiration Rate, day^{-1}
u_micro= Specific Bacterial Growth Rate (light & temperature dependent), day^{-1}

Few models incorporate the effects of bioflocculation which continues for a short distance immediately downstream of a wastewater treatment plant (Bhargava, 1986). This may be accounted for in the model by assigning a value of bacterial biomass to the outflow of the wastewater treatment plant. It is assumed that this mass settles as a floc mass nearly completely from the water column within a short distance (a few miles) downstream since these nutrient processing effects may not be significant for the remainder of the stream length. This may be accomodated by assigning a large settling factor to the bacterial mass which may be assumed to be in the form of loosely aggregated, settling floc.

6.4.3 Suspended Solids:

Adsorption of dissolved substances to suspended solids is a potential sink term for dissolved phosphorus compounds. Suspended sediment load is calculated in the model in one of two ways:

- o Option 1: as a function of velocity, or
- o Option 2: by using source/sink terms.

With Option 1, suspended sediment concentration may be estimated as a function of the average velocity of a reach. The relationship is treated as non-liner or linear at the users' descretion by the incorporation of either linear or nonlinear coefficients. A third term is provided for base bed load contributions. The relationship is as follows:

$$\text{SuspendSed} = (\text{Kv1} * \text{velocity}) + (\text{Kv2} * \text{velocity}^2) + \text{Cvs}$$

where:

Kv1 = linear suspended solids coefficient
Kv2 = nonlinear suspended solids coefficient
Cvs = base bed load concentration of suspended solids, mg/l
velocity= average reach velocity, ft/sec
= Reach Distance / Time of travel interval

Using this relationship, both resuspension and settling are treated at the same time. The linear or the nonlinear regime may be used in combination or deselected by setting the coefficient which is not desired to zero. Linear coefficents may be provided for high flow regimes. Nonlinear or a combination of linear and nonlinear are recommended for low flow regimes. Velocity is computed automatically by the model from time of travel and distance information provided for each reach.

Using Option 2, suspended sediment concentration decreases with distance using a constant settling rate. Sediment is added to the system from bed load when a scour velocity is reached. Using the following equation to calculate the scour velocity (Camp, 1946), the sediment source term is defined:

$$vs = ((8 * ks * (sg - 1) * g * dia) / f)^{0.5}$$

where:

vs = scour velocity, ft/sec
ks = sediment scour constant
= 0.04 for sand and 0.06 for mud
sg = specific gravity of the sediment
g = gravity, ft/sec
dia = average particle size, ft

Change in Suspended sediment =
Suspended sediment scoured
\- Suspended sediment settled

-OR-

$$dSuspSed/dt = (o8 * (vh > vs)) - (o7 * Susp\_sed)$$

where:
o7 = sediment settling rate, ft/sec
o8 = sediment resuspension rate, mg/l-sec
vh = horizontal water velocity, ft/sec

The horizontal water velocity, vh, is calculated by the simulation from the average time of travel for the reach.

6.4.3.1 Colloidal Material.

Colloidal material consists of minute particles of solids which are maintained in suspension in the water column and are not subject to retention on an 0.45 micron filter. Generally they are not subject to settling unless their mass is increased due to coalescence. Colloids are particularly germane to this model since they function as an intermediate site for the conversion of dissolved organic phosphorus to dissolved inorganic phosphorus. The transformation process takes place at a given rate, unless high concentrations of inorganic metallic ions are present. These cations will complex with the colloid-phosphorus complexes and prevent the transformation to FRP. Concern for colloid concentration is only for that fraction of the colloid pool which has been "bound-up" with metallic-phosphate complexes. These are taken into account in the calculation of colloidal phosphorus concentrations.

6.4.4 Phosphorus.

The primary nutrient modeled is phosphorus and its major species. Species modeled include organic phosphorus and filterable reactive phosphorus. Organic phosphorus is subdivided

into a particulate phosphorus component and a dissolved organic component. Filterable Reactive phosphorus is modled as a colloidal complex component and a dissolved component.

6.4.4.1 Organic Phosphorus:

Organic phosphorus is simulated primarily as that portion of the phosphorus pool which is incorporated into biomass and thereby suspended in the water column. Algal and bacterial biomass are treated separately and are broken out from the dissolved phosphorus as Particulate Organic Phosphorus (POP). Typical losses include organic compounds containing phosphorus which are catabolized during the respiration process. These may be transformed into dissolved P or colloidal P and the latter of which after coalescence, settles out of the water column. A fraction of the biomass also settles out of the water column. POP is calculated directly from the biomass concentrations. Since biomass calculations have already taken into account the loss due to biomass death and settling, POP calculation becomes a simple ratio.

```
Particulate Organic Phosphorus =
     Portion of Algal Biomass which is P
          + Portion of Bacterial Biomass which is P

                          -OR-

      POP = (a2 * Algae) + (a7 * Bacteria)
```

```
Change in Dissolved Organic Phosphorus Concentration =
     fraction algal biomass converted by respiration
      + fraction bacterial biomass converted by
        respiration
      - quantity transformed directly to dissolved P
      - quantity transformed to colloidal_P

                          -OR-

     dOrganicP/dt := (a2 * pa * Algae)
                   + (a8 * pm * Microb)
                   - (b4 * Organic P)
                   - (b6 * Organic P)
```

where:

Algae= Algal Biomass, mg/l
Microb= Bacterial Biomass, mg/l
a2 = Algal Biomass P Fraction, mgP/mg A
a8 = Bacterial Biomass P Fraction, mg P/mg B
b4 = Decay Rate Organic P to Dissolved, 1/day
b5 = Transformation Rate Organic P to Colloidal P, 1/day
p = Algal Respiration Rate, day^{-1}
pm = Bacterial Respiration Rate

6.4.4.2 Colloidal Phosphorus:

Colloidal phosphorus is that portion of the phosphorus pool which is adsorbed to inorganic colloids and is still capable of passing through an 0.45 micron filter. This is separated from the other filterable phosphorus in that it is not immediately available for biological assimilation. According to Lean (1973) this is a necessary intermediate step in the transformation of dissolved organic phosphorus to dissolved inorganic phosphorus. The process may be blocked by the presence of cations in solution which will complex with the colloids and prevent the transformation to dissolved P.

The cation-colloid complexing is simulated in the model in a stepwise fashion. Metallic cations in solution are represented as capable of complexing with colloidal-P in some proportion to their concentration. This forms a metallic-colloid-complex. The change in concentration of cation is estimated as a soluble release relative to flow minus metal complex which has coalesced and settled.

$$dMetal/dt = (a9 * Flow) - ((1 - fm) * o9 * TMetal)$$

where:

a9 = rate of cation solubilization
fm = (free) fraction of cations not complexed with colloidal P.
o9 = Setling rate for Cation-colloid complex, 1/day
TMetal = Total cation in the river water, mg/l

A portion of the metal is complexed with free colloid:

$$MetalColloidComplex = (b8 * fc * Colloidal\ P)$$

where:

b8 = rate of metal-colloid complexing, 1/day
fc = (free) fraction of colloidal P not bound to cations

The amount of cation-colloid complex is limited in the above equation by the amount of available colloid. It is also limited by the amount of available cation by adjusting the pool of available cations:

```
dfreemetal/dt := (a9 * Flow)
                 - (MetalColloidComplex / PM_Ratio)
```

where: P/M Ratio = Stochiometric coefficient to maintain cation-colloid proportionality.

Lastly, a new free cation fraction is calculated:

```
freemetal = freemetal / TMetal
```

In a similar manner, the concentration of colloidal P is estimated.

Change in Colloidal_P concentration =
Organic P transformed to Colloidal P
+ FRP conversion to colloidal P
- Colloidal P transformed into Dissolved P
- Settled Cation-Colloidal P complex

-OR-

```
dColloidalP/dt := (b5 * OrganicP) + (b7 * FRP)
                  - (fc * b6 * Colloidal P)
                  - ( (1 - fc) * o9 * Colloidal P)
```

where:

b5 = transformation rate of organic to colloidal P, 1/day
b6 = transformation rate of colloidal to dissolved P, 1/day
b7 = rate of FRP conversion to colloidal P, 1/day
fc = (free) fraction of colloidal P not bound to cations
o9 = Setling rate for Cation-colloid complex, 1/day

The change in the amount of free colloid is estimated as a portion of the total colloid in a similar fashion to that of free metal.

```
dfreecolloid/dt = (b5 * Organic P) + (b7 * FRP)
                       - (fc * b6 * Colloidal_P)

        fc = freecolloid / Colloidal P
```

6.4.4.3 Dissolved Phosphorus.

Filterable reactive phosphorus is that portion of the total phosphorus pool which may not be retained by microfiltration through a filter with an average pore size of 0.45 microns, reacts with the colorimetric reagents, and is considered the most available for biological assimilation. It is modeled as the dissolved inorganic phosphorus portion of the total phosphorus pool. Sources include organic phosphorus from cell lysis which has been transformed to dissolved phosphorus, and that which is released from the bottom sediments. Loss terms include absorption dissolved phosphorus absorbed by algae and bacteria and dissolved phosphorus which adsorbs to suspended sediment and colloidal matter.

```
Change in FRP Concentration =
     Transformation of Colloidal P to Dissolved P
     + Transformation of Organic P to Dissolved P
          + Transfer from the Benthos
          - Amount utilized by Algae
          - Amount utilized by bacteria

                    -OR-

dFRP/dt = (b4 * Organic P) + (o2 / Depth)
          + (fc * b6 * Colloidal_P
          - (a8 * u_Micro * Microb)
          - (a2 * u_algae * Algae)
          - (b9 * Suspended Sed)
```

where:

Depth = Mean River Depth, feet
a2 = Algal Biomass P Fraction, mgP/mg A
a8 = Bacterial Biomass P Fraction, mg/mg M
b4 = Transformation rate Organic to Dissolved P, 1/day
b9 = Adsorption rate of Dissolved on Suspended Sediment, 1/day
o2 = Benthos Source Rate for Dissolved P, mgP /ft2 day
u_algae = Specific Algal Growth Rate, 1/day
u_micro = Specific Bacteria Growth Rate

6.4.5 Nitrogen.

Nitrogen is simulated in the model in a four step oxidation. The cycle starts with organic nitrogen as excretion products from algal and bacterial respiration. It is then successively deaminated ammonia, and oxidized to nitrite and, finally, nitrate. The cycle is completed with the biological incorporation of dissolved ammonia or nitrates to organic nitrogen by algae and bacteria.

6.4.5.1 Organic Nitrogen.

The source term for organic nitrogen is manifest as a fraction of the algal and bacterial metabolic products. While functionally not correct, the respiration rate terms, p for algae and pm for bacteria, are used to approximate the rate of release of organic nitrogen as a fraction of algal and bacterial excretions. These are the same terms that were used in calculating endogenous respiration. Organic nitrogen is lost through hydrolysis to ammonia, and settling to the benthos. Conceptually the process is represented as follows:

Change in Organic Nitrogen Concentration =
fraction algal biomass converted by respiration
+ fraction bacterial biomass converted by respiration
- Amount hydrolyzed to Ammonia
- fraction transferred to the Benthos

-OR-

```
dOrganicN/dt = (a1 * p * Algae)
             + (a10 * pm * Microb)
             - (b3 *  Organic_N)
             - (o4 * Organic_N)
```

where:

a1 = Nitrogen fraction of Algal Biomass, mg N/mgA
a10 = Nitrogen fraction bacterial biomass, mg N/mgB
b3 = Hydrolysis rate of organic-N to NH_3, 1/day
o4 = Organic N Settling Rate, 1/day
p = Algal Respiration Rate, 1/day

6.4.5.2 Ammonia Nitrogen.

Ammonia nitrogen is a product of the hydrolysis of organic compounds containing nitrogen. A portion may be lost to the benthos or may be further oxidized by bacteria to nitrite. In addition, a portion of the ammonia may be utilized by algae in lieu of or in addition to nitrate. An algal preference factor, F1, is introduced to account for that the proportion of the total nitrogen usage by algae which is ammonia.

Change in Ammonia Nitrogen Concentration =
Amount of hydrolyzed organic nitrogen
- Amount oxidized to nitrite
+ Amount contributed by the benthos
- Algal incorporation

-OR-

dAmmoniaN/dt = (b3 * Organic_N)
- (b1 * Ammonia_N)
+ (o3/depth)
- (F1 * a1 * u * Algae)

where:
b1 = Oxidation Rate constant NH_3 to NO_2,day^{-1}
b3 = Hydrolysis rate organic-N to NH_3, day^{-1}
o3 = Benthos source rate for ammonia-N, mg O/ft^2 day
u = Algal specific growth rate, day^{-1}
F1 = Fraction of total algal nitrogen usage which is ammonia

6.4.5.3 Nitrite Nitrogen.

Nitrite nitrogen results as the product of the oxidation of ammonia by chemoautotrophic bacteria which produce nitrite during respiration. Similarly, nitrite is lost to the system by a conversion to nitrate by a different chemoautotrophic bacteria. Conceptually, the change in nitrite concentration is as follows:

Change in Nitrite Nitrogen concentration =
Amount transformed form ammonia N
- Amount oxidized to Nitrate

-OR-

dNitriteN/dt = (b1 * Ammonia_N)
- (b2 * Nitrite_N

where:
b1 = Oxidation Rate constant NH_3 to NO_2
b2 = Bio-oxidation rate of NO_2 to NO_3

6.4.5.4 Nitrate Nitrogen:

The source of nitrate is from the oxidation of nitrite by chemoautotrophic bacteria. Loss of nitrate from the system occurs from algal assimilation. While nitrate is generally the nitrogen form prefered by algae, they are capable of assimilating ammonia as well. Therefore, algal nitrate assimilation becomes the difference in total assimilated nitrogen minus the amount of ammonia nitrogen utilized.

Change in Nitrate Nitrogen concentration =
Amount transformed from Nitrite N
- Amount assimilated during algal photosynthesis

-OR-

$$\text{dNitrateN}/dt = (b2 * \text{Nitrite\_N}) - ((a1 * u * \text{Algae} * (1 - F1))$$

where:
a1 = Algal Biomass Nitrogen Factor, mgN/mgA
b2 = Bio-oxidation rate of NO_2 to NO_3, day^{-1}
u = Specific Algal Growth Rate, day^{-1}
F1 = Fraction of total algal nitrogen usage which is ammonia

6.4.6 Dissolved Oxygen and CBOD.

The concentration of dissolved oxygen and oxygen demand have classically been considered the primary measure of water quality associated with the discharge of domestic effluents.

To increase model flexibility, equations have been incorporated to simulate these two processes. Biological oxygen demand is generally broken down into nitrogenous oxygen demand and carbonaceous oxygen demand. Since nitrogenous components have already been considered in the nutrient equations, carbonaceous demand is considered separately.

6.4.6.1 Carbonaceous Oxygen Demand:

Change in Carbonaceous Oxygen Demand =
Amount of carbonaceous oxygen demand
- BOD lost to sediment
- BOD Satisfied

-OR-

$$dCBOD/dt = (K1 * CBOD) - (K3 * CBOD)$$

where:
K1 = Carbonaceous Deoxygenation Rate
K3 = BOD Loss rate due to settling

6.4.6.2 Dissolved Oxygen.

Change in dissolved oxygen concentration =
Atmospheric reaeration
+ Algal photosynthesis contribution
- Amount consumed by aerobic Bacteria
- Carbonaceous oxygen demand
- Amount consumed by sediment demand
- Amount consumed by Ammonia Oxidation
- Amount consumed by nitrite oxidation

-OR-

$$\begin{aligned} dO/dT = {} & (K2*(Ox - DOxygen)\ ) \\ & + (\ ((a3 * u) - (a4 * p)) * Algae) \\ & - (a4 * pm * Microb) \\ & - (K1 * CBOD) - (K4 / depth) \\ & - (a5 * b1 * Ammonia\_N) \\ & - (a6 * b2 * Nitrite\_N) \end{aligned}$$

where:

depth= Mean River Depth, feet
a3 = O_2 production/unit Algae, mg O_2/ mg A
a4 = O_2 uptake / unit Algae-Bacteria, mg O_2/mg A
a5 = O_2 uptake / unit NH_3 oxidation, mg O_2/Mg N
a6 = O_2 uptake / unit NO_2 oxidation, mg O_2/mg N
b1 = Oxidation Rate constant NH_3 to NO_2,day^{-1}
b2 = Bio-oxidation rate of NO_2 to NO_3,day^{-1}
p = Algal Respiration Rate, day^{-1}
pm = Bacterial Respiration Rate, day^{-1}
u = Specific Algal Growth Rate, day^{-1}
K1 = Carbonaceous Deoxygenation Rate, day^{-1}
K4 = Sediment Oxygen Demand Rate, mg O_2/ft^2-day

6.4.6.3 Reaearation.

The process of reaeration has been well documented in the literature with references dating from the 1950's. Most reaeration equations derived can be condensed to the following general equation:

$$K2 = \text{Constant} \times \text{velocity}^{a} \times \text{slope}^{b} / \text{depth}^{c}$$

Values for the constant and the coefficients a, b and c are documented in the literature to be as follows:

Table 6.1: Reaeration Equation Constants and Coefficients

	Constant	a	b	c
2 - O Connor & Dobbins (1958)	12.9	0.500	0	1.500
3 - Churchill et.al. (1962)	11.6	0.969	0	1.673
4 - Owens et.al (1964a)	21.7	0.67	0	1.85
5 - Owens et.al (1964b)	23.3	0.73	0	1.75
6 - Bennett & Rathbun (1972a)	106.0	0.413	0.273	1.408
7 - Bennett & Rathbun (1972b)	20.2	0.607	0	1.689

The predefined constant and coefficent combinations may be selected or the user may manually provide values under a User Defined Option.

6.5 Temperature Related Coefficients.

Coefficients for several processes, to include those for settling, decay and adsorption, are modeled as temperature dependent. Values for these coefficients are entered into the model at a reference temperature of 20 degrees Centigrade and are adjusted for temperature using the following formula:

$$\text{coefficient}_t = \text{coefficient}_{20} * \text{factor}^{(\text{temp}-20)}$$

Factors corrected for temperature include K1..K4, b1..b4, and o1..o5.

PART 7

MODEL TESTING

7.1 GENERAL

Nutrient processing in the Neuse River, was demonstrated to be variable when comparing water samples collected in April with those which were collected in September. While the April samples displayed decreases in both phosphorus and nitrogen species downstream of the wastewater treatment plant, observation of September data showed little to no nutrient processing. The Stream Nutrient Processing Simulation (SNUPS) model, as described in Chapter six, was constructed to test two hypothesis:

- The retention of phosphorus in the colloid pool as a (metal) cation-colloid-P complex.
- Microbial assimilation of phosphorus immediately downstream of the wastewater treatment plant.

7.2 MODEL VARIABLES AND SENSITIVITY TESTING

The SNUPS Model requires the input of boundary conditions and several reaction coefficients for proper execution. The boundary conditions include the initial physical, chemical and biological data for the starting reach of the model and for point source and tributary contributions along the length of the river to be simulated. These variables are outlined in Table 7.1 through Table 7.2. Values demonstrated were those which were measured at the sampling site or estimated from measured values.

Sensitivity testing was performed on each of the parameters to determine the range of values for which effects of the variable were observable and for which the variable produced believable results. This was performed by setting interacting parameters to zero and observing the effects of increasing the test variable. The value in the low end of the range is the point at which effects of the variable were discernable. The high end value is the point at which effects were maximum (the affected constituent went to zero) or the simulation went out of control (the affected constituent concentration rise was not believable). Values in the "range" column of Tables 7.3 were the results of sensitivity testing. Table 7.4 represents miscellaneous coefficients which were taken from the Handbook for the EPA Qual-IIe model (1987) or the EPA Handbook of "Rates, Constants and Kinetics Formulation for Surface Water Quality Modeling" (1985).

Table 7.1. Hydrologic Variables
Values Used for each Reach

Reach Length	Value	Time of Travel	Value
H[1].Miles	0.0	H[1].TOT	0.0000
H[2].Miles	3.8	H[2].TOT	0.2917
H[3].Miles	4.0	H[3].TOT	0.2292
H[4].Miles	3.0	H[4].TOT	0.2083
H[5].Miles	5.4	H[5].TOT	0.3333
H[6].Miles	5.0	H[6].TOT	0.2708

Note: [n] denotes reach index.

Table 7.2. Initial Boundary Conditions
Physical and Chemical Parameters

Variable	Treatment Plant	River Reach, 0
Flow	20-60	237.29
Algae	0	10
Microbe	5.0	0.01
PartOrg_P	0.01	0.02
Organic_P	0.01	0.06
Colloidal_P	0.01	0.02
FRP	6.22	0.23
Organic_N	3.63	1.05
Ammonia_N	0.19	0.07
Nitrite_N	0.01	0.01
Nitrate_N	10.9	0.47
DOxygen	2.0	7.30
CBOD	50.0	10.0
Susp_Sed	5.0	16.0
TMetal	15.0	10.0

Reaction rate coefficients must be provided as displayed in Table 7.3. Values for these variables were chosen within the ranges of those provided in the reference, "Rates, Constants, and Formulations in Surface Water Quality Modeling" (US EPA, 1985).

These variables were varied within the model and observed for their effect upon model performance.

Table 7.3. Reaction Rate Coefficients

Coef	Val	Description	Units	Range
a0	0.55	Ratio Chlorophyll-a to Biomass	mgCha/mgA	0.10-1.00
a1	0.08	Algal Biomass Nitrogen Factor	mg-N/mg/A	0.08-0.12
a2	0.01	Algal Biomass Phosphorus Fract	mg-P/mg-A	0.01-0.03
a3	1.80	O_2 Production / unit algae	mg-O/mg-A	1.40-1.80
a4	1.60	O_2 Uptake / unit Algae	mg-O/mg-A	1.60-2.30
a5	3.00	O_2 Uptake / unit NH_3 oxidation	mg-O/mg-N	3.00-4.00
a6	1.00	O_2 Uptake / unit NO_2 oxidation	mg-O/Mg-N	1.00-1.14
a7	0.03	Microbal biomass Nitrogen fact	mg-N/mg-M	0.03
a8	0.02	Microbial Biomass P Fraction	mg-P/mg-M	0.02
a9	0.00	Dissolved Metal source factor	mg/cu.ft	0-0.0001
b1	0.80	Oxidation Rate con NH^3 to NO_2	1/day	.003-0.10
b2	2.00	Bio-oxidation rate NO2 to NO3	1/day	0.10-2.00
b3	0.02	Hydrolysis rate organic-N to NH_3	1/day	0.02-0.40
b4	0.01	Decay Rate Organic P to Dissolve	1/day	0.01-0.70
b5	0.02	Transfer Organic to Colloidal P	1/day	.001-0.02
b6	0.01	Transfer rate Colloidal P to FRP	1/day	0.01-5.00
b7	0.001	Transfer Rate FRP to Colloidal	1/day	.001-5.00
b8	0.01	Metal:Colloid complexing rate	1/day	0.01-10.0
b9	0.01	FRP adsorb/desorb to Susp Solids	1/day	0.01-0.10
o1	0.50	Algal Settling Rate	ft/day	0.05-0.50
o2	0.01	Benthos source rate Dissolved P	mg/ft2-day	
o3	0.01	Benthos source rate Ammonia N	mg/ft2-day	
o4	0.00	Organic N Settling Rate	1/day	0.001-0.1
o5	0.001	Organic P Settling Rate	1/day	0.001-0.1
o6	10.0	Bacterial Settling Rate	1/day	0.50-10.0
o9	0.05	colloid-metal floc-settle rate	1/day	0.05-2.00

Table 7.4. Miscellaneous Variables

Var	Value	Description	Units	Range
fc	0	Bound colloid metal fract of colloid		
fm	0	Bound colloid metal fract of metal		
PM_Ratio	2	Colloid/metal stochiometric weight ratio		
p	0.1	Algal Respiratrion Rate	1/day	0.05-0.15
pm	0.045	Microbial Respiration Rate	1/day	0.03-0.06
u	1.271603	Specific Algal Growth Rate	1/day	
u_micro	"	Specific Microbial Growth Rate	1/day	
Fv1	-10.4694	Velocity 1st Order Coeff (data regression)		
Fv2	8.0236	Velocity 2nd Order Coeff (data regression)		
Cvs	14.4247	Velocity constant (data regression)		
KL	5.0	Michaelis-Menten Half-sat light	BTU/ft2-min	
Kn	0.4	Michaelis-Menten Half-sat N	mg-N/l	0.025-0.4
Kp	0.03	Michaelis-Menten Half-sat P	mg-P/l	.0005-.03
Ky	0	Suspended Solids Shading Factor		
K1	0.02	Carbonaceous Deoxygenation rate	1/day	0.01-0.6
K2	5	Atmospheric Reaeration Rate	1/day	
K3	0.18	BOD Loss Rate due to settling	1/day	0.02-0.92
K4	1	Sediment Oxygen Demand Rate		
I_Max	100.0	Maximum Solar Incident Radiation	BTU/ft2-hr	
IMin	50.0	Minimum Solar Incident Radiation	BTU/ft2-hr	
u_Max	15.0	Maximum Algal Growth Rate	1/day	1.30-2.50
O_Sat	9.0	Equilibrium O_2 Conc @ non-std Pressure		
Pa	1.0	Atmospheric Pressure	atm	
PNH4	0.5	Algal Ammonia Preference Factor		0-1
tMax	18.6	temperature maximum	degree C	
tMin	12.0	temperature minimum	degree C	
tK1	1.047	K1 temperature correction coefficient		
tK2	1.024	K2 temperature correction coefficient		
tK3	1.024	K3 temperature correction coefficient		
tK4	1.060	K4 temperature correction coefficient		
tb1	1.083	b1 temperature correction coefficient		
tb2	1.047	b2 temperature correction coefficient		
tb3	1.047	b3 temperature correction coefficient		
tb4	1.047	b4 temperature correction coefficient		
tb5	1.083	b5 temperature correction coefficient		
to1	1.024	o1 temperature correction coefficient		
to2	1.074	o2 temperature correction coefficient		
to3	1.074	o3 temperature correction coefficient		
to4	1.024	o4 temperature correction coefficient		
to5	1.024	o5 temperature correction coefficient		
to6	1.024	o6 temperature correction coefficient		
tu	1.047	u temperature correction coefficient		
tp	1.047	p temperature correction coefficient		

7.3 MODEL FIT.

The model was initially tested and calibrated to fit the data from April run 1. Parameters and coefficients in Tables 7.1 through 7.4 in the values column represent the resultant values of the calibration. In each case, parameters which affected the test hypothesis were factored out of the calibration by evaluation at a value at which they would produce little to no effect. These included factors affecting microbial assimilation and settling, cation-colloid-P formation and suspended solids adsorption.

Model fit is represented graphically in Figure 7.1 through Figure 7.6 against actual field data from the first April run. Good fit is demonstrated for Particulate Organic Phosphorus (POP) which was calculated as the difference between the analyzed Total Phosphorus (TP) and Total Filterable Phosphorus (TFP) (Figure 7.1). Organic phosphorus was calculated from the actual data as the difference between TFP and Filterable Reactive Phosphorus (FRP). The model results fit four out of the six actual data points (Figure 7.2). FRP was analyzed directly and demonstrates good fit with the model predictions (figure 7.3), however, the model values do not appear to level off at the 10 mile mark as they are demonstrated to do in the data (see Figure 5.5).

The simulated nitrogen species, ammonia and nitrate, were tested against the actual data. Ammonia demonstrated reasonable fit for four out of six actual data points (Figure 7.4). Concentrations immediately downstream of the wastewater treatment plant were slightly lower for the simulation than they were in the actual data set. This may be due to an overestimation of dilution by the treatment plant waters. Simulated nitrate provided good fit with the actual data (Figure 7.5).

Dissolved oxygen was simulated as a test parameter to determine if the model was functioning in a believable fashion in response to diurnal cycle and temperature fluctuations. Simulation results for dissolved oxygen fluctuated diurnally in consort with the actual data and the values for the first half of the simulation were within the correct range (Figure 7.6). The second half of the simulation produces higher than actual dissolved oxygen values. This is because the model assumes temperature to fluctuate the same over twenty-four hour periods. The second half of the simulation represented activity on a second day. On the second day of the actual data, the temperature was slightly higher causing the dissolved oxygen saturation to lower. These produced lower actual values over the simulated ones.

FIG. 7.1: MODEL FIT RUN 1, POP

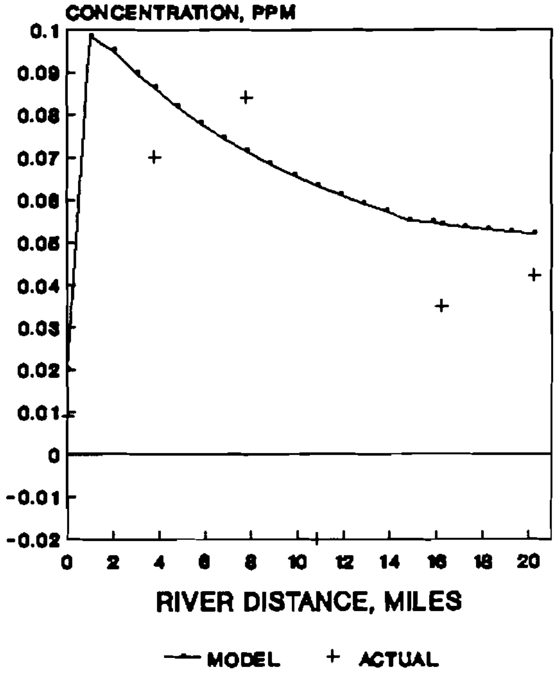


FIG. 7.2: MODEL FIT RUN 1, ORGANIC P

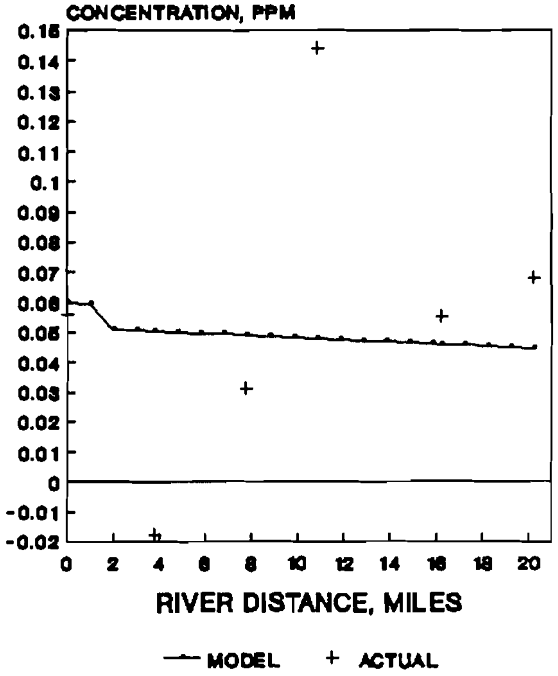


FIG. 7.3: MODEL FIT RUN 1, FRP

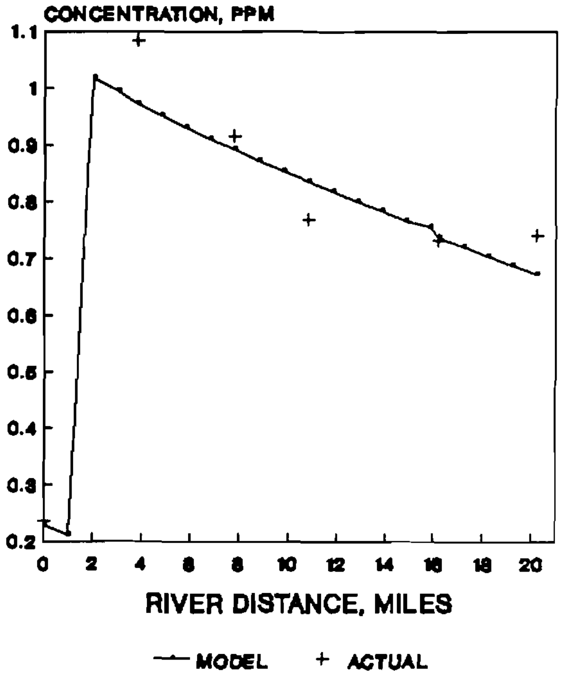
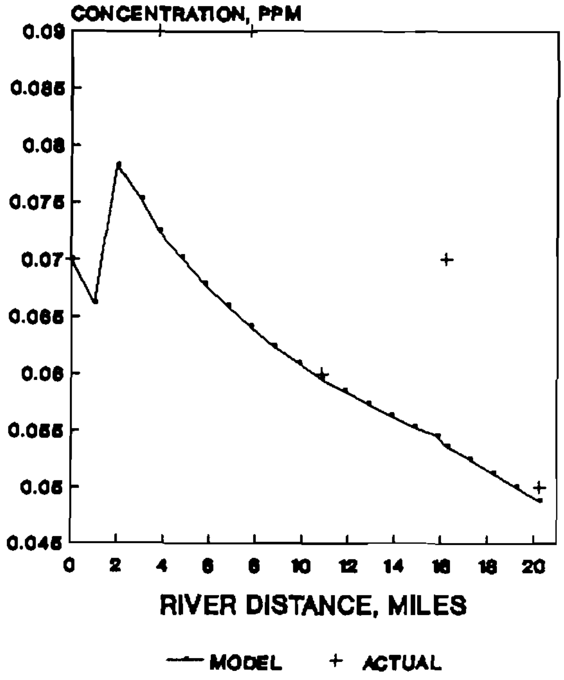


FIG. 7.4: MODEL FIT RUN 1, NH3



7.4 HYPOTHESIS TESTING

Using the calibrated parameters as a base, variables which would effect the two hypothesis were tested. The hypothesis addressed were :

1. The retention of phosphorus in the colloid pool as a (metal) cation-colloid-P complex. This complex is postulated to be measured as FRP during analysis using the molybedenum blue method; and
2. Microbial assimilation of dissolved phosphorus immediately downstream of the wastewater treatment plant.

The cation-colloid-P complex hypothesis was tested by running the model using the calibrated default values (Table 7.3) and coefficients adjusted to the maximum to determine the affect upon FRP processing for the September runs. Two coefficient adjustments were tested. The first adjustment took into account only the blocking of organic phosphorus transfer to dissolved phosphorus by the formation of cation-colloidal-P complexes. The second adjustment added the transfer of FRP as dissolved phosphorus into a colloidal phase. The coefficient adjustments are as follows:

FIG. 7.5: MODEL FIT RUN 1, NO3

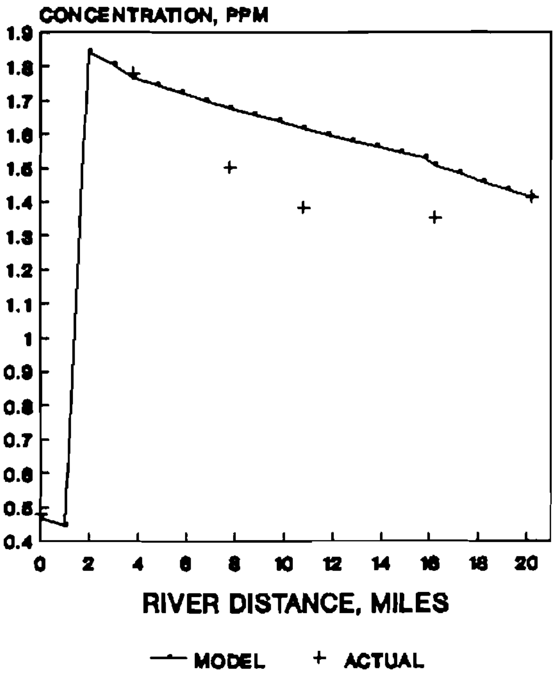
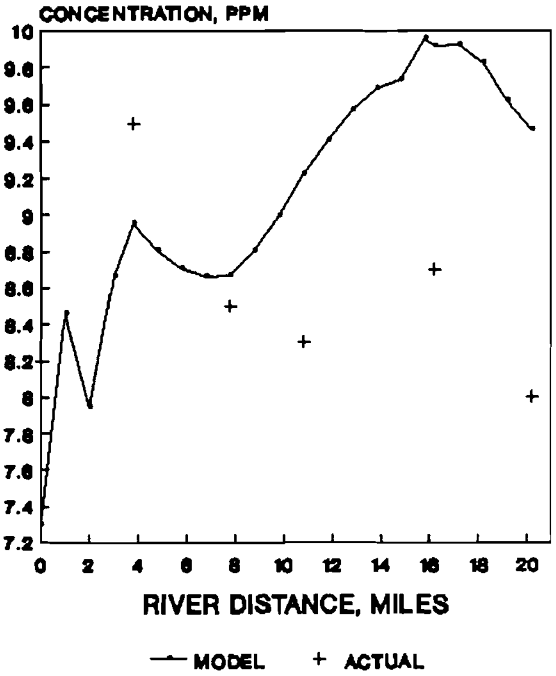


FIG. 7.6: MODEL FIT RUN 1, DO



Coefficient	Default	Colloid Block	Dissolve to Colloid
b4	0.01	0.01	0.01
b5	0.02	0.02	0.02
b6	0.01	0.01	0.01
b7	0.001	0.001	5.00
b8	0.01	10.00	10.00

In addition, the two adjustments included the addition of metal ion at the equivalent of site number 4 of the sample runs. The results of the organic P contribution alone to the colloid compartment are presented in Figure 7.7. It is indicated that there can be little affect on the dissolved "die-off" of dissolved phosphorus from this mechanism alone since there is so little organic phosphorus relative to the amount of dissolved phosphorus discharged by the wastewater treatment plant.

Figure 7.8 demonstrates the affect on phosphorus processing if dissolved phosphorus is moved into the colloid P compartment. This option demonstrates a substantial contribution to colloidal P which reaches a relative plateau in concentration at the ten mile point in the river. This is consistent with the location where there was no longer apparent reduction of FRP in the actual data runs. However, the simulation conditions in this option are fictitious in that it assumes the transfer of dissolved P into the colloid phase by an unidentified mechanism. This option, however is more complex than the testing of dilution only in that the complexing is dependent upon the availability of free cations which may not be in excess.

Results of both simulations are demonstrated in Figure 7.9 relative to using the default coefficient values with adjusted boundary conditions and temperature. Very little effect is seen from the blocking of colloid alone when compared to the default values from the calibration. This is primarily due to the small amount of organic phosphorous generated relative to the amount of dissolved FRP discharged by the treatment plant. These results of the transfer of dissolved phosphorus into the colloid compartment demonstrates a better fit to the actual data.

The cation-colloid-P complexing scenario assumes that the processing of phosphorus in April was the normal condition and that there was some mechanism that was responsible for blockage of FRP processing in September. The observation that April processing appeared to occur only for the first ten miles for run 1 suggests the existence of a mechanism which exists for a finite time in the river. Discharge of microbes from the wastewater treatment plant in irregular occurring intervals which are already "tuned" to phosphorus assimilation, represents a possible process. Figure 7.10 represents the results of simulation of microbial discharge relative to April data. Microbial concentrations of 100 ppm, 200 ppm and 500 ppm are presented against a

FIG.7.7: COLLOID INHIBIT TO FRP PROCESS HYPOTHESIS TESTING

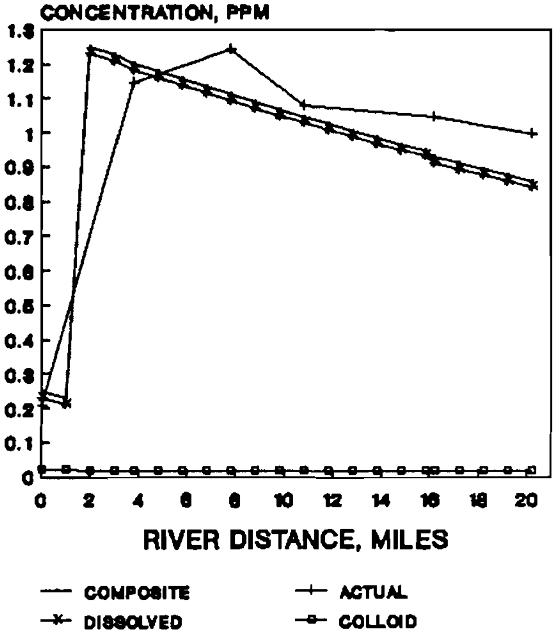
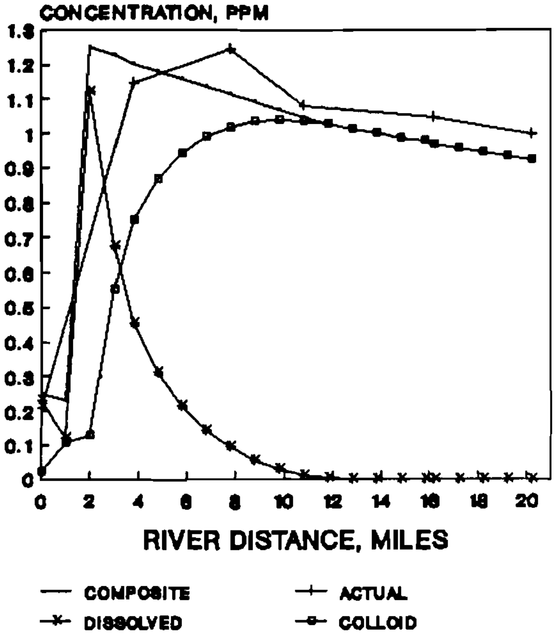


FIG.7.8: DISS P TRANSFER TO COLLOID HYPOTHESIS TESTING



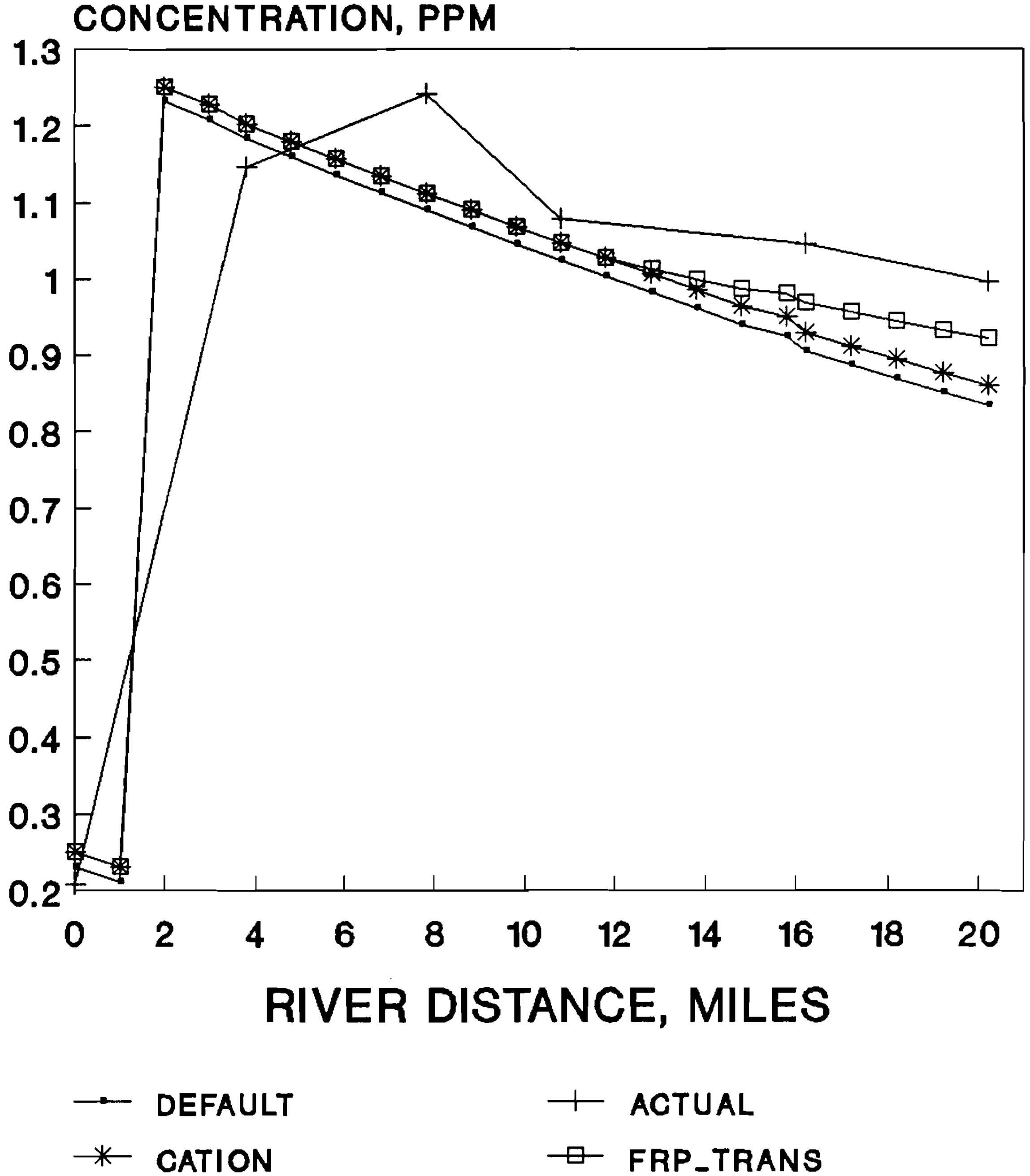
baseline in which all primary production is negated. The baseline case represents the affects of dilution of phosphorus alone. Algal productivity is discounted in all cases. The simulations demonstrate enhancement of phosphorus reduction, especially in the area immediately downstream of the treatment plant as the microbial concentration is increased. However, the corresponding microbial effect upon the processing of nitrates is almost non-existent in the absence of algae (Figure 7.11). The good model prediction of nitrate "die-off" in the original data fitting (Figure 7.5) indicates that both of these mechanisms may have been available at the same time. In reality, the concentration of microbes from the treatment plant necessary to produce these results is high and might only occur as a result of sloughing of biomass from treatment plant discharge weirs.

7.5 CONCLUSIONS

The hypothesis that there was a cation-colloidal P complex which inhibited processing of FRP was tested against the Neuse River data for September when little to no processing was evident using calibration data from the April months when reduction in FRP occurred downstream of the wastewater treatment plant. Colloid formed as an intermediate between organic phosphorus and dissolved inorganic phosphorus was not adequate to produce the lack of

FIG.7.9: COLLOID P HYPOTHESIS TEST

HYPOTHESIS TESTING



FRP processing observed. Transfer of dissolved phosphorus into the colloidal phase, however, does appear to produce the desired results. A mechanism to explain this interaction needs to be investigated.

Microbial degradation of phosphorus downstream of the wastewater treatment plant outfall remains a viable option, but only during periods of low maintenance of treatment plant discharge overflow weirs. The high concentration of microbial mass that is necessary to provide the desired effects does not justify this option as a regularly occurring mechanism. Microbial coefficients used in this simulation which affected the rate of phosphorus processing were those found in the literature for river ambient microbes. Further investigation may be warranted in observing the effects of increasing the phosphorus processing related coefficients to those which may be exhibited by microbes which have acclimation to a high phosphorus concentration.

FIG. 7.10: WWTP MICROBIAL FRP PROCESS HYPOTHESIS TESTING

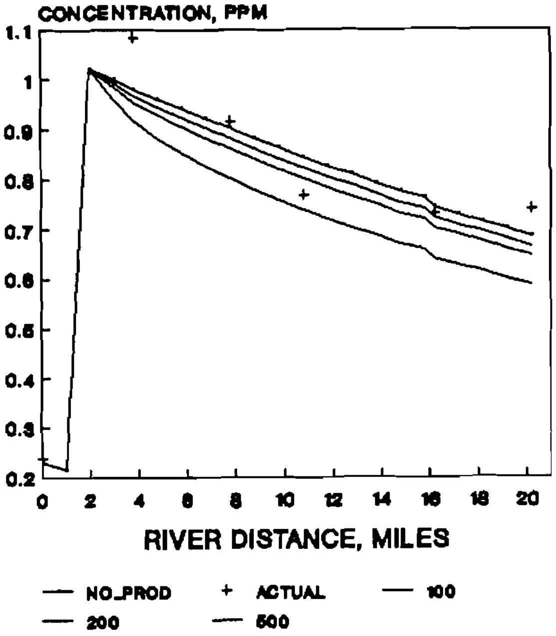
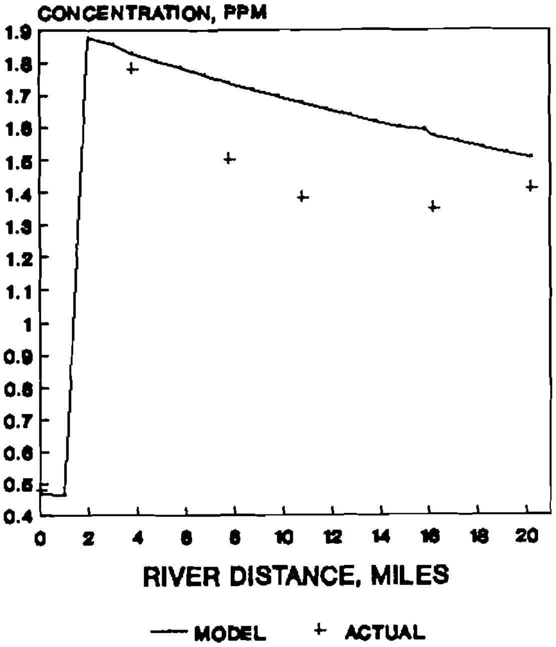


FIG. 7.11: WWTP MICROBIAL NO3 PROCESS HYPOTHESIS TESTING



PART 8

DISCUSSION AND CONCLUSIONS

Analysis of the data from the study of the Neuse River downstream of the Raleigh, North Carolina wastewater treatment plant produced inconsistent results. A decrease in both total phosphorus and FRP was observed in samples that were collected in April of 1986 but no decrease was evident in samples collected during September of the same year. This was not expected as the conditions found in September were more favorable for phosphorus processing than those observed in April. During September, the water temperature was warmer and there was a visible growth of periphyton that was not apparent in April.

One can only conclude that conditions in September existed that were not present in April that discouraged the phosphorus processing in the river. Comparison of data on both dates for phosphorus species and the support parameters which were analyzed revealed a possible anomoly at site 4 located approximately ten miles downstream of the treatment plant. This lead to the hypothesis that the water chemisty had changed significantly enough in September to discourage phosphorus reduction in the river. The formation of a cation-colloidal-P complex which blocked the complete transformation of organic phosphorus to dissolved phosphorus was proposed as a possible mechanism. The increase of metal ion concentration, especially that of iron, at the ten mile site gave support to this theory.

A second hypothesis was offered in which bacteria from the wastewater treatment plant might be discharged to the river, and be responsible for processing immediately downstream of the treatment plant. These organisms, which are "geared" to phosphorus uptake, might continue to remove phosphorus while exposed to the river environment. This would proceed until they became dilute or they are removed from the water column through settling. In April, processing was observed for a short distance downstream of the treatment plant outfall. The discharge of treatment plant bacteria was proposed as a condition that existed in April which promoted processing of phosphorus for samples collected during that month.

These two hypothesis were subjected to testing using the "Stream Nutrient Processing Simulation" (SNUPS) Model. Neither hypothesis proved to be satisfactory mechanisms for the observations that were made. Insufficient organic phosphorus was present relative to the quantity of phosphorus discharged by the wastewater treatment plant to allow the cation-colloid-P complex to maintain phosphorus river loading at the observed September level. It was noted during simulation, however, that should the treatment plant phosphorus consist of a bound phosphorus rather than a reactive form of phosphorus, reduction of phosphorus in the river would not be apparent. This leads to a conclusion that in studying the affect of rivers in the processing of nutrients, it may be as important to perform all analysis upon the wastewater treatment plant effluent as it is for the river water. The character of the wastewater effluent in September may have been such that reactive forms of phosphorus were not present.

The hypothesis that microbes discharged from the wastewater treatment plant might continue to process nutrients in the river appeared to be possible only with the release of large quantities of microbial mass. The model demonstrated that up to 500 mg/L of bacterial mass was necessary to mediate the observed decrease of phosphorus in April. This mechanism may be of interest, however, when coupled with algal processing. Also, more accurate asessment of the micrbial respiration and growth coefficients in the model might provide more favorable results.

Suggestions for further research include the following:

- Further work need be performed to define the interaction between colloidal-P and cations in freshwater.
- Studies should be conducted to determine the influence of the composition of the treatment plant waste stream upon reduction of phosphorus in the river.
- Field sampling should be performed to provide data on the effects of treatment plant microbial mass discharged to the river upon nutrient processing.

PART 9

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CONTENTS OF APPENDIX

APPENDIX A

APPENDIX B

APPENDIX A

RAW DATA - CONCENTRATIONS

RUN /STA NUMBER		RIVER Miles	TIME	TSS mg/l	TDS mg/l	TEMP DegC	D.O. mg/l	pH
RUN 1	1	-1.8	8.75	17.6	91.0	12.2	8.2	7.00
	2	2.0	13.75	11.3	115.0	16.7	9.5	6.66
	3	6.0	19.25	26.1	185.0	16.5	8.5	6.91
	4	9.0	23.25	14.3	105.5	14.5	8.3	6.82
	5	14.4	30.25	11.7	101.0	12.0	8.7	7.10
	6	19.4	35.25	16.7	104.5	15.5	8.0	6.88
RUN 2	1	-1.8	10.75			14.0	8.7	7.01
	2	2.0	15.75			17.3	9.5	6.81
	3	6.0	21.25			15.0	8.7	6.83
	4	9.0						
	5	14.4	32.25			13.5	8.3	7.01
	6	19.4	37.15			18.6	7.9	6.52
RUN 3	1	-1.8	13:00	14.3		23	7.1	7.45
	2	2.0	20:00	11.6		23.5	7.45	6.51
	3	6.0	01:30	14.1		22.2	7.1	6.46
	4	9.0	06:30	20.8		21	7.1	6.43
	5	14.4	14:30	12.0		22.8	6.9	7.23
	6	19.4	21:00	13.5		21	6.9	6.66
RUN 4	1	-1.8	15:00			23.9	7.2	6.62
	2	2.0	22:00			23.2	7.5	6.77
	3	6.0	03:30			NA	NA	NA
	4	9.0	08:30			21.4	6.8	6.7
	5	14.4	16:30			22.3	7.45	7.27
	6	19.4	23:00			21.2	6.85	6.58
RUN 5	1	-1.8	05:00	17.1		19	6.5	NA
	2	2.0	12:00	11.8		20.5	6.85	6.58
	3	6.0	17:30	13.1		21.2	7.8	6.9
	4	9.0	22:30	9.2		20.4	7.5	6.6
	5	14.4	07:00	NA		19.8	7.1	6.8
	6	19.4	13:00	12.6				
RUN 6	1	-1.8	07:00			19.5	6.45	7.3
	2	2.0	14:00			21.2	6.85	7.4
	3	6.0	19:30			21.1	7.8	6.85
	4	9.0	00:30			NA	NA	NA
	5	14.4	09:00			20.3	6.8	7.49
	6	19.4	15:00					

RUN /STA NUMBER		RIVER Miles	TIME	SECCHI in.	COND umhos	ALK mg/l CaCO3	TURB NTU	FRP ug/l
RUN 1	1	-1.8	8.75	26.0	183		5.0	237
	2	2.0	13.75	29.0	230		3.7	1085
	3	6.0	19.25		371		4.8	917
	4	9.0	23.25		211		4.9	768
	5	14.4	30.25	21.0	202		5.5	733
	6	19.4	35.25	25.0	209		5.7	740
RUN 2	1	-1.8	10.75	27.5				245
	2	2.0	15.75	29.5				1223
	3	6.0	21.25					1078
	4	9.0						NA
	5	14.4	32.25	28.0				845
	6	19.4	37.15	27.0				742
RUN 3	1	-1.8	13:00	30	147.0	NA	7.6	208.33
	2	2.0	20:00	0	205.0	29.5	7.8	1146.67
	3	6.0	01:30	0	235.0	NA	5.9	1241.67
	4	9.0	06:30	0	216.0	NA	8.2	1078.33
	5	14.4	14:30	37.5	219.0	30.0	9.8	1045.00
	6	19.4	21:00	0	225.0	33.5	12.0	995.00
RUN 4	1	-1.8	15:00	NA				151.67
	2	2.0	22:00	0				1088.33
	3	6.0	03:30	NA				NA
	4	9.0	08:30	25.5				1110.00
	5	14.4	16:30	29				1080.00
	6	19.4	23:00	0				1051.67
RUN 5	1	-1.8	05:00	NA	195.0	NA	11.0	271.67
	2	2.0	12:00	32	240.0	NA	6.6	703.33
	3	6.0	17:30	29	219.0	28.5	7.4	805.00
	4	9.0	22:30	0	221.0	34.0	9.4	721.67
	5	14.4	07:00	0	NA	NA		698.33
	6	19.4	13:00		224.0	32.5	7.0	785.00
RUN 6	1	-1.8	07:00	0				271.67
	2	2.0	14:00	34				920.00
	3	6.0	19:30	0				828.33
	4	9.0	00:30	NA				NA
	5	14.4	09:00	32				795.00
	6	19.4	15:00					748.33

RUN /STA NUMBER		RIVER Miles	TIME	TFP ug/l	Total-P ug/l	NO2 mg/l	NO3 mg/l
RUN 1	1	-1.8	8.75	293	302		0.48
	2	2.0	13.75	1067	1137		1.78
	3	6.0	19.25	948	1032		1.50
	4	9.0	23.25	912	892		1.38
	5	14.4	30.25	788	823		1.35
	6	19.4	35.25	808	850		1.41
RUN 2	1	-1.8	10.75	282	255		0.46
	2	2.0	15.75	1247	1262		1.97
	3	6.0	21.25	1130	1152		1.50
	4	9.0		NA	NA		NA
	5	14.4	32.25	878	912		1.46
	6	19.4	37.15	797	863		1.45
RUN 3	1	-1.8	13:00	238.33	251.67	<0.01	0.76
	2	2.0	20:00	1158.33	1195.00	<0.01	>2.00
	3	6.0	01:30	1226.67	1286.67	<0.01	3.53
	4	9.0	06:30	1148.33	1231.67	<0.01	3.43
	5	14.4	14:30	1071.67	1170.00	<0.01	>2.00
	6	19.4	21:00	1025.00	1110.00	<0.01	>2.00
RUN 4	1	-1.8	15:00	205.00	251.67	<0.01	0.77
	2	2.0	22:00	1120.00	1186.67	<0.01	1.93
	3	6.0	03:30	NA	NA	<0.01	NA
	4	9.0	08:30	1146.67	1263.33	<0.01	2.97
	5	14.4	16:30	1088.33	1153.33	<0.01	3.04
	6	19.4	23:00	1060.00	1136.67	<0.01	3.01
RUN 5	1	-1.8	05:00	276.67	315.00	<0.01	0.84
	2	2.0	12:00	698.33	736.67	<0.01	1.87
	3	6.0	17:30	771.67	793.33	<0.01	2.11
	4	9.0	22:30	751.67	781.67	<0.01	2.21
	5	14.4	07:00	768.33	790.00	<0.01	1.75
	6	19.4	13:00	823.33	NA	<0.01	2.74
RUN 6	1	-1.8	07:00	276.67	315.00	<0.01	0.84
	2	2.0	14:00	1032.50	936.67	<0.01	3.09
	3	6.0	19:30	938.33	890.00	<0.01	2.00
	4	9.0	00:30	NA	NA	<0.01	NA
	5	14.4	09:00	900.00	880.00	<0.01	1.80
	6	19.4	15:00	898.33	880.00	<0.01	1.83

RUN /STA NUMBER		RIVER Miles	TIME	NH4+ mg/l	Cl- mg/l	SO4 mg/l	Ca+ mg/l	Mg+ mg/l
RUN 1	1	-1.8	8.75	0.07	13.00	13.40	2.70	2.65
	2	2.0	13.75	0.09	20.13	12.77	2.70	2.75
	3	6.0	19.25	0.09	17.50	14.47	2.57	2.61
	4	9.0	23.25	0.06	14.00	12.43	2.67	2.62
	5	14.4	30.25	0.07	17.50	13.17	2.63	2.63
	6	19.4	35.25	0.05	18.80	13.17	2.60	2.60
RUN 2	1	-1.8	10.75	0.07	7.00	10.70	2.70	2.68
	2	2.0	15.75	0.08	21.20	14.47	2.87	2.77
	3	6.0	21.25	0.09	18.30	12.63	3.03	2.76
	4	9.0		NA	NA	NA	NA	NA
	5	14.4	32.25	0.07	16.53	13.53	3.00	2.70
	6	19.4	37.15	0.04	17.73	13.40	2.53	2.50
RUN 3	1	-1.8	13:00	<0.01	12.81	4.30	8.20	2.86
	2	2.0	20:00	<0.01	16.06	6.43	9.40	2.87
	3	6.0	01:30	0.02	16.07	6.81	9.63	2.94
	4	9.0	06:30	<0.01	16.07	6.84	9.47	2.92
	5	14.4	14:30	<0.01	NA	NA	9.27	2.91
	6	19.4	21:00	0.01	16.07	6.80	9.40	2.92
RUN 4	1	-1.8	15:00	0.02	12.64	3.34	8.23	2.88
	2	2.0	22:00	<0.01	13.37	5.50	9.47	2.95
	3	6.0	03:30	NA	NA	NA	NA	NA
	4	9.0	08:30	0.01	18.86	6.42	9.43	2.84
	5	14.4	16:30	<0.01	20.35	6.27	9.27	2.86
	6	19.4	23:00	<0.01	19.95	6.69	9.30	2.87
RUN 5	1	-1.8	05:00	<0.01	9.40	9.66	9.10	3.02
	2	2.0	12:00	<0.01	15.31	10.15	9.57	2.92
	3	6.0	17:30	0.01	18.84	10.04	9.57	2.89
	4	9.0	22:30	0.01	16.77	9.94	9.60	2.92
	5	14.4	07:00	<0.01	18.84	10.33	9.67	2.95
	6	19.4	13:00	<0.01	23.69	10.70	9.63	2.95
RUN 6	1	-1.8	07:00	<0.01	9.40	9.66	9.10	3.02
	2	2.0	14:00	<0.01	24.83	11.85	9.97	3.04
	3	6.0	19:30	<0.01	NA	NA	9.70	3.00
	4	9.0	00:30	NA	NA	NA	NA	NA
	5	14.4	09:00	0.01	NA	NA	9.73	3.03
	6	19.4	15:00	0.01	NA	NA	9.63	2.95

RUN /STA NUMBER		RIVER Miles	TIME	Na+ mg/l	K+ mg/l	Fe mg/l	Cu mg/l	Mn mg/l
RUN 1	1	-1.8	8.75	24.33	2.97	0.56		0.17
	2	2.0	13.75	35.33	4.40	0.60		0.18
	3	6.0	19.25	33.67	3.87	0.63		0.15
	4	9.0	23.25	31.20	4.10	0.76		0.18
	5	14.4	30.25	31.07	3.87	0.71		0.16
	6	19.4	35.25	28.33	4.00	0.74		0.12
RUN 2	1	-1.8	10.75	26.67	2.97	0.57		0.19
	2	2.0	15.75	28.90	4.83	0.48		0.12
	3	6.0	21.25	37.33	4.63	0.53		0.16
	4	9.0		NA	NA	NA		NA
	5	14.4	32.25	32.40	4.20	0.66		0.14
	6	19.4	37.15	30.33	4.83	0.79		0.14
RUN 3	1	-1.8	13:00	14.00	3.07	0.51	0.15	0.24
	2	2.0	20:00	27.33	5.08	0.50	0.10	0.18
	3	6.0	01:30	29.67	5.30	0.49	0.08	0.15
	4	9.0	06:30	28.50	5.23	0.62	0.07	0.15
	5	14.4	14:30	29.00	5.13	0.48	0.04	0.10
	6	19.4	21:00	30.00	5.20	0.45	0.04	0.10
RUN 4	1	-1.8	15:00	13.00	3.08	0.56	0.09	0.24
	2	2.0	22:00	27.67	5.13	0.50	0.05	0.17
	3	6.0	03:30	NA	NA	NA	NA	NA
	4	9.0	08:30	27.67	4.85	0.59	0.03	0.15
	5	14.4	16:30	29.33	4.78	0.46	0.02	0.10
	6	19.4	23:00	30.00	4.87	0.49	0.02	0.10
RUN 5	1	-1.8	05:00	26.50	3.33	0.61	0.04	0.29
	2	2.0	12:00	32.33	4.33	0.47	0.03	0.19
	3	6.0	17:30	32.83	4.42	0.48	0.03	0.16
	4	9.0	22:30	32.67	4.50	0.53	0.02	0.14
	5	14.4	07:00	32.50	4.43	0.53	0.03	0.13
	6	19.4	13:00	33.00	4.58	0.50	0.04	0.11
RUN 6	1	-1.8	07:00	26.50	3.33	0.61	0.04	NA
	2	2.0	14:00	36.33	4.80	0.45	0.02	0.19
	3	6.0	19:30	34.83	4.48	0.47	0.02	0.16
	4	9.0	00:30	NA	NA	NA	NA	NA
	5	14.4	09:00	34.67	4.48	0.52	0.03	0.13
	6	19.4	15:00	33.00	4.50	0.47	0.04	0.10

RUN /STA NUMBER		RIVER Miles	TIME	Chla ug/l	Pheo ug/l	TKN mg/l
RUN 1	1	-1.8	8.75			NA
	2	2.0	13.75			NA
	3	6.0	19.25			NA
	4	9.0	23.25			NA
	5	14.4	30.25			NA
	6	19.4	35.25			NA
RUN 2	1	-1.8	10.75			NA
	2	2.0	15.75			NA
	3	6.0	21.25			NA
	4	9.0				NA
	5	14.4	32.25			NA
	6	19.4	37.15			NA
RUN 3	1	-1.8	13:00	0.29	0.25	0.63
	2	2.0	20:00			1.29
	3	6.0	01:30			1.48
	4	9.0	06:30	0.17	0.36	1.69
	5	14.4	14:30	0.17	0.17	1.13
	6	19.4	21:00			1.85
RUN 4	1	-1.8	15:00			1.04
	2	2.0	22:00			1.33
	3	6.0	03:30			NA
	4	9.0	08:30			1.50
	5	14.4	16:30			1.36
	6	19.4	23:00			1.34
RUN 5	1	-1.8	05:00	0.32	0.29	NA
	2	2.0	12:00	0.26	0.28	1.24
	3	6.0	17:30		1.18	1.34
	4	9.0	22:30			1.40
	5	14.4	07:00			1.37
	6	19.4	13:00		0.59	1.68
RUN 6	1	-1.8	07:00			1.57
	2	2.0	14:00			1.09
	3	6.0	19:30			1.48
	4	9.0	00:30			NA
	5	14.4	09:00			1.34
	6	19.4	15:00			1.48

APPENDIX B

RAW DATA - CONSTITUENT LOADINGS

RUN /STA NUMBER		RIVER Miles	TIME	FLOW cuft/s	TSS lb/day	SRP lb/day
RUN 1	1	-1.8	8.75	229.75	21785	293.36
	2	2.0	13.75	265.63	16172	1552.78
	3	6.0	19.25	273.93	38519	1353.34
	4	9.0	23.25	280.15	21584	1159.19
	5	14.4	30.25	291.35	18366	1150.59
	6	19.4	35.25	301.72	27147	1202.93
RUN 2	1	-1.8	10.75	229.75	21785	303.26
	2	2.0	15.75	279.56	17020	1842.07
	3	6.0	21.25	287.86	40478	1671.86
	4	9.0		294.08	22657	NA
	5	14.4	32.25	305.28	19244	1389.82
	6	19.4	37.15	315.66	28401	1261.87
RUN 3	1	-1.8	13:00	237.29	43807	266.33
	2	2.0	20:00	294.92	44167	1821.97
	3	6.0	01:30	309.57	56353	2070.93
	4	9.0	06:30	320.56	86081	1862.35
	5	14.4	14:30	340.34	52726	1916.14
	6	19.4	21:00	358.65	62509	1922.63
RUN 4	1	-1.8	15:00	237.29	43807	193.89
	2	2.0	22:00	296.47	44399	1738.36
	3	6.0	03:30	311.12	56634	NA
	4	9.0	08:30	322.11	86496	1926.30
	5	14.4	16:30	341.89	52966	1989.32
	6	19.4	23:00	360.20	62779	2040.90
RUN 5	1	-1.8	05:00	237.29	52384	347.30
	2	2.0	12:00	266.28	40566	1009.03
	3	6.0	17:30	280.93	47513	1218.42
	4	9.0	22:30	291.92	34673	1135.02
	5	14.4	07:00	311.70	NA	1172.73
	6	19.4	13:00	330.02	53683	1395.73
RUN 6	1	-1.8	07:00	237.29	52384	347.30
	2	2.0	14:00	270.15	41155	1339.05
	3	6.0	19:30	284.80	48167	1271.01
	4	9.0	00:30	295.79	35132	NA
	5	14.4	09:00	315.57	NA	1351.65
	6	19.4	15:00	333.89	54313	1346.14

APPENDIX B

RAW DATA - CONSTITUENT LOADINGS

RUN /STA NUMBER		RIVER Miles	TIME	TFP lb/day	Total-P lb/day	TFP-FRP
RUN 1	1	-1.8	8.75	362.68	373.82	69.32
	2	2.0	13.75	1527.02	1627.20	-25.76
	3	6.0	19.25	1399.09	1523.06	45.75
	4	9.0	23.25	1376.53	1346.35	217.35
	5	14.4	30.25	1236.92	1291.86	86.33
	6	19.4	35.25	1313.47	1381.74	110.54
RUN 2	1	-1.8	10.75	349.06	315.64	45.80
	2	2.0	15.75	1878.22	1900.81	36.15
	3	6.0	21.25	1752.51	1786.63	80.65
	4	9.0		NA	NA	NA
	5	14.4	32.25	1444.10	1500.02	54.28
	6	19.4	37.15	1355.41	1467.65	93.53
RUN 3	1	-1.8	13:00	304.69	321.73	38.35
	2	2.0	20:00	1840.50	1898.76	18.54
	3	6.0	01:30	2045.91	2145.98	-25.02
	4	9.0	06:30	1983.24	2127.16	120.89
	5	14.4	14:30	1965.03	2145.34	48.90
	6	19.4	21:00	1980.60	2144.85	57.97
RUN 4	1	-1.8	15:00	262.07	321.73	68.18
	2	2.0	22:00	1788.94	1895.42	50.58
	3	6.0	03:30	NA	NA	NA
	4	9.0	08:30	1989.93	2192.39	63.63
	5	14.4	16:30	2004.67	2124.40	15.35
	6	19.4	23:00	2057.07	2205.85	16.17
RUN 5	1	-1.8	05:00	353.69	402.70	6.39
	2	2.0	12:00	1001.85	1056.85	-7.17
	3	6.0	17:30	1167.97	1200.77	-50.45
	4	9.0	22:30	1182.20	1229.38	47.18
	5	14.4	07:00	1290.29	1326.67	117.55
	6	19.4	13:00	1463.89	NA	68.16
RUN 6	1	-1.8	07:00	353.69	402.70	6.39
	2	2.0	14:00	1502.79	1363.30	163.74
	3	6.0	19:30	1439.80	1365.63	168.79
	4	9.0	00:30	NA	NA	NA
	5	14.4	09:00	1530.17	1496.16	178.52
	6	19.4	15:00	1615.97	1582.99	269.83

APPENDIX B

RAW DATA - CONSTITUENT LOADINGS

RUN /STA NUMBER		RIVER Miles	TIME	TP-TFP	TP-FRP	NO2 lb/day
RUN 1	1	-1.8	8.75	11.14	80.46	0.00
	2	2.0	13.75	100.18	74.42	
	3	6.0	19.25	123.97	169.72	
	4	9.0	23.25	-30.19	187.16	
	5	14.4	30.25	54.94	141.27	
	6	19.4	35.25	68.27	178.81	
RUN 2	1	-1.8	10.75	-33.42	12.38	
	2	2.0	15.75	22.59	58.74	
	3	6.0	21.25	34.12	114.77	
	4	9.0		NA	NA	
	5	14.4	32.25	55.92	110.20	
	6	19.4	37.15	112.24	205.78	
RUN 3	1	-1.8	13:00	17.05	55.40	
	2	2.0	20:00	58.26	76.80	
	3	6.0	01:30	100.07	75.05	
	4	9.0	06:30	143.92	264.82	
	5	14.4	14:30	180.31	229.20	
	6	19.4	21:00	164.24	222.21	
RUN 4	1	-1.8	15:00	59.66	127.84	
	2	2.0	22:00	106.48	157.06	
	3	6.0	03:30	NA	NA	
	4	9.0	08:30	202.46	266.09	
	5	14.4	16:30	119.73	135.08	
	6	19.4	23:00	148.78	164.95	
RUN 5	1	-1.8	05:00	49.01	55.40	
	2	2.0	12:00	54.99	47.82	
	3	6.0	17:30	32.79	-17.66	
	4	9.0	22:30	47.18	94.37	
	5	14.4	07:00	36.39	153.94	
	6	19.4	13:00	NA	NA	
RUN 6	1	-1.8	07:00	49.01	55.40	
	2	2.0	14:00	-139.48	24.26	
	3	6.0	19:30	-74.16	94.62	
	4	9.0	00:30	NA	NA	
	5	14.4	09:00	-34.00	144.52	
	6	19.4	15:00	-32.98	236.85	

APPENDIX B

RAW DATA - CONSTITUENT LOADINGS

RUN /STA NUMBER		RIVER Miles	TIME	NO3 lb/day	NH4+ lb/day	Cl- lb/day
RUN 1	1	-1.8	8.75	594.15	86.65	16091.53
	2	2.0	13.75	2547.41	128.80	28808.65
	3	6.0	19.25	2213.75	132.82	25827.03
	4	9.0	23.25	2082.91	90.56	21130.98
	5	14.4	30.25	2119.10	109.88	27469.77
	6	19.4	35.25	2292.06	81.28	30560.83
RUN 2	1	-1.8	10.75	569.39	86.65	8664.67
	2	2.0	15.75	2967.20	120.50	31931.24
	3	6.0	21.25	2326.34	139.58	28381.30
	4	9.0		NA	NA	NA
	5	14.4	32.25	2401.35	115.13	27187.90
	6	19.4	37.15	2465.92	68.03	30152.28
RUN 3	1	-1.8	13:00	967.33	12.78	16376.39
	2	2.0	20:00		15.89	25518.12
	3	6.0	01:30	5879.21	33.36	26802.50
	4	9.0	06:30	5923.82	17.27	27753.87
	5	14.4	14:30		18.34	NA
	6	19.4	21:00		25.76	31051.95
RUN 4	1	-1.8	15:00	984.37	25.57	16159.06
	2	2.0	22:00	3074.73	15.97	21355.42
	3	6.0	03:30	NA	NA	NA
	4	9.0	08:30	5154.14	17.35	32735.45
	5	14.4	16:30	5593.43	18.42	37483.97
	6	19.4	23:00	5834.84	19.41	38709.16
RUN 5	1	-1.8	05:00	1073.86	12.78	12017.02
	2	2.0	12:00	2682.77	14.35	21964.25
	3	6.0	17:30	3193.63	20.18	28510.61
	4	9.0	22:30	3481.07	15.73	26380.62
	5	14.4	07:00	2938.83	16.79	31630.26
	6	19.4	13:00	4865.80	17.78	42120.90
RUN 6	1	-1.8	07:00	1073.86	12.78	12017.02
	2	2.0	14:00	4492.59	14.55	36144.53
	3	6.0	19:30	3068.84	15.34	NA
	4	9.0	00:30	NA	NA	NA
	5	14.4	09:00	3060.33	11.33	NA
	6	19.4	15:00	3297.90	17.99	NA

APPENDIX B

RAW DATA - CONSTITUENT LOADINGS

RUN /STA NUMBER		RIVER Miles	TIME	SO4 lb/day	Ca+ lb/day	Mg+ lb/day
RUN 1	1	-1.8	8.75	16586.66	3342.09	3280.20
	2	2.0	13.75	18275.53	3864.05	3935.61
	3	6.0	19.25	21355.27	3792.88	3851.92
	4	9.0	23.25	18761.29	4029.98	3954.51
	5	14.4	30.25	20672.96	4128.31	4128.31
	6	19.4	35.25	21408.84	4226.50	4226.50
RUN 2	1	-1.8	10.75	13244.57	3342.09	3317.33
	2	2.0	15.75	21794.57	4322.77	4172.15
	3	6.0	21.25	19587.75	4699.20	4280.46
	4	9.0		NA	NA	NA
	5	14.4	32.25	22253.62	4934.28	4440.85
	6	19.4	37.15	22788.52	4302.61	4251.59
RUN 3	1	-1.8	13:00	5492.89	10482.93	3660.50
	2	2.0	20:00	10216.78	14935.89	4560.21
	3	6.0	01:30	11352.56	16067.05	4897.95
	4	9.0	06:30	11818.86	16349.51	5048.78
	5	14.4	14:30	NA	16991.58	5329.73
	6	19.4	21:00	13139.59	18163.56	5648.74
RUN 4	1	-1.8	15:00	4269.88	10525.55	3677.55
	2	2.0	22:00	8784.95	15120.77	4706.61
	3	6.0	03:30	NA	NA	NA
	4	9.0	08:30	11141.28	16370.62	4922.75
	5	14.4	16:30	11555.25	17068.87	5274.16
	6	19.4	23:00	12989.31	18047.89	5563.15
RUN 5	1	-1.8	05:00	12353.67	11633.50	3860.79
	2	2.0	12:00	14556.76	13724.67	4193.91
	3	6.0	17:30	15191.19	14479.82	4379.26
	4	9.0	22:30	15633.35	15098.60	4587.25
	5	14.4	07:00	17339.12	16233.56	4959.63
	6	19.4	13:00	19030.56	17128.10	5245.11
RUN 6	1	-1.8	07:00	12353.67	11633.50	3860.79
	2	2.0	14:00	17252.34	14506.33	4424.67
	3	6.0	19:30	NA	14883.87	4608.37
	4	9.0	00:30	NA	NA	NA
	5	14.4	09:00	NA	16548.46	5145.89
	6	19.4	15:00	NA	17328.95	5312.61

APPENDIX B

RAW DATA - CONSTITUENT LOADINGS

RUN /STA NUMBER		RIVER Miles	TIME	Na+ lb/day	K+ lb/day	Fe lb/day
RUN 1	1	-1.8	8.75	30115.92	3676.30	693.17
	2	2.0	13.75	50561.84	6296.97	858.68
	3	6.0	19.25	49691.21	5711.46	929.77
	4	9.0	23.25	47091.90	6188.36	1147.11
	5	14.4	30.25	48770.61	6074.74	1114.49
	6	19.4	35.25	46052.57	6502.30	1202.93
RUN 2	1	-1.8	10.75	33012.40	3676.30	705.55
	2	2.0	15.75	43528.90	7274.90	722.97
	3	6.0	21.25	57894.74	7180.62	821.97
	4	9.0		NA	NA	NA
	5	14.4	32.25	53290.25	6908.00	1085.54
	6	19.4	37.15	51580.29	8214.07	1343.50
RUN 3	1	-1.8	13:00	17897.69	3920.45	647.73
	2	2.0	20:00	43430.60	8077.03	794.46
	3	6.0	01:30	49479.84	8839.66	822.81
	4	9.0	06:30	49221.24	9038.29	1070.78
	5	14.4	14:30	53175.10	9412.60	880.14
	6	19.4	21:00	57968.80	10047.92	869.53
RUN 4	1	-1.8	15:00	16619.29	3941.75	715.91
	2	2.0	22:00	44190.98	8199.29	798.63
	3	6.0	03:30	NA	NA	NA
	4	9.0	08:30	48012.77	8416.70	1018.10
	5	14.4	16:30	54030.94	8810.73	853.44
	6	19.4	23:00	58219.00	9444.42	957.38
RUN 5	1	-1.8	05:00	33877.77	4261.36	775.57
	2	2.0	12:00	46386.51	6216.75	679.06
	3	6.0	17:30	49695.54	6684.93	726.51
	4	9.0	22:30	51377.19	7077.47	838.81
	5	14.4	07:00	54578.35	7445.05	895.64
	6	19.4	13:00	58674.11	8149.18	889.00
RUN 6	1	-1.8	07:00	33877.77	4261.36	775.57
	2	2.0	14:00	52882.60	6986.32	650.12
	3	6.0	19:30	53448.95	6879.31	726.29
	4	9.0	00:30	NA	NA	NA
	5	14.4	09:00	58939.71	7622.49	878.43
	6	19.4	15:00	59362.16	8094.84	851.46

APPENDIX B

RAW DATA - CONSTITUENT LOADINGS

RUN /STA NUMBER		RIVER Miles	TIME	Cu lb/day	Mn lb/day	TKN lb/day
RUN 1	1	-1.8	8.75	0.00	210.43	NA
	2	2.0	13.75	0.00	257.60	NA
	3	6.0	19.25	0.00	221.37	NA
	4	9.0	23.25	0.00	271.68	NA
	5	14.4	30.25	0.00	251.15	NA
	6	19.4	35.25	0.00	195.07	NA
RUN 2	1	-1.8	10.75	0.00	235.18	NA
	2	2.0	15.75	0.00	180.74	NA
	3	6.0	21.25	0.00	248.14	NA
	4	9.0		0.00	NA	NA
	5	14.4	32.25	0.00	230.27	NA
	6	19.4	37.15	0.00	238.09	NA
RUN 3	1	-1.8	13:00	196.02	311.08	805.40
	2	2.0	20:00	164.19	280.71	2049.71
	3	6.0	01:30	127.87	255.74	2468.43
	4	9.0	06:30	120.89	253.30	2918.73
	5	14.4	14:30	79.46	189.47	2072.00
	6	19.4	21:00	70.85	186.79	3574.74
RUN 4	1	-1.8	15:00	119.32	306.82	1329.54
	2	2.0	22:00	74.54	271.53	2124.36
	3	6.0	03:30	NA	NA	NA
	4	9.0	08:30	46.28	254.53	2603.10
	5	14.4	16:30	30.70	184.20	2505.07
	6	19.4	23:00	32.34	200.53	2600.45
RUN 5	1	-1.8	05:00	46.87	375.00	NA
	2	2.0	12:00	43.04	272.58	1778.95
	3	6.0	17:30	45.41	237.13	2028.18
	4	9.0	22:30	31.46	220.19	2201.88
	5	14.4	07:00	44.78	212.72	2300.69
	6	19.4	13:00	71.12	189.65	2987.05
RUN 6	1	-1.8	07:00	46.87	NA	2007.10
	2	2.0	14:00	33.96	271.69	1586.48
	3	6.0	19:30	30.69	245.51	2270.94
	4	9.0	00:30	NA	NA	NA
	5	14.4	09:00	45.34	221.02	2278.25
	6	19.4	15:00	71.95	179.89	2662.30