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The Effects of a Phosphate Detergent Ban on a Biological Nutrient Removal Plant and Anaerobic Digester

by

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(ABSTRACT)

This study investigated the effects of the detergent phosphorus ban implemented on January 1, 1988 in Virginia, on the treatment streams of the York River Wastewater Treatment Plant, a biological nutrient removal (BNR) system. Evaluation of the available historical data indicated that the influent phosphorus load entering the plant in the post-ban period had decreased 27% compared to the pre-ban period. The influent phosphorus concentration had decreased 29% from the pre- to the post-ban period. No definitive conclusion could be reached concerning the effects of the influent phosphorus decrease on the treatment efficiency due to operational changes which occurred at the time of the ban implementation. The combination of operational changes and the phosphorus ban resulted in 54% and 59% decreases in the effluent phosphorus load and concentration, respectively.

Measurements and modelling of the anaerobic digester contents indicated that several minor changes had occurred in the digester which may be attributable to the phosphorus ban, but the equilibria of the digester regarding phosphorus compounds had not been dramatically altered. This was primarily due to improved operation of the clarifiers and sludge thickeners, which delivered similar phosphorus loads to the digester in the pre- and post-ban periods.

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GLOSSARY

A/O - Anaerobic/Oxic - a patented wastewater treatment system which removes phosphorus biologically (a BPR system).

A2/O - Anaerobic/Anoxic/Oxic - a patented modification of the A/O process which removes nitrogen and phosphorus biologically (a BNR system).

BNR - biological nutrient removal - a wastewater treatment system that removes nutrients (nitrogen and phosphorus) without chemical addition. Used to describe plants that remove both nitrogen and phosphorus, or as a general term for plants removing either nutrient.

BPR - biological phosphorus removal - a wastewater treatment system which removes phosphorus without chemical addition.

SRT - solids retention time - an average time a solid will remain in the treatment system, based on the solids wasting rate and the total mass of solids maintained in the system. Also called mean cell residence time (MCRT).

GLOSSARY (continued)

VIP - Virginia Initiative Plant - a wastewater treatment process which removes nitrogen and phosphorus biologically (a BNR system). Actually a high-rate University of Cape Town (UCT) BNR process.

CHEMICAL COMPOUNDS

aluminum hydroxide - $Al(OH)_3$

aluminum phosphate - $AlPO_4$

amorphous calcium phosphate - ACP - $Ca_9(PO_4)_6$

bobierrite - magnesium phosphate - $Mg_3(PO_4)_2 \cdot 8H_2O$

brushite - calcium phosphate dihydrate - $CaHPO_4 \cdot 2H_2O$

calcite - calcium carbonate - $CaCO_3$

chlorapatite - $Ca_5(PO_4)_3Cl$

dicalcium phosphate - DCP - $CaHPO_4 \cdot H_2O$

ferric hydroxide - $Fe(OH)_3$

ferrous ammonium phosphate - $FeNH_4PO_4$

ferrous hydroxide - $Fe(OH)_2$

fluorapatite - $Ca_5(PO_4)_3F$

hydroxyapatite - $Ca_5(PO_4)_3OH$

Newberyite - $MgHPO_4 \cdot 3H_2O$

octacalcium(octocalcium) phosphate -OCP- $Ca_8H_2(PO_4)_6 \cdot 5H_2O$

sarcopside - $(Fe\text{-}Mg)_3(PO_4)_2$

siderite - ferrous carbonate - $FeCO_3$

GLOSSARY (continued)

strengite - ferric phosphate - $FePO_4$

struvite - magnesium ammonium phosphate - $MgNH_4PO_4$

ß-tricalcium phosphate - TCP - $(Ca\text{-}Mg)_9(PO_4)_6$ or

ß-$Ca_3(PO_4)_2$

vivianite - $Fe_3(PO_4)_2 \cdot 8H_2O$

CHAPTER I

INTRODUCTION

Increasing concern over eutrophication of the Chesapeake Bay and other water bodies has encouraged new efforts in the reduction of nutrients from both point and non-point sources. Both enacted legislation and the anticipation of legislation have led to the implementation of various nutrient control techniques and technologies. Efforts aimed at non-point sources are comprised primarily of land management practices that minimize the nutrient transport to the water body.

Identifiable point sources (usually industrial and municipal wastewater treatment plants) have been the focus of techniques that remove the nutrients from the water column or ameliorate their deleterious effects. For example, nitrification with or without denitrification has been practiced in many instances to decrease the effects of ammonia/nitrogen discharge into receiving waters. Measures to affect both point and non-point sources have taken the form of limitations on the nutrient content of materials. Many efforts have concentrated on phosphorus since it is more often the limiting nutrient for plant and algal growth in the fresh waters that feed the Bay (1). In the Bay itself, the situation is dependent on the salinity of the water, the season of the year, and the dynamics of oxygen and nitrogen consumption in the water (2).

Phosphorus in municipal wastewater derives primarily from laundry detergents and other cleaners, and human waste, including waste food disposal (3). Historically, 10 mg/L has been considered an average concentration of phosphorus in wastewater, with 50% from detergent phosphate building agents and the remainder from human and food waste(4). Reformulation of many detergents reduced the average concentration for many localities in the late 1970s to the 7-9 mg/L range (1). Locations with large industrial contributions to their wastewater (especially from food industries) may have considerably higher influent phosphorus concentrations.

Wastewater treatment plants remove phosphorus either by chemical precipitation and coagulation, or by incorporation of the phosphorus into biological solids which are periodically wasted from the treatment process. Since, in both cases, the phosphorus is removed as part of the waste sludge, the ultimate disposal and fate of this sludge is of primary importance for phosphorus removal.

Sludge handling and disposal is of particular concern because it may account for 50% or more of the capital and operation costs of a wastewater treatment plant (4). This makes minimizing and concentrating the sludge highly desirable. Most large treatment plants are equipped with anaerobic digesters which stabilize and reduce the volume of the sludge. The digested sludge is then dewatered by gravitational or mechanical techniques. The liquid removed from the sludge and any digester supernatant or other internal recycle streams are usually recycled to the head of the treatment plant.

In anticipation of legislation limiting the discharge of phosphorus into the tributaries of the Chesapeake Bay,the York River Wastewater Treatment Plant (Seaford, Virginia) began operating with biological phosphorus removal in August, 1986. Because the York River Plant utilizes anaerobic digestion for sludge reduction, sampling schemes and studies were undertaken to follow the impact of the plant recycles on phosphorus removal (6,7). These studies indicated that chemical removal mechanisms in the plant and anaerobic digester prevented the saturation of the biological mechanism (6, 7). These chemical mechanisms were driven by the increased phosphorus concentrations resulting from biological phosphorus removal (6).

A phosphate detergent ban was instituted in Virginia in January, 1988, which restricted the phosphorus content of laundry detergents to trace (<0.5%) amounts (19). With the anticipated reduction in the influent phosphorus concentration of the wastewater load, questions arose concerning the chemical equilibrium conditions which would exist in the anaerobic digester at the York River facility. This study was undertaken to investigate the overall issue of the impact of the phosphate ban on the York River Wastewater Treatment Plant. Specific objectives were to:

1. quantify the effect of the phosphorus ban on the influent and effluent phosphorus loads and concentrations at the York River Wastewater Treatment Plant;

2. investigate the effects of the lower influent phosphorus concentrations on the phosphorus loads in various liquid flow streams within the plant; and,

3. investigate the effect of the lower influent phosphorus concentrations on the phosphorus load to and the chemical equilibria of the primary anaerobic digester at the York River Wastewater Treatment Plant.

CHAPTER II

LITERATURE REVIEW

This literature review chapter is divided into sections relevant to phosphorus bans, biological phosphorus removal, anaerobic digestion, and phosphate chemistry.

PHOSPHATE DETERGENT BANS

A phosphate detergent ban restricting the phosphorus content of laundry detergents to 0.5% went into effect throughout Virginia on January 1, 1988. Virginia joined a growing number of states which have implemented restrictions or bans on phosphorus content in laundry detergents due to concern over eutrophication of water bodies. States that have imposed bans or restrictions on detergent phosphate content are shown in Table 1 along with the date of the legislation's effectiveness.

Phosphates in detergents are used to soften the wash water and keep the dirt in suspension so that the surfactants may clean clothes more effectively (8). Phosphates are considered the best "builders" available, and have been used widely for years (8). Identification of detergents as a major source of phosphorus impacting on lakes in the late 1960s and early 1970s led to reformulation of detergents by soap manufacturers (1). Concurrently, many states began

Table 1. Dates of Legistated Laundry Detergent Phosphorus Limitations (after Maki *et al.*, (9)).

	Intermediate Ban		Date of Ban to 0.5% Phosphorus
Location	Date	P Limit	
New York	1/1/72	8.7 %	6/1/73
Connecticut	2/1/72	8.7 %	--
Indiana	2/22/72	8.7 %	1/1/73
Maine	6/1/72	8.7 %	--
Michigan	7/1/72	8.7 %	10/1/77
Florida	12/31/72	8.7 %	--
Vermont	--	--	4/1/78
Wisconsin	--	--	7/1/79[a]
Minnesota	--	--	8/30/79[b]
Maryland	--	--	12/1/85[c]
Washington, D.C.	--	--	9/1/86
Virginia	--	--	1/1/88
North Carolina	--	--	1/1/88
Pennsylvania	--	--	3/30/90 & 3/30/91[d]

a. The Wisconsin ban expired on July 30, 1982, and was reinstated on January 1, 1984.

b. The ban in Minnesota was enacted to take effect in late 1976, but legal challenges delayed the official date until August 30, 1979. Shipment of phosphate detergents into Minnesota stopped in late 1976.

c. The Maryland ban had an initial expiration date of December 1, 1989, but the legislature voted to reenact the ban.

d. Pennsylvania has required the Susquehanna River Basin and the Lake Erie areas to meet the ban limitations in 1990, and the rest of the state in 1991.

restricting the phosphorus content of detergents. Phosphorus levels in detergents decreased by 50% or more (9), from approximately 11% in the early 1970s (1) to 5% phosphorus in the late 1970s (10).Cleansers involved in food and dairy processing (including dish washing detergents), hospitals, and specific industries have been exempted from using reduced phosphate detergents(8).

Early U.S. impetus for a phosphate ban surrounded the Great Lakes, and mirrored the concern on the Canadian side of these lakes. Concern about accelerated eutrophication of the Great Lakes in the mid- and late 1960s led to studies which identified phosphorus as the most easily controlled pollutant in certain sections of the Great Lakes (8). Since human activity was regarded as one of the major causes of the water quality deterioration in the Great Lakes (11),and municipal treatment plants were the largest phosphorus source (12, 13), the Canadian government in July, 1970,limited the phosphorus content of detergents to 8.7% (9).In 1972, as states on the American side of the Great Lakes began enacting initial restrictions on detergent phosphorus levels at 8.7% (9), the Canadians government further reduced the maximum phosphorus level in detergents to 2.2%(12). In addition, Ohio and Illinois, although not adopting state-wide bans, enacted local bans for the cities of Chicago and Akron and the northern areas bordering the Great Lakes (12).

Although the Great Lakes prompted much of the early discussion on phosphorus bans, accelerated eutrophication of water bodies was occurring in many locations. The information in Table 1 shows that Florida and several states in New England adopted detergent restrictions at the same time as the states bordering the Great Lakes. The detergent reformulations later decreased the phosphorus content enough to make the Florida, Maine, and Connecticut bans meaningless.

The result of the measures around the Great Lakes was reported in 1981 as a 50% reduction in municipal wastewater phosphorus loads into the Great Lakes when compared to 1975 levels (9). Agricultural and urban run-off became a larger source of phosphorus into the Lakes than municipal wastewater (13). Canadian municipal plant influent phosphorus concentrations decreased from 8-9 mg/L to 5.5-6.8 mg/L, a 20-30% reduction (14), while effluent concentrations decreased 36% (12).

Despite assertions that Lake Ontario improvements were noted relatively quickly and National Oceanic and Atmospheric Administration reports that phosphorus levels were reduced more quickly than expected (8), actual improvements in lake water quality were not easy to document and were harder to specifically attribute to phosphorus bans. Indiana, the first state in the United States to enact a ban on phosphate detergents, could only attribute a dramatic decrease in the phosphorus levels in Lake Michigan to the ban by "good circumstantial evidence"(8). A study of New York lakes from 1971-1978 concluded that the New York phosphorus ban produced no measurable impact on water quality (9).

The effects of the New York phosphorus ban were also observed at the Tallman Island Pollution Control Plant, as described by Sharfstein, et al. (15). The initial legislation affecting detergent phosphorus (effective January 1, 1972) restricted household cleaners only, with a limit of 8.7% phosphorus by weight. This restriction resulted in a 24% reduction in the total phosphorus concentration entering the Tallman Island Plant and a 21% reduction in the orthophosphate concentration. After June 1, 1973, household cleaners were restricted to trace (0.5% by weight) amounts of phosphorus, resulting in decreases of 47% and 51% in the influent total phosphorus and orthophosphate concentrations, respectively. The orthophosphate concentration in the East River also decreased 24% (15). These values are included in Table 2 with a review of the reported effects of phosphorus bans on various flows.

Sharfstein et al., (15) also reported an 18% decrease in the East River orthophosphate concentration

Table 2. Literature Review of Phosphorus Ban Impacts on Wastewater Treatment Plants

Location/Date of Detergent Phosphorus Ban	Detergent P Limit		Change in Phosphorus Concentration (unless noted otherwise)		
	From	To	Flow Affected	% Change	measurement
Canada, 1972	8.7%	2.2%	Influent Effluent	20-30% 36%	total total
New York, 1972	>8.7 %	8.7%	Influent Influent	24% 20%	total ortho-P
New York, 1973	8.7%	0.5%	Influent Influent East River	47% 51% 24%	total ortho-P ortho-P
Minnesota, 1976	a	0.5%	Lake Load[b]	13%	total load
Wisconsin, 1979	5.0%	0.5%	Influent	16-34%	total load
Wisconsin, 1982[c]	0.5%	up	Influent	3-26%	total load
Michigan, 1977[d]	5.7%	0.5%	Influent Effluent Effluent	23% 24% 20%	total total total load
Michigan, 1977[d]	5.7%	0.5%	Influent	13-15%	total load
Maryland, 1985	a	0.5%	Influent	32%	total
Maryland, 1985	a	0.5%	Effluent	16-21%	total load
Virginia, 1988	a	0.5%	Influent Effluent[e]	31% 52%	total total
Virginia, 1988	a	0.5%	Influent Effluent Effluent	32% 50% 42%	total total total load

a. This value was not reported in the literature.

b. The decrease noted is in the total load of phosphorus entering a number of lakes.

c. These data reflect the lapsing of the Wisconsin ban and the subsequent increase in phosphorus loads. The percent change is the percent increase.

d. Several authors discussed the same Michigan data with different statistics, and reached different conclusions.

e. This effluent value excludes plants that practiced any deliberate phosphorus removal.

resulting from legislation which expanded the phosphorus restrictions to all commercial products (except dish washing powders, and products used in food and beverage processing and dairy equipment). The secondary effluent of the Tallman Island Plant and water from the East River formed the culture medium of an aquaculture protein production plant on the Tallman Island Pollution Control Plant site. The effects of the phosphorus restrictions on this aquaculture plant was also reported by Sharfstein et al., (15). The reduction of phosphorus in the culture medium altered the performance of the aquaculture by shifting the system from being nitrogen limited to phosphorus limited, as the N:P ratio changed from 9:1 to 21:1. Production of protein was reduced more than 50% (15).

The impact of the Minnesota phosphorus ban on lakes was studied from 1975-1976 (pre-ban) and 1977-1980 (post-ban) by Runke; the results were subsequently summarized by Maki et al., (9). Although the Minnesota ban was to become effective in late 1976, legal challenges delayed the actual date of enactment to August, 1979. The study preceded the actual ban, but the detergent industry stopped the shipment of phosphate detergents into Minnesota in late 1976 (9). Lakes were evaluated in pairs, with lakes having no point source inputs of wastewater phosphorus acting as controls for similar lakes with wastewater point sources. This was an attempt to have a set of controls to better establish the natural variation of the parameters monitored during the study. The external phosphorus load entering the lakes decreased by 13% as a result of the ban; however, the loading reductions did not result in any water quality improvements when compared with the natural fluctuation in water quality parameters (9).

The Wisconsin phosphorus ban passed by the 1978 legislature became effective on July 1, 1979, but had a "sunset provision" so that unless specifically reenacted prior to June 30, 1981, the ban would expire (10). In the interim, the effect of the ban would be evaluated and the results would aid the legislators in their decision. In July, 1979, the "sunset" was extended to June 30, 1982, to give more time for assessment of the ban's effects. Data were not collected specifically to study the effects of the ban (10), and although the load of phosphorus was reduced in many sewers (9), major improvements to wastewater treatment plants made the phosphorus reductions resulting from the ban difficult to assess (8). No direct evidence of water quality improvements could be shown (8, 9). The ban was allowed to lapse, and detergents with phosphates began to reappear in July, 1982 (10). Prior to the ban the average detergent phosphorus content had been approximately 5%, but no determination was presented of the content after the ban lifted, or the extent of phosphate reemergence in the market. In October, 1983, Wisconsin passed another phosphorus ban which became effective on January 1, 1984(9).

A thorough intervention analysis of the data from several Wisconsin treatment plants evaluated the effects of the first phosphorus ban and the lifting of the first ban. The ban reduced the influent load 26% (+/- 9%), and the lifting of the ban resulted in a 13% (+/- 11%) increase in the influent phosphorus load (10).

Michigan banned detergent phosphorus concentrations to trace levels on October 1, 1977. The average phosphorus content in laundry detergent before the ban was 5.7% (12). According to an analysis by Hartig et al., (12), using the two sample t-test, without a significant difference inflow, the influent total phosphorus concentration decreased by 23%; the effluent total phosphorus concentration decreased by 24%; and the total effluent phosphorus load decreased by approximately 20%. A critique and alternative analysis of the same data by Berthouex et al., (16), questioned these conclusions because the use of a paired t-test assumed the data were independent though sequential data may be dependent (16) and significant changes in the operation of the largest plant in the study skewed the results (13). The separate analysis concluded that the reduction of the influent phosphorus load attributable to the ban was 13-15% (16).

Further discussion by Hartig claimed that the initial analysis was conservative because data from after the ban were included in the analysis as data before the ban (16). Hartig et al., (17), also noted in another analysis that the existing stocks of phosphorus detergents were allowed to sell out after the ban. This analysis evaluated nine Michigan treatment plants which did not alter treatment over the time of the data and calculated influent total phosphorus concentration reductions ranging from 14-41% (17). The authors also had conflicting claims regarding observable effects of the Michigan phosphorus ban. One paper claimed no observable improvement in the water quality of the lakes (13), while another touted reductions in tributary and near- shore phosphorus levels and algae (12).

This ban experience seemed typical of most described in the literature. Significant and similar decreases in influent and effluent phosphorus concentrations and loads were reported in many instances, but improvements in water quality relied on qualitative evidence. Improvements were also difficult to attribute solely to the ban, because phosphorus bans are usually an adjunct to other phosphorus reduction and control strategies. Operational changes in the wastewater treatment plants make data on effluent phosphorus concentrations and loads especially difficult to interpret. This has created some discrepancy in the conclusions concerning the effectiveness of bans. Bans evaluated on the basis of water quality improvements conclude that bans are ineffective, especially when the collective result and magnitude of all active random factors are considered. If the goal of a phosphorus ban is to reduce the phosphorus delivered to the receiving water then bans are clearly effective, although the detergent industry claims that bans are less cost-effective than removal of phosphorus at municipal wastewater treatment facilities (8).

Because the regulatory agencies have begun to require phosphorus removal more often, recent evaluations of phosphorus bans have concentrated on the cost reductions in wastewater treatment. The reduction of the influent phosphorus loads reduces the use of chemical additives to meet effluent standards and the amount of sludge produced (17). Since handling and disposal of sludge is often a major fraction of the cost of wastewater treatment (3), the reduction of sludge production can result in substantial savings to the service authority (1, 17). In Maryland, the potential for cost avoidance positioned the large Washington Suburban Sanitary

Commission (WSSC) as a strong supporter and lobby for a phosphorus ban (1).

The Maryland ban was the most heavily lobbied bill of the 1985 session but passed and became effective on December 1, 1985 (1). As a result of concern about the Chesapeake Bay's condition and productivity, and in recognition of its economic importance, the governments surrounding the Bay had been considering phosphorus bans and various other nutrient control measures. The city of Washington, D.C., followed the example of Maryland and passed a ban that became effective in September, 1986 (1). Designation of "nutrient enriched waters" in Virginia affected discharge into many of the Bay's tributaries (18). Ban legislation finally passed in the 1987 session of the Virginia state legislature to become effective on January 1, 1988 (19). Pennsylvania also passed legislation in 1989 to ban phosphorus detergents beginning after March 30, 1990.

The impact of the Maryland ban on the effluent of wastewater treatment plants has been watched closely (20). Based on only three months of post-ban data, the WSSC reported a 32% decrease in the influent total phosphorus concentration with similar flow-rates (1). The total phosphorus load discharged from all Maryland plants dropped 37%, from 10,550 lbs/d in 1985, to 6,680 lbs/d in 1986, due to the ban and operational changes (20).

Treatment plants without phosphorus removal (representing 17% of the total effluent flow) accounted for an estimated 43-58% of the effluent load reduction (20). The flow-weighted average of total phosphorus in the effluent from Maryland treatment plants without phosphorus removal decreased from 4.2 mg/L to 2.4 mg/L, a 43% reduction (20). Chemical addition at WSSC's large Blue Plains Advanced Wastewater Treatment facility in Washington, D.C., was reduced 30% as a result of a 26% reduction in the influent phosphorus load (1). Other WSSC plants have cut chemical addition by 53% and 57% (1). Cost figures have not been published to verify the expected cost savings associated with the reduction in chemical costs and sludge handling, but would appear to be substantial (20).

Another treatment facility was noted that had reduced chemical addition by 55%. The same plant recorded only an 18% decrease in influent phosphorus concentrations. The influent phosphorus concentration to the Seneca Wastewater treatment facility (operated by the WSSC) could not be sampled until after the plant recycle flows had joined the influent stream (1). Based on similar plants in the area with similar chemical reductions, the influent reduction would be estimated at approximately 30%. The 18% reduction reported implies that the decrease in phosphorus from the ban does not proportionately affect the recycle concentrations.

The percent chemical reduction from the Maryland ban was not equivalent to the percent phosphorus reduction. This illustrates the role of background mechanisms of phosphorus uptake. Biological and physical/chemical background mechanisms removed 35-60% of the influent phosphorus at treatment plants which were evaluated in the metropolitan Washington, D.C. area (1). A portion of this removal was from the inclusion of phosphorus in the created cellular material, and some results from the influent water chemistry. The ban did not appear to affect the background uptake mechanisms (1) at one of the WSSC plants which operated without phosphorus removal.

The contribution of detergent phosphorus to the phosphorus concentration entering WSSC waste treatment facilities is illustrated in Figure 1. Detergents in 1970 contained approximately 11% phosphorus and contributed 50-70% of the load reaching treatment plants (1). As reformulations reduced detergent phosphorus to values in the 5-6% range (1, 10), the contribution of detergents to the total load decreased. The estimates for the WSSC area are higher than the 20-30% (9, 10) contribution often cited for this similar time period in other locations. The 2.7 mg/L, or 27%, reduction in the

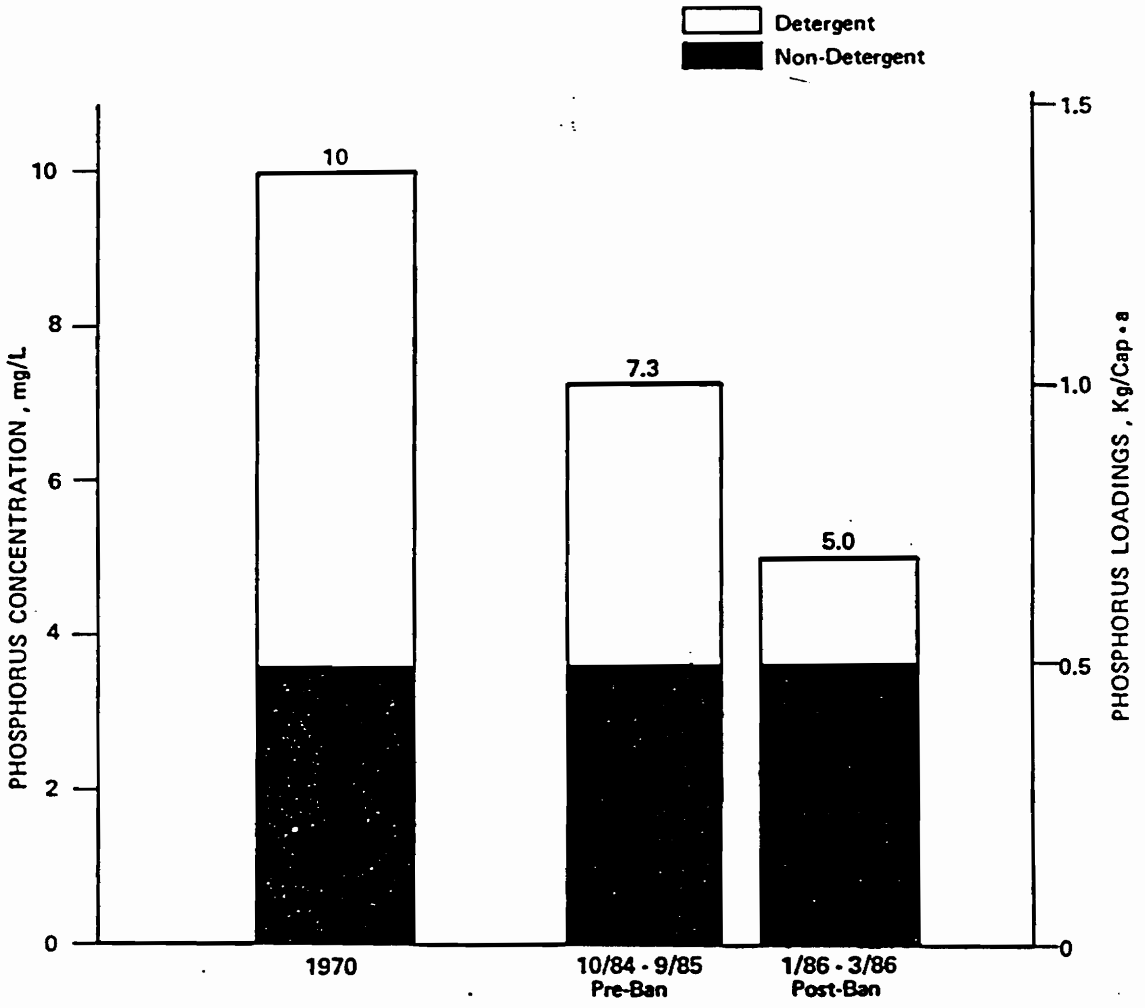

Figure 1. Generalized Trend in Raw Wastewater Phosphorus Concentrations at Washington Suburban Sanitary Commission Wastewater Treatment Facilities (from Jones and Hubbard, (1)).

phosphorus concentration is typical of decreases reported for this time period (the 1970s) when considering municipal wastewater. The phosphorus ban resulted in another 2.3 mg/L decrease, or 32%, in the influent phosphorus concentration (1).

The Virginia phosphorus ban resulted in a 31% decrease in the influent total phosphorus concentration for a flow-weighted average of 37 plants receiving primarily municipal waste (19). The concentration decreased from 7.37 mg/L to 5.09 mg/L. The decrease in effluent total phosphorus concentration for the 26 plants without phosphorus removal was 52%, decreasing to 2.54 mg/L from 5.25 mg/L. A longer time series for the nine treatment plants operated by the HRSD calculated a reduction of 32% in the influent total phosphorus concentrations, from 7.95 mg/L in 1985, to 5.39 mg/L in the first nine months of 1988. There was an 11% increase in flow over this time which may in part have been due to increased rainfall in early 1988 (19). Most of the flow increase was due to expanded service, so dilution effects have not been considered, but the 32% decrease in influent concentration represents the maximum reduction in the phosphorus concentration. Effluent load reductions excluding the York River Plant (due to significant operational changes between the years of comparison) calculated a reduction of 50% from 5.31 mg/L to 2.64 mg/L, but again noting that this represents the maximum change that may have occurred. The effluent load reduction was 42% (19).

BIOLOGICAL PHOSPHORUS REMOVAL

Biological phosphorus removal concentrates phosphorus in the biological solids of an activated sludge plant. Conventional activated sludges incorporate phosphorus in stoichiometric proportions according to the generally accepted empirical formula for cellular material developed by McCarty as: $C_{60}H_{87}O_{23}N_{12}P$ (21), which calculates to 2.3% phosphorus by weight. A typical phosphorus content of microbial solids is 1.5-2.0% of the dry weight (5). Biological phosphorus removal sludges usually contain 4-7% phosphorus on a dry weight basis (22), but sludges with 9-10% (23) and 14% (24) phosphorus content have been reported.

Various theories have attempted to attribute the phosphorus removal in excess of stoichiometric amounts to chemical or biological mechanisms. Investigations of both mechanisms have demonstrated phosphorus removal, and evidence shows the mechanisms are interrelated (25); the relative importance of the two mechanisms is unresolved. A summary presenting the involved mechanisms from a review by Arvin (26) is repeated here as Table 3.

Table 3. Summary of Phosphorus Removal Mechanisms (26)

Biological Mechanisms	Chemical Mechanisms
1. Normal P Assimilation: 1-2.5% removal (based on SS). Net removal increases with increasing BOD/P ratio in the wastewater. 2. Polyphosphate Accumulation: up to a P-content of 5-7%. Requires alternating anaerobic/aerobic sludge treatment.	1. Bulk Precipitation: • Normal Bulk Precipitation: Stimulated by a relatively high pH (>7.5), Ca, and F concentrations, low Mg, pyrophosphate, and bicarbonate concentrations. • Accelerated Bulk Precipitation: Accelerated by the high P concentration created by anaerobic poly-P stripping from bacteria. Factors affecting normal bulk precipitation apply. 2. Biofilm Precipitation: Created by bacterial denitrification in biofilms. Factors affecting normal bulk precipitation apply. Inhibited by filamentous growth.

The distinguishing feature of biological phosphorus removal systems is an anaerobic zone (excluding nitrates and oxygen (25)) within the treatment scheme. The anaerobic zone conditions the sludge to remove excess phosphorus, apparently by selecting microorganisms which are able to accumulate polyphosphate (27), seen as volutin granules under a microscope. Besides polyphosphates, volutin granules include RNA, lipid, protein, and the stabilizing cation Mg^{++} (25) or in some organisms, Ca^{++} (28). Another metabolic product which plays a role in biological phosphorus removal is poly-b-hydroxybutyrate (PHB).

Polyphosphate and poly-b-hydroxybutyrate are microbial storage products of phosphate and carbon, respectively. Storage occurs when the substrate is available from exogenous sources in excess of the immediate requirements of the cell. This stored substrate may be degraded as a suitable energy source when the exogenous energy supply is no longer sufficient for optimal cell maintenance (29). Only certain species of aerobic bacteria accumulate PHB, and only when deprived of sufficient oxygen, not carbon or nitrogen (29). The species most often identified with uptake of excess phosphorus are _Acinetobacter_ species (7), obligate aerobes which use mainly acetic acid as substrate (25). Pure cultures of Acinetobacter have accumulated 6-10% phosphorus content by weight (5).

There are two mechanisms that allow microbes to accumulate excess phosphorus; polyphosphate overplus, and luxury uptake (29). The former of these mechanisms is induced by subjecting the microbe to a phosphate depleted environment; subsequent exposure to an abundance of phosphorus results in the synthesis of polyphosphates (25).If the lack of oxygen in the anaerobic zone of the treatment plant curtails the active transfer of exogenous phosphorus into strict aerobes (29), that may simulate a phosphorus depleted environment and lead to polyphosphate overplus.

The latter mechanism, luxury uptake, is uptake in the absence of growth (30). Luxury uptake occurs when an essential element other than phosphorus is limited, but sufficient energy is available to transfer phosphorus into the cell (29). Certain bacteria use alternate metabolic pathways when deprived of one key element of metabolism (29). The production of polyphosphates may act as a storage mechanism for excess phosphorus which becomes energy (29) either through ATP, or perhaps directly from hydrolysis of the polyphosphate bonds (31).

The accepted scheme is that the cyclic anaerobic/aerobic conditions stress the microbes and derepress or induce enzyme systems in the microbes that allow them to accumulate polyphosphate. The anaerobic stress alone is not sufficient to stimulate phosphorus uptake, even in the presence of a carbon source, but requires a period of acclimation (22). The accumulation of polyphosphates occurs in the aerobic zones and becomes an energy source (directly (31) or possibly indirectly through ATP (29)) for cell maintenance and PHB synthesis in the anaerobic zone (31). The polyphosphate may also supply energy for translocation of cations to restore the proton motive force of the cells as they absorb acetic acid (31). The PHB serves as the carbon supply for the bacteria to compete in the aerobic zone (31) or as the proton and electron sink for the microbe to survive the stress of the anaerobic zone (29). In the aerobic zone, the microbes utilize the PHB for cell growth and phosphorus accumulation. The amount of phosphorus uptake exceeds the amount of release for a net removal of phosphorus (7). The role of the accumulated carbon (PHB) in acquiring phosphorus has led to the use of influent total BOD_5 to total phosphorus ratios (TBOD:TP) or soluble BOD_5 to soluble phosphorus (SBOD:SP) ratios to assess the potential of biological phosphorus removal. Total and soluble BOD:P ratios greater than 20-25 and 12-15 respectively are considered necessary to achieve 1 mg/L effluent phosphorus concentrations (27).

Despite the uncertainty of the biochemical roles of the storage products, the consequences of their roles have been observed in many studies. Release of phosphorus as orthophosphate (32) occurs in the anaerobic zone. This results from hydrolysis of polyphosphate bonds for energy to accumulate organic material which will become PHB. Polyphosphates are hydrolyzed in proportion to the BOD absorbed (23). The rate of phosphorus release in the anaerobic zone slows after extracellular substrate depletion; it also slows after a fixed loss of phosphorus even in the presence of excess substrate (33). This fixed loss apparently represents the depletion of thelow-molecular weight polyphosphate pool (34). The low-molecular weight pool has been observed to be one of the phosphorus pools present in sludge that varied most widely between biological phosphorus removal and conventional activated sludge plants (34) and represents the bulk of the acid extractable pool identified as responsible for the hydrolysis in the anaerobic zone (32) that accompanies substrate absorption.

In addition to exerting pressure that favors polyphosphate-accumulating microbes, the anaerobic zone may be equally or more important as a selection zone for populations that produce low molecular weight fatty acids (LFA) (31). Observations show that a readily biodegradable substrate must be present in the anaerobic zone for biological phosphorus removal (27) and suggest that LFA production is linked with phosphorus release (31). Since substrate is the most important selective pressure in a microbiological system (35), the presence of LFAs may be crucial in selecting Acinetobacter since it favors acetic acid. The formation of LFAs is often completed in part during wastewater transmission through sewers, especially pumped mains (25), where sewage remains in the system for extended periods. A logical corollary is that an overdesigned anaerobic zone will remove phosphorus consistently and effectively (25), even increasing the phosphorus removal 66-96% based on removal per unit MLSS (36) in one study. The role of the anaerobic zone for conditioning of the sludge is crucial (37), but may vary with the septicity of the arriving sewage.

The anaerobic zone is also important for the chemical mechanism implicated in biological phosphorus removal. As mentioned previously, polyphosphate is accompanied in microbial cells by Mg^{++} or Ca^{++} which may be released concurrent with the release of phosphorus in the anaerobic zone. Mention was also made that the energy derived from the hydrolysis of phosphate bonds may have a role in balancing the proton motive force of the microbial cell by expelling cations (31). Under anaerobic conditions, the high soluble phosphorus concentrations, along with the metal cations present in the wastewater and released by the microbe, increase the driving force for phosphate precipitation at a pH greater than 7 (27). In a biological phosphorus removal plant that ascribed the high removal of phosphorus to chemical precipitation, removals were greatly reduced when the anaerobic conditioning was removed (38).

Some early studies of biological phosphorus removal by Mulbarger et al., (39) concluded that the high oxygenation rates in the aeration basins stripped out carbon dioxide and increased the pH in the basin so that all of the excess removal was due to precipitation of calcium phosphate. In work reported by Kerdachi and Roberts (25), the cell production in several plants operated at long solids retention times was not considered adequate to have achieved the phosphorus removals recorded. They presumed a chemical mechanism of phosphorus removal despite high phosphorus content in the Acinetobacter present in the sludge. In a lab-scale system operated by Lan (40), increased aeration did result in a pH increase and calcium phosphate precipitation, but this accounted for only 15-27% of the total phosphorus removed. In a plant in the soft water area of the Western Cape of South Africa, about 16% of the removal of phosphates could be attributed to precipitation (25). The amount of chemical precipitation present is variable (37), and would depend on factors listed in Table 3.

Simultaneous chemical precipitation of phosphorus caused by cations improves the performance of the biological phosphorus removal system (27). The increase in the phosphorus concentration will mediate precipitation in the macroenvironment of the basin and also in the microenvironment surrounding the biomass by accelerating precipitation and inducing nucleation (26). Denitrifying systems will also encourage precipitation by elevating the pH in the microenvironment of the biofilm or bio-floc (26). Phosphorus release in the anoxic zone of a denitrifying system when the pH is increasing will precipitate readily and no longer be available to the system (25). Further interpretation of experience with long solids retention times, leads to the conclusion that either the phosphate pool becomes more stable or precipitation of phosphates occurs (25).

The metal cations present in the wastewater and released by the microbes will determine which chemical precipitates form. The release of cations with phosphorus has been reported by several authors; a summary of their results is listed in Table 4 (after Sen (6)). Calcium present in the wastewater forms calcium phosphates which may have been responsible for high phosphorus removals, especially in the pH range 7.5-9.5, and in the absence of

Table 4. Literature Reports of Cation:Phosphorus Molar Ratios During Concomitant Release and Uptake in Biological Nutrient Removal Sludges (after Sen, (6)).

Researcher	1	2	3	4	5	6	7	8	9
Mg^{++}/P	0.26	0.32	0.24	0.28	0.27	0.29	0.26	0.27	0.25
K^{+}/P	0.27	0.23	0.34	0.20	0.23	0.23	0.24	0.28	0.25
Ca^{++}/P	0.00	--	0.06	0.09	0.12	0.07	--	0.02	--
Na^{+}/P	--	--	0.00	0.00	0.00	--	--	--	--
Sum of charges	0.79	0.87	0.94	0.94	1.01	0.95	0.76	0.86	0.75
P transport	rel	rel	rel	rel	upt	rel	r/u	rel	r/u
Reference	(6)	(6)	(6)	(6)	(6)	(6)	(6)	(31)	(36)

Sum of charges = $(2*Mg^{++}/P) + K^{+}/P + (2*Ca^{++}/P) + Na^{+}/P$

P transport = release (rel) or uptake (upt) of P by the cell

Researchers:

1. Miyimato-Mills <u>et al</u>, 1983
2. Arvin and Kristensen, 1983
3 - 5. Comeau <u>et al</u>, 1985
6. Brannan, 1985
7. Sen, 1987
8. Comeau <u>et al</u>, 1985
9. Gerber and Winter, 1985

high alkalinity and magnesium levels (41). Magnesium and potassium have most often been cited as cations concomitantly released with the phosphorus in the anaerobic zone. A sludge with polyphosphate accumulation exhibited higher molar ratios (based on % MLSS) of magnesium and potassium than a non-accumulating sludge (23). The molar ratios of the cations in excess of the conventional sludge were 0.25 and 0.28 for potassium and magnesium, respectively, which agree well with the ratios presented in Table 4.

Studies have also evaluated the correlation between phosphorus uptake and release with other cations. Various studies have concluded that calcium has no role in the concomitant release of cations (23, 36), while information contained in Table 4 shows that certain studies have implied that calcium has a role (6). The relative unimportance of calcium release is surprising since calcium is, according to scanning electron microscopy work by Buchan (35), the only cation consistently associated with the polyphosphates in Acinetobacter cells. The lack of calcium will also prevent polyphosphate accumulation by the overplus mechanism (25). However, co-transport of ions across the membrane may not be representative of the ions stabilizing the polyphosphate chain (6). Other cations such as iron (36), aluminum (23), sodium (36), copper

(36), and the anion chloride (36) have shown no significant relationship to the release or uptake of phosphorus.

Solid phases of precipitates in wastewater treatment trains have been described but few other than calcium phosphate have been identified. A significant portion of the phosphate can be mineral bound to calcium (26). The presence of silica-dioxides (quartz) has been reported to make X-ray diffraction of sludges difficult (38). As mentioned in the previous paragraph, a biological phosphorus removal sludge containing magnesium and potassium was described (23). Other sludges have contained aluminum, iron, magnesium, and calcium (43). Sludge extract data showed that nearly one-half of the phosphorus in along solids retention time (SRT) plant was in a mineral rather than a biological form (43). The net composition of the mineral was reported as $Ca_{10.5}Fe_{2.5}(PO_4)_{4.5}(OH)_{15}$ (43); but some of the calcium may be simply bound to the biomass by ion exchange (26). Solid phases with iron, calcium and phosphate have also been noted elsewhere (38). Work describing the metal phosphates in the digester of a biological phosphorus removal plant is discussed later in this chapter.

The extent of chemical precipitation in a biological phosphorus removal system may be related in part to solids retention time. Sludge from very long sludge ages (38 and 69 days) held anaerobic with a carbon source for 2 hours released less than 6% of the total phosphorus content (38). The lack of leaching of phosphorus in the clarifiers or the return sludge presented further indirect proof of an extracellular precipitation or adsorption mechanism (38). An unidentified solid phosphate was noted in the sludge (38).

Systems for biological phosphorus removal (BPR) operate at different solids retention times. Biological phosphorus removal is often coupled in the treatment system with nitrification/denitrification for nitrogen removal and referred to as a biological nutrient removal (BNR) system. Early BNR plants (Bardenpho and University of Capetown) utilized long solids retention times in order to assure nitrification and denitrification. Two BNR systems with short solids retention times are the A2/O (anaerobic/anoxic/oxic) and the Virginia Initiative Plant (VIP) systems whose configurations are shown as Figure 2. Both systems are characterized by an anaerobic zone, an anoxic zone, and an aerobic zone in series and provide recycling of nitrified mixed liquor from the aerobic to the anoxic zone (44). In the VIP process, return activated sludge is directed to the anoxic zone for denitrification and a separate recycle stream is taken from the end of the anoxic zone to provide denitrified mixed liquor to the

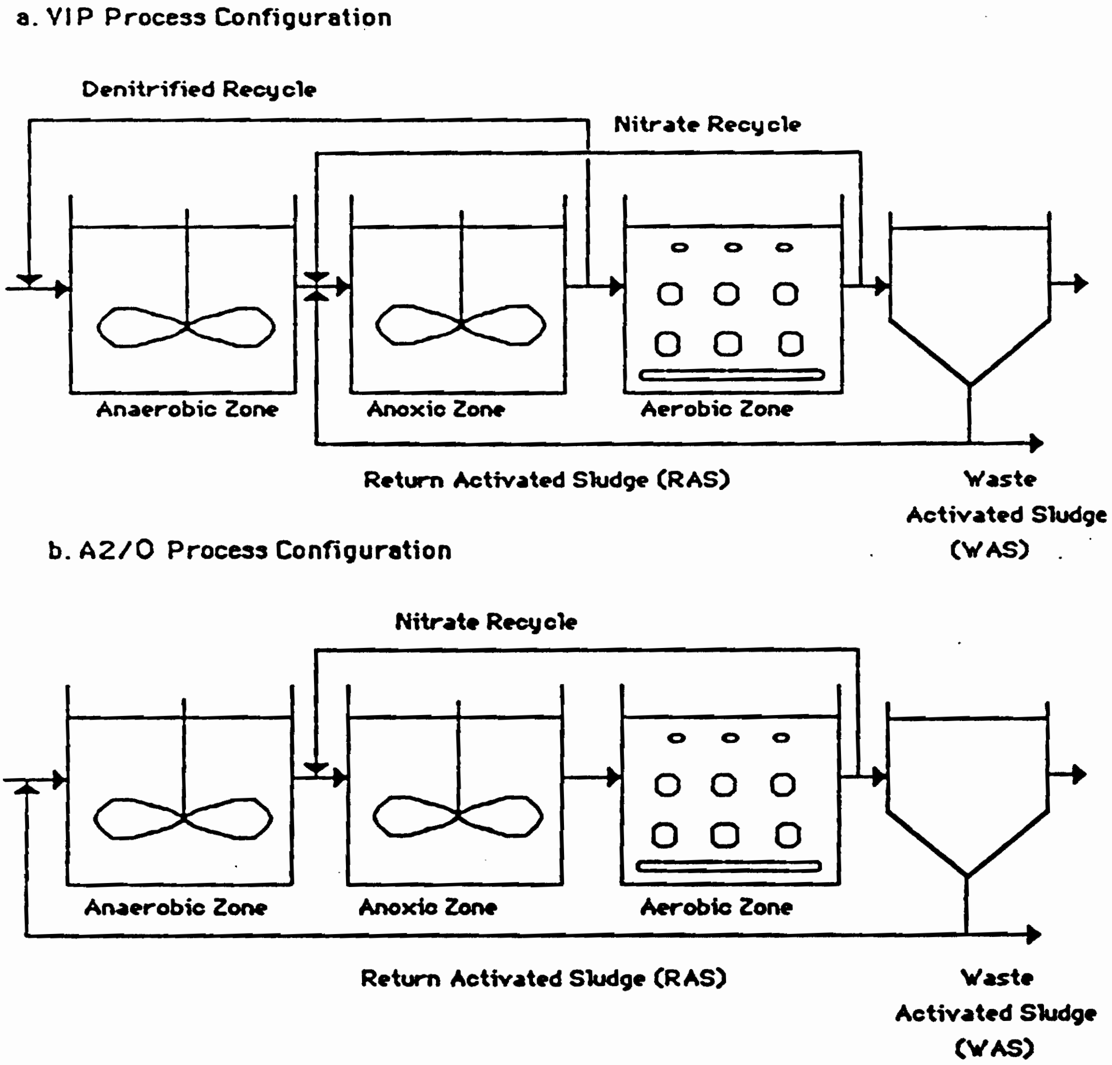

Figure 2. Process and Recycle Configurations for the a) VIP process and the b) A2/O process

anaerobic zone (44). In the A2/O process, return activated sludge, which may contain nitrate, is returned directly to the anaerobic zone (44).

The VIP process is similar in configuration to the University of Capetown, or UCT process, but differs by having staged reactors. It also operates at a high rate (low solids retention time), and, therefore has a more active biomass (44). The A2/O process is an extension of the A/O (anaerobic/oxic) process, and is identical to a three-stage modified Bardenpho plant (2).

The VIP process has shown superior phosphorus removal efficiency when compared to the A2/O process in a pilot plant study. The VIP process accumulated more phosphorus (14% P/VSS) than the A2/O (9% P/VSS), and operated effectively at TBOD:TP ratios as low as 10:1. Phosphorus removal in the A2/O system decreased when the TBOD:TP ratio decreased into the 18-20:1 range (44). The VIP process maintained a high phosphorus removal efficiency even at phosphorus additions to the influent which overwhelmed the A2/O system (44).

A comparison at a high rate BPR/BNR plant was not able to distinguish between the phosphorus removal potentials of the high rate processes used due to multiple operational changes and a phosphorus ban that altered influent phosphorus concentrations during the study (45). From limited data, the phosphorus removal performance of the A2/O system appeared better than the A/O process (45). Also, the nitrifying VIP process evidenced better phosphorus removal than the A/O process (45).

Higher sludge yields associated with low solids retention times would logically increase the phosphorus removal capacity for the systems (5). The VIP process has shown significant advantages for operation at high rate compared to a low-rate UCT system (44). Specifically, the VIP process demonstrated improved aerobic zone phosphorus uptake kinetics and increased sludge production (44). Five-stage modified Bardenpho facilities with low rates operated at similar influent TBOD:TP ratios had higher effluent soluble phosphorus levels than other BPR plants operating at higher rates (5). In work reported by Daigger et al., (44), an increase in the hydraulic retention time of a VIP process reduced phosphorus removal almost immediately.

For effective treatment the accumulated phosphorus (whether biologically or chemically held) is removed with the biological solids in the waste activated sludge. Achievement of effluent phosphorus concentrations lower than 1-2 mg/L total phosphorus requires efficient clarification which achieves less than a 20 mg/L TSS concentration or the use of tertiary filters (5). If sludge is not removed from the bottom of the clarifiers, phosphorus release will occur as the sludge blanket becomes anaerobic; and less phosphorus removal will occur. Since they produce more sludge, high-rate systems have a greater capacity to remove phosphorus, and have the added advantage in many systems of reduced clarifier retention times.

ANAEROBIC DIGESTION

Anaerobic digestion is commonly used to reduce the volume of sludge from wastewater treatment plants. Many of the pollutants responsible for the offensive and noxious nature of untreated wastewater are stabilized in the digestion process (46). Anaerobic digestion will also solubilize much of the organic matter present in the waste sludge (46). Resolubilization is a major operational concern in biological nutrient removal systems (7) because the excess phosphorus will also be released in the anaerobic conditions of the digester (14). Recycle of the digester contents to the head of the plant could overload the phosphorus removal capacity of the activated sludge system (5). Such considerations have led to recommendations that biological phosphorus removal sludge be handled aerobically, or without supernatant return from the digester to the plant (37).

A biological phosphorus removal sludge from a pilot plant described by Deakyne <u>et al.</u>, (47) (total phosphorus 724 mg/L; 5% phosphorus by weight), when subjected to anaerobic conditions, released phosphorus at a rate of 10 mg/L/hour for 24 hours, then at a reduced rate of 3.3 mg/L/hour for several days. The soluble phosphorus level went from 13 mg/L to 428 mg/L over 96 hours. Reaeration caused an uptake of phosphorus at a rate of 19.2 mg/L/hour over 6 hours; the phosphorus easily precipitated with a combination of ferric chloride and lime, decreasing to less than 1 mg/L in 10 minutes or less depending on the concentrations of iron and lime used (47).

Actual experience with anaerobic digestion of phosphorus removal sludges is limited because plants have avoided combining the two processes due to the predictions of the literature. A plant in Pontiac, Michigan, operating in an A/O mode, conducted studies operating with and without anaerobic digester supernatant recycle to the head of the treatment plant. The results indicated the impact of the digester recycle was minimal (5). The digester supernatant phosphorus levels indicated a minimal release of soluble phosphorus in the anaerobic digester (5), possibly due in part to the long solids retention time (for an A/O process) of 16-24 days and chemical precipitation. The plant consistently removed phosphorus to an effluent concentration of 0.3-0.7 mg/L; but may have been limited in process performance by the long solids retention time, the low influent phosphorus concentrations

(3-4 mg/L), and the recycle of nitrates to the anaerobic zone (5).

More intensive and specific studies have been conducted on the effect of operation as a biological phosphorus removal system on the anaerobic digester of the York River Wastewater Treatment Plant, in Seaford, Virginia. Change of the plant operation from conventional activated sludge to BPR resulted in significant increases in the phosphorus and metal ion loadings to the anaerobic digester (48). Total phosphorus, and total recoverable magnesium and potassium concentrations increased in the digester (48), and entered primarily through the flotation-thickened secondary sludge (7). The release of magnesium and potassium as soluble species accompanying phosphorus release in the flotation thickener and the digester indicated a biological accumulation rather than chemical precipitation as the principal phosphorus removal mechanism during waste treatment (7). The long contact time of the released phosphorus with the metal ions in the digester provided the opportunity for chemical precipitation in the digester (7).

Precipitation in digesters has often focused on the formation of struvite ($MgNH_4PO_4(s)$), because struvite tends to adhere to pipes and clog sludge transmission lines (49). In conventional activated sludge plants, the decrease in temperature and the loss of CO_2 associated with pumping the digester effluent have been identified as the factors which enhance struvite precipitation (49).

When operated conventionally, the total phosphorus in the York River digester averaged 340 mg/L, 85% of which was present in chemical precipitates (7). The soluble phosphorus concentration averaged 49 mg/L (6). Calcium precipitates accounted for 65% of the phosphate precipitates; extraction resulted in high molar ratios of Ca:P, suggesting a large presence of calcium carbonates or other non-phosphate calcium precipitates, also (7). The remaining phosphates were associated with magnesium (20%) and iron (15%), primarily in the ferrous state (7). A computer model (discussed later in Chapter III) calculated that the digester was slightly undersaturated with respect to struvite (6).

The introduction of biological phosphorus removal at the facility increased the total phosphorus content of the digester to an average of 1,100 mg/L; only 71% (780 mg/L) was associated with precipitates (7). Soluble phosphorus concentrations increased to 316 mg/L (6). The increases in the phosphorus concentrations are illustrated by Figure 3, taken from Sen (6). The soluble phosphorus increase was more extensive than the metal cation increase (7). The Ca:P ratio decreased, indicating that a greater percentage of the calcium was associated with

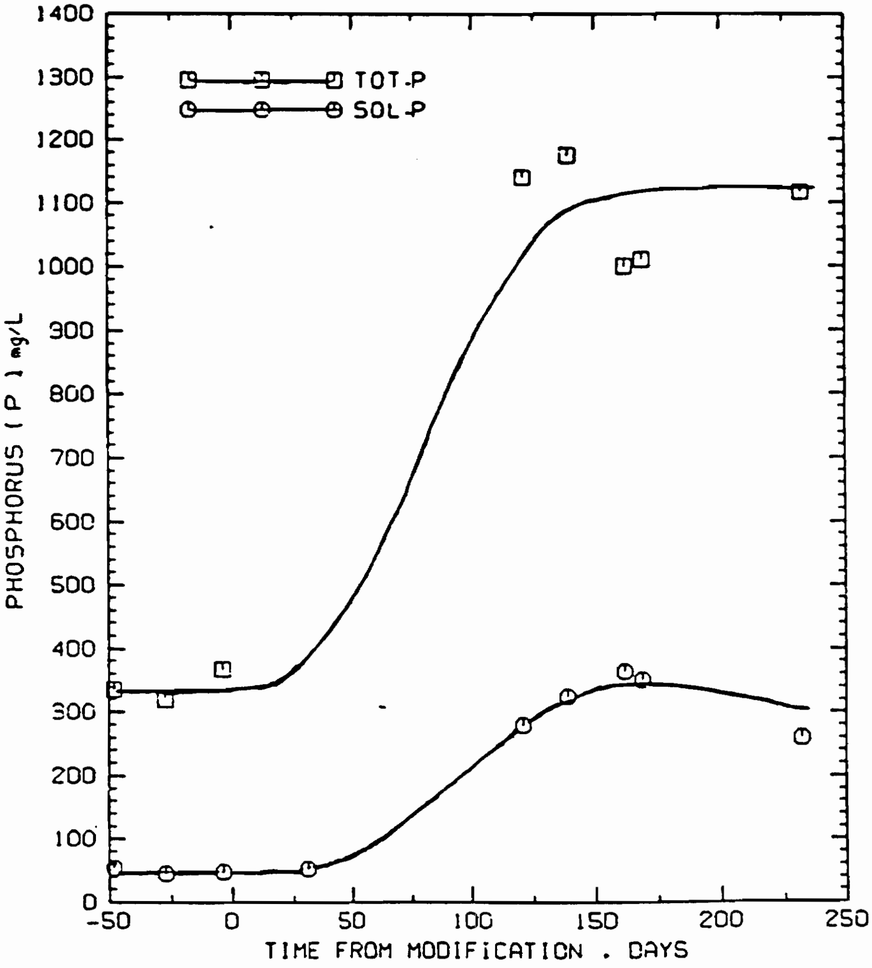

Figure 3. Trend in Total and Soluble Phosphorus Loads in the Primary Digester with Time from BNR Modification (from Sen (6)).

phosphates, but calcium phosphates only accounted for 50% of the phosphate precipitates (7). Struvite precipitates accounted for 30-40% of the remainder (7, 48); vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) accounted for 15%, and ferric phosphate ($FePO_4(s)$) accounted for the last 5% (7). A high percentage of the precipitated struvite was present as microcrystals on the surface of the biomass (48), which seemed to explain why dismantling the digester effluent piping never revealed any struvite deposition (50). It was hypothesized that the high phosphorus levels in the digester and, specifically, in the immediate microenvironment of the bacteria favored the formation of struvite (6). This accelerated local precipitation did not require the pH increase or temperature decrease in the effluent line (6). The soluble magnesium was, therefore, depleted in the primary digester and did not precipitate in the sludge transmission pipes (6).

With the advent of BPR, all of the total metal ion concentrations increased (Ca, Mg, Fe, K, and Na slightly), as shown in Figure 4, taken from Sen (6). The soluble magnesium concentration was constant, and the soluble calcium concentration decreased, as shown in Figure 5, also from Sen (6). This indicated that magnesium and calcium precipitated (48).

Laboratory work by Sen, discussed by Knocke _et al._, (48), simulated the species concentrations present in

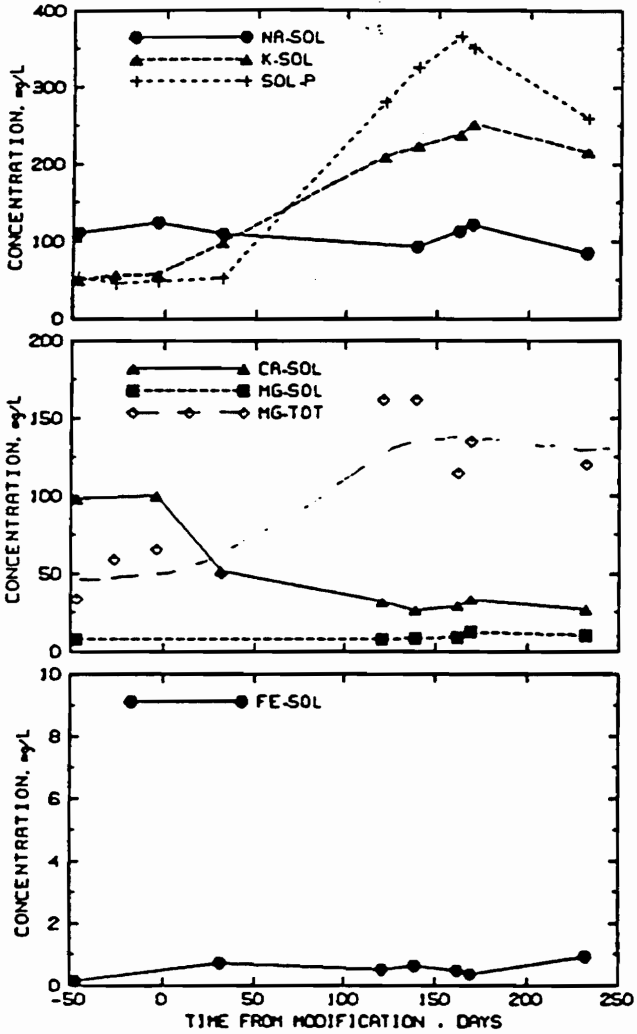

Figure 4. Trend in Soluble Metal Concentrations in the Primary Digester with Time from BNR Modification (from Sen (6)).

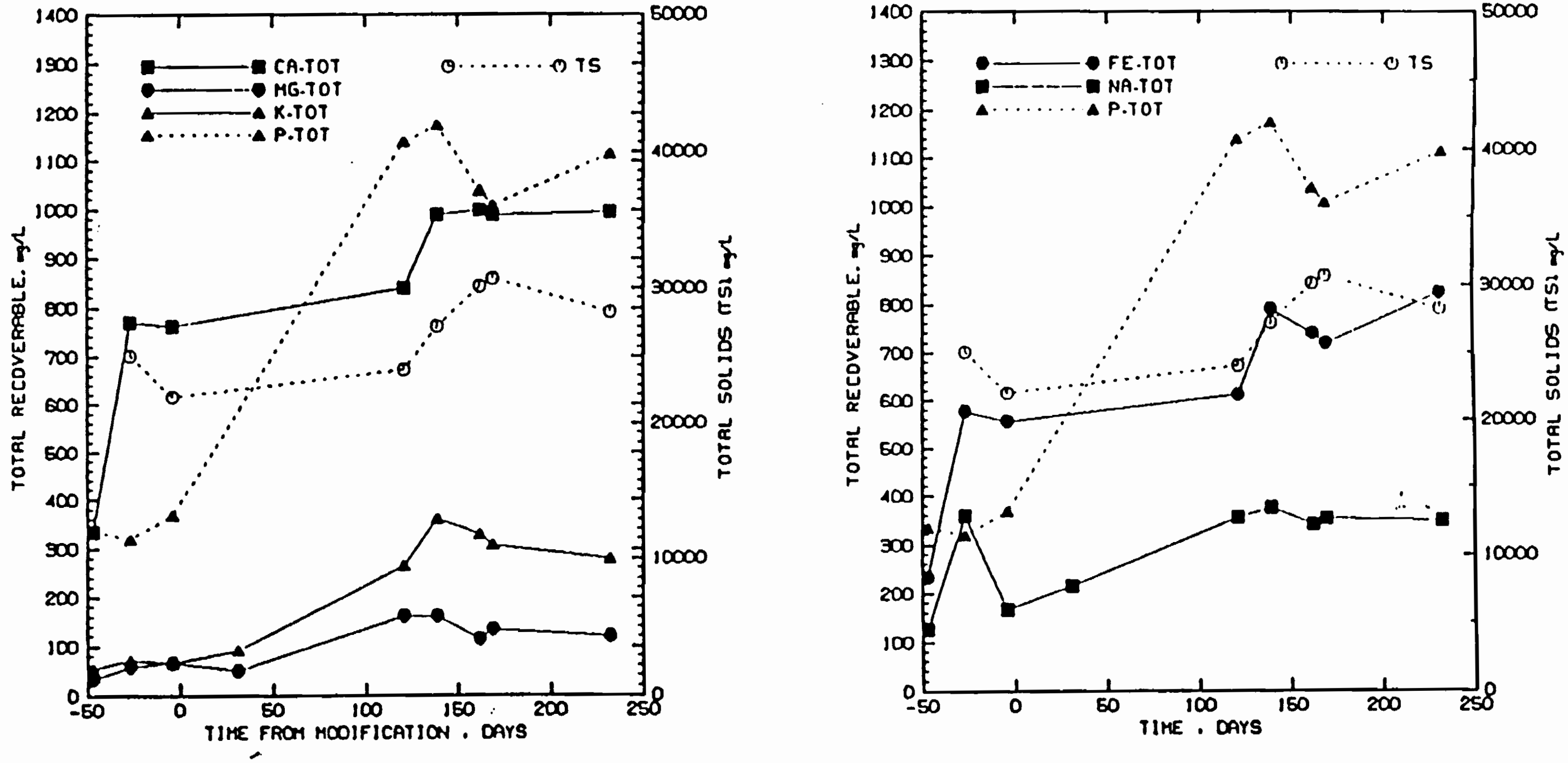

Figure 5. Trend in Total Metal Concentrations in the Primary Digester with Time from BNR Modification (from Sen (6)).

the York River digesters. These studies indicated that struvite formation was kinetically rapid; further, no magnesium precipitates were observed to form in the absence of ammonium. Calcium phosphate precipitates tended to be initially amorphous. Their formation kinetics were slowed by the presence of struvite. The Ca:P ratio for the calcium phosphate precipitates increased from 1 to 1.7 over several days in the presence of struvite; however, calcium phosphate precipitation had no effect on the formation of struvite. Slow rates of calcium phosphate precipitation should result in higher levels of soluble calcium present in the digester than thermodynamics might predict (6). One hypothesized treatment scenario was that waters with higher levels of hardness (especially magnesium hardness) should precipitate more metal phosphates in the digester, reducing the digester effluent soluble phosphorus concentrations and further minimizing the potential for struvite formation in pipes (48).

The effects of anaerobic digestion on iron phosphate precipitates has been studied because of the use of iron coagulants in wastewater treatment. For example, Singer (51) studied facilities that have employed ferric salts addition for orthophosphorus precipitation; little release of phosphorus was noted in the digester (51). Singer also observed lower phosphorus concentrations in the anaerobic digester supernatant of plants using ferric iron addition than was present for plants with no ferric addition. The difference was ascribed to ferrous iron precipitates. Singer further examined primary sludges from several plants using ferrous iron addition by X-ray diffraction analysis. The results showed vivianite precipitates to be present in significant quantities. Anaerobic digestion of these sludges did not release phosphorus. The apparent insolubility of ferric or ferrous phosphate under anaerobic conditions suggests either kinetic stability of ferric phosphate or insolubility of ferrous phosphate (52).

ANAEROBIC DIGESTION AND PHOSPHATE CHEMISTRY

Two models are used for chemical reactions: thermodynamic models and kinetic models. Thermodynamic, or equilibrium, models are more extensively developed than kinetic models because they are simpler and require less information. Thermodynamic models assume homogeneous distributions of material, fixed temperature and pressure,and a specified total number of moles (53). Thermodynamic information enables the user to identify chemical reactions that are possible; however, the rate at which equilibrium is attained cannot be predicted by this information alone (53).

Violations of the assumptions and attempts to predict what compounds are present lead to the use of kinetic models. The lack of detailed kinetic data on the rate and mechanism of the various hydrolysis reactions as they occur in natural waters or wastewater and the constant violation of thermodynamic assumptions make application of chemical models difficult to many systems, and specifically to wastewater treatment (3).

One of the major problems with applying equilibrium calculations to real problems of water chemistry is the large variation in the values of reported equilibrium constants for the same chemical reactions. Only overall solubility trends can be predicted in many chemical systems. The extensive hydrolysis and polynuclear complexes with slow kinetics for specific metals of interest to wastewater treatment (iron and aluminum) only complicate matters further (3).

For a phosphate removal process to be effective, nearly all the phosphate entering the digester must also leave the digester in an insoluble form. Anaerobic digestion of aluminum, ferric, or ferrous phosphate does not release phosphorus. Calcium phosphate precipitates will tend to dissolve at the lower pH values encountered in anaerobic digestion or in the blanket of the secondary clarifier (52).

In biological systems and inorganic model systems, well defined calcium phosphates never form (26) because the rate of attainment of equilibrium is extremely slow

(53). The involvement of impurities and the existence of precursors make the formation of true apatites (for example, hydoxyapatite - HAP - $Ca_5(PO_4)_3OH$, or fluorapatite- FAP - $Ca_5(PO_4)_3F$) rare (6). The solid phase formed incipiently is metastable with respect to a thermodynamically more stable solid phase (53). The Ostwald-Lussac step rule states that the less thermodynamically stable and, hence, the more soluble form, of a polymorphous solid is generally the most readily precipitable (54). Amorphous phosphate precipitates are formed in preference to crystalline ones (54), and the more amorphous the calcium phosphate solid the more soluble it is in solution (26). The active microcrystalline precipitate (with disordered lattice) may persist in metastable equilibrium with the solution and convert (age) only slowly to a more thermodynamically stable form (53). The final solid form is a function of the supersaturation ratio and the physical characteristics of the treatment process that determine the time and conditions under which the sludge ripens into crystalline form (54). Precipitation of calcium phosphate is strongly influenced by the kinetics of nucleation and crystal growth and the chemical composition of the medium (52).

Precursors to the biological apatites (calcium phosphates) are amorphous calcium phosphate (ACP - $Ca_9(PO_4)_6(s)$), beta-tricalcium phosphate (TCP - (Ca-

$Mg)_9(PO_4)_6(s)$ or $ß\text{-}Ca_3(PO_4)_2(s)$), octacalcium phosphate (OCP - $Ca_8H_2(PO_4)_6 \cdot 5H_2O(s)$), and dicalcium phosphate (DCP - $CaHPO_4 \cdot H_2O(s)$) (26). The order of stability at pH 7 and 37° C has been predicted by Nancallos (7) as: hydroxyapatite (HAP) > TCP > OCP > DCP > ACP. Formation of HAP may be direct but only in a solution with low supersaturation (7). Ions in wastewater stabilize the ACP phase; as a result, OCP and substituted apatites may never form (26).

Magnesium stabilizes ACP, leading to TCP instead of HAP formation (7). Magnesium also inhibits nucleation of calcium apatites (7) and is especially good at decreasing the phosphorus removal at pH values less than 9, although whether the mechanism is kinetic or thermodynamic is unclear (41). Magnesium also inhibits calcium carbonate formation, which may increase calcium phosphate precipitation (41). Carbonate decreases the rate of calcium phosphate precipitation (26) by affecting the solubility of phosphate (41). Carbonate can also substitute for phosphate in apatite, which reduces the phosphorus removal and makes the solid more soluble (41). Pyrophosphates strongly inhibit crystal growth and dissolution in part by stabilizing ACP (26). Other inhibitors of HAP formation are zinc, aluminum, and ferric and ferrous iron (7). Fluoride promotes apatite crystal growth and decreases the solubility of apatites (26).

When phosphorus is removed with lime precipitation, the calcium phosphate solid found is often octacalcium phosphate (54). Octacalcium phosphate also best fits the field data for pH trends during phosphorus removal (41). Menar and Jenkins (7) reported that the residual phosphate concentration in wastewater is governed by the calcium phosphate equilibrium and that tricalcium phosphate and hydroxyapatite were the calcium phosphate species precipitated in biological treatment systems. Calcium phosphate precipitation used to achieve high phosphate removals would be compatible with anaerobic digestion and supernatant return (41).

Aluminum precipitates are present only to small degrees in plants that do not utilize alum addition. Aluminum phosphate precipitation is favored thermodynamically and kinetically over aluminum hydroxide precipitation; therefore, aluminum removes phosphorus preferentially, and the complicated chemical considerations associated with calcium and iron do not occur (52). The actual solid formed is probably an amorphous mixture of the hydroxide and the phosphate that would improve phosphorus removal if recycled. Adsorption of ortho-condensed phosphates probably also occurs to further aid phosphorus removal (52).

Iron may be stable in either the ferric or ferrous forms at different points in the waste treatment scheme(52). Ferric iron forms strengite ($FePO_4$ (s)) in the presence of phosphate at an optimal pH of 5, while the optimal pH for ferric hydroxide formation is 9 (7). Both are likely to be present. In anaerobic digestion, reduced ferrous iron is more prevalent (7), and the transformation of ferric iron to ferrous iron should resolubilize the iron, but it remains insoluble apparently as vivianite (51). Ferrous iron may also be present as ferrous hydroxide, ferrous ammonium phosphate and ferrous carbonate (7). Ferrous interactions with phosphorus are not well understood (52). Iron exerts a negative influence on the coprecipitation of phosphate on calcite (55).

Magnesium is most often found in anaerobic digestion as struvite. Another possible precipitate is Newberyite ($MgHPO_4 \cdot 3H_2O$), but the formation of Newberyite is easily inhibited by pyrophosphate, copper, strontium, and manganese (7). The problems associated with formation of struvite have already been mentioned previously.

SUMMARY OF LITERATURE REVIEW

The deleterious effects of phosphorus on water bodies led to the implementation of detergent phosphorus bans and the development of treatment processes to remove phosphorus. The effect of a detergent phosphorus ban on the wastewater treatment plants designed to remove phosphorus biologically had not been previously reported. This study investigated the effect of the phosphorus ban on the influent and effluent of the York River Wastewater Treatment Plant, a biological phosphorus removal plant; other liquid flow streams within the plant were also investigated. The recycle of supernatant from anaerobic digestion at the York River Plant prompted prior work evaluating the digester contents. The present study continued the previous work by reassessing the digester contents.

CHAPTER III

METHODS AND MATERIALS

The research effort was divided into several phases, requiring the analysis of data from several sources. The first phase involved the analysis of historical data (56) collected by Hampton Roads Sanitation District personnel with respect to their routine monitoring of the York River Treatment Plant. These data allowed investigation of the impact of the phosphorus ban on the flows into and throughout the treatment plant. Phosphorus loads, flow magnitudes, and plant operating procedures were all evaluated by the review of this historical data (56). Discussion and conclusions of a previously performed analysis of a partial collection of the data (45) were a part of the information available for this study. The second phase involved measurement of metal, phosphorus, and solids loadings across the York River Wastewater Treatment Plant and in the digesters to generate data for comparison with prior plant sampling data, collected prior to the ban (6, 7). The next phase involved computer modelling with data collected during the second phase. Data and information were often used in several phases of the research.

Description of the York River Treatment Plant

At the time of this study, the York River Wastewater Treatment Plant was operated to treat 6.5 MGD in a biological nutrient removal mode known as the VIP process.The actual influent flow ranged from 6-12 MGD over the course of this study. The influent flow was principally domestic wastewater, with little or no industrial contribution. The wastewater was pumped to the plant from various locations in the Hampton Roads Sanitation District,and may have spent up to 24 hours in the collection system prior to entering the plant. The influent passed through a bar screen, grit chamber, a preaeration basin and then underwent primary clarification. The primary sludge was sent from the bottom of the primary clarifiers to gravity thickeners. The primary clarifier effluent flowed into an activated sludge mixed liquor tank.

The mixed liquor tank had six parallel units, each with a volume of 0.674 million gallons (MG). Prior to the switch to operation for biological nutrient removal in August, 1986, three units were in operation. Two units were modified to allow operation in a biological nutrient removal mode. Various nutrient removal modes have been utilized at the plant. Prior to the phosphorus ban, the plant had been operating in an A2/O mode. The change to the VIP process occurred in February, 1988, but the process was not established until late March due to difficulties with the nitrate recycle. The plant schematic shown in Figure 6 depicts the VIP operation.

The aeration tank effluent was settled in secondary clarifiers. The clarified effluent was then chlorinated and released, with some recycling back into the plant as non-potable water. Secondary sludge was collected from the bottom of the secondary clarifiers and recycled to the head of the anaerobic section as return activated sludge or sent as waste activated sludge to flotation thickeners.

The thickened sludges were then sent to the primary digester. The other flows from the thickeners contributed to the combined head recycle, which combined the thickener flows, belt filtrate flow, septage deliveries, scum concentrator flow, floor drains, plant facilities sewage, and any flows from draining plant units. The combined recycle returned to the plant ahead of the bar screen and grit chamber.

The primary digester was mixed and maintained at 35°C by pumping its mixed liquor through heat exchangers. The mixed liquor from the primary digester was sent into a secondary digester, which operated as a holding tank for sludge. The detention time for each digester was 45 days or more. The underflow from the secondary digester was dewatered in a belt filter press. The belt filtrate, a major part of which was non-potable water used to wash the

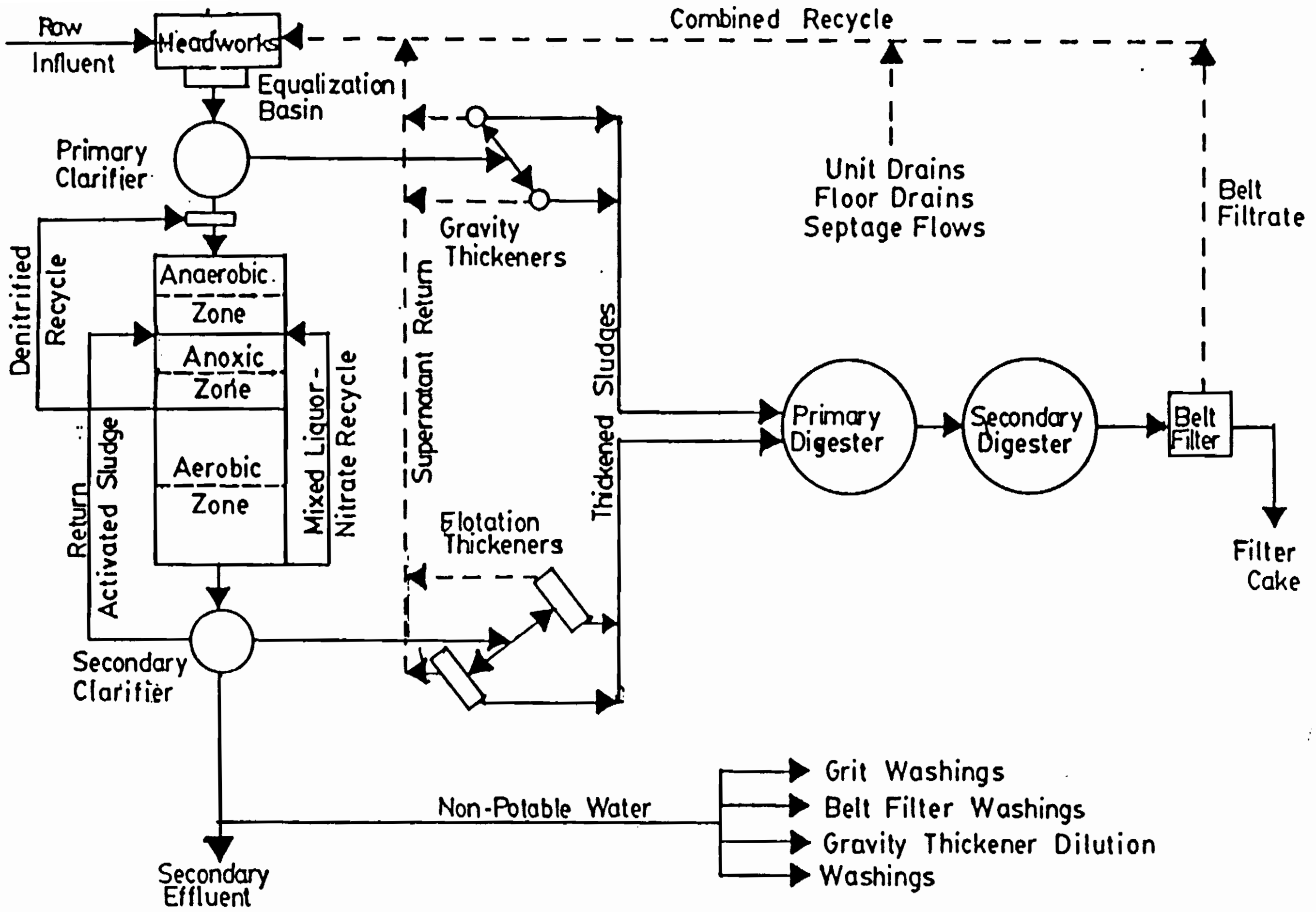

FIGURE 6. Schematic of the York River Wastewater Treatment Plant during VIP Operation.

belts, became part of the combined head recycle. The filter cake was sent to the plant's compost facility. Typical monthly averages for the various waste streams in the VIP process are shown in Table 5.

Plant operation in different treatment modes only required the alteration of recycle lines surrounding the mixed liquor tank. Both the A/O and the A2/O processes did not have the denitrified mixed liquor recycle; instead, the return activated sludge was recycled into the anaerobic zone and not the anoxic zone. The A/O process also omitted the nitrate recycle since nitrogen removal was not part of the process.

The various treatment modes and the dates of their use are shown in Table 6. Variations in the operation of the recycle lines and aeration equipment made actual operation much more variable than the information in Table 6 suggests.

Chemical use in the plant was limited over the course of the biological nutrient removal operation. Chlorine was added to the gravity thickener for odor control on a regular basis. Polymers were added to the belt filter feed for enhanced dewatering and, occasionally, to the secondary clarifier to enhance settling. Ammonia was also added to the secondary clarifier during denitrification transition periods like May, 1988, and June, 1989, in order to maintain a chlorine

Table 5. Average Waste Stream Flows at the York River Wastewater Treatment Plant for November 1988 (56).

Waste Stream	Flow (MGD)
Raw Influent	6.78
Plant Influent	8.03
Denitrified Recycle	7.36
Nitrate Recycle	4.03
Return Activated Sludge	6.27
Waste Activated Sludge	0.081
Primary Clarifier Underflow	0.331
Thickened Primary Sludge	0.014
Gravity Thickener Diluent	0.006
Gravity Thickener Supernatant	0.324
Thickened Waste Sludge	0.017
Flotation Thickener Subnatant	0.064
Primary Digester Feed	0.031
Secondary Digester Underflow	0.027
Belt Filter Feed Sludge	0.027
Belt Filtrate	0.050
Filter Press Wash	0.026
Combined Head Recycle	1.25

Table 6. York River Treatment Plant Operation Scheme and Date of Implementation.

Conventional Activated Sludge		pre August 4, 1986
A/O	--	August 4, 1986
A2/O	--	August 4, 1987
A/O	during modifications[1]	November 11, 1987
VIP	modifications completed	February 10, 1988
"A/O"	nitrate recycle off	February 12, 1988
VIP	nitrate recycle on	March 7, 1988
"A/O"	nitrate recycle off	June 4, 1988
VIP	nitrate recycle on	June 21, 1988

[1] While the necessary modifications for VIP operation were being completed, the plant operated in an A/O mode.

residual. A brief trial of ferric chloride addition to the belt filter feed for dewatering took place in June, 1988. Otherwise, chlorine and sulfur dioxide addition to the plant effluent were the only use of chemicals during the study period.

PHASE I

The relevant historical data from the York River Plant are included in Appendix A. Analysis of the data is also discussed in Chapter IV. Calculations of means and standard deviations were performed by formulae taken from Probability and Statistics for Engineers, by Miller and Freund (57). Data from the four month period of November, 1987, through February, 1988, were excluded from analysis as a transition period for institution of the ban.

The mean values were calculated by averaging the data for the time period under consideration. The standard deviation, s, of each time series was calculated by the equation,

$$s = \sqrt{\frac{\Sigma\ (x_i - x)^2}{n - 1}}$$

Further analysis of the data was attempted by application of the student t-test, but the lack of independence of the data rendered the test inappropriate.

An alternate analysis suggested by the work of Pallesen _et al._, (10) was also applied to the data. This second analysis minimized the sum of the squared differences between adjacent data to create a weighting function for the data. The weighting function accounted for random variation of the datum measurements as well as drift in the data. The short length of the available time series (around 30 data points) was not sufficient to account for the seasonal variation of the data. This resulted in the weighting of the data surrounding the gap (specifically, October, 1987, and March, 1988) to the near-exclusion of the remaining data. This analysis was abandoned since the weighting proved unsuited to the seasonal nature of the York River data. Only the mean values and standard deviations of the data are presented.

Phosphorus concentration values exhibited considerable daily variation; in some instances, values judged not representative were discarded. Judgement relied on the corresponding TSS concentration. For example, the influent total phosphorus data from March, 1987, exhibited two values which were 2 and 4 times greater than other values for that month. These values, 14.94 mg/L on the 3rd and 29.05 mg/L on the 19th, were evaluated based on the corresponding influent TSS concentrations.

The TSS data, 312 mg/L on the 3rd and 86 mg/L on the 19th, were compared to the monthly average of 146 mg/L.

The significantly elevated TSS concentration on the 3rd resulted in the inclusion of the phosphorus concentration of the 3rd in the monthly average as explained below, while the datum from the 19th was excluded. Few data were discarded in this manner; most values were included in monthly averages by weighting the concentration datum based on the estimated number of days the unusual condition existed. Estimation of the number of days for an unusual phosphorus concentration was based on aberrations in TSS concentrations in the same flow. This was necessary because the phosphorus data was generated only 3 days a week, while TSS measurements were taken each day. For example, if the previous example is continued, the phosphorus concentration of the 3rd would be weighted by the number of days of the TSS elevation - in this case one day. The remaining phosphorus concentration data for the month (excluding the datum from the 19th) would be averaged together and multiplied by the remaining number of days in the month, 30. The two products are added, then divided by 31 days to yield an average monthly total phosphorus concentration for inclusion in Appendix A and use in the statistical analysis.

PHASE II

Samples collected during the second phase of the research were analyzed and compared to the previous data collected by Sen (6). Comparisons utilized the two sample t-test to evaluate means from before and after the phosphorus ban. Data from the four month period of November, 1987, through February, 1988, were excluded from analysis as a transition period for institution of the ban.

The t-test formulae and the statistical table of t-values were taken from *Probability and Statistics for Engineers*, by Miller and Freund (57). The formula for calculating the t-statistic was

$$t = \frac{(x_1 - x_2) - d}{\sqrt{(n_1 - 1)s^2 + (n_2 - 1)s^2}} \sqrt{\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}}$$

where x, n, and s represent the mean of the time series, the number of samples in the series, and the standard deviation in the series, respectively. The subscripts represent the different time series involved, usually before and after the phosphate detergent ban. The d represents the difference in the means, which, in all cases, was assumed to be zero. The standard deviation was calculated by the formula previously given.

Sample Sites

Samples were collected at seven sites within the York River Plant. The sites included sampling of the raw influent, the final effluent, the primary and secondary digester contents, the feed to the belt filter press, the belt filtrate, and the filter cake. Sampling occurred on the dates given in Table 7. The sites sampled on each sampling date are shown in Table 8.

The influent sampling site was located in the headworks building of the plant. A valve allowed side stream flow through a small-diameter pipe for sampling of the raw influent. Effluent sampling was accomplished at a flowing pipe outside the chlorination/dechlorination building. The digesters were sampled on the lower floor of the digester building at the sink and spigots provided for sampling. Valve wrenches began the flow of gases and digester contents into the sinks. Prior to sampling, the flows from the digesters were allowed to reach a consistent flow without escaping gases.

The samples surrounding the belt filter press were collected in the large room housing the filter presses. The belt feed from the secondary digester was sampled at the spigot in the upright pipe near the head of the filter presses. Belt filtrate samples were collected by placing the sample bottle under the filtrate and washwater stream

Table 7. Sample Collection Dates at the York River Wastewater Treatment Plant.

Date of Sampling	Abbrev.
March 31, 1989	3/31
April 22, 1989	4/22
May 6, 1989	5/6
May 25, 1989	5/25
June 13, 1989	6/13
June 20, 1989	6/20
July 14, 1989	7/14
August 15, 1989	8/15

Table 8. Sample Collection Sites and Dates of Sample Collection at the York River Wastewater Treatment Plant.

	Date							
Site	3/31	4/22	5/6	5/25	6/13	6/20	7/14	8/15
Plant Influent	X	X	X	X	X	X	--	X
Plant Effluent	X	X	X	X	X	--	X	X
Primary Digester	X	Xs	X	X	X	X	X	X
Secondary Digester	--	X	X	Xs	X	X	X	X
Belt Press Feed	--	X	--	X	X	X	X	--
Belt Press Filtrate	--	X	--	X	X	X	X	X
Belt Filter Cake	--	Xs	--	Xs	Xs	Xs	Xs	Xs

X = sample taken
-- = no sample taken
Xs = sample taken, soluble test not completed

chute at mid-length of the filter presses. Filter cake samples were collected at the scraper of the filter presses and placed into sample bottles.

Sample Collection and Preservation

Sample collection and preservation were dictated by the tests which each sample underwent and the field equipment available. Measurements on each sample, except the filter cake, evaluated dissolved metals (referred to herein as soluble metals), orthophosphate phosphorus (referred to as soluble phosphorus), total recoverable metals (often referred to herein as total metals), total phosphorus, and solids content. The filter cake was evaluated for total metals, total phosphorus, and solids content. The preservation measures suggested by Methods for Chemical Analysis of Water and Wastes (58) for the relevant tests are shown in Table 9.

Solids content tests required no preservation and were collected directly in empty plastic bottles, then refrigerated. Total phosphorus and metals samples were collected in bottles containing the appropriate acid and then refrigerated. Soluble phosphorus and metal samples required filtration as described below.

Table 9. Sample Preservation Guidelines (58).

Test	Volume Required (mL)	Handling	Acid Addition	Maximum Holding Time (days)
Dissolved Metals	200	F	HNO_3, to pH<2	180
Total Recoverable Metals	200	--	HNO_3, 5 mL/L	180
Orthophosphate	50	F, R	--	2
Total Phosphorus	50	R	H_2SO_4 to pH<2	28
Filterable Solids	100	R	--	7
Non-Filterable Solids	100	R	--	7
Volatile Solids	100	R	--	7

F = requires filtration
R = requires refrigeration

Sample Filtration

The soluble tests required filtration as part of preservation. The digester samples, including the belt feed, required centrifugation prior to filtration. Centrifugation and filtration was performed as soon as feasible within 48 hours for all digester samples, usually within 8-24 hours. During transport to the lab, these samples were refrigerated.

Different centrifugation schemes ranging from 5-45 minutes at 12,000-18,000 rpm on a Beckman, Model J-21C centrifuge, created no discernible difference in time required to filter a sample, so short centrifugation times were generally selected. These samples were then filtered sequentially through 1.2mm pore size, 5.5 cm diameter GF/C glass microfibre filter papers (Whatman Ltd., Maidstone, England) and then 0.45mm pore size, 47 mm diameter GN-6 filter papers (Metricel Membrane Filter, Gelman Metricel, Inc.). Occasionally, samples were centrifuged and directly filtered through 0.45mm pore size filters.

The remaining liquid samples - influent, effluent, and belt filtrate - were filtered on-site into two collection bottles. Filtration was achieved with a syringe filter unit and 0.45mm pore size, 25 mm diameter GN-6 filter papers (Metricel Membrane Filter, Gelman Metricel, Inc.). Belt filtrate filtration required a preliminary filtration using a 1.2mm pore size, 2.4 cm diameter, 934-AH filter papers (Whatman Ltd., Maidstone, England). One of the collection bottles contained acid for soluble metal sample preservation, and the other was empty.

Analytical Procedures

The analytical procedures were selected to give results directly comparable to previous work done at the same plant (6, 7).

Calcium, Magnesium, Sodium, Potassium, and Iron

The concentrations of these cations in solution were measured by analyzing the 0.45mm filtered samples using a Model 703, Perkin-Elmer (Norwalk, CN) Atomic Absorption Spectrophotometer. The samples were preserved by acidifying them with concentrated nitric acid.

In order to analyze for the total recoverable metal fraction, a method suggested by USEPA (58) was followed. The samples were digested by adding 5.0 mL of concentrated hydrochloric acid to 100 mL of the sample or an appropriate dilution of it, and boiled to decrease the volume to between 10 and 15 mL. After digestion, the sample was cooled, diluted to 100 mL, and filtered through a coarse filter (Whatman, 7.0 cm diameter, number 4 Qualitative filter paper) to remove the particulate matter. The filtered samples were then analyzed using the Atomic Absorption Spectrophotometer described above.

Phosphorus: Soluble and Total

Soluble phosphorus was measured on the 0.45m filtered samples within 48 hours of sampling. The analysis was conducted according to Standard Methods(59), Section 424F. A new standard curve was generated for each set of samples. The sample concentrations were kept in the range of 0.15 to 1.0 mg/L by controlled dilution in accordance with the 1 cm light path and Standard Method guidelines. The colorimetric measurements were done using a Beckman Instruments, Inc. (Irvine, CA) DU-6 Spectrophotometer with a one centimeter light path at a wavelength of 880 nm.

The total phosphorus content of samples was measured by first using the persulfate digestion method, Section 424C, Standard Methods(59) as a preliminary digestion step; this was followed by the Abscorbic Acid Method, Section 424F, Standard Methods(59) to colorimetrically measure for orthophosphates in the digested sample. The standard curve was again developed for each new set of samples for the same range as the soluble phosphorus measurements.

Solids Determinations

The mixed liquor total solids (TS) concentrations were measured in accordance with Section 209A of Standard Methods (59). Total volatile solids (TVS) were determined by igniting the dried sample (103°C for at least 2 hours) at 550°C for 45 minutes and measuring the difference in sample weight. Total dissolved solids (TDS) were measured by drying a known volume of a filtered sample (0.45 mm pore size filter) at 103 to 105°C for at least two hours.

In samples where the suspended solids content was less than 1000 mg/L, the total suspended solids (TSS) concentration was measured by filtering a known volume through a Whatman (Whatman Limited, Maidstone, England) 934-AH glass fiber filter paper, then drying and weighing the filter. For more concentrated samples, TSS was calculated by subtracting the measured total dissolved solids value from measured total solids value.

PHASE III

Thermodynamic Modelling

A computer model (STRUV1) developed by Sen (18) was used with the gathered data to predict the thermodynamic equilibrium for a number of compounds. The computer model (written in FORTRAN 77) resided on the IBM 3090 Mainframe computer at VPI & SU. The program calculated the degree of supersaturation with respect to 72 compounds, most of which were phosphorus or carbonate precipitates of calcium, magnesium, and/or iron. Ionic strength effects were incorporated in the model.

Data entered into the model for the primary digester simulations included temperature, pH, alkalinity, and concentrations of ammonia, acetate, chloride, and soluble phosphorus, and soluble metal concentrations for iron (ferrous and ferric), calcium, magnesium, potassium, and sodium. The model allowed selection of compounds to be evaluated.

Solubility products for the compounds were calculated in an auxiliary program (STRAUX1) using standard free energies (ΔG^{o}) when available; otherwise, reported Ksp_{25} values were substituted. The auxiliary program avoided unnecessary repetition of calculations. The formula used to calculate Ksp_{25} values from standard free energies was

$$\Delta G^0 = -RT \ln Ksp_{25}$$

where $\Delta G^0 = (\Sigma v_i G^0)_{products} - (\Sigma v_i G^0)_{reactants}$

v_i = stoichiometric coefficient

G^0 = free energy (kJ/mole) at 25^0C and 1 atmosphere

R = universal gas constant

and $T = 298$ K (25^0C).

Temperature corrections on the acid dissociation constants and solubility products were also calculated in the auxiliary program by the Van't Hoff equation

$$\ln \frac{K_{25}}{K_T} = \frac{\Delta H^0}{R} \left(\frac{1}{T_T} - \frac{1}{T_{25}} \right)$$

where $\Delta H^0 = (\Sigma v_i H^0)_{products} - (\Sigma v_i H^0)_{reactants}$

v_i = stoichiometric coefficient

H^0 = enthalpy (kJ/mole) at 25°C and 1 atmosphere

R = universal gas constant

T = temperature in K

and K = solubility product or acid dissociation constant.

The main program utilized the output file from the auxiliary program and the entered digester environment and species information to calculate the degree of supersaturation for the selected compounds. To calculate the supersaturation the model performed the following tasks:

1. It speciated the anionic species based on the pH entered for the system.

2. The ionic strength was calculated iteratively by modification of the hydrolysis constants until successive calculations differed by less than 0.01. The formula used to calculate ionic strength was

$$I = \frac{1}{2} \Sigma C_i Z_i^2$$

where Z_i = charge on a species i

C_i = concentration of the species i.

3. Activity coefficients (f) for ionic strengths less than 0.1 were calculated by the Debye-Huckel formula

$$\log f = - AZ^2 \sqrt{I}.$$

For ionic strengths greater than 0.1 the formula used was:

$$\log f = - AZ^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$$

where $A = 1.82 \times 10^6 (DEC * T)^{3/2}$

DEC = dielectric constant of water, as calculated by extrapolating from a multiple regression fit of values in Table 3.5 of the CRC Handbook of Chemistry and Physics, 65th edition, page 56 (6).

4. The final calculation of the degree of supersaturation was performed on a log scale by subtraction of the log of the calculated solubility product (Ksp) from the log of the reaction quotient (Qsp).

The final outputs of the model were the calculated degrees of supersaturation (expressed in log units) for the selected compounds. Supersaturation values of zero indicated that the compound was approximating thermodynamic equilibrium and the precipitate was likely to be present. A highly negative value indicated the degree of under saturation and probable absence of the compound. A large positive value suggested that the thermodynamic considerations were not sufficient to describe the equilibrium for that compound.

CHAPTER IV

RESULTS

The experimental results are presented in the following subsections in approximately the same order as presented in Chapter III. The treatment plant conditions prior to and after the phosphorus ban were compared by using the calculated mean values and standard deviations of the historical data. All data analyses comparing the conditions in the primary digester prior to and following the implementation of the ban were completed using the two-sample student t-test. The confidence interval used in the t-test was 95%. The t-test was limited by the assumption of independence of monthly averages, but attempts to use another statistical analysis were severely affected by the small number of values available for the time series. Seasonal variations and datum spikes distorted the alternate intervention analysis; however, these variations had much less effect on the t-test.

Data came from the monthly averages calculated from the data supplied by the York River Plant from July, 1986, to July, 1989 (included as Appendix A), and the data from Sen (6) in Appendix B. Data collected during the present study are included in Appendix C. A four month gap (November, 1987, through February, 1988) was omitted as a transition period for comparing data before and after the phosphate ban. Since composite phosphorus sampling began in November, 1986, many analyses began with that month. Additional months were omitted for the statistical tests when data were not available.

COMPARISON OF THE PRE- AND POST-BAN PLANT PERFORMANCE

The York River Wastewater Treatment Plant performance was evaluated using the historical data gathered by the plant personnel (Appendix A). Influent flow data for the period from November, 1986, to July, 1989, are shown in Figure 7. This period was selected to coincide with the beginning of composite sample analyses for phosphorus concentrations. The calculated mean value for the influent flow was higher in the post-ban period than in the pre-ban period. The calculated mean values were 7.77 MGD before the ban, and 8.21 MGD after the ban, for a calculated 5.7% increase in flow. The calculated mean values and standard deviations are shown in Table 10. The increase in flow was hypothesized to be due to an increase in the number of customers discharging into the sewer system, and, in part, from the wet early months of 1989.

Data for soluble and total influent phosphorus concentrations for the treatment plant are shown in Figure 8. The mean values and standard deviations for influent phosphorus concentrations before and after the

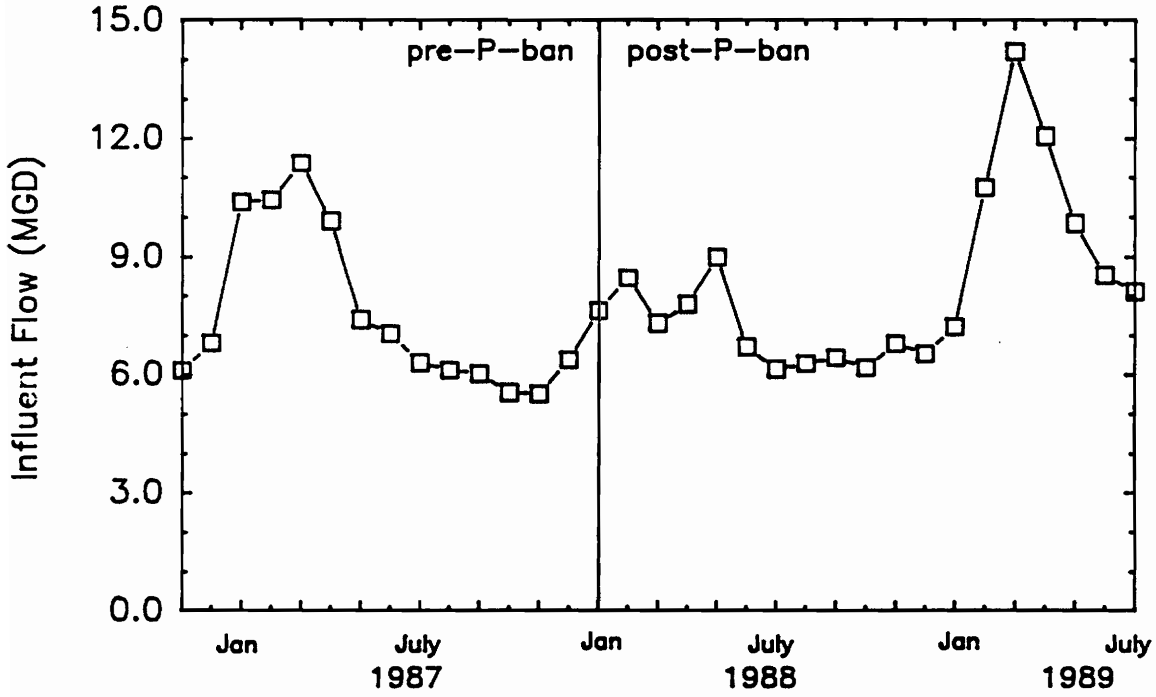

Figure 7. York River Wastewater Treatment Plant Average Monthly Raw Influent Flow

Table 10. Influent and Effluent Phosphorus Data Mean Values and Standard Deviations

	Time Period	Mean	St.Dev
Raw Influent Phosphorus Load			
pre-ban	11/86-10/87	583	176
post-ban	3/88-7/89	428	107
Raw Influent Flow			
pre-ban	11/86-10/87	7.77	2.34
post-ban	3/88-7/89	8.21	1.09
Raw Influent Total Phosphorus Concentration			
pre-ban	11/86-10/87	9.34	2.82
post-ban	3/88-7/89	6.54	1.63
Raw Influent Soluble Phosphorus Concentration			
pre-ban	11/86-10/87	6.64	2.00
post-ban	3/88-7/89	4.19	1.05
Effluent Phosphorus Load			
pre-ban	11/86-10/87	229	69
post-ban	3/88-7/89	106	27
Effluent Flow			
pre-ban	11/86-10/87	7.38	2.22
post-ban	3/88-7/89	8.20	2.05
Effluent Total Phosphorus Concentration			
pre-ban	11/86-10/87	3.76	1.13
post-ban	3/88-7/89	1.55	0.39
Phosphorus Load Removal			
pre-ban	11/86-10/87	354	107
post-ban	3/88-7/89	322	81

Notes: Loads are in lbs/day; Concentrations are in mg/L.
Flow is in million gallons per day (MGD).

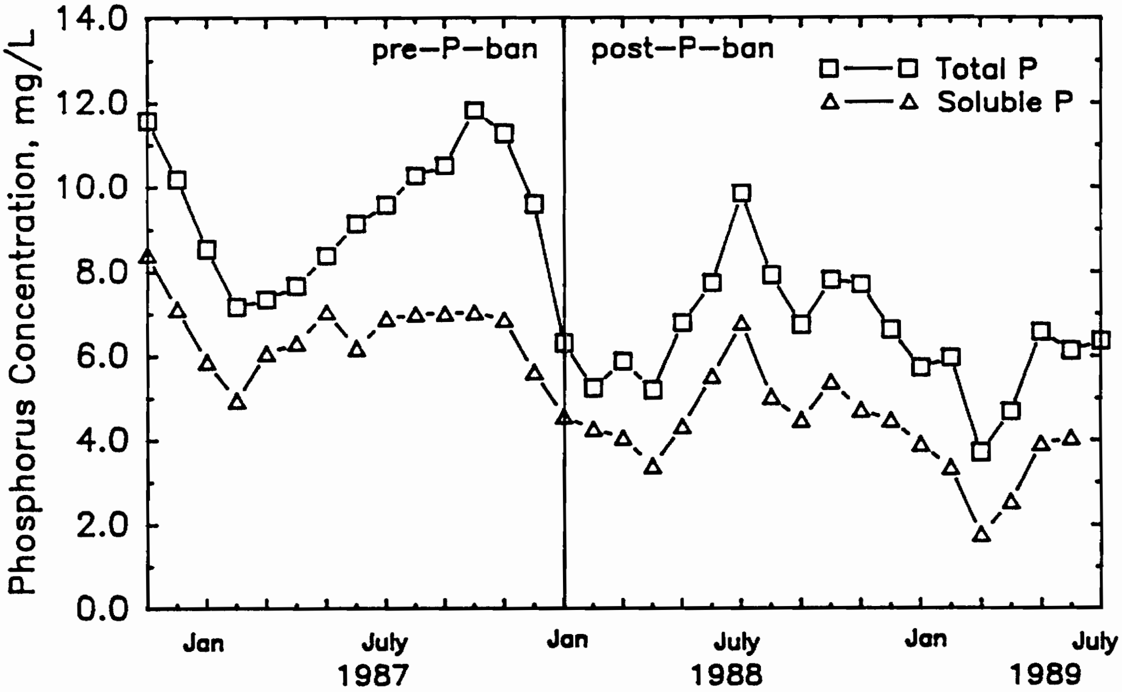

Figure 8. York River Wastewater Treatment Plant Average Monthly Raw Influent Phosphorus Concentrations

ban are included in Table 10. The mean total phosphorus concentration decreased from 9.34 mg/L to 6.54 mg/L. The 2.80 mg/L decrease in total phosphorus represents a 30% reduction. The mean soluble phosphorus concentration decreased over the time of the ban implementation from 6.64 mg/L to 4.19 mg/L. This 2.45 mg/L decrease was a 37% decrease. The decrease in the soluble portion of the influent phosphorus equals 87.5% of the reduction in the total phosphorus concentration. The increased rainfall accounts for part of the decrease because of dilution; but assuming that all of the flow increase was due to increase drain only reduces the effect of the ban to 25% and 32% decreases in total and soluble phosphorus, respectively.

The phosphorus loads entering the York River Plant were calculated from the flow and concentration data presented above, and are shown in Figure 9. The mean value for influent phosphorus load decreased as a result of the ban; mean values pre-ban and post-ban, respectively, were 583 lbs/day, and 428 lbs/day, for a reduction of 155 lbs/day or 27%. These data are shown in Table 10. The phosphorus ban apparently resulted in a decrease in the influent phosphorus load to the York River Wastewater Treatment Plant on the order of 27 percent.

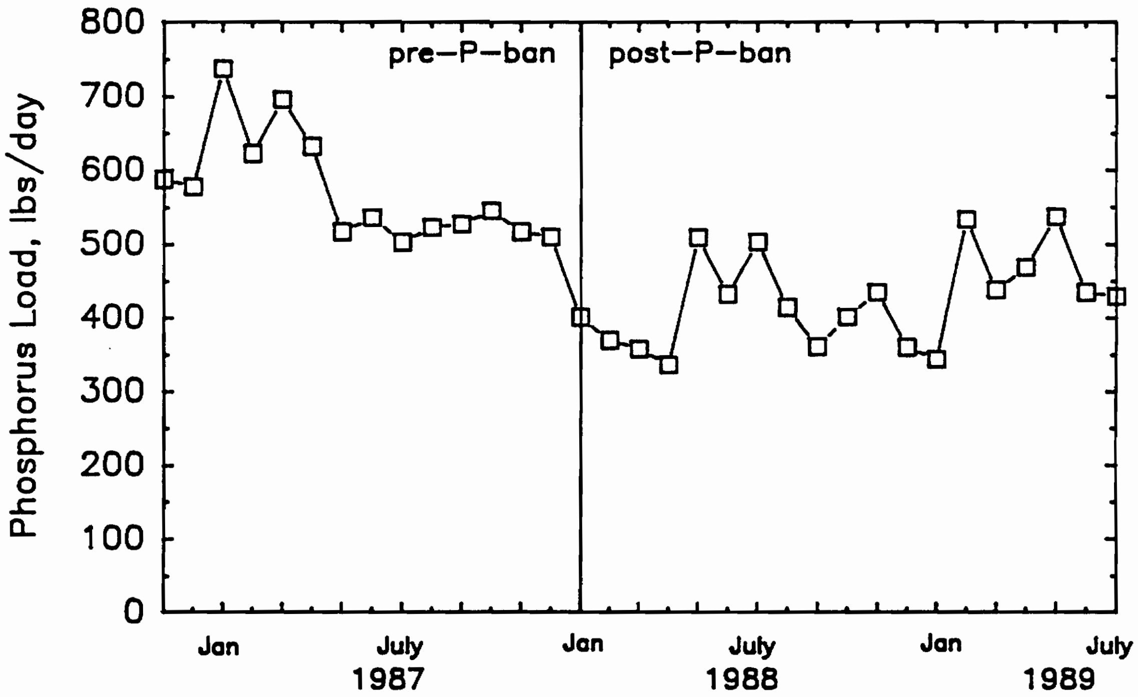

Figure 9. Average Monthly Influent Phosphorus Load to the York River Wastewater Treatment Plant

Analysis of the effluent attempted to evaluate the effect of the reduced influent phosphorus load on the phosphorus load discharged from the plant. The effluent phosphorus load discharged from the treatment plant was again calculated using the flow and phosphorus concentration data. For effluent flow, the calculated mean value was higher in the post-ban period than in the pre-ban period (shown in Table 10). The calculated mean values were 7.38 MGD before the ban, and 8.20 MGD after the ban, an 11% increase.

The effluent phosphorus concentration mean values decreased from 3.76 mg/L to 1.55 mg/L. The decrease, when attributed to the phosphorus ban, becomes a 2.21 mg/L decrease in total phosphorus, a 59% reduction. This reduction was 79% of the reduction in the influent total phosphorus concentration, suggesting that most of the decrease may have carried through the treatment process to impact on the effluent. The 20+% that did not impact the effluent may indicate a decrease in treatment performance. The influent and effluent total phosphorus concentrations are graphed together in Figure 10.

The calculated effluent phosphorus load was graphed in Figure 11, with the calculated mean values and standard deviations for the pre- and post-ban periods included in Table 10. The pre-ban effluent phosphorus load mean value, 229 lbs/day, and post-ban load mean

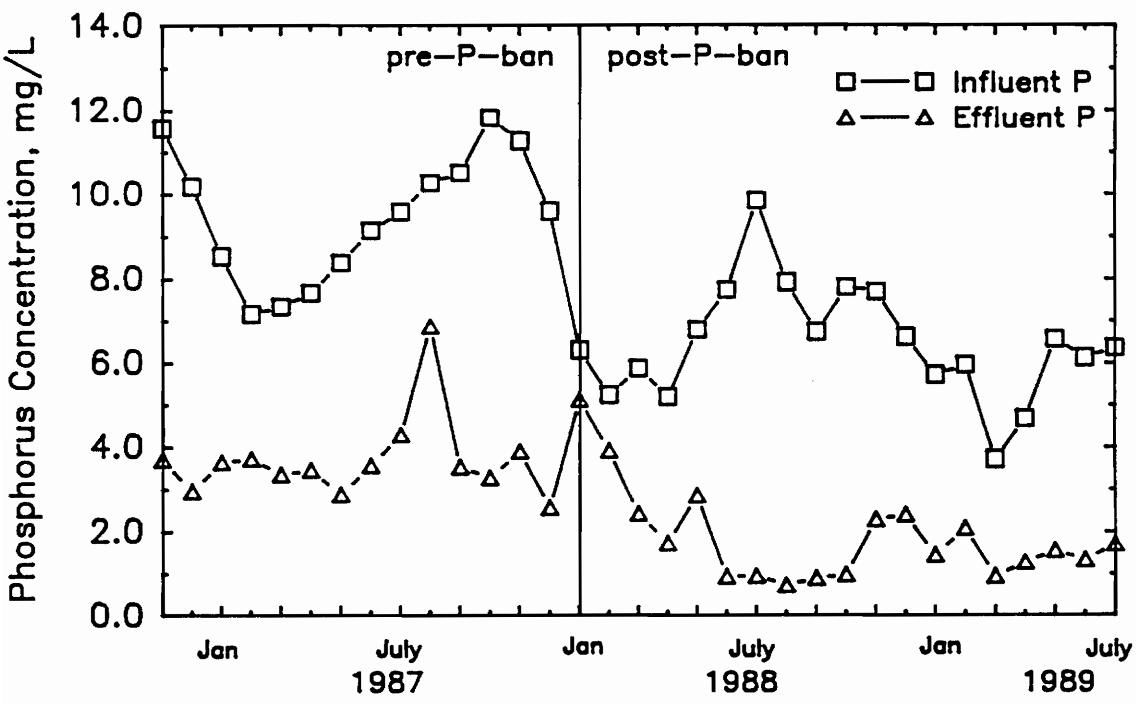

Figure 10. York River Wastewater Treatment Plant Average Monthly Influent and Effluent Phosphorus Concentrations

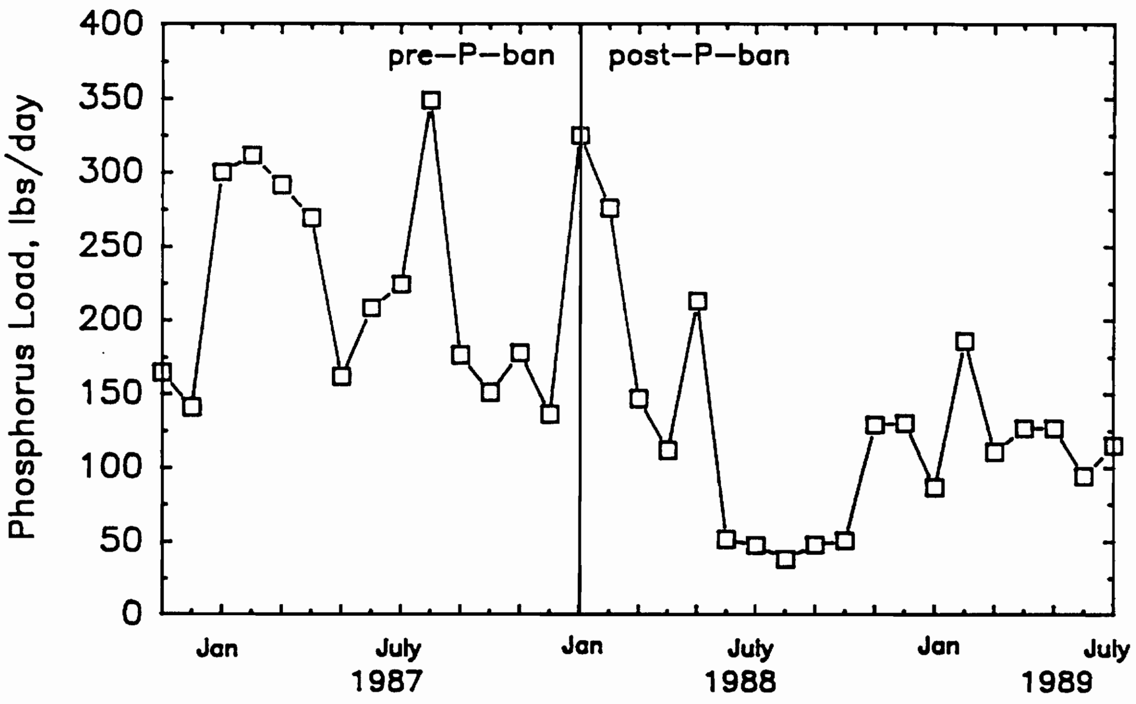

Figure 11. Average Monthly Effluent Phosphorus Load from the York River Wastewater Treatment Plant

value, 106 lbs/day, reflecting a 54% decrease; but the impact of the ban cannot be clearly assessed because of operational changes which were undertaken concurrent with the ban which may have impacted the effluent load. Assuming the operational changes did not alter phosphorus removal by the plant would lead to a calculated decrease of 123 lbs/day in the phosphorus discharge. This decrease represents 79% of the decrease in the influent total phosphorus. The difference between the influent and effluent load changes due to the ban implies that the removal of phosphorus within the plant has been altered by the ban and operational changes.

The difference between the two loads was evaluated as the plant removal. The phosphorus removed was calculated by subtracting the effluent phosphorus load from the influent phosphorus load. The phosphorus removed (lbs/day) is graphed in Figure 12. The mean values pre-ban and post-ban, respectively, were 354 lbs/day, and 322 lbs/day, for a reduction of 32 lbs/day or 9%. The apparent (though slight) decrease in phosphorus removed suggests a decrease in the treatment effectiveness, but the size of the decrease makes conclusions concerning the the removal before and after the ban impossible.

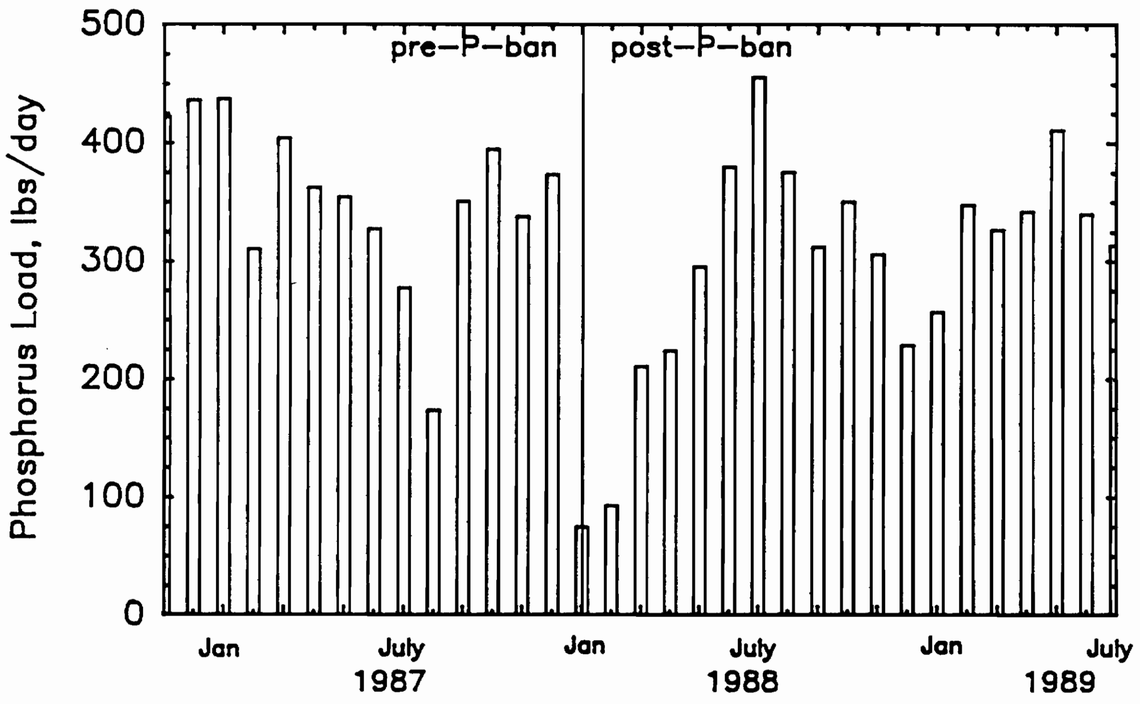

Figure 12. Average Monthly Phosphorus Load Removed by the York River Wastewater Treatment Plant

COMPARISON OF THE PRE- AND POST-BAN PRIMARY DIGESTER LOADS

The primary digester loads were evaluated using the historical data gathered by the plant personnel (Appendix A). The loading to the digester comes from two sources, the gravity thickener and the flotation thickener. The gravity thickener receives the primary sludge from the primary clarifier. Phosphorus may exit the thickener in a supernatant stream which recycles back to the head of the plant, and in the underflow which goes to the primary digester. The flotation thickener receives the secondary sludge which flows to the primary digester, while the thickener subnatant recycles to the head of the plant.

The nutrient removal changes instituted in August,1986, were assumed for this study to have affected the phosphorus loads to the gravity thickener and the flotation thickener in January, 1987, and September, 1986, respectively, and so data analysis began at these dates. Figures 13 and 14 show the phosphorus load entering each thickener. The gravity thickener influent phosphorus load had to be calculated by subtracting the calculated phosphorus load in the primary effluent from the calculated total phosphorus entering the primary clarifier (influent phosphorus plus the recycle phosphorus load). The phosphorus entering the flotation

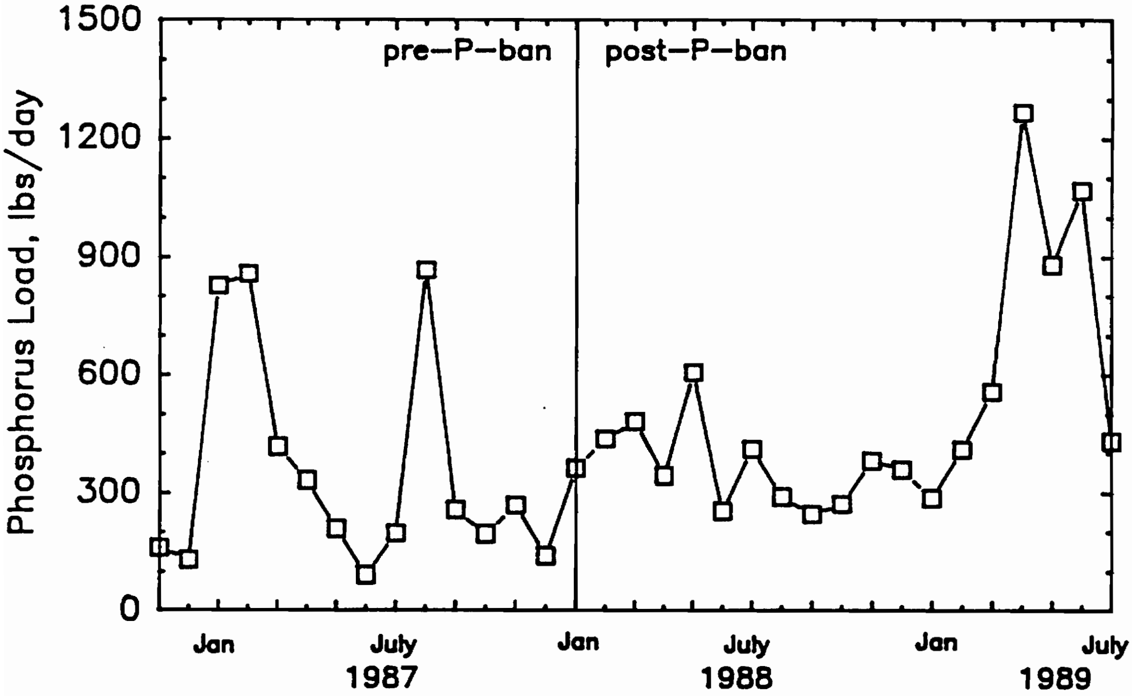

Figure 13. Average Monthly Phosphorus Load Entering the Gravity Thickener at the York River Wastewater Treatment Plant

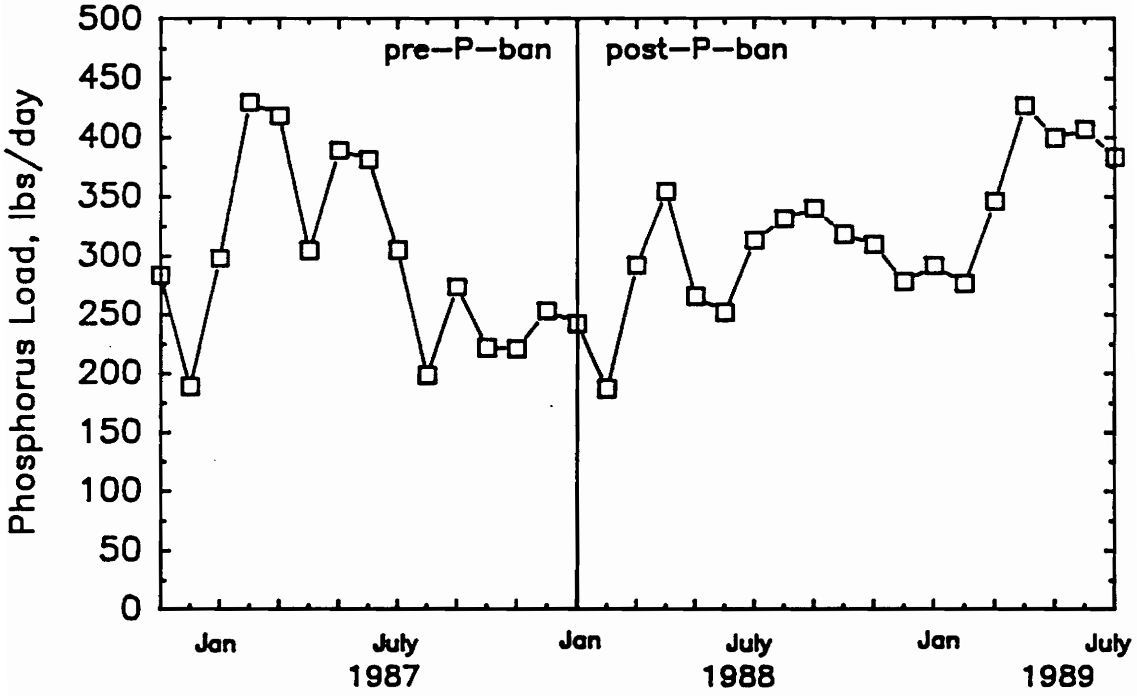

Figure 14. Average Monthly Phosphorus Load Entering the Flotation Thickener at the York River Wastewater Treatment Plant

thickener was calculated by multiplying the waste sludge flow by the phosphorus concentration of the return activated sludge.

Analysis of the phosphorus loads entering the thickeners indicated only small changes over the time of the ban for either thickener. Both thickeners did trend upward, however. The mean values and standard deviations are included in Table 11. The gravity thickener influent phosphorus load went from 424 lbs/day to 494 lbs/day, a 17% increase. The flotation thickener mean influent phosphorus load increased from 306 lbs/day to 328 lbs/day, only a 7% increase. Both thickeners were subject to wide daily and monthly variability in phosphorus load which is reflected by the standard deviations for the thickeners. This variablility did not change from the pre-ban to the post-ban periods as shown by the similar standard deviations in each period for each thickener.

The phosphorus loads transferred from the thickeners to the primary digester were calculated by subtracting the supernatant or subnatant phosphorus load (as appropriate) from the phosphorus loads entering each thickener. The phosphorus loads sent to the primary digester increased after the phosphorus ban. The t-test information for both thickeners is included in Table 11. Prior to the ban, the gravity thickener delivered a mean phosphorus load of 323 lbs/day to the primary digester.

Table 11. Thickener Phosphorus Load Data Mean Values and Standard Deviations

	Time Period	Mean	St.Dev
Gravity Thickener Phosphorus Load			
pre-ban	1/87-10/87	424	141
post-ban	3/88-7/89	494	124
Flotation Thickener Phosphorus Load			
pre-ban	9/86-10/87	306	85
post-ban	3/88-7/89	328	82
Gravity Thickener Transfer Phosphorus Load			
pre-ban	1/87-10/87	323	107
post-ban	3/88-7/89	418	105
Flotation Thickener Transfer Phosphorus Load			
pre-ban	9/86-10/87	272	76
post-ban	3/88-7/89	313	78
Primary Digester Phosphorus Load			
pre-ban	1/87-10/87	611	204
post-ban	3/88-7/89	731	183

Notes: Loads are in lbs/day.

After the ban, 418 lbs/day, or 30% more phosphorus went to the primary digester. The flotation thickener phosphorus load to the digester changed considerably less than the gravity thickener load, from 272 lbs/day to 313 lbs/day, or 41 lbs/day, a 15% increase. The phosphorus loads transferred from the thickeners are graphed in Figures 15 and 16. The increases in the phosphorus loads leaving the thickeners and entering the primary digester could not have resulted from the phosphorus ban but resulted from the operational changes.

To further evaluate the increases in the delivery of phosphorus from the thickeners to the digester while the influent phosphorus to the plant decreased, the TSS loads into the thickeners and digester were calculated. The TSS loads entering the gravity thickener were estimated based on the raw influent and primary effluent TSS loads, and ignoring any contribution from the recycle flows (because data was not available). The flotation thickener TSS load was calculated based on the waste sludge flow and the return activated sludge suspended solids concentration. The results from the mean value and standard deviation calculations for the TSS loads are included in Table 12. The primary effluent TSS load decreased by 3% in the post-ban period compared to the pre-ban period. Combined with the earlier observation that more TSS entered the plant, the decrease in TSS

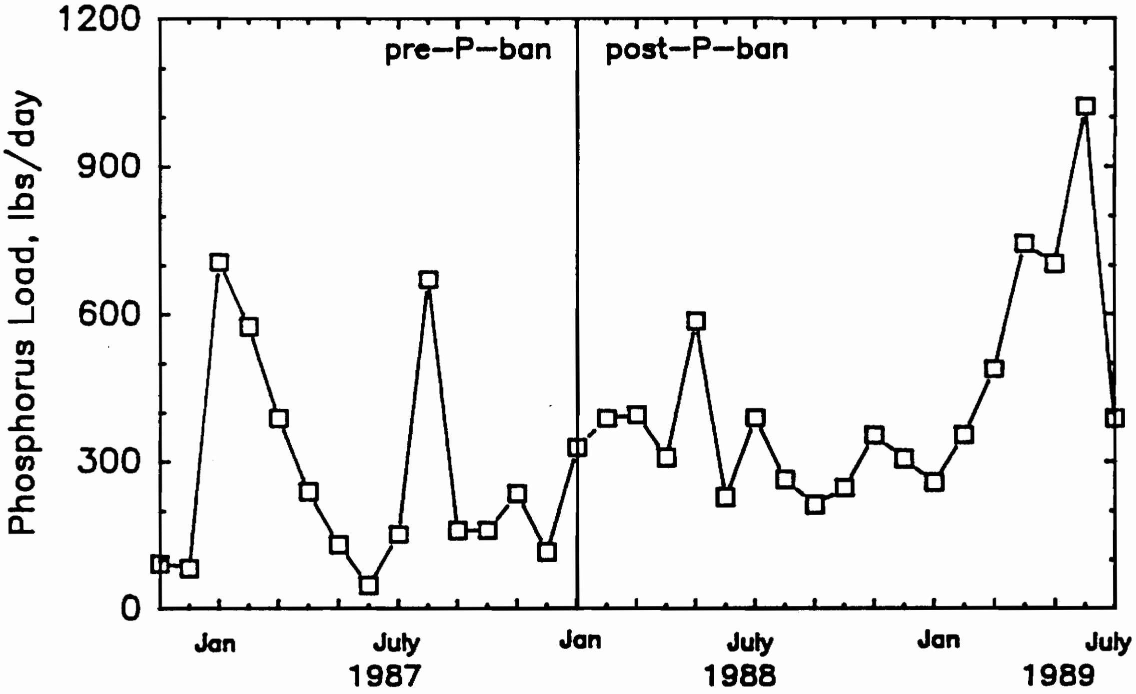

Figure 15. Average Monthly Phosphorus Load Transferred from the Gravity Thickener to the Primary Digester at the York River Wastewater Treatment Plant

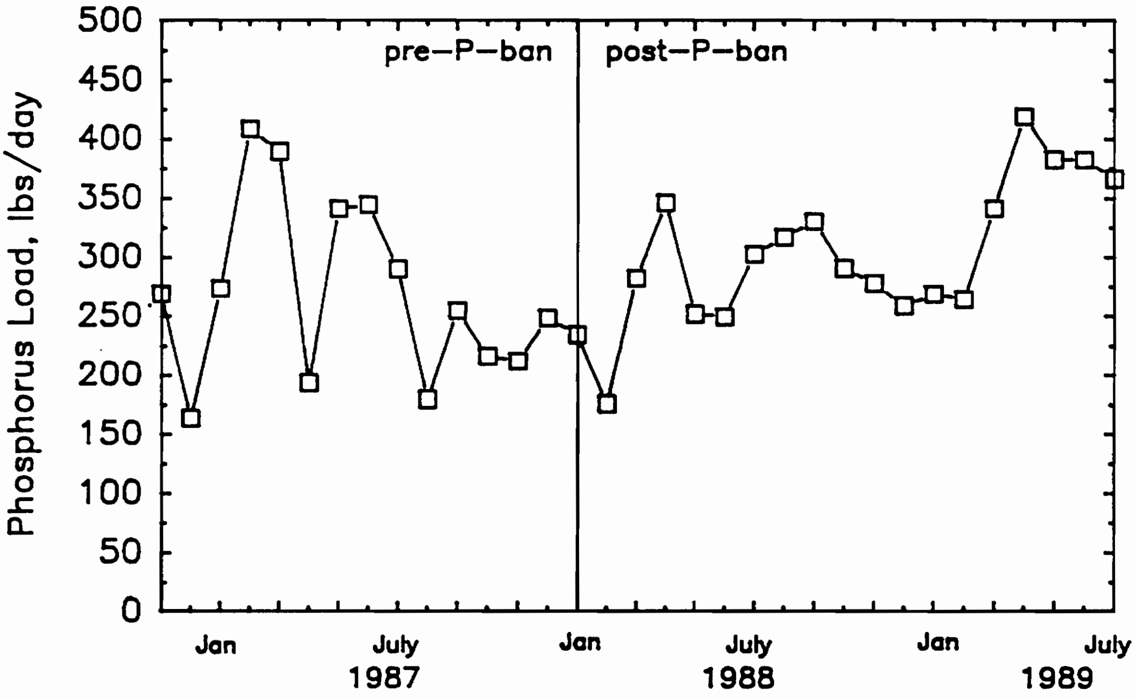

Figure 16. Average Monthly Phosphorus Load Transferred from the Flotation Thickener to the Primary Digester at the York River Wastewater Treatment Plant

Table 12. Thickener TSS Load Data Mean Values and Standard Deviations

	Time Period	Mean	St.Dev
Primary Effluent TSS Load			
pre-ban	9/86-10/87	6,870	1,910
post-ban	3/88-7/89	6,550	1,640
Primary Sludge (Gravity Thickener Influent) TSS Load			
pre-ban	9/86-10/87	5,750	1,660
post-ban	3/88-7/89	6,430	1,610
Gravity Thickener Supernatant TSS Load			
pre-ban	9/86-10/87	2,580	720
post-ban	3/88-7/89	2,700	680
Secondary Sludge (Flotation Thickener Influent) TSS Load			
pre-ban	9/86-10/87	4,080	1,130
post-ban	3/88-7/89	6,320	1,580
Flotation Thickener Supernatant TSS Load			
pre-ban	9/86-10/87	144	40
post-ban	3/88-7/89	61	15
Flotation Thickener Transfer TSS Load			
pre-ban	9/86-10/87	3,930	1,090
post-ban	3/88-7/89	6,260	1,560

Notes: Loads are in lbs/day.

leaving in the primary clarifier effluent required an increase in the TSS in the primary sludge and therefore entering the gravity thickener. The calculated increase in TSS to the gravity thickener, as shown in Table 12, was 12%. The supernatant TSS load increased by 120 lbs/day (5%), which when coupled with the 680 lbs/day increase in TSS load to the thickener, results in a calculated increase of 560 lbs/day (from 3,170 lbs/day to 3,730 lbs/day) of TSS to the digester.

The flotation thickener TSS load increased 55% after the ban, from 4,080 lbs/day to 6,320 lbs/day. This increase, as shown in Table 12, can be attributed in part to an increase in the secondary (waste) sludge and in part to an increase in the sludge suspended solids concentration. The subnatant TSS load decreased significantly from 144 lbs/day to 61 lbs/day, but compared to the magnitude of the total load involved this change is inconsequential. The decrease in the standard deviation of the subnatant load does indicate that the thickener was operated more efficiently in the post-ban period. The TSS load to the digester from the flotation thickener increased significantly over the time of the ban. The increase, as shown in Table 12, was from 3,930 lbs/day to 6,260 lbs/day. The calculated increase in total TSS delivered to the primary digester from both thickeners over the time of the ban was 2,880 lbs/day, a 41% increase, from 7,100 lbs/day to 9,980 lbs/day.

A comparison of the changes in the phosphorus loadings and the TSS loadings around the thickeners is summarized as Table 13. The increases in the TSS loads surrounding the thickeners offer a partial explanation of the increase in the phosphorus loads to and from the thickeners despite a phosphorus ban. The disparity between the TSS and phosphorus increases for the flotation thickener influent and transfer loads indicated the impact of the phosphorus ban on the biological accumulation of phosphorus by the secondary sludge at the York River Plant. The gravity thickener was clearly not affected in the same manner.

The phosphorus load delivered to the primary digester through the thickened sludges was calculated from the plant data presented previously beginning from January, 1987, to exclude data prior to "equilibrium" in both sludge thickeners. The total phosphorus load to the digester is shown in Figure 17 as the sum of the two thickener transfer loads. The calculated mean value prior to the ban was 611 lbs/day, and after the ban the mean value was 731 lbs/day, a difference of 120 lbs/day, or 20%. The increase would appear to be in part due to increased loads entering both thickeners and, in part, to a decrease in loss of phosphorus in the super- and

Table 13. Thickener Phosphorus and TSS Load Percent Changes

Flow Stream		Phosphorus	TSS
Influent	GT	+17	+12
	FT	+7	+55
-Natant	GT	-25	+5
	FT	-56	-58
Transfer	GT	+30	+18
	FT	+15	+59

GT = Gravity Thickener; FT = Flotation Thickener

All percentages are calculated based on lbs/day.

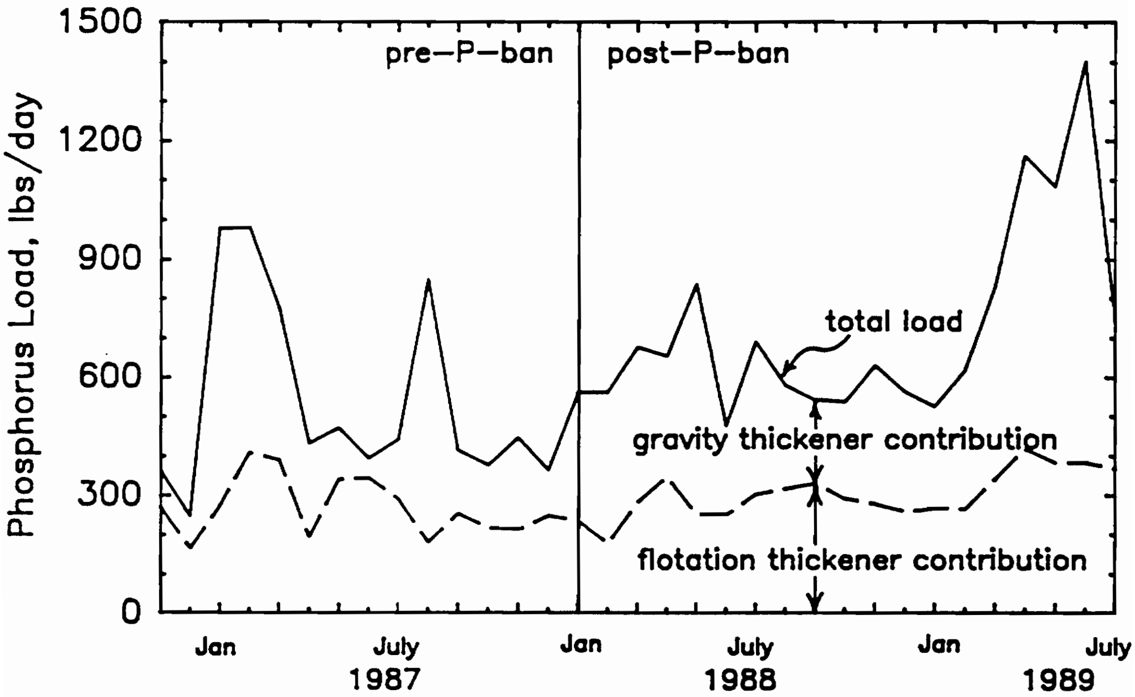

Figure 17. Average Monthly Sum of the Phosphorus Loads from the Thickeners to the Primary Digester at the York River Wastewater Treatment Plant

subnatants of the thickeners. Though the estimated TSS load to the digester increased 41%, as discussed in the previous paragraph, the phosphorus load increased only 20%.

EFFECTS OF THE PHOSPHORUS BAN ON BELT FILTRATE AND RECYCLE FLOWS

Another indicator of the phosphorus in the primary digester is the phosphorus load exiting the digester. The underflow of the primary digester goes to a second digester for holding prior to dewatering on a belt filter press. The phosphorus in the filtrate from the belt filter press reflects the soluble phosphorus concentration in the digesters. Verification that the belt filter press feed from the secondary digester is adequate to describe the contents of the primary digester is discussed later.

Belt filtrate sample collection requires sampling a filtrate-filter press washwater mixture which dilutes the filtrate samples. The dilution flow as a percent of the total filtrate flow before and after the phosphorus ban decreased 14% as shown in Table 14. Evaluation of the filtrate concentrations, total and soluble, before and after the phosphorus ban, indicated that neither concentration had changed significantly as a result of the ban. The mean total phosphorus concentration

Table 14. Filtrate, Recycle, and Process Data Mean Values and Standard Deviations

	Time Period	Mean	St.Dev
Filter Dilution Flow (as a percentage of the filtrate flow)			
pre-ban	11/86-10/87	0.51	0.15
post-ban	3/88-7/89	0.44	0.12
Belt Filtrate Total Phosphorus Concentration			
pre-ban	11/86-10/87	125	38
post-ban	3/88-7/89	140	37
Belt Filtrate Soluble Phosphorus Concentration			
pre-ban	12/86-10/87	109	33
post-ban	3/88-7/89	113	30
Combined Head Recycle Phosphorus Load			
pre-ban	1/87-10/87	669	223
post-ban	3/88-7/89	579	145
Treatment Process Phosphorus Load			
pre-ban	1/87-10/87	1,250	420
post-ban	3/88-7/89	1,010	250

Notes: Loads are in lbs/day; Concentrations are in mg/L.

increased slightly from 121 mg/L to 137 mg/L while the mean soluble phosphorus concentration went from 106 mg/L to 113 mg/L. These modest increases of 13% and 7% agree with the idea that the phosphorus load to the digester had not changed to a large degree as a result of the ban. The similar percent decrease in the dilution flow may account for the modest increases in the measured concentrations. These mean values and standard deviations for these measurements are also included in Table 14.

The combined head recycle combines the belt filtrate flow and the supernatant and subnatant flows from the thickeners with several unmeasured streams and returns them to the head of the treatment process. The treatment process receives the combined phosphorus load of the influent and the combined head recycle. The average combined recycle flow contributes slightly more phosphorus to the system than the influent load. The recycle phosphorus contribution also has a propensity to generate high peak loads due to the intermittent nature of the recycle flows. The flows which are not measured and enter the plant by way of the combined recycle include flows from the scum concentrator, floor drains, septage deliveries, and drains to empty units at the plant. These unmeasured flows account for roughly a third of the total phosphorus load entering the treatment process, with the bulk of the load coming from emptying the secondary clarifiers or the sludge thickeners. The total phosphorus load to the process is shown in Figure 18 as the sum of the influent load and the combined recycle load, both the measured and unmeasured portions.

The combined recycle and the treatment process phosphorus loads had not changed greatly since the ban, but both loads had decreased. The mean values are shown in Table 14. The combined recycle mean value decreased from 669 lbs/day before the ban to 579 lbs/day after the ban, a reduction of 13%. The plant process phosphorus load was reduced 240 lbs/day, or 20%, by the ban, decreasing from 1250 lbs/day to 1010 lbs/day.

EFFECTS OF THE PHOSPHORUS BAN ON THE CONTENTS OF THE PRIMARY DIGESTER

The comparisons of pre- and post-ban data for concentrations of phosphorus and selected cations within the primary digester are shown as Tables 15, 16 and 17, along with the t-test parameters and results. Pre-ban data came directly from Sen (6) and are included in Appendix B; post-ban data (generated for this study) are included in Appendix C. The data points from both studies were few and acquired over a much shorter period of time than the data for the previous analyses. The data were compared for evaluation of the phosphorus ban on the

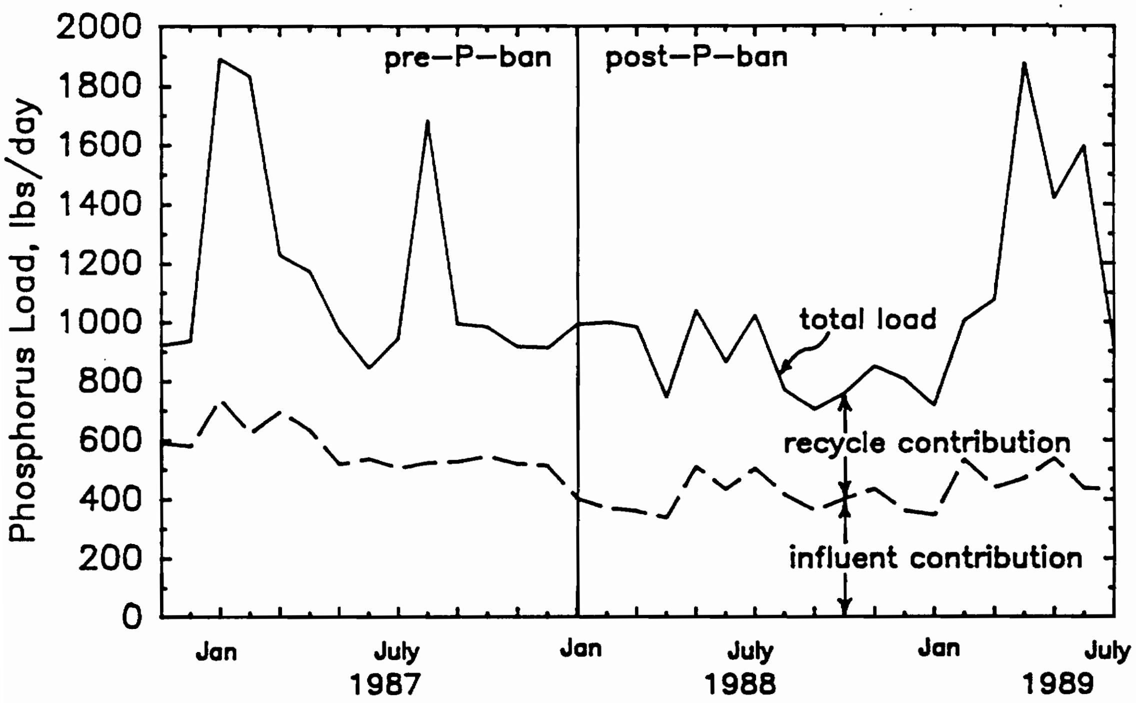

Figure 18. Average Monthly Phosphorus Load Entering the Treatment Process at the York River Wastewater Treatment Plant

Table 15. Primary Digester Phosphorus Concentrations
T-test Results

Hypothesis: $H_o:\mu_1 = \mu_2$ $H_1:\mu_1 \neq \mu_2$

	Time Period	Mean	St.Dev	t-calc	t-95%	accept H_o
Primary Digester Total Phosphorus Concentration						
pre-ban	12/86-3/87(5)	1,100	70			
post-ban	3/89-8/89(8)	1,070	190	-0.25	-2.20	accept
Primary Digester Soluble Phosphorus Concentration						
pre-ban	12/86-3/87(5)	316	45			
post-ban	3/89-8/89(7)	175	61	-4.36	-2.23	reject

Notes: Loads are in lbs/day; Concentrations are in mg/L.

Parentheses indicate the number of data points available for the analysis.

Table 16. Primary Digester Soluble Metal Concentrations T-test Results

Hypothesis: $H_o: \mu_1 = \mu_2$ $H_1: \mu_1 \neq \mu_2$

	Time Period	Mean	St.Dev	t-calc	t-95%	accept H_o
Iron Concentration						
pre-ban	12/86-3/87(5)	0.58	0.22			
post-ban	3/89-8/89(7)	0.27	0.11	-3.32	-2.23	reject
Calcium Concentration						
pre-ban	12/86-3/87(5)	29.4	3.1			
post-ban	3/89-8/89(7)	32.8	9.3	0.79	2.23	accept
Magnesium Concentration						
pre-ban	12/86-3/87(5)	9.4	1.8			
post-ban	3/89-8/89(7)	21.1	12.8	2.00	2.23	accept
Sodium Concentration						
pre-ban	12/86-3/87(4)	103	17			
post-ban	3/89-8/89(7)	74.5	18.3	-2.57	-2.26	reject
Potassium Concentration						
pre-ban	12/86-3/87(5)	228	17			
post-ban	3/89-8/89(7)	143	33	-5.33	-2.23	reject

Notes: Loads are in lbs/day; Concentrations are in mg/L.

Table 17. Primary Digester Total Recoverable Metal Concentration T-test Results

Hypothesis: $H_o:\mu_1 = \mu_2$ $H_1:\mu_1 \neq \mu_2$

	Time Period	Mean	St.Dev	t-calc	t-95%	accept H_o
Iron Concentration						
pre-ban	12/86-3/87(5)	737	82			
post-ban	3/89-8/89(7)	864	205	1.30	2.23	accept
Calcium Concentration						
pre-ban	12/86-3/87(5)	963	69			
post-ban	3/89-8/89(7)	937	186	-0.30	-2.23	accept
Magnesium Concentration						
pre-ban	12/86-3/87(5)	138	21			
post-ban	3/89-8/89(7)	191	50	2.24	2.23	reject
Sodium Concentration						
pre-ban	12/86-3/87(5)	354	13			
post-ban	3/89-8/89(7)	150	20	-19.8	-2.23	reject
Potassium Concentration						
pre-ban	12/86-3/87(5)	307	35			
post-ban	3/89-8/89(7)	213	42	-4.08	-2.23	reject

Notes: Loads are in lbs/day; Concentrations are in mg/L.

digester contents and then used in the computer model (18) to further assess the impact of the phosphorus ban on the precipitates in the digester.

Primary Digester Phosphorus and Metal Concentrations

The t-test results indicated that soluble phosphorus concentrations in the digester had changed significantly since the phosphorus ban. Soluble phosphorus decreased from a mean value of 316 mg/L to 175 mg/L, a 45% decrease. Total phosphorus, however, decreased less than 3%, from 1,100 mg/L to 1,070 mg/L, a difference which was not distinguishable statistically. The t-test results for these concentrations are included in Table 15. A graph illustrating the phosphorus trend in the digester from before the modification to remove phosphorus through the implementation of the phosphorus ban is included as Figure 19.

The two sample t-test was applied to the soluble metal concentrations in the digester; the results are found in Table 16. Soluble iron, sodium, and potassium concentrations decreased significantly over the time of the phosphorus ban. Soluble sodium and potassium decreased 28% and 37%, respectively. Figure 20 shows the soluble sodium and potassium trend, including the data from operation as a conventional activated sludge plant.

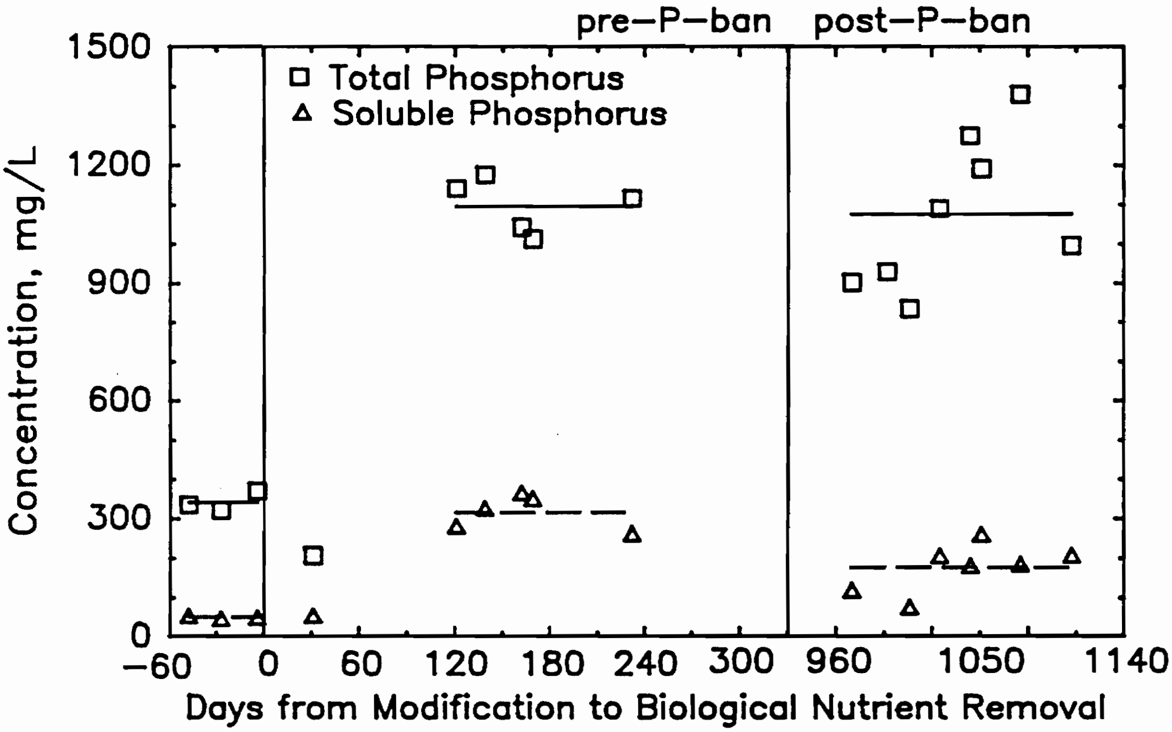

Figure 19. Phosphorus Concentrations in the Primary Digester at the York River Wastewater Treatment Plant (Period Averages: Soluble –– Total ——)

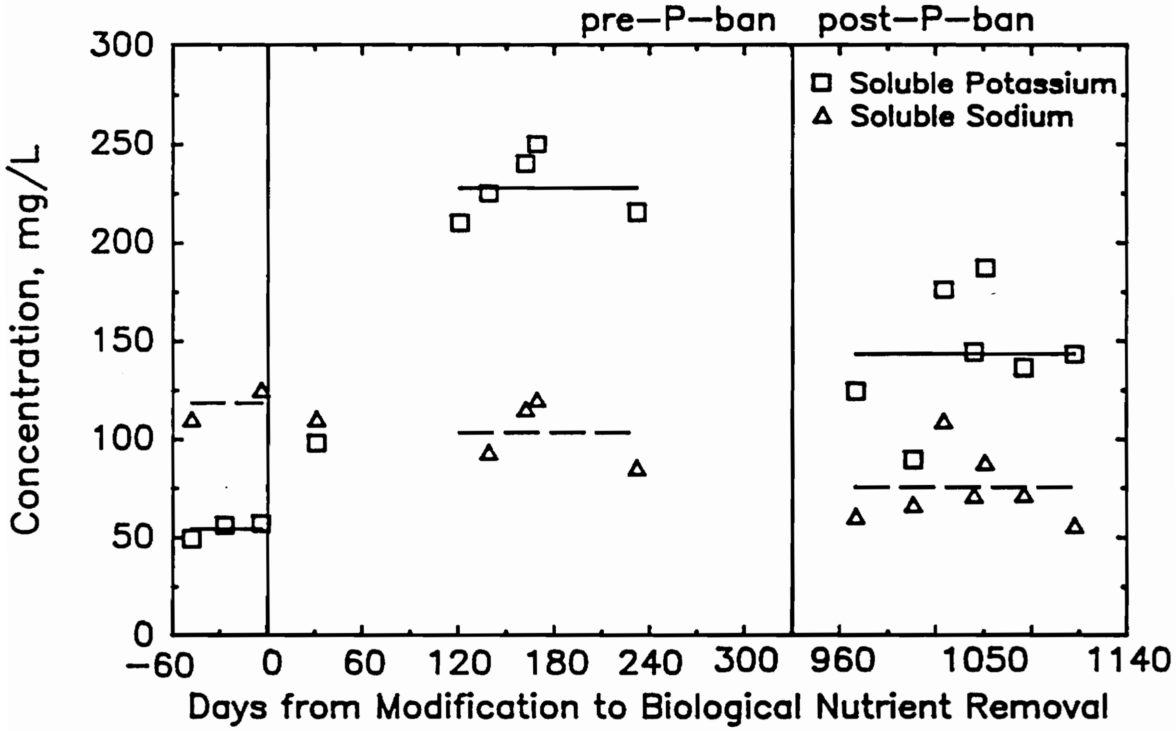

Figure 20. Soluble Sodium and Potassium Concentrations in the Primary Digester at the York River Wastewater Treatment Plant (Period Averages: Potassium —— Sodium ––)

The iron concentration decreased 54%, but the concentrations were small enough (<1 mg/l) that the change was considered inconsequential. The iron data are graphed in Figure 21.

Soluble calcium and magnesium concentrations increased by 12% and 124%, respectively, from before to after the phosphorus ban. The changes in the calcium and magnesium concentrations are graphed in Figure 22. Soluble calcium and magnesium concentrations could not be statistically distinguished before and after the phosphorus ban using the 95% confidence interval. The large variability in the soluble magnesium data, as reflected by the standard deviation values listed in Table 16, made statistical examination unlikely to differentiate between pre- and post-ban concentrations.

When evaluated with the two sample t-test, the total recoverable metal concentration data indicated that "total" magnesium, sodium, and potassium changed significantly over the time of the phosphorus ban. Complete t-test results for the total recoverable metals concentrations are included in Table 17. Total sodium and potassium concentrations both decreased (by 58% and 31%, respectively) while the magnesium concentration increased by 39%. Total iron and calcium concentrations could not be statistically distinguished before and after the phosphorus ban with a 95% confidence interval; iron

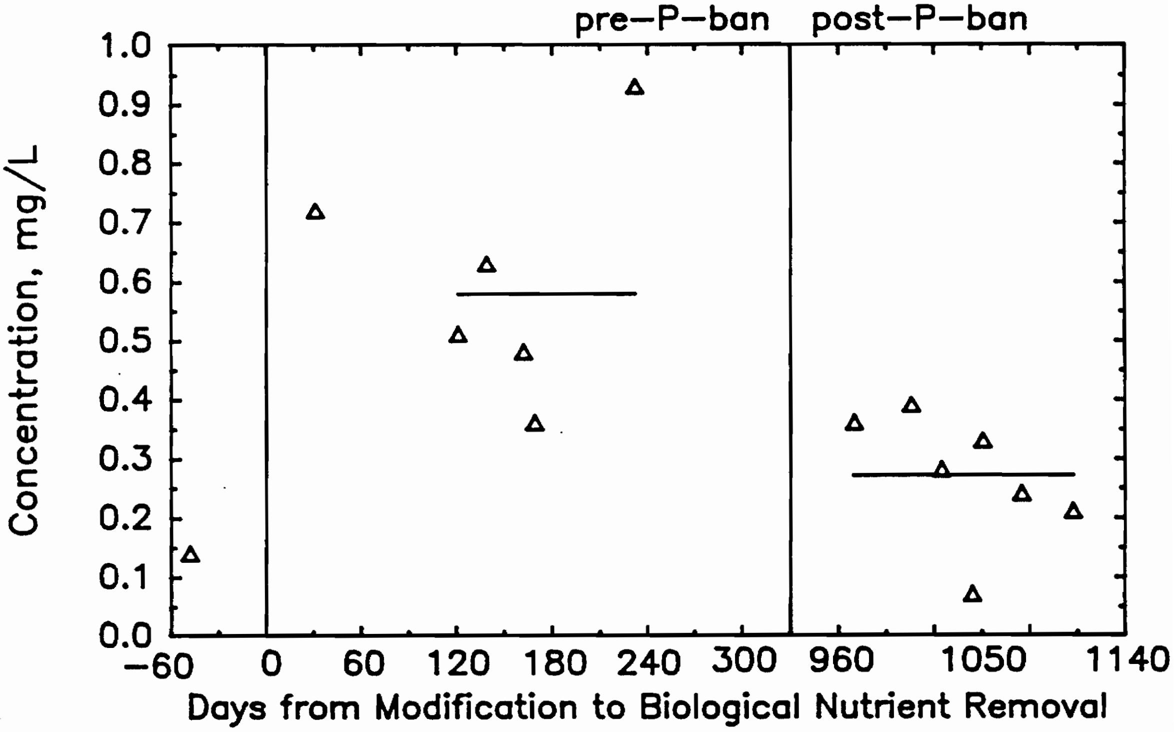

Figure 21. Soluble Iron Concentrations in the Primary Digester at the York River Wastewater Treatment Plant (Period Averages ——)

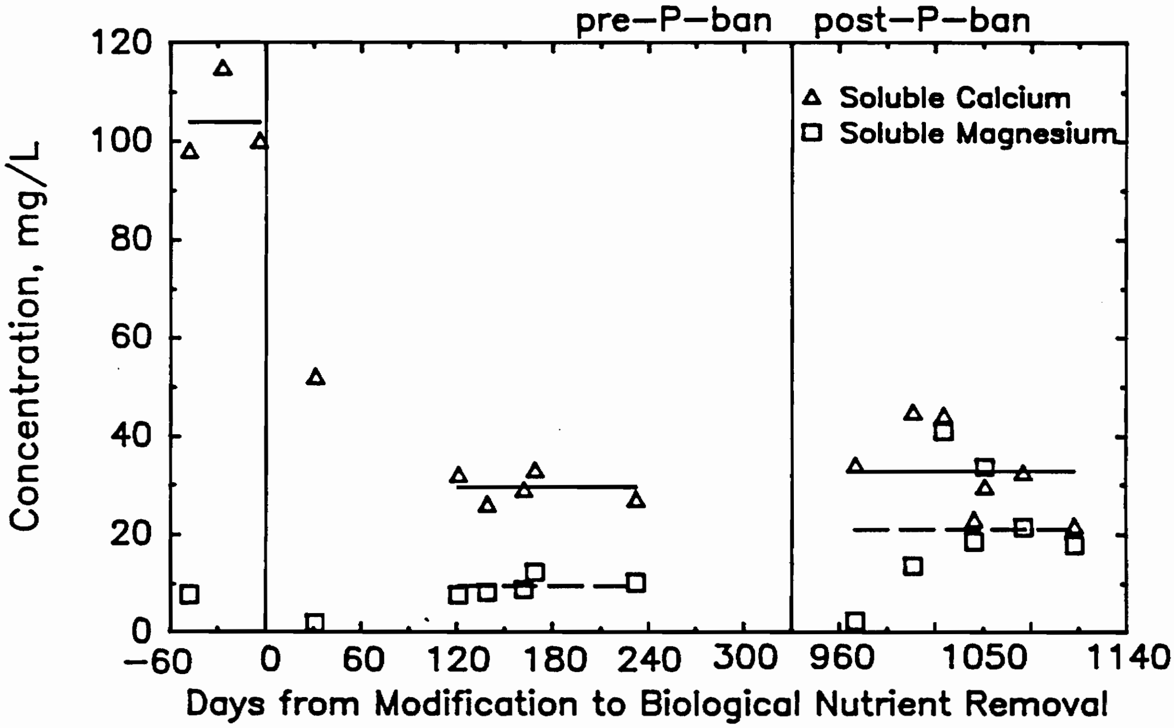

Figure 22. Soluble Calcium and Magnesium Concentrations in the Primary Digester at the York River Wastewater Treatment Plant (Period Averages: Calcium —— Magnesium – –)

increased 17%, while the calcium concentration decreased slightly (less than 3%). The sodium and potassium concentration data are graphed in Figure 23; iron and calcium in Figure 24; and magnesium in Figure 25.

Primary Digester Contents and Subsequent Flows

As previously discussed, the primary digester contents travel to the secondary digester and eventually to the belt filter press. Ultimately, the digester contents leave the plant in the filter cake destined for the compost facility or return to the plant in the belt filtrate. Since the secondary digester differs from the primary digester, the potential exists for the primary digester contents to alter during the time required to exit the plant. The differences in the digesters are that no mixing occurs in the secondary digester, and gases are vented to the atmosphere from the floating cover on the secondary digester. Additionally, samples from the secondary digester are collected from a lower portion of the stratified digester, so measured concentrations tend to be higher for the same constituent than in the primary digester or in the feed to the filter press, which comes from multiple levels in the secondary digester. The two sample t-test was used to compare the phosphorus and metal concentrations measured in the samples from the two digesters and the belt feed. These tests were to

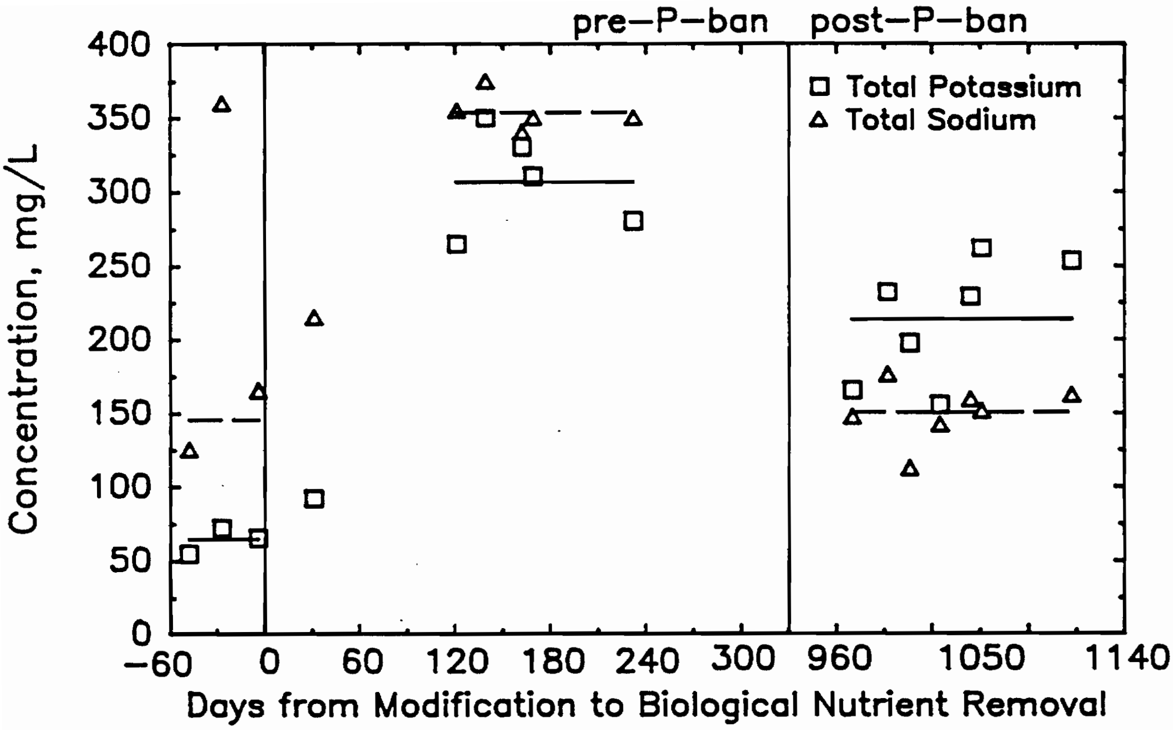

Figure 23. Total Potassium and Sodium Concentrations in the Primary Digester at the York River Wastewater Treatment Plant (Period Averages: Potassium—— Sodium ––)

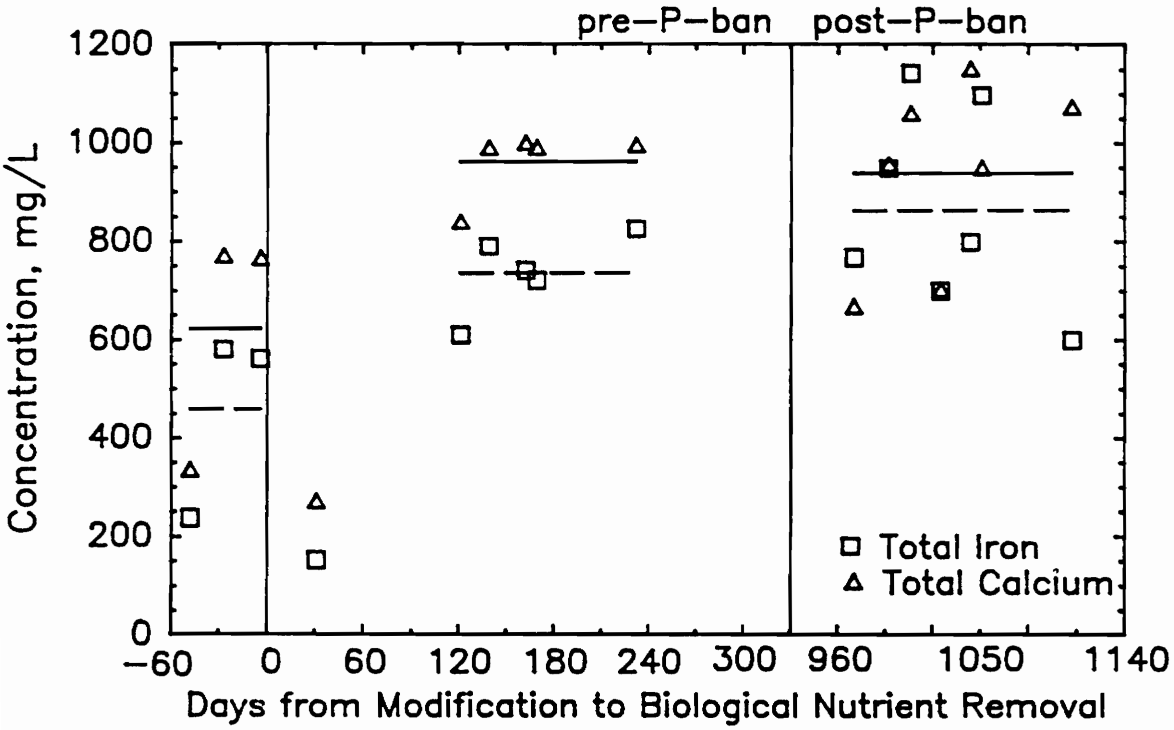

Figure 24. Total Iron and Calcium Concentrations in the Primary Digester at the York River Wastewater Treatment Plant (Period Averages: Iron –– Calcium ——)

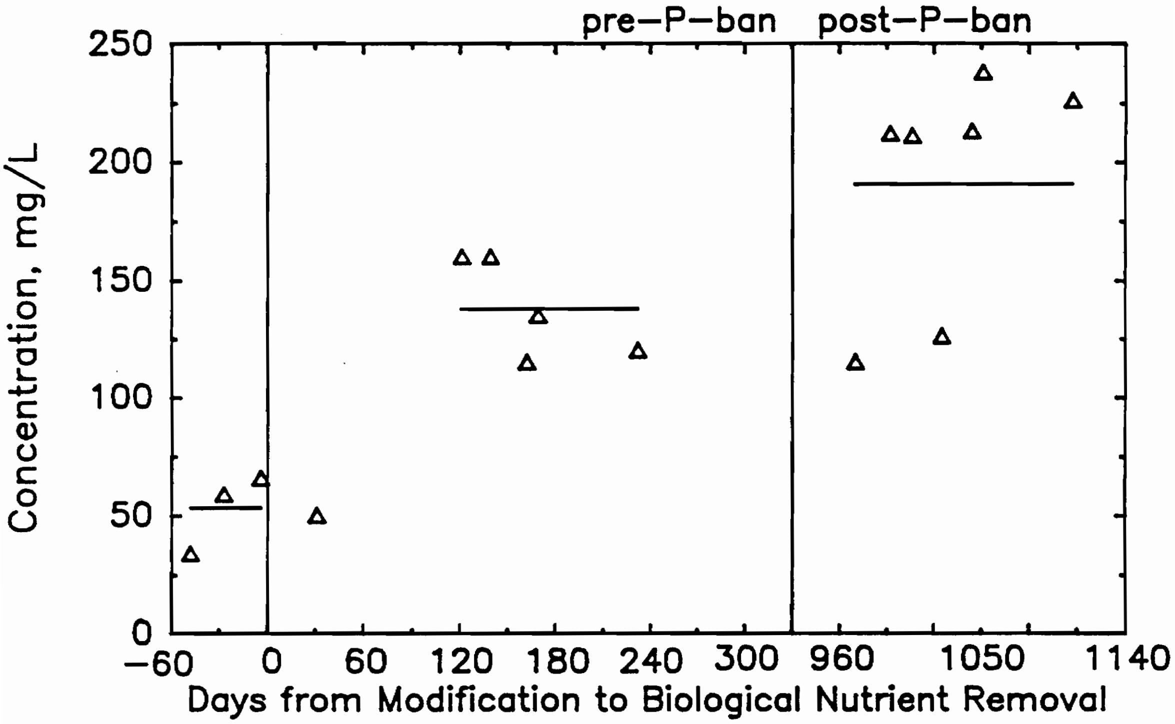

Figure 25. Total Magnesium Concentration in the Primary Digester at the York River Wastewater Treatment Plant (Period Averages: ——)

determine if the differences in the operation of the digesters, or the extra detention time, altered the chemical constituents in the second digester, and if the belt feed accurately represented the contents of the primary digester.

A comparison of the primary digester contents to the secondary digester contents using a 95% confidence interval could not show that the mean values differed for any constituent measured in the digesters. Although this implies that the concentrations might have been equal, such a conclusion cannot be proven; but has not been disproven. Likewise, a comparison of the primary digester contents with the contents in the belt filter press feed provided no indication that the belt feed was different than the primary digester content with regard to any constituent evaluated. These results support the assumptions that the filter feed accurately represents the primary digester, and that there was not a major difference in the phosphorus and metal content of the primary and secondary digesters.

Thermodynamic Modelling of the Primary Digester

Changes in the soluble concentrations of metals and phosphorus in the primary digester reflect an alteration in the chemical equilibrium since the phosphorus ban. To evaluate the potential precipitates present in the digester, the concentrations and pH values measured after the ban (found in Appendix C) were entered into the computer model developed by Sen (18). These precipitates and their supersaturation ratios (log Q/K_{sp}) were compared with values from Sen (6) to assess the changes resulting from the phosphorus ban and operational changes.

Simulations were performed using the average daily pH and alkalinity of the primary digester in the post-ban period (from HRSD data (56)), and using the chloride, ammonium, and acetate concentrations (125 mg/L, 750 mg/L, and 400 mg/L, respectively) used by Sen in previous simulations (6); another simulation used a pH of 7.3 to attempt a better correlation with the previous simulations performed by Sen (6). Filtration of the sample through the 0.45 mm filter altered the actual pH of the samples that were analyzed for the soluble metal species. The pH increase was usually near 1 pH unit. The soluble iron was speciated into 80% ferrous and 20% ferric, after Nash (7).

Computer simulation using the average concentrations of the ions measured for this study yielded the results in the first two columns of Table 18. The third column of Table 18 contains data from before the phosphorus ban taken from Sen (6). The values given are the log of the reaction quotients (Q) minus the log of the solubility

Table 18. Computer Model Supersaturation Values (log Q/K_{sp})

Chemical Compounds	pH =7.0	pH =7.3	From Sen[b] pH =7.3
Struvite	0.08	0.50	0.23
Bobierrite[a]	0.75	1.60	no data
Octacalcium Phosphate[a]	5.88	7.85	no data
Hydroxyapatite	19.54	22.70	23.5
Chlorapatite	21.07	23.63	24.0
ß-tricalcium Phosphate	7.27	8.12	8.0
Brushite	0.60	0.73	1.0
Sarcopside[a]	-2.90	-2.04	-0.8
Vivianite[a]	3.23	4.08	5.3
Ferrous Ammonium Phosphate[a]	-1.92	-1.49	-1.1
Ferrous Hydroxide	-3.37	-2.77	-2.5
Siderite	-0.01	0.32	0.7
Strengite	13.66	14.09	14.5
Ferric Hydroxide	10.68	11.57	11.7

All values are expressed in log units.

a. These values were calculated at 25° Celsius, rather than at 35° Celsius.

b. These data were interpreted from graphs from Sen (6).

products (K_{sp}) to yield the degree of supersaturation at a pH of 7.3 (for direct comparison) and at the average daily pH of 7.0. A value near zero (especially slightly above) was interpreted to mean that the precipitate was favored and likely to be present. Highly negative values indicate the degree of undersaturation and the likely absence of precipitation. High positive values suggest a driving force for precipitation that was limited by kinetics, nucleation, or inhibitory factors; certain of these precipitates may be present.

From results presented in Column One of Table 18, magnesium should be present primarily as struvite but also as bobierrite, calcium as brushite, and iron as siderite. The presence of vivianite was likely, as was octacalcium phosphate, b-tricalcium phosphate, ferric hydroxide, strengite, hydroxyapatite, and chlorapatite. The relative amounts of these precipitates will depend on the kinetics involved.

Comparison of the second column of Table 18 with the third column indicates that none of the precipitates likely to be present has changed since the phosphorus ban. All of the supersaturation values are similar for the individual compounds. Comparison of all three columns shows that the effect of the pH change has had a greater effect than the slight changes in metal and phosphorus concentrations. The average pH in the primary digester has decreased since Sen's work. Still, the simulations conducted here do identify the same trends and relative magnitudes in the supersaturation levels, suggesting that the changes in the metal and phosphorus concentrations in the primary digester brought on by the phosphorus ban and operational changes have not been sufficient to drastically alter the precipitates formed in the digester.

CHAPTER V

DISCUSSION

EFFECTS OF THE PHOSPHORUS BAN ON THE TREATMENT PLANT AND OPERATION

The phosphorus ban in Virginia has resulted in a 27% reduction, or 155 lbs/day, in the phosphorus entering the York River Wastewater Treatment Plant. This decrease in the influent phosphorus load is similar to the reduction (26%) seen when Wisconsin implemented a ban (10). The influent total phosphorus concentration decreased 2.8 mg/L, or 30%, which is consistent with the effect on the influent load, and agrees with concentration reductions seen in Maryland (2.3 mg/L or 32%)(1), Virginia (2.3 mg/L or 31%)(19), and Michigan (23%)(12). The Maryland and Virginia reductions were based on limited data which resulted in comparisons of Summer and Fall months of the year to the early Winter months; thus, the reductions in concentration may have been partly inflated due to dilution effects which were not considered in evaluating the data. The influent soluble phosphorus concentration at the York River Plant decreased 2.5 mg/L due to the ban, almost 90% of the reduction in the total phosphorus concentration. This is consistent with literature assertions that the phosphate in detergents is readily hydrolyzed and should arrive at the treatment plant solubilized (9). Clearly most, if not all, of the decrease in influent phosphorus to the treatment plant was in the soluble fraction.

In addition, the phosphorus ban may have reduced the variability of the phosphorus load entering the treatment plant. For all of the measurements of phosphorus found in Table 10, the standard deviation decreased from the pre-ban period to the post-ban period. This may have aided the operation of the treatment plant.

The decrease in influent phosphorus may have affected treatment at the York River Plant. The actual effect of the ban on treatment is difficult to discern because of the operational changes which occurred coincident with the implementation of the ban. The phosphorus load removed by the plant decreased by 32 lbs/day. While this decrease was small, it may indicate a change in the treatment due to the ban and the operational changes. The 2.2 mg/L reduction in the effluent total phosphorus concentration is only 79% of the decrease (2.8 mg/L) which occurred in the influent concentration, which also suggests that treatment may not have been as effective after the ban (though not necessarily because of the ban).

The effluent load from the York River Plant decreased by 54% as a result of the ban and operational changes. This is considerably higher than literature reports of 13-15% (16) and 20% (12) in Michigan, and 16-21% (20) in Maryland, but more consistent with the reductions of 42% reported herein for the HRSD treatment plants. The higher effluent load reduction is clearly due to the phosphorus removal at the York River plant. Phosphorus removal plants typically are excluded from calculations of effluent concentration and load reductions. The change in the effluent phosphorus load at the York River was proportionately higher than at other locations because the effluent loads were smaller.

The effluent concentration reductions calculated for Virginia were 52% (19) for plants without phosphorus removal, and 50% for the HRSD plants (excluding the York River Plant) (19). The York River Plant effluent phosphorus concentration decreased 59% over the time of the ban. These reductions were higher than the decrease reported for Michigan (24%). The HRSD data compare 1985 data to the first 9 months of 1988, and are, therefore, slightly biased toward the wet months of 1988, but much less than the Virginia data which again is based on limited data from a single year being compared seasonally. These seasonal dilution effects cannot explain the more than doubling of the decrease in the Michigan study by the decrease reported in the Virginia study. Differences in operation efficiency and treatment design may account for the considerable difference. The large York River percent decrease is not surprising because of the smaller effluent concentrations at the plant due to phosphorus removal.

Evaluation of the effects of the phosphorus ban on phosphorus removal and the effluent at the York River Plant required separate consideration of the effects of the ban and operational changes. The impact of the operational change to the VIP process from the A2/O process was difficult to assess due to limited comparison information in the literature. According to Daigger et al. (24), the VIP process is able to achieve higher phosphorus removals at less favorable (lower) $TBOD_5$:TP ratios. The ratio of usable BOD_5 or COD to phosphorus in the influent to the plant process will determine whether or not the bacteria can reduce the effluent soluble phosphorus concentration to less than 1.0 mg/L (27). The $TBOD_5$:TP ratio of the process influent (primary effluent) at the York River, according to calculations from Wable et al. (45), had a large increase after the ban from 11.2 to 17.7, a 58% increase. The analysis by Wable included data from prior to operation and stabilization as a BPR system which may have affected the calculations. A more limited series of the data on organic to phosphorus ratios from Wable et al. (45) is included in Table 19. The increase in the primary effluent $TBOD_5$:TP ratio calculated here was from 13.3 to

Table 19. Organic to Phosphorus Ratios at the York River Wastewater Treatment Plant (from Wable <u>et al</u>, (45)).

	Raw Influent		Primary Effluent
	TBOD:TP	TCOD:TP	TBOD:TP
1986 December	19.3	46.1	10.6
1987 January	19.9	39.3	13.0
February	20.5	43.7	10.2
March	17.4	42.4	9.2
April	18.1	48.6	9.1
May	20.6	45.9	9.2
June	23.6	40.1	10.3
July	26.7	39.4	15.9
August	24.5	37.8	12.9
September	27.1	37.8	17.4
October	22.5	36.2	17.4
November	22.9	51.2	18.8
December	24.9	51.1	18.6
Pre-Ban Average	22.1	43.0	13.3
1988 January	25.0	63.4	18.4
February	24.3	67.4	12.1
March	26.0	61.9	13.5
April	33.0	67.5	22.0
May	35.7	79.8	20.8
June	28.7	61.5	20.4
July	31.1	61.5	20.0
August	25.8	57.1	14.7
Post-Ban Average	28.7	65.0	17.7

17.7. Either increase in the $TBOD_5$:TP ratio resulting from the phosphate ban should have enhanced the potential of the York River Plant to reach low effluent soluble phosphorus concentrations. The operational change to the VIP process and the phosphorus ban both had the potential to increase the phosphorus load removal at the York River Plant. Despite potential benefits from the ban and the operational change, the load of phosphorus removed at the York River Plant did not increase, but decreased by 32 lbs/day.

Prior to the ban, the A2/O process at the York River was limited in the removal of phosphorus by the influent organic load (45). The $TBOD_5$:TP ratio entering the treatment process (13.3) was well below the optimal range for phosphorus removal in BPR plants (>20-25) (27). The unfavorable $TBOD_5$:TP ratio resulted from the large phosphorus load in the recycle stream. The effect of this recycle phosphorus load on the treatment efficiency of the plant is evidenced by the high effluent phosphorus concentrations. As a result of the ban the organic:phosphorus ratio increased, which increased the phosphorus load removal potential for the process. The inability of the VIP process to remove an increased load of phosphorus resulted from the lower phosphorus concentrations. The phosphorus concentration decreased sufficiently to limit the VIP process. The phosphorus removal change at the York River Plant appears to have resulted from the limitation of phosphorus to the system due to the ban and not the operational changes.

As a result of the increased TBOD:TP ratio after the ban, either process should have operated similarly or better than before the ban. Although actual comparison of the treatment processes before and after the ban was not possible, the VIP process would be expected to operate better than the A2/O process under the pre-ban conditions with the low TBOD:TP ratio. The hydraulic loading of the plant was usually over the design flow of the system and was likely responsible for many of the difficulties in achieving low effluent concentrations of phosphorus (45). Clearly, there are many unanswered questions resulting from the concurrent alteration of the influent phosphorus and the operation at the York River.

EFFECTS OF THE PHOSPHORUS BAN ON SLUDGE THICKENING AND RECYCLE FLOW STREAMS

The phosphorus load entering the gravity and flotation thickeners at the York River Wastewater Treatment Plant increased after the implementation of the phosphorus ban. The increase in phosphorus is best explained by the increase in TSS which occurred at the same time. The TSS loads entering the gravity and flotation thickener increased by 12% and 55%, respectively. The primary sludge flow to the gravity thickener increased 12% over the same period, which explains the increase in the TSS load to the gravity thickener. The gravity thickener phosphorus load increased by 17%, an increase similar to the TSS and flow increases, which indicates that the phosphorus ban had little effect on the phosphorus present in the primary sludge. The phosphorus present in the primary sludge would be expected to be primarily insoluble, either incorporated in the biomass, or present in chemical precipitates. Since it primarily affected the soluble phosphorus in the influent, the ban would not be expected to have a direct effect on the primary sludge.

The flotation thickener phosphorus load increased by only 7% despite a large increase (55%) in the TSS load (shown in Table 13). This reflects the effect of the phosphorus ban on the accumulation of excess phosphorus by the biomass. The large TSS load increase was due to a 9% increase in waste sludge flow and a significant (36%) increase (over 2,000 mg/L) in the MLSS of the secondary sludge. Thus, the large TSS load increase seems clearly due to operational differences in the pre- and post-ban periods; the disparity between the TSS changes and the phosphorus changes can be attributed to the phosphorus ban. This disparity is illustrated by the decrease (shown in Table 20) of the % P/TSS for the flotation thickener flow to the primary digester from the pre- to the post-ban period.

Both thickeners delivered more phosphorus to the digester after the ban than before, partially as a result of better thickening, but primarily due to the increased sludge flows and better clarification in the secondary clarifiers. The gravity thickener received more phosphorus and delivered more phosphorus to the primary digester. The gravity thickener contributed 323 lbs/day and 418 lbs/day pre- and post-ban, respectively. The flotation thickener contributed 272 lbs/day or 289 lbs/day in the pre-ban period (depending on the time period used for the evaluation) and 313 lbs/day in the post-ban period. The contribution of the gravity thickener to the digester increased from 53% to 57% of the total phosphorus load, as shown in Table 20. This underscores the importance of background and chemical (normal and accelerated) phosphorus removal mechanisms in the York River Plant. The importance of the background and chemical removals has likely increased since the ban, judging from the increase of the gravity thickeners relative phosphorus contribution to the primary digester and the slight increase in the % P/TSS in the flows from the gravity thickener shown in Table 20.

Table 20. York River Wastewater Treatment Plant Primary Digester Phosphorus and TSS Loadings, Pre- and Post-Ban

Total Load to Digester	Pre-Ban	% of Total	Post-Ban	% of Total
Phosphorus Total	611	--	731	--
- from Gravity Thickener	322	53	418	57
- from Flotation Thickener	289	47	313	43
TSS Total	7,100	--	9,990	--
- from Gravity Thickener	3,170	45	3,730	37
- from Flotation Thickener	3,930	55	6,260	63
Phosphorus/TSS (in % lbs-P/lbs-TSS)				
Total Flow to Digester	8.6	--	7.3	--
- from Gravity Thickener	10.2	--	11.2	--
- from Flotation Thickener	7.4	--	5.0	--

All loads are expressed in lbs/day.

The combined head recycle may be of interest in evaluating the gravity thickener performance and the importance of chemical precipitation in biological phosphorus removal at the York River. The recycle carries large amounts of soluble phosphorus to the head of the treatment process, where cations present in the influent wastewater may react and form precipitates that, if the precipitation kinetics permit, will be removed in the primary sludge. If, as suggested by the Seneca Wastewater Treatment Plant (20) data, the recycle flows are not affected proportionately by the phosphorus ban, chemical mechanisms of phosphorus removal may be disproportionately maintained. At the York River plant, the combined head recycle phosphorus load decreased 13% over the time of the ban, only half of the 27% reduction in the raw influent phosphorus load. This reasoning could be used to account for the 5% difference in phosphorus and TSS load increases in the flow from the gravity thickener to the primary digester. Unfortunately, the nature of the mass balances required to calculate the primary sludge and gravity thickener phosphorus loads make such conclusions to be purely of a speculative nature only.

Recycle flows from digesters and sludge processing, like the combined head recycle at the York River, have been viewed as a liability to biological phosphorus removal systems. The experience at Pontiac, Michigan (5), and the experience at the York River Plant seem to indicate that chemical precipitation will ameliorate the disruption of biological removal by digester recycles. The return of digester supernatant to the plant at Pontiac, unlike the York River filtrate recycle, did not even result in a large return of phosphorus into the treatment process, perhaps due to the combination of low influent phosphorus, long solids retention times, and precipitation of phosphates in the digester (5). At the York River facility, the precipitation of phosphate compounds in the digester clearly lowered phosphorus levels in the recycle streams, but the recycle stream still doubled the amount of phosphorus seen by the treatment process. Prior to the phosphorus ban, the plant phosphorus removal was limited by the organic load as a result of the large phosphorus load in the recycle stream. According to the work of Daigger _et al._ (24), the change of operation which coincided with implementation of the phosphorus ban, should have allowed more efficient phosphorus removal despite the low $TBOD_5$:TP ratio. Since the phosphorus ban raised the $TBOD_5$:TP ratio, the impact of the recycle phosphorus decreased and the two operation modes could not be directly compared.

The return of this phosphorus rich recycle to the head of the plant may have promoted the chemical mechanisms of phosphorus removal within the plant. The soluble phosphorus recycle would precipitate easily, based on the chemical precipitation studies by Deakyne et al. (47). Further, the influent wastewater at the York River plant has a low (6-12 mg/L) magnesium concentration and a moderate (50-60 mg/L) calcium concentration, both of which favor precipitation of calcium phosphate precipitates (26). This may provide a clue to the high phosphorus loads contained in the gravity thickener stream in both the pre- and post- ban periods. During both periods the phosphorus load in the gravity thickened sludge was greater than the load in the flotation thickened sludge, especially when the phosphorus load was expressed as a percent of the TSS. The recycle of soluble phosphorus to the head of the treatment process appears to strongly favor chemical removal mechanisms in the York River Plant. The hydraulic and solids retention times, and the chemical composition of the influent wastewater would also affect the relative importance of the chemical and biological removal mechanisms.

EFFECTS OF THE PHOSPHORUS BAN ON THE PRIMARY DIGESTER

The phosphorus and TSS loads to the digester increased 20% and 41% over the time of the ban, respectively. The increase in phosphorus to the digester was clearly not a direct consequence of the phosphorus ban, but resulted from better clarification and thickening and the increased sludge flows. The filter cake total solids load and the filter cake volume both increased significantly, the former by 51% and the latter by 24% (data from 56), so the increased phosphorus load did not result in an increase in the phosphorus concentrations in the digester. From comparison of data gathered by Sen (6) with the data of this study, the total phosphorus concentration in the primary digester remained essentially the same, while the soluble phosphorus concentration decreased by 45%.

The change in the proportion of phosphorus present in the soluble form (decreased from 29% to 16% of the total) is consistent with various combinations of an increased delivery of insoluble phosphate compounds to the digester; a reduction of the biological accumulation (and subsequent release in the digester); and an increase in digester precipitation. A reduction in the biological accumulation of phosphorus has been previously discussed as a likely consequence of the phosphorus ban, based on the flotation thickener flow stream data. The possibility of an increased delivery of insoluble phosphate compounds has been alluded to in regard to the gravity thickener and the combined recycle, but no direct evidence of such an occurrence was collected.

The possibility of increased precipitation in the primary digester was evaluated by comparing the changes in the molar concentrations of the solid phases of the metals and phosphorus, shown in Table 21. Solid phase concentrations were calculated by subtracting the soluble concentrations from the total recoverable concentrations. The agreement of the calculated change in the solid phase of phosphorus with the sum of the calculated changes in the solid phases of iron, calcium, and magnesium is good circumstantial evidence that increased precipitation of phosphates occurred. Identification of actual precipitates was not accomplished.

The concomitant release of cations with phosphorus under anaerobic conditions was discussed previously. The potassium concentrations (shown in Figures 20 and 23) agreed with the expectations of concomitant release. As a result of the phosphorus ban, the total recoverable and soluble potassium concentrations decreased (31% and 37%, respectively) to a level intermediate to the conventional activated sludge operation and the pre-ban operation of biological phosphorus removal. The soluble potassium

Table 21. Changes in the Molar Concentrations of the Solid Phases of Phosphorus and Selected Cations within the Primary Digester.

	Pre-Ban	Post-Ban	Change
Phosphorus	25.3	28.9	+3.6
Cations			
- Iron	13.2	15.5	+2.3
- Magnesium	5.3	7.0	+1.7
- Calcium	23.3	22.6	-0.7
Total Cations	41.8	45.1	+3.3

All values are given in millimoles.

reduction accounted for over 90% of the total potassium decrease. The decrease of soluble potassium due to the reduced phosphorus at the York River plant is consistent with the proposed role of potassium in the transport of phosphorus across the bacterial cell membrane.

Using the molar ratio of the release of potassium with phosphorus as 0.25, the reduction of soluble phosphorus released can be estimated based on the change in the digester potassium. Potassium decreased 85 mg/L, or 2.18 mM (millimolar).

$$\frac{2.18 \text{ mM K}}{0.25 \text{ mM K/ mM P}} * 31.0 \text{ mg P/ mMole P} = 270 \text{ mg/L P}$$

This is greater than the observed decrease (141 mg/L) in the soluble phosphorus concentration in the digester. As previously discussed, much of the decrease in soluble phosphorus can be accounted for on the basis of precipitation. Neither precipitation nor concomitant mechanism is likely to account for the changes in phosphorus alone, and the data collected for this study provide no clear insight into the relationship between the mechanisms.

The increase in the soluble and total magnesium concentrations cannot be explained based upon concomitant release of magnesium from the nutrient removal sludge. The concentrations of magnesium were expected to react similarly to the potassium concentrations and decrease to a level intermediate to the conventional and pre-ban concentrations. Inexplicably, the soluble and total magnesium concentrations increased 124% and 39%, respectively. The soluble concentration data varied from 2.2 mg/L to 41 mg/L, a range that limited the statistical tests ability to differentiate the post-ban period from the pre-ban. The total concentration varied widely also, but the t-test could distinguish between the two time periods using the 95% confidence interval. The increase in the total concentration (53 mg/L) was larger than that of the soluble concentration (12 mg/L), indicating an increase in magnesium precipitates. One possibility, apart from sampling, preservation, and lab errors, was that the magnesium compounds had not reached equilibrium in the pre-ban digester. The kinetics of struvite formation are rapid and could not be responsible for such a mechanism, but the formation of a kinetically very slow precipitate offers a potential explanation. Bobierrite precipitation was never observed in lab studies with a 95 day incubation period (6), but the supersaturation value calculated by the computer model for the digester (0.75) indicates the possibility of bobierrite formation, which may offer a partial explanation of the magnesium increase.

The effect of the phosphorus ban on the sodium concentrations in the digester was also difficult to interpret. The total concentration decreased from the pre-ban period down to levels similar to those prior to biological phosphorus removal at the plant. Sodium does not participate in the phosphorus release according to the literature (6), and would be expected to be constant throughout the various studies. No clear explanation of the large increase in sodium concentrations after phosphorus removal began was forwarded in the work of Sen (6). One possible explanation might be a seasonal effect peculiar to the pre-ban data of winter, 1987. Unusual snows may have resulted in an increase of sodium entering the waste flows through run-off. The soluble concentration did not follow the trend of the total sodium, but decreased at each interval.

The calcium concentrations in the primary digester did not change significantly as a result of the ban. Soluble calcium increased 12% (3.4 mg/L) and the total concentration decreased 3%. Most of the calcium has remained insoluble since modification to remove phosphorus. Many calcium compounds are supersaturated in the digester (Table 16); the many inhibitors, nucleation effects, and kinetics involved will determine the actual compounds present. The calcium, which enters primarily in the thickened primary sludge (6), may not precipitate to the same degree in the post-ban period due to the reduced phosphorus concentrations released from the thickened secondary (waste) sludge. The calcium concentration data does not support a mechanism of concomitant release of calcium with phosphorus, but this was not specifically investigated. The total calcium concentration in the digester has not changed as a result of the operational changes at the plant or the phosphorus ban, as illustrated in Figure 26, which shows the total iron and calcium concentrations as a percent of the total solids of the digester sample.

Changes in the iron concentrations in the digester could not be distinguished statistically. The soluble iron concentration remained below 1 mg/L, and although it decreased 54%, the low levels and the wide variability in the data make the decrease inconsequential. As Singer (51) has noted, the iron in the anaerobic digester remains insoluble. The computer model suggested a variety of iron compounds potentially present, including vivianite, siderite, strengite, and ferric hydroxide. The iron phosphate most likely to be present is vivianite, but iron is more likely to be present in other non-phosphate forms (siderite). The wide variability in the iron data makes the 17% increase in the total recoverable iron difficult to interpret and unlikely to be meaningful. The total iron data shown as a percent of the total solids in Figure 26 indicate that the ban and

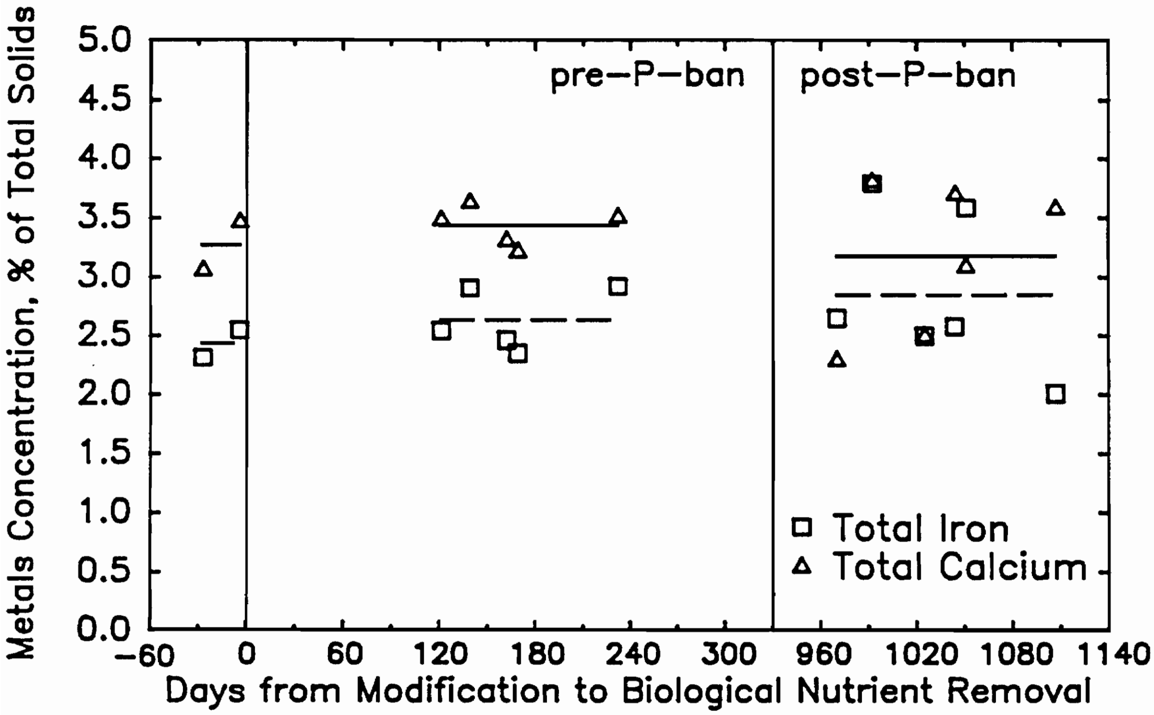

Figure 26. Total Iron and Calcium Concentrations as Percentages of the Total Solids of the York River Wastewater Plant Primary Digester Samples (Period Averages: Iron – – Calcium —)

previous changes have not altered the iron present in the primary digester.

The digester altered little as a result of the ban due to changes in the operation of several plant units which compensated. The concentration of several cations did significantly change, but the computer model indicated that the potential compounds in the digester altered more as a result of the decrease in pH than element concentrations.

CHAPTER VI

CONCLUSIONS

This investigation attempted to describe the changes resulting from the implementation of a state-wide detergent phosphorus ban on various treatment streams within the York River Wastewater Treatment Plant and the contents of the anaerobic digester at the plant. Data was gathered from the Plant Monthly Operation Reports, previous studies of the plant sludges and primary digester, and original plant sampling. Based on the analysis of the data collected, the following conclusions are advanced:

1. The phosphorus ban in Virginia resulted in a 27% reduction in the mean influent phosphorus load, and a 29% reduction in the mean influent concentration to the York River Wastewater Treatment Plant.

2. The mean effluent load at the York River Plant was reduced 54%, likely as a result of the phosphorus ban. The mean effluent total phosphorus concentration decreased 59%.

3. The phosphorus load delivered to the digesters has not been affected by the phosphorus ban due to compensation by the clarifiers and sludge thickeners.

4. Chemical equilibria and precipitates within the digester have probably not changed significantly as a result of the phosphorus ban.

Operational changes coinciding with the implementation of the phosphorus ban made evaluation of the effects of the ban on the treatment process inconclusive. Conversely, the phosphorus ban made comparison of the two treatment processes (A2/O and VIP) impossible. Full-scale comparison of the VIP and A2/O processes would have been of considerable value, especially in the organic-limited wastewater prior to the ban. The effects of a phosphorus ban on the phosphorus content of the primary and secondary sludges and primary digester without the operational changes would have offered better insight into the fate of phosphorus in the treatment system.

Future investigations of the operation of biological nutrient removal systems should attempt to establish the factors affecting the relative contributions of chemical and biological mechanisms to the removal of phosphorus. Better characterization and comparisons of the phosphorus present in the primary and secondary sludges may offer insight into the phosphorus removal mechanisms. The effects of digester, belt filtrate, or other phosphorus-rich recycle flows has not been investigated. These recycles would be expected to have significant effects on the chemical mechanisms of phosphorus removal. The effects of such recycles on the organic:phosphorus ratio entering the treatment process and the resulting phosphorus content of the primary and secondary sludges could be investigated, also.

Additional work could identify chemical precipitates in the digester and in the plant. Microbiological work could attempt to identify the actual mechanism of cation release with the phosphorus.

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APPENDICES:

APPENDIX A: HISTORICAL PLANT DATA FOR THE YORK RIVER WASTEWATER TREATMENT PLANT (56).

APPENDIX B: YORK RIVER WASTEWATER TREATMENT PLANT PRIMARY DIGESTER DATA, FROM SEN (6).

APPENDIX C: YORK RIVER WASTEWATER TREATMENT PLANT POST-BNR, POST-BAN DATA, FROM THIS STUDY.

APPENDIX A: HISTORICAL PLANT DATA FOR THE YORK RIVER WASTEWATER TREATMENT PLANT (56)

Table A1: York River Plant Influent Data: Pre-Ban					
Month		Flow	Phosphorus		
		MGD	Soluble mg/L	Total (C) mg/L	Load[b] lbs/day
1986	June	5.77	--	--	--
	July	6.12	--	--	--
	August	6.19	6.64	--	--
	September	6.24	7.15	--	--
	October	6.13	8.09	--	--
	November	6.09	8.39	11.55	586
	December	6.80	7.10	10.17	577
1987	January	10.38	5.85	8.52	737
	February	10.43	4.93	7.15	622
	March	11.36	6.06	7.34[a]	695
	April	9.88	6.30	7.66	631
	May	7.38	7.04	8.38	516
	June	7.03	6.17	9.14	536
	July	6.28	6.88	9.58	502
	August	6.10	6.99	10.27	522
	September	6.01	7.00	10.51	527
	October	5.53	7.03	11.82	545
	November	5.50	6.85	11.25	516
	December	6.37	5.60	9.58	509

(C) These data acquired from composite sampling.

a. High daily values on the raw data sheet were not included in this average.

b. The values in this column were calculated.
Load = Flow * Concentration * 8.34 lbs/gallon

Table A1: York River Plant Influent Data: Post-Ban					
Month		Flow	Phosphorus		
		MGD	Soluble mg/L	Total (C) mg/L	Load[b] lbs/day
1988	January	7.62	4.55	6.29	400
	February	8.46	4.25	5.22	368
	March	7.29	4.04	5.87	357
	April	7.78	3.37	5.17	335
	May	8.99	4.32	6.78	508
	June	6.69	5.51	7.73	431
	July	6.12	6.77	9.85	503
	August	6.27	5.01	7.90	413
	September	6.42	4.46	6.72	360
	October	6.16	5.37[c]	7.80[c]	401
	November	6.78	4.70[c]	7.69[c]	435
	December	6.52	4.46	6.60	359
1989	January	7.21	3.88	5.70	343
	February	10.74	3.33	5.95	533
	March	14.20	1.75	3.69	437
	April	12.03	2.53	4.67	469
	May	9.82	3.90	6.56	537
	June	8.51	4.04	6.11	434
	July	8.09	3.82	6.35	420

(C) These data acquired from composite sampling.

b. The values in this column were calculated.
Load = Flow * Concentration * 8.34 lbs/gallon

c. High daily values for the phosphorus in the raw data sheet were weighted according to how many days the TSS concentrations were also elevated.

Table A2: York River Plant Effluent Data: Pre-Ban					
Month		Flow	Phosphorus		
		MGD	Total (C) mg/L	Load[b] lbs/d	Removed[b] lbs/d
1986	June	5.42	--	--	--
	July	6.14	--	--	--
	August	6.21	--	--	--
	September	6.15	--	--	--
	October	5.63	--	--	--
	November	5.34	3.68	164	422
	December	5.73	2.94	140	437
1987	January	9.91	3.63	300	438
	February	10.06	3.71	311	311
	March	10.45	3.34	291	404
	April	9.34	3.45	269	362
	May	6.76	2.86	161	355
	June	7.03	3.55	208	328
	July	6.28	4.28	224	277
	August	6.10	6.86	349	174
	September	6.01	3.51	176	351
	October	5.53	3.26	150	395
	November	5.50	3.88	178	338
	December	6.37	2.55	136	374

b. The values in this column were calculated.

Load = Flow * Concentration * 8.34 lbs/gallon
Load Removed = Influent Load - Effluent Load

Table A2: York River Plant Effluent Data: Post-Ban

Month		Flow	Phosphorus		
		MGD	Total (C) mg/L	Load[b] lbs/d	Removed[b] lbs/d
1988	January	7.62	5.11	325	75
	February	8.47	3.90	275	93
	March	7.29	2.41	146	211
	April	7.78	1.71	111	224
	May	8.99	2.84	213	296
	June	6.65	0.92	51	380
	July	6.01	0.94	47	456
	August	6.27	0.72	38	375
	September	6.42	0.89	48	312
	October	6.16	0.98	50	350
	November	6.78	2.28	129	306
	December	6.52	2.39	130	229
1989	January	7.21	1.43	86	257
	February	10.74	2.07	186	348
	March	14.20	0.93	110	327
	April	12.03	1.26	126	342
	May	9.82	1.54	126	411
	June	8.51	1.32	94	340
	July	8.09	1.70	115	314

b. The values in this column were calculated.

Load = Flow * Concentration * 8.34 lbs/gallon
Load Removed = Influent Load - Effluent Load

Table A3: York River Plant Thickener Data: Pre-Ban					
Month		Thickener Phosphorus Loads (lbs/d)			
		Gravity Thickener		Flotation Thickener	
		Influent	Transfer to Digester	Influent	Transfer to Digester
1986	June	--	--	--	--
	July	102	51	85	71
	August	79	21	82	72
	September	89	38	295	248
	October	137	79	300	243
	November	159	92	283	269
	December	129	82	188	163
1987	January	826	706	298	273
	February	857	573	430	408
	March	416	387	418	389
	April	330	238	304	193
	May	208	130	389	341
	June	90	48	381	344
	July	197	152	304	289
	August	867	671	198	179
	September	256	159	273	254
	October	193	160	221	215
	November	225	191	221	212
	December	139	115	253	248

Load = Flow * Concentration * 8.34 lbs/gallon
Load Transferred = Influent Load - (Sub- or Supernatant Load)

Table A3: York River Plant Thickener Data: Post-Ban					
Month		Thickener Phosphorus Loads (lbs/d)			
		Gravity Thickener		Flotation Thickener	
		Influent	Transfer to Digester	Influent	Transfer to Digester
1988	January	362	328	242	234
	February	436	387	186	175
	March	481	395	292	282
	April	342	307	354	346
	May	606	586	265	251
	June	132	106	251	249
	July	410	389	313	302
	August	289	262	331	317
	September	245	211	340	330
	October	271	246	318	290
	November	381	353	309	277
	December	358	304	277	258
1989	January	285	256	292	268
	February	409	353	276	264
	March	556	487	346	341
	April	1,270	743	427	419
	May	878	701	399	382
	June	1,070	1,020	406	382
	July	428	386	382	365

Load = Flow * Concentration * 8.34 lbs/gallon
Load Transferred = Influent Load - (Sub- or Supernatant Load)

Table A4: York River Plant Thickener Data: Pre-Ban

Month	Thickener TSS Loads (lbs/d)			
	Gravity Thickener		Flotation Thickener	
	Influent	Transfer to Digester	Influent	Transfer to Digester
1986 June	3,390	2,840	2,470	2,410
July	2,830	1,930	2,800	2,770
August	4,900	3,490	2,110	2,050
September	4,190	3,260	3,550	3,480
October	5,710	3,890	3,050	2,940
November	7,200	6,160	3,430	3,410
December	6,440	5,500	2,340	2,280
1987 January	2,530	-4,360[a]	4,440	4,240
February	3,060	-8,540[a]	8,050	7,700
March	5,410	4,460	6,390	6,320
April	5,790	3,550	4,930	3,980
May	6,700	4,540	4,290	4,200
June	7,880	6,900	3,620	3,590
July	6,700	5,890	3,910	3,900
August	7,320	2,780	2,960	2,940
September	4,720	1,160	3,310	3,290
October	4,140	3,750	2,830	2,810
November	3,210	2,870	3,040	3,010
December	2,370	2,130	3,830	3,830

[a] These negative values were due to high supernatant concentrations. Analysis of the data omitted these values.

Load = Flow * Concentration * 8.34 lbs/gallon
Load Transferred = Influent Load - (Sub- or Supernatant Load)

Table A4: York River Plant Thickener Data: Post-Ban

Month		Thickener TSS Loads (lbs/d)			
		Gravity Thickener		Flotation Thickener	
		Influent	Transfer to Digester	Influent	Transfer to Digester
1988	January	2,460	1,660	4,760	4,750
	February	2,550	-5,550[a]	5,250	5,230
	March	3,730	-570[a]	6,430	6,330
	April	6,250	3,650	6,590	6,570
	May	7,740	7,110	5,350	5,310
	June	6,840	6,180	5,100	5,060
	July	5,940	5,260	4,850	4,810
	August	7,140	6,560	5,020	4,990
	September	6,800	5,160	3,890	3,870
	October	6,260	5,410	4,300	4,270
	November	6,790	4,150	5,720	5,680
	December	6,120	3,180	6,260	6,200
1989	January	5,910	4,800	7,310	7,190
	February	9,350	8,130	7,420	7,310
	March	1,480	-340[a]	9,800	9,790
	April	4,180	-10,050[a]	9,050	8,890
	May	5,850	-2,000[a]	8,350	8,280
	June	9,070	7,570	6,540	6,490
	July	9,850	9,140	5,340	5,300

a. These negative values were due to high supernatant concentrations. Analysis of the data omitted these values.

Load = Flow * Concentration * 8.34 lbs/gallon
Load Transferred = Influent Load - (Sub- or Supernatant Load)

Table A5: York River Plant Stream Data: Pre-Ban						
Month		Phosphorus Loads			Filtrate P Concentrations	
		Belt Recycle	Combined Influent	Primary Digester	Soluble	Total
1986	June	--	--	--	--	--
	July	230	697	123	--	--
	August	217	663	92	20.2	24.0
	September	270	749	286	25.8	33.8
	October	373	871	322	64.5	85.7
	November	334	920	361	95.6	103
	December	361	937	245	124	144
1987	January	1,150	1,890	979	105	117
	February	1,210	1,830	982	80.7	92.0
	March	531	1,230	776	96.5	110
	April	539	1,170	430	70.1	84.2
	May	452	968	471	85.7	100
	June	307	842	392	105	118
	July	443	944	441	116	141
	August	1,160	1,680	850	135	148
	September	464	991	413	130	146
	October	436	981	375	117	129
	November	397	913	403	106	119
	December	399	908	363	125	142

Table A5: York River Plant Stream Data: Post-Ban

Month		Phosphorus Loads			Filtrate P Concentrations	
		Belt Recycle	Combined Influent	Primary Digester	Soluble	Total
1988	January	594	994	562	--	--
	February	633	1,000	562	119	131
	March	624	981	676	91.6	103
	April	407	742	653	83.5	90.5
	May	532	1,040	837	95.4	103
	June	431	862	355	--	--
	July	521	1,020	691	100	119
	August	355	768	579	141	190
	September	341	701	541	163	198
	October	357	758	536	177	207
	November	415	850	630	168	209
	December	446	805	562	136	165
1989	January	372	715	524	116	134
	February	472	1,010	617	90.7	121
	March	639	1,080	828	72.5	89.8
	April	1,410	1,880	1,160	60.3	75.2
	May	881	1,420	1,080	86.2	115
	June	1,160	1,600	1,400	94.9	119
	July	488	916	751	134	153

APPENDIX B: YORK RIVER WASTEWATER TREATMENT PLANT PRIMARY DIGESTER DATA, FROM SEN (6)

TABLE B1: PRE-BNR, PRE-BAN AND NEAR-BNR, PRE-BAN PRIMARY DIGESTER DATA

TABLE B2: POST-BNR, PRE-BAN PRIMARY DIGESTER DATA

Table B1: York River Wastewater Treatment Plant Primary Digester Concentration Data: Pre-BNR, Pre-Ban and Near-BNR, Pre-Ban (from Sen (6)).

	Pre-BNR, Pre-Ban			Near-BNR, Pre-Ban
Date	6/17/86	7/08/86	7/31/86	9/04/86
Days Since BNR	-48	-27	-4	31
Soluble P	53	45	48	53
Total P	335	320	370	205
Soluble Fe	0.14	--	--	0.72
Total Fe	235	580	560	150
Soluble Ca	98	115	100	52
Total Ca	335	770	765	270
Soluble Mg	7.60	--	--	1.76
Total Mg	34	59	66	50
Soluble Na	110	--	125	110
Total Na	125	360	165	215
Soluble K	49	56	57	98
Total K	54	72	65	92
Total Solids-TS	--	25,100	22,000	--

Note: All values are given in mg/L.

Table B2: York River Wastewater Treatment Plant Primary Digester Concentration Data: Post-BNR, Pre-Ban (from Sen (6)).

Date	12/3/86	12/21/86	1/13/87	1/20/87	3/24/87
Days Since BNR	121	139	162	169	232
Soluble P	280	325	365	350	260
Total P	1,140	1,175	1,040	1,010	1,115
Soluble Fe	0.51	0.63	0.48	0.36	0.93
Total Fe	610	790	740	720	825
Soluble Ca	32	26	29	33	27
Total Ca	840	990	1,000	990	995
Soluble Mg	7.70	8.25	8.83	12.3	10.1
Total Mg	160	160	115	135	120
Soluble Na	--	93	115	120	85
Total Na	355	375	340	350	350
Soluble K	210	225	240	250	215
Total K	265	350	330	310	280
Total Solids-TS	24,000	27,200	30,100	30,700	28,300

Note: All values are given in mg/L.

APPENDIX C: YORK RIVER WASTEWATER TREATMENT PLANT POST-BNR, POST-BAN DATA, FROM THIS STUDY

TABLE C1: INFLUENT

TABLE C2: EFFLUENT

TABLE C3: PRIMARY DIGESTER

TABLE C4: SECONDARY DIGESTER

TABLE C5: BELT FEED

TABLE C6: BELT FILTRATE

TABLE C7: FILTER CAKE

Table C1: York River Wastewater Treatment Plant Treatment Plant Influent Concentration Data: Post-BNR, Post-Ban

Date	3/31/89	4/22/89	5/6/89	5/25/89
Days Since BNR	970	992	1,006	1,025
Soluble P	--	--	--	3.58
Total P	3.24	3.82	3.53	5.10
Soluble Fe	0.35	0.40	0.33	0.22
Total Fe	2.66	4.21	3.88	5.08
Soluble Ca	66.3	61.4	55.4	68.2
Total Ca	72.3	66.0	61.8	58.9
Soluble Mg	11.2	5.99	6.13	11.0
Total Mg	13.1	8.21	8.34	12.5
Soluble Na	54.4	63.0	56.0	98.8
Total Na	45.4	70.0	79.8	100
Soluble K	7.00	14.6	7.00	9.70
Total K	7.06	7.68	8.34	10.9
TS	1,000	410	970	720
TDS	--	2,100*	380	540
TVS	--	--	--	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C1: York River Wastewater Treatment Plant Treatment Plant Influent Concentration Data: Post-BNR, Post-Ban				
Date	6/13/89	6/20/89	7/14/89	8/15/89
Days Since BNR	1,044	1,051	1,075	1,107
Soluble P	4.28	4.17	--	2.00
Total P	5.62	5.80	--	5.32
Soluble Fe	0.11	0.13	--	0.36
Total Fe	2.34	2.92	--	3.35
Soluble Ca	53.0	35.2	--	39.8
Total Ca	57.9	53.4	--	53.0
Soluble Mg	6.23	4.84	--	6.70
Total Mg	6.69	5.46	--	7.39
Soluble Na	69.4	74.6	--	53.7
Total Na	80.0	82.0	--	81.0
Soluble K	12.0	11.4	--	10.4
Total K	9.58	9.88	--	9.40
TS	600	600	--	690
TDS	540	730	--	5,300*
TVS	200	--	--	343
TSS	100	320	--	173

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C2: York River Wastewater Treatment Plant Treatment Plant Effluent Concentration Data: Post-BNR, Post-Ban

Date	3/31/89	4/22/89	5/6/89	5/25/89
Days Since BNR	970	992	1,006	1,025
Soluble P	--	--	--	6.63
Total P	2.40	0.54	2.47	7.15
Soluble Fe	0.08	0.17	0.21	0.14
Total Fe	0.47	0.57	0.91	0.33
Soluble Ca	69.3	65.6	56.1	61.8
Total Ca	69.1	66.0	55.6	58.0
Soluble Mg	7.17	7.11	5.89	9.33
Total Mg	9.04	8.06	7.29	9.85
Soluble Na	68.7	67.6	66.4	84.8
Total Na	59.3	68.2	81.6	91.7
Soluble K	10.3	7.80	9.20	11.7
Total K	8.19	8.60	8.26	12.5
TS	980	1,100	430	560
TDS	--	1,760*	540	--
TVS	--	--	--	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C2: York River Wastewater Treatment Plant Treatment Plant Effluent Concentration Data: Post-BNR, Post-Ban

Date	6/13/89	6/20/89	7/14/89	8/15/89
Days Since BNR	1,044	1,051	1,075	1,107
Soluble P	0.54	--	0.17	0.10
Total P	0.75	--	0.44	0.22
Soluble Fe	--	--	0.14	0.17
Total Fe	0.39	--	0.37	1.48
Soluble Ca	43.0	--	45.7	40.7
Total Ca	57.9	--	52.4	47.4
Soluble Mg	5.50	--	4.84	4.96
Total Mg	6.86	--	4.80	5.04
Soluble Na	82.2	--	60.6	59.6
Total Na	103	--	93.6	106
Soluble K	10.9	--	9.50	11.9
Total K	8.96	--	8.30	8.80
TS	600	--	510	460
TDS	500	--	2,880*	3,070*
TVS	100	--	220	360
TSS	3	--	<10	13

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C3: York River Wastewater Treatment Plant Treatment Plant Primary Digester Concentration Data: Post-BNR, Post-Ban

Date	3/31/89	4/22/89	5/6/89	5/25/89
Days Since BNR	970	992	1,006	1,025
Soluble P	118	--	74.0	205
Total P	899	928	832	1,090
Soluble Fe	0.36	--	0.39	0.28
Total Fe	766	948	1,140	698
Soluble Ca	34.1	--	44.9	44.2
Total Ca	667	956	1,060	701
Soluble Mg	2.22	--	13.6	41.0
Total Mg	115	212	211	126
Soluble Na	60.4	--	66.4	109
Total Na	147	176	112	142
Soluble K	124	--	89.0	176
Total K	165	232	197	155
TS	29,000	25,000	11,400	28,000
TDS	1,700	--	760	650
TVS	--	--	--	--
TSS	--	--	--	--
Alkalinity	3,050	1,350	1,500	1,800
pH	7.20	7.00	7.00	7.00

Note: All values are given in mg/L, except pH.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C3: York River Wastewater Treatment Plant Treatment Plant Primary Digester Concentration Data: Post-BNR, Post-Ban

Date	6/13/89	6/20/89	7/14/89	8/15/89
Days Since BNR	1,044	1,051	1,075	1,107
Soluble P	179	259	183	206
Total P	1,270	1,190	1,380	993
Soluble Fe	0.07	0.33	0.24	0.21
Total Fe	798	1,097	--	598
Soluble Ca	22.9	29.6	32.5	21.6
Total Ca	1,151	948	-	1,073
Soluble Mg	18.4	33.6	21.3	17.7
Total Mg	213	238	--	226
Soluble Na	71.0	87.8	71.4	55.7
Total Na	159	151	--	162
Soluble K	144	187	136	143
Total K	229	262	--	253
TS	31,000	30,600	27,600	29,900
TDS	2,100	2,800	2,840	4,500
TVS	18,000	11,000*	16,300	18,400
TSS	--	--	--	--
Alkalinity	1,500	1,300	2,000	--
pH	7.30	6.80	7.00	--

Note: All values are given in mg/L, except pH.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C4: York River Wastewater Treatment Plant Treatment Plant Secondary Digester Concentration Data: Post-BNR, Post-Ban				
Date	3/31/89	4/22/89	5/6/89	5/25/89
Days Since BNR	970	992	1,006	1,025
Soluble P	--	169	123	--
Total P	--	1,380	1,310	1,010
Soluble Fe	--	0.20	0.42	--
Total Fe	--	963	1,360	910
Soluble Ca	--	33.2	39.2	--
Total Ca	--	980	1,380	869
Soluble Mg	--	0.98	3.94	--
Total Mg	--	193	281	178
Soluble Na	--	52.0	75.0	--
Total Na	--	123	--	140
Soluble K	--	135	152	--
Total K	--	223	182	191
TS	--	34,000	36,000	29,000
TDS	--	--	1,200	--
TVS	--	--	--	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C4: York River Wastewater Treatment Plant Treatment Plant Secondary Digester Concentration Data: Post-BNR, Post-Ban				
Date	6/13/89	6/20/89	7/14/89	8/15/89
Days Since BNR	1,044	1,051	1,075	1,107
Soluble P	148	195	188	--
Total P	1,730	1,280	1,190	1,010
Soluble Fe	0.02	0.21	0.69	0.10
Total Fe	1,500	1,070	816	946
Soluble Ca	33.9	32.7	28.6	15.4
Total Ca	1,410	960	987	1,170
Soluble Mg	13.4	20.1	13.2	11.3
Total Mg	260	199	242	195
Soluble Na	71.6	74.2	77.4	42.1
Total Na	153	204	147	178
Soluble K	141	165	180	105
Total K	239	238	226	269
TS	46,000	33,000	27,900	27,500
TDS	2,700	3,300	3,500	5,100
TVS	24,000	18,000	15,900	15,800
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C5: York River Wastewater Treatment Plant Treatment Plant Belt Feed Concentration Data: Post-BNR, Post-Ban

Date	3/31/89	4/22/89	5/6/89	5/25/89
Days Since BNR	970	992	1,006	1,025
Soluble P	--	132	--	86.7
Total P	--	1,080	--	1,050
Soluble Fe	--	0.19	--	1.97
Total Fe	--	810	--	773
Soluble Ca	--	32.3	--	28.6
Total Ca	--	793	--	778
Soluble Mg	--	5.24	--	9.70
Total Mg	--	158	--	154
Soluble Na	--	60.6	--	76.4
Total Na	--	136	--	118
Soluble K	--	140	--	133
Total K	--	213	--	160
TS	--	--	--	30,000
TDS	--	1,200	--	620
TVS	--	--	--	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C5: York River Wastewater Treatment Plant Treatment Plant Belt Feed Concentration Data: Post-BNR, Post-Ban

Date	6/13/89	6/20/89	7/14/89	8/15/89
Days Since BNR	1,044	1,051	1,075	1,107
Soluble P	173	153	191	--
Total P	1,070	1,040	1,250	--
Soluble Fe	0.29	0.10	0.38	--
Total Fe	787	853	817	--
Soluble Ca	26.8	28.1	32.7	--
Total Ca	839	806	874	--
Soluble Mg	12.0	16.7	12.3	--
Total Mg	191	195	225	--
Soluble Na	160	72.6	75.6	--
Total Na	181	176	151	--
Soluble K	114	155	181	--
Total K	237	256	218	--
TS	27,000	28,000	31,500	--
TDS	2,700	2,600	3,200	--
TVS	15,000	16,000	18,100	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C6: York River Wastewater Treatment Plant Treatment Plant Belt Filtrate Concentration Data: Post-BNR, Post-Ban

Date	3/31/89	4/22/89	5/6/89	5/25/89
Days Since BNR	970	992	1,006	1,025
Soluble P	--	113	--	108
Total P	--	106	--	148
Soluble Fe	--	1.56	--	0.31
Total Fe	--	6.26	--	2.30
Soluble Ca	--	62.0	--	51.7
Total Ca	--	48.1	--	41.4
Soluble Mg	--	27.1	--	31.7
Total Mg	--	21.4	--	19.4
Soluble Na	--	92.0	--	88.4
Total Na	--	84.0	--	81.4
Soluble K	--	110	--	134
Total K	--	115	--	123
TS	--	3,400	--	1,200
TDS	--	3,500	--	860
TVS	--	--	--	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C6: York River Wastewater Treatment Plant Treatment Plant Belt Filtrate Concentration Data: Post-BNR, Post-Ban

Date	6/13/89	6/20/89	7/14/89	8/15/89
Days Since BNR	1,044	1,051	1,075	1,107
Soluble P	160	50.6	173	146
Total P	94.5	71.1	169	183
Soluble Fe	--	0.45	0.17	0.24
Total Fe	1.40	7.05	2.15	3.90
Soluble Ca	36.3	42.4	32.1	36.1
Total Ca	39.0	46.6	35.3	37.7
Soluble Mg	32.1	59.2	24.4	29.0
Total Mg	28.8	33.4	27.3	30.2
Soluble Na	81.6	58.8	101	82.0
Total Na	103	110	100	124
Soluble K	125	76.8	142	112
Total K	131	138	116	133
TS	1,000	1,100	1,300	122,000*
TDS	470	2,800	3,700*	6,900*
TVS	200	--	460	880
TSS	66	335	98	183

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C7: York River Wastewater Treatment Plant Treatment Plant Filter Cake Concentration Data: Post-BNR, Post-Ban

Date	3/31/89	4/22/89	5/6/89	5/25/89
Days Since BNR	970	992	1,006	1,025
Soluble P	--	--	--	--
Total P	--	7.8	--	9.0
Soluble Fe	--	--	--	--
Total Fe	--	34.8	--	34.6
Soluble Ca	--	--	--	--
Total Ca	--	22.5	--	25.1
Soluble Mg	--	--	--	--
Total Mg	--	6.16	--	7.68
Soluble Na	--	--	--	--
Total Na	--	0.96	--	1.58
Soluble K	--	--	--	--
Total K	--	1.88	--	2.06
TS	--	--	--	--
TDS	--	--	--	--
TVS	--	--	--	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

Table C7: York River Wastewater Treatment Plant Treatment Plant Filter Cake Concentration Data: Post-BNR, Post-Ban				
Date	6/13/89	6/20/89	7/14/89	8/15/89
Days Since BNR	1,044	1,051	1,075	1,107
Soluble P	--	--	--	--
Total P	6.8	7.7	16.2	19.0
Soluble Fe	--	--	--	--
Total Fe	33.9	34.5	25.7	26.7
Soluble Ca	--	--	--	--
Total Ca	26.6	25.8	23.1	22.1
Soluble Mg	--	--	--	--
Total Mg	8.59	9.29	6.16	8.90
Soluble Na	--	--	--	--
Total Na	2.02	1.04	1.80	1.60
Soluble K	--	--	--	--
Total K	2.50	2.54	3.34	3.14
TS	--	--	--	--
TDS	--	--	--	--
TVS	62%	62%	65%	--
TSS	--	--	--	--

Note: All values are given in mg/L.

*. Values were unusual and were not considered representative of the sample. These values were not used in analysis of the data.

VITA

William O. Randall was born July 17,1963 in Lexington, Kentucky. He received a Bachelor of Science in Civil Engineering from Virginia Polytechnic Institute and State University in 1985. Later in 1985, he entered the Medical College of Virginia in Richmond, Virginia. After completing the classroon portion of medical training, he left medical school in the fall of 1987. After working briefly for the consulting firm of R. Stuart Royer and Associates, Inc., in Richmond, Virginia, he enrolled in the Environmental Engineering department at Virginia Poltechnic Institute and State University in 1988. Towards the end of this work he did part-time work with the consulting firm of Anderson and Associates. In the fall of 1990, he will begin work towards a Doctorate degree at the University of North Carolina, Chapel Hill.

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