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Determination of Nutrient Levels and Proposed Predictive Models for Phosphate in the Lafayette River, Norfolk, Virginia

John R. Montgomery Old Dominion University

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DETERMINATION OF NUTRIENT LEVELS AND PROPOSED PREDICTIVE MODELS FOR PHOSPHATE IN THE LAFAYETTE RIVER, NORFOLK, VIRGINIA

JOHN R. MONTGOMERY

A thesis presented 1n partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE'

INSTITUTE OF OCEANOGRAPHY OLD DOMINION UNIVERSITY July, 1972

SUPERVISORY COMMITTEE

Thesis Director Donald D. Adams

Ronald E. Johnson

ABSTRACT

The Lafayette River, an urban, well-mixed estuarine embayment, was sampled from October, 1970 to January, 1972
for phosphate, nitrate, nitrite, oxygen, water temperature and salinity. The mean values found for these samples were: 0X7gen saturation from 69% to 106%, nitrite from O to 4 microgram-atoms per liter, and salinity from 13°/oo.
to 24°/oo. The mouth of the Elizabeth River to Hampton Roads was also sampled from May, 1971 to August, 1971. The Lafa7ette and Elizabeth Rivers were also sampled over a 24 hour period in the summer of 1971 and the Lafayette River again ln the winter ot 1972. The mean concentration • of phosphate in the auamer varied from) to 16 microgramatoms per liter for the Lafayette River and from 2 to 12
microgram-atoms per liter for the Elizabeth River. The microgram-atoms per liter for the Elizabeth River. highest values of phosphate occurred in the awmaer months and the lowest in the winter. The mean concentration of phosphate tor the Elizabeth River ranged from 3 to *s.1* miorogram-atom.s per liter with the highest value in June, 1971. The mean oonoentratlon of phosphate *tor* the Lafayette River ranged from 1.9 to 8.6 microgram-atoms per liter with the highest value in August, 1971.

Multiple linear regression models revealed that the dailJ concentration or phosphate ls related to the stage of the tide, and rate of flow of phosphate from the Lamberts Point sewage outfall as follows:

1. The concentrat1on·ot phosphate **increases** on the ebb tide and decreases on the flood tide because of the diluting effect ot the Hampton Roads water.

2. The concentration of phosphate is also directly related to the rate of flow of phosphate from the Lamberts
• Point sewage outfall on the flood tide but quantitively is not as important as the diluting effects of the Hampton Roads water. Seasonal multiple linear regression models show a direct relation of temperature to the concentration of phosphate and an indirect relatian with the amount of rainfall. The effect or temperature was ascribed to increased bilological activity and the effect of rainfall to the dilution of the water in the Lafayette River.

ACKNOWLEDGMENT

•Nature hides her secrets through her intrinsic grandeur, but not through deception[#]

Albert Einstein

The statement **above is a** highly optimistic philosophy. **However,** without a similar optimism, a project such as a Master's thesis can appear hopeless.

I would like to thank the following graduate students for their sharing of the load: B. Golub. G. White, B. Weiss. J. Haluska, J. Melchor and C. Belin. Jim Melchor deserves special thanks for arranging with Mrs. E. P. Worthington for the use of her cruiser, Miss Priss III. Robert Bray and Gene Doty were especially helpful 1n collecting data in the early stages of the study. Gene Doty deserves special mention for his aid 1n collecting samples from the icy waters of the Lafayette River. I also wish to thank the following people for their aid in the collection or data and other information pertaining to the River: Mr. W. T. Brownley, Mr. Gene Goffigon, Director of Treatment, H.R.S.D., Mr. Lawrence, H.R.S.D., A. Winemann, N.A.s.A. 0 Mr. J. Day, State Department of Shellfish, Mr. R. s. Mcivor, Virginia State water Control Board, Dr. Kent Price, u. of Delaware, Mr. Madhu Paranjape, Bedford Institute, Tom Purcell, Biology Department, o.D.u.,

Mr. Murphy, for technical aid, Dr. J. F. Slowey, for suggesting the thesis topic and of course, all the other students and **staff** for their encouragement and criticisms. I also wish to acknowledge Steve Yates, Pete Nickolas, John Balonas, and James White; and Mrs. Diane Bakaysa for typing this thesis. A thesis or any other publication, must **be reviewed by** others in the same field. This has been accomplished by a very conscientious and hard working thesis committee. Although not on my committee I would like to acknowledge the extensive aid and encouragement I received from Dr. J. c. Ludwick on regression analysis. I would like to extend my special thanks to the hard working chairman of my committee, Donald D. Adams, tor his extensive **review** of the thesis.

As you can see, although there is only one author on the title page there were many who aided in the completion of this thesis. One who is remembered with affection and pride for her hard work, in collection of samples, typing, rewriting, and encouragement is my wife, Sarah.

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CHAPTER I

THE PROBLEM AND DEFINITIONS OF TERMS

Many variables can effect the productivity and aesthetic qualities of an urban estuarine embayment, some of which are salinity, dissolved oxygen, availability of sunlight, pH, pollution by-products, circulation, morphometry of the embayment. water temperature. land run-off. and nutrient concentrations in the water (Steward and Rohlich, 1967). Although it is difficult to state which of these is the most important to the embayments' ecology. the nutrients, especially phosphate, play an important role (Redfield, 1958 and Likens, 1972). Pritchard states (1969), that when the total phosphate concentration exceeds 3.3 microgram-atoms phosphate phosphorous per liter, that undesirable conditions associated with eutrophication occur.

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Statement of the purpose. At this time, there are no published studies for nutrient concentrations in the Lafayette River. The Lafayette River has recreational and aesthetic value for the citizens of Norfolk, Virginia, and provides a breeding and feeding site for numerous species

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of wildlife. It is imperative to obtain a basic knowledge of the nutrient cycles in the Lafayette River to be used in determining the present base levels of these nutrients in the Lafayette River for comparison with the nutrient levels of future studies.

Statement of the problem. It is the purpose of this study to determine the yearly cycle of phosphate, oxygen. nitrate. and nitrite concentrations in the Lafayette and Elizabeth Rivers. A portion of this data will be used to attempt to answer the following questions:

- 1. Does the Lafayette River's concentration of phosphate exceed the value of 3.3 microgramatoms per liter as stated by Pritchard (1969).
- 2. If the concentration of phosphate in the Lafayette River does exceed the 3.3 microgramatoms phosphate per liter, what are the explanations for this phenomenom?
- 3. How do the levels of phosphate in the Lafayette River compare to sther estuaries?

Statement of the Research Hypothesis. The Lafayette River is a small, shallow urban estuary that drains a large paved watershed. The Lamberts Point Sewage Plant, a large primary treatment plant, is located at the mouth of the river. It was postulated that the levels of phosphate in the Lafayette River would show a change in concentration over a twenty four hour period. The concentration would increase on the flood tide and decrease on the ebb tide.

 $\mathbf{2}$

This increase in phosphate would be due to the tidal currents moving the sewage laden waters from the Lamberts Point Sewage outfall into the Lafayette River. On the ebb tide the inverse or flushing would occur. The wind direction could either increase the flow of sewage into the river or decrease the flow depending on its direction. It was further postulated that over a longer seasonal time period, wind direction, urban storm water runoff and sluggish water circulation would increase the levels of phosphate in the Lafayette River over those levels found in Hampton Roads.

II. DEFINITIONS OF TERMS USED

Multiple linear regression model. The model is of the form (Draper and Smith, 1967; Snedecor and Cochran. 1968; Sokal and Rohlf, 1969):

 $Y = a + B_1X_1 + B_2X_2 + \cdots + B_nX_n + E^1$

a is the constant or Y intercept.

 B_n are the regression coefficients of the independent wariables, X., used to predict the estimation of the dependent variable Y.

B_oX_o is the joint effect of all the terms omitted from the n wariable models.

 E^1 is the residual or error term and is assumed to be distributed independently of the X⁸s with zero mean and variance. 6²

The model is of Type I (Sokal and Rohlf. 1969). This means that the predicted \hat{x} or phosphate concentration is dependent on "error free" independent variables. i.e. variables that can essentially be said to be measured with no, or more realistically, small error. Notice that \hat{Y} is the predicted value and therefore, has a statistically normally distributed range of values for each set of independent variables. The linear least squares fit for the model is a Y on X regression.

Primary treated sewage. This term refers to the treatment involved in the mechanical settling out and screening of large sewage particles. After this has been accomplished, the final effluent is heavily dosed with chlorine to kill pathogenic organisms. This treatment has little or no effect on nutrient levels in the sewage.

Elizabeth River and Lafayette River. As the Lafayette River and the Elizabeth River have a common mouth, the sampling section D refers to the Elizabeth River and sections A. B. and C refer to the Lafayette River. Sampling sections were labelled A, B, C. or D. Sampling stations are the individual sampling locations within the sections and have a letter and number designation; \mathcal{L}^{max}

Tidal samples. The term will refer to multiple samples collected from one or more sampling stations over a partial or complete tidal cycle.

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Daily samples. The term refers to multiple samples collected from one or more sampling stations over a twenty-four hour period.

Seasons. The seasons will be defined as follows: Summer - the months of June, July, and August. Fall - the months of September, October, and November. Winter - the months of December, January, and February. Spring - the months of March, April, and May.

Cosine theta. The wind direction will be expressed numerically as the cosine theta. Theta is the angle the resultant wind makes to the main Lafayette River channel. The main Lafayette River channel bears 028⁰ true at the mouth of the river.

Wind component. The wind velocity is a vector designated as cosine theta times the wind speed in knots.

P value. A statistical parameter used to determine the significance of a regression equation. It is the ratio of the mean square for the regression divided by the variance of the regression.

F value. When used in nutrient calibration curves. it is equal to the nutrient concentration divided by the corrected absorbance. (Strickland & Parsons, 1965)

Tide stages. The stage of tide was expressed numerically in order to include the tidal parameter in the regression equations. Beginning ebb tide is expressed as 1 (one) and includes all values up to but not including 2 (two). Beginning flood tide is expressed as 2 (two) and

includes all values up to but not including 3 (three). Therefore 1.5 designates a sampling point halfway into the ebb tide and 2.75 indicates a sampling point three quarters into the flood tide.

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CHAPTER II

REVIEW OF THE STUDY AREA AND RELATED RESEARCH

REVIEW OF THE STUDY AREA \mathbf{I} .

Bacteriological. The Lafayette River (see Figures 1 and 2) was once called Tanners Creek but has been called the Lafayette River since 1934. In 1916, an investigation of the oyster beds in the Hampton Roads area (cited in Crohurst and Sullinon, 1935) concluded that oysters from the Elizabeth River and its tributaries, which includes the Lafayette River, could not be safely used for human consumption. The Crohurst report of December, 1935 (Crohurst and Sullinon, 1935) showed the coliform values in the Lafayette River to vary from 1700 to 4400 per 100 pubic centimeters and concluded #...the stream obviously is grossly polluted under all tidal conditions." This could hardly be otherwise since raw sewage from an estimated population of 10.000 was deposited from 35 public sewers directly into the Elizabeth and Lafayette Rivers (Smith. 1950). In addition to the sbove public sewers, there were approximately 300 family sewage units with direct connections to the Lafayette River and its branches. The water quality survey by the Virginia State Department of Health in August, 1950 showed the Lafayette River to have a median

Report Follows

coliform density of over 500 per 100 milliliters. Since the construction of the Hampton Roads Sanitation District's Army Base Plant and Lamberts Point (see Figure 2) Plant in 1947 and 1948, respectively (Gene Goffigon, personal communication Hampton Roads Sanitation District, 1972), there is no known direct raw sewage input into either the Lafayette or the Elizabeth River. However, the present total coliform count data from the Norfolk Department of Health (Wise, 1970) remains or is higher than the values in 1934 and 1949, especially in the summer months.

Algal studies. Marshall (1967. 1968. 1969) has compiled plankton surveys on the Lafayette and Elizabeth Rivers. Diatoms were shown to predominate in the Lafayette River in April and June. 1964 with a ratio to phytoflagellates of 7:1 and 317:1. respectively. Skeletonema costatum was the major constituent on both these dates. This also held true for the Eastern and Western branches of the Elizabeth **River.** $\sigma \sim 100$

REVIEW OF RELATED RESEARCH $II.$

Nutrients in the Elizabeth River. No other published nutrient studies or bacterial studies for the Lafayette could be found: However, the State Water Control Board of Virginia (Jennings, 1965) performed a survey on the Eastern Branch of the Elizabeth River. Daily exygen profiles were prepared from August 10-11, 1964, as well as monthly surface samples from March to August, 1964, were taken. The samples

A.

covered various stages of the tidal cycle and included chlorophyll extractables, biomass, as total organic volatile substance, total phosphate, orthophosphates. biological oxygen demand, ammonia. and coliform counts. Table I lists the orthophosphate trends and total phosphate concentration as extracted from this survey report. Jennings (1965), assuming 15 milligrams per liter of phosphorous in the primary treated sewage effluents deposited in the Eastern Branch of the Elizabeth River, calculated that 123 pounds of phosphorous per day would be discharged into the river with an effluent discharge rate of approximately one million gallons per day. The total quantity of phosphorous in pounds, calculated from the concentration of phosphorous found in the water and the depth of the river. "...far exceeds that which could be discharged to this stream each day from sewage treatment plants. Therefore, it appears that buildup of nutrient material has occurred, or there is a substantial contribution from some other source."

The State Water Control Board of Virginia periodically monitors the Eastern and Southern Branches of the Elizabeth River for nutrients, oxygen, biological oxygen demand, alkalinity, and other parameters. A partial summary of this data is shown in Table II.

Phosphate levels in similar estuaries. Dissolved inorganic phosphate is higher in coastal waters and does not have a 15:1 atomic ratio of nitrogen/phosphorous as is found

Orthophosphate Concentration Trends and Total Phosphate.

TABLE 1

in Microgram-atoms Per Liter for the Eastern

Branch of the Elizabeth River

The samples were taken at bridges crossing the river. The data in this table was compiled by Jennings (1965).

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TABLE II

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A Summary of the Orthophosphate and Nitrate Concentration Values in Microgram-atoms Per Liter, and Trends for the Eastern and Southern Branches of the Elizabeth River Norfolk, Virginia, 1971, as Reported by the State Water Control Board

a. The values for nutrients as shown in the above table are suspect as the water samples were not adequately preserved.

in the open ocean. This is probably due to the low nitrogen/phosphorous rationfound on land (Sverdrup, et al., 1942; Pomeroy, et al., 1972). Although dissolved inorganic phosphate appears to be always in excess in coastal waters and nitrogen to be limiting to phytoplankton (Ryther and Dunstan, 1971; Likens, 1972), it is possible for dissolved inorganic phosphate to be used as an index or pollution (Ketchwa, 1967; Ryther and Dunstan, 1971). The levels or phosphate found for other estuaries are shown in Table III.

•

Daily cycles of phosphate. It has been noted **(Hewoombe** and Lang, 19)9; Newcombe and Brust, 1940; Kuenzler, McKellar and Muse, 1970; McKellar, 1971), that a daily cycle of dissolved inorganic phosphate exists in **estuaries.** The dissolved inorganic phosphate increases during the night and decreases during the day. McKellar ascribes this to an increase in the flux of phosphate from the sediment (McKellar, personal communication, 1972.). \therefore This study was done in a sewage waste pond where the level of dissolved inorganic phosphate was approx1matel7 *S0-60* microgram-atoms phosphate phosphorous per liter. Newcombe and Lang (1939) believe the daily fluctuations "...to be due to an acoelerated regeneration and reduced utilization of phosphate **as a** oorollaey of poor light penetration.•

Atypical cycles of phosphate in estuaries. Pomeroy summarizes and defines *atypical* cycles of phosphates in estuaries (Pomeroy, et al., 1972). In an *atypical* cycle

TABLE III

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Comparison of the Dissolved Orthophosphate in the Lafayette/

Elizabeth River to its Concentration in Other Estuaries

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of phosphate, the level of phosphate is greatest in the summer and least in the winter; This is, in general, the epposite of the cycle in the open ocean where phosphate is a limiting nutrient and is greatest in the winter and least in the summer; This atypical cycle has been noted by others (Newcombe, et al., 1939, 1940; Hutchinson and Bowen, 1947, 1950; Pratt, 1950; Rochford, 1951; Reimold. 1965; Gooch, 1968; McKellar, 1971) and their explanations can be summarized as follows:

1. Accelerated regeneration and reduced utilization. as a corollary of poor light penetration (Newcombe and Brust, 1940).

2. Uptake and release of large amounts of loosely bound inorganic phosphate adsorbed on clay particles (Reimold, 1965; Pomeroy, et al., 1965).

110 3. Increase of pH and/or Eh which releases phosphate from estuarine sediments (Carrit and Goodgal, 1954; Jitts, 1959: Young, 1968);

4. Remineralization of phosphate by sulfate reducing bacteria or other microorganisms (Teal and Kanwisher, 1961; Oppenheimer and Ward, 1963; Gooch, 1968), including equilibrium reactions of dissolved inorganic phosphate. dissolved organic phosphate and particulate phosphorous (Hutchinson and Bowen. 1950: Rigler. 1956).

S. S. Nutrient enrichment of the estuaries and slow exchange between estuaries and the open seas (Jeffries: - 実業の会社 1962; Barlow, et alv, 1963);

6: Shifting of the rates of metabolic processes that move phosphate from sediments to the water (Pomeroy, et al., 1972)

7. Greater wind generated interaction between bottom deposits and the water column in shallow areas (Aurand. 1968).

8. Excretion and rapid liberation of phosphate from zooplankton, especially in the summer (Hayes, 1963; McKellar, 1971 .

9. A seasonal regeneration and adsorption equilibrium ovele where in spring, adsorption is greater than regeneration and the opposite in the summer. In winter, adsorption equals regeneration due to reduced biological activity (Redfield, et al., 1963; Odum, 1971).

Pomeroy (1972) postulated a model of dissolved inorganic phosphate for Georgia salt marshes, rivers, and sounds which had several parameters that are very similar to the present study area. These parameters are:

1. Norphometry. The Duplin River has a water area of 1.3 x 10^6 miles² at mean low water as compared to the Lafayette River's water area of 7.12×10^6 miles² and 1 x 10⁷ miles³ volume as compared to 4.3 x 10⁶ miles³ for the Lafayette River.

2. Annual cycle of dissolved inorganic phosphate varied from a high in the summer to a low in the winter.

3. The levels of dissolved inorganic phosphate in the Duplin River were several orders of magnitude higher

than the coastal zone. The range was 1 to 4 microgram-atoms phosphate phosphorous per liter. $\sqrt{2}$

The major differences for the areas are:

1. The Georgia area is not polluted.

2. The Georgia area is not heavily urbanized. The Duplin River and the Lafayette River areas are similar in amount of rainfall and water temperature. The model postulated by Pomeroy is as follows (Pomeroy, et al., 1972, page 283, figure 7):

Initial concentrations, $X_n(0)$ are in microgram-atoms phosphate phosphorous per liter.

 C_1 and C_2 describe seasonal variations in the transfer of dissolved inorganic phosphate from sediments to Spartina and vice versa.

Pomeroy found that levels of phosphate in the Duplin River decreased with an increase in rainfall and increased with an increase in water temperature.

This increase of phosphate with an increase of temperature was ascribed to a alight shift in the equilibriwa of the dissolved inorganic phosphate from the sediment to the water because of an alteration of metabolic activity. The seasonal cycle of concentrations of phosphate in the Georgia salt marshes (Pomeroy, et al., 1972) is primarily controlled by the marsh grass (Spartina) metabolic processes and secondarily by sediment/water interactions.

Especially interesting was the high values of up to 10 microgram-atoms phosphate phosphorous per liter found in the water even in the winter due to a lag in the Spartina/ sediment system.

CHAPTER III

METHODS AND MATERIALS

I. DESCRIPTION OF THE STUDY ABBA

Description *gt* the general area. The Lafayette River is located within the urban Norfolk, Virginia environs at 360 *55'* Wand 760 201 N. The general area is shown in Figure 1 and the sampling area in Figure 2. The physical parameters are shown in Table IV.

The Lafayette River is lined with private residences, high rise apartments, three yacht clubs, a public park and zoo, and a u. s. Public Health Hospital. There is no industry of any consequence on the river. However, the Elizabeth River and Hamptons Roads area is heavily polluted by primary treated domestic wastes and commercial and U.S. Navy shipping. There is a dredge spoil depository at Craney Island at the juncture of the Lafayette River-Elizabeth River moqth. Furthermore, at the western edge of the juncture of the two rivers, there **is a** Hampton Roads Sanitation District sewage plant, called the Lamberts Point Plant, with a $19-31$ million gallons per day capacity. On the Elizabeth River, the city of Portsmouth has at Pinners Point a sewage plant with a 16 million gallons per day capacity. Hampton Roads Sanitation District also has

FIGURE 1

Chart of the General Study Area The sampling area, outlined by the rectangle is shown in greater detail in Figure 2. S indicates sewage plants.

FIGURE 2

A Chart of the Lafayette/Elizabeth River Study Area With
Sampling Sections and Locations

Sewer outfalls are marked O.F. Day markers are marked D.M.

TABLE IV

Physical Parameters of the Lafayette River

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a plant on the Elizabeth River near the Pinners Point plant with an outflow of 2-4 million gallons per day of secondary treated sewage and the Army Base plant outside of the mouth of the Elizabeth River with an outflow of 10-12 million gallons per day. The Lamberts Point and Army Base plants are primary treatment plants and are shown in Figure 2. The flow data for these plants is in Appendix B and C.

Description of the sampling area. The sampling area was divided into four sections (Figure 2) labelled A, B, C, and D.

Section A-1 through A-7 is the area from Lafayette Park up to. but not including. Day Marker 20. Section B-1 through B-21 is the area from Day Marker 20 to Day Marker 4 at the mouth of the Lafayette River. Section C-1 through C-4 is the area within the confines of the common mouth of the Elizabeth and Lafayette Rivers. Section D-1 through D-11 is the Elizabeth River mouth out to Hampton Roads.

EXECUTE: COLLECTION OF SAMPLES

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Sampling times. All samples were collected either from an eleven foot skiff, the twenty-eight foot R/V African Queen, the nineteen foot R/V Pangea. the thirtyfour foot Miss Priss III, from bridges spanning the Lafayette River, or from docks. In general, surface and bottom samples were taken at each station. The values for each sampling station are shown in Appendix A. The August, 1971

daily samples were collected from the R/V African Queen at stations B-18, $C-4$, and D-10. The January, 1972 daily samples were taken from the Miss Priss III anchored at statian B-16. The May, 1971 tidal data was sampled from station B-16 using the Norfolk Yacht Club dock. The lio,,...,,..r, 1971 tidal **aamp].es were** obtained from stations B-14, B-15, and B-16 using docks at these points. Times. dates, sections, wind velocity and tidal stages are shown in Table V for the sampling period 1970-1972.

Temperature, All **temperature** values are 1n degrees Centigrade (^OC) and were obtained using either a bucket thermometer or the thermocouple circuit on the Beckman RS5 Induction Salinometer.

Salinity. A Beckman RS5 Induction Salinometer with a fifty foot cable was utilized to obtain the salinity in the field. The induction salinometer was calibrated prior to each sampling interval.

Oxygen. When the macro-Winkler technique was used. all oxygen samples were collected with a polyvinylchloride Van Dorn'bottle. The first 100 milliliters of the sample was allowed to drain out before the oxygen sample was taken. The sample was then drained into the bottom of a 300 milliliter Biological Oxygen Demand bottle using rubber tubing. All precautions were taken to preyent the trapping of air bubbles in the sample container. The samples were stored, after addition of the reagents, at ambient temperature in the dark.

TABLE V

Sampling Information for All Dates for the Study Area

Over the Sampling Period 1970-1972
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Nutrients. The samples were collected with either a Van Dorn bottle or by dipping a polyethylene bottle just below the surface. All samples were stored in the dark on ice. All nutrient samples were analyzed within 3 to 4 hours for most studies or within 30 minutes for the daily survey.

III. TIDE AND WEATHER DATA

Tidal data. The tidal data was obtained from standard tide tables for Lamberts Point, Virginia (U. s. Department

of Commerce, Tidal Current Tables, 1970-1972).
Weather data. Wind information was procurred from the National Weather service at Norfolk Regional Airport.

IV. SEWAGE PUMPING BATE

This rate is expressed in million gallons per day **and was** taken from the flow records of the Hampton Roads Sanitation District. The sewage pumping rate over a twenty-" ' • four hour period for August 4 and *S,* 19?1 and January 11 and 12. 1972 for the Lamberts Point Sewage Plant is found in Appendix C. The mean monthly sewage pumping rate for the Lamberts Point Plant and the Army Base Plant is shown 1n Appendix B. おとも こうかい 酒 いっぱ

ANAIYTICAL V.

Nutrients. All samples were shaken and brought to room temperature prior to analysis. At this point, the various reagents for nutrient assay were added. A one centimeter pathlength was used in the Bausch and Lomb Spectronic 20 spectrophotometer. The wavelength for the determination of phosphate was 705 nm and for the determination of nitrate and nitrite. 525 nm. Corrections were made for turbidity, reagent, and tube to tube effects for all absorbance readings. The Hach Chemical Company method" was used for all nutrients. The Hach method for phosphate involves the formation of a phosphomolybdenum blue complex which is reduced by stannous chloride to a blue compound. The nitrate method reduces the nitrate, with an activated cadmium compound to nitrite. The nitrite then forms a diazo dye compound as in the Griess reaction.

Preparation of calibration curves; All of the methods used for determination of nutrients were based on a chemical reaction which produces a colored product. The absorbance of this colored product is directly proportional to the mutrient concentrations in the sample. Therefore, varying concentrations of the nutrient must be assayed by the \mathbb{R}^n \mathcal{A} particular method in question, so that a calibration curve

R_{Hach} Chemical Company, Ames, Iowa.

of absorbancy versus concentration can be prepared. A least squares fit of the curve is adopted to produce a regression equation. This equation can then be employed to predict the unknown nutrient concentration in a sample.

However, some of the methods utilized are subject to salt errors. If this is so, the calibration curves should be done in waters whose salinities approach that of the study areas. If a salt error is detected, then a calibration should be carried out in water taken from the study area. This will insure that the salt error is truly a salt error and not due to other factors peculiar to the water quality of the study area. Since the Hach methods for nutrient analyses were not in common use at the time this study was conducted, they must be compared to a standard method. The standard methods for this study are those contained in Strickland and Parsons (1965). The efficacy of the Hach method calibration curves over an extended period must be examined to determine if the curves are stable.

The preparation of the calibration curves were examined for:

. 14 Preparation of the Hach^Q method calibration curves in different artificial salinities and distilled water

2. Determination and statistical comparison of the curves to detect the presence of any salt error

 $\mathbf{x}^{(i)} = \mathbf{y} \mathbf{z}^{(i)} = \mathbf{y}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)} \mathbf{z}^{(i)}$

3. Comparison of the Hach[{]calibration curves in artificially prepared saline waters with those in Lafayette **River water**

4. Comparison of the Hach^p method for phosphate and nitrite and the standard methods

5. Comparison of recent Hach^Amethod calibration ourves with previous calibration curves.

Oxygen.

Macro Winkler method. The method used is outlined in Hydrographic Office Publication 607 (U.S. Navy Oceanographic Office, 1968) except that 0.025N phenylarsineoxide (P.A.O., Hach Chemical Company, Ames. Iowa) was used in place of 0.01N sodium thiosulfate. The manganous salt and alkaline iodide were added immediately to the water sample. shaken once, the brown precipate allowed to settle halfway, then reshaken. The samples were stored in the dark. The sulfurio acid was added in the laboratory just prior to titration with phenylarsineoxide. Duplicate aliquots of the sample were always analyzed. The mean of the two titrations was employed to compute the exygen in milliliters per liter at standard temperature. and pressure. The oxygen saturation, in per cent, was computed from a nomograph (Gilbert, et al., 1968).

 \ldots Oxygen meter A Yellow Spring International (Y.S.I.-51-A) oxygen meter was utilized to obtain in situ oxygen values. The machine was calibrated prior to each use and

checked with the macrowinkler method. The machine can be adjusted to compensate for different temperatures. salinities. and ambient pressures, so that the concentration of oxygen can be read from the machine.

VII. STATISTICAL METHODS

Test for null hypothesis. Unless otherwise stated. all tests were run at the p greater than 0.05 level. The significance test for the null hypothesis that the two population means are equal was based upon the "t" statistic (Snedecor and Cochren. 1968).

Analysis of variance for the regression. Draper and Smith (1967) have shown that the sum of the squares about the mean equals the sum of the squares about the regression plus the sum of the squares due to the regression. This allows the deviation from the regression line to be partitioned into two parts. Therefore, it can be applied in the assessment of the usefulness of the regression line. When the sum of the squares (S. S.) due to the regression is much greater than the sum of the squares about the Sum of the squares due to regression
Sum of the squares about the mean regression or R^2 equals is not too far from unity, then the regression appears to be a useful predictor. This does not hold true when the number of variables is nearly as large as the number of observations. It would then be possible to get a spuriously high R^Z or multiple correlation coefficient. The method

in Table VI served to construct the analysis of variance (anovar) table. The actual computation was done by an I.B.M. 1130 or 360 digital computer (Dixon, 1970).

Stepwise multiple regression. To obtain a regression equation of the form $Y = B_0 + B_1X_1 + B_2X_2$ $B_nX_n + e$ (Equation III-1) (Draper and Smith, 1967), where the variables in the regression may have interrelationships, the order of insertion in the regression could determine the significance and fit of the regression. The Biomedical Research Program for stepwise multiple regression was adopted (Dixon, 1970). This program allows the variables to be inserted in the regression equation if their partial F criterion is greater than a preselected percentage of the appropriate F distribution. If all variables are greater than the percentage of the F value, then the most highly correlated is inserted. The program computes and prints the multiple correlation coefficient, means, standard deviation, anovar table, F values, partial correlation coefficients and constants, and a summary of the increase in R^2 . and the state of the state

TABLE VI

Computation of the Analysis of the Regression Table

(Draper end Smith, 1967, P• 15)

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CHAPTER IV

RESULTS OP THE STUDY

The results of this. study have been divided into three sections. The first section, laboratory results, will deal with the statistical examination of the nutrient calibration curves. This examination will determine if the curves are significant and whether a "salt error" exists for the Hach methods. Special attention will be paid to the method for phosphate, and the oxygen meter will be compared to the Winkler method. The second section entitled field results will list the concentrations of oxygen, nitrate, nitrite, salinity, water temperature and phosphate for the tidal oycle, daily, seasonal and annual samples. The last section will **examine** proposed multiple linear regression predictive models for concentrations of phosphate. These models will be utilized in an attempt to determine the relationship of phosphate to the following parameters: tide, phosphate in sewage, rain, wind direction, and water temperature.

I. • **·lABOBl'l'OBY** BESUL!S

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The results of the statistical tests of the calibration curves for the H ach $^{\alpha}$ method are:

1. Dissolved inorganic phosphate. There is a definite salt effect that appears to cause a difference in the slope and intercept of the regression equations between distilled and saline water. The regression equations for the various salinities are shown in Table VII.

2. Nitrate. The slope of the regression equations for the Hach method in distilled water was not significantly different from those in saline waters. However, the intercepts are significantly different indicating a possible salt effect for this method. All the regression equations were significant at the p greater than *0.05* level (Table VII).

:,. Nitrite. The results ·tor this method are the same as those for the method for nitrate (Table VII).

Comparison of the Hach Methods with the Standard Methods for distilled water.

1. Dissolved inorganic phosphate. The Hach method tor dissolved phosphate in distilled water and at different salinities compares favorably with the standard method. (Table VIII).

2. Nitrate. Although the regression equation was significant, the Hach $^{\mathcal{C}}$ method displayed very erratic results. It was never possible to consistently repeat the Hach^{*} determination of nitrate and get the same regression . .
equation. Therefore, a calibration curve was prepared before every daily study and the resulting regression equation used for that determination. The concentrations

TABLE VII

Hach[&]Method Calibration Curve Data for Nutrients

The nutrients were dissolved in waters of different salinities. The concentration ranges for the nutrients are: 1.3 to 12.5 microgram-atoms phosphate phosphorous per liter, 5 to 30 microgram-atoms nitrate nitrogen per liter, 0.05 to 3.04 microgram-atoms nitrite nitrogen per liter. All the regressions are significant at the p greater than 0.05 level.

TABLE VIII

Comparison of the Standard Method Regression Data and the Hach^eMethod Regression Data for Dissolved

Inorganic Phosphate

a. The F value was determined using only this concentration of phosphate (Strickland and Parsons, 1965).

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of nitrate are not presented in the main body of the paper because of inacouracies in the Haeh method. They are listed 1n Appendix A.

3. Nitrite. The Hach method for nitrite compares very favorably with the standard method (Strickland and Parsons, 1965), however, it is not as sensitive nor as precise as the standard method.

One sample, from station B-16, of Lafayette River water was analyzed in quadruplicate by the Hach^a and standard phosphate method, giving the following results: $1.4 + 0.01$ microgramatoms per liter for the Hach² method and 1.6 ± 0.01 microgramatoms per liter for the standard method. The Hach method for phosphate was also shown to be stable for at least a year by using the $*t*$ test and comparing the mean F value (defined on page *S,* this thesis) of curves Pl plus P2 plus PJ with ourve P4 (Table IX).

Comparison of Yellow Springs International oxygen meter, model 51A, with the Macrowinkler oxygen determination. The oxygen meter was compared with oxygen values as determined by the macroWinkler method in waters with different concentrations of oxygen (Table X).

II. FIELD RESULTS

Oxygen.

B&nge., The range of saturation of 0X7gen for the Lafayette River was from 56 to 143 per cent (Appendix A).

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TABLE IX

Comparison of the Hach^a Method Calibration Curves for Dissolved Inorganic Phosphate Over an

Extended Period, 1970-1972

TABLE X

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Comparison of Yellow Springs International Oxygen Meter,

4S1-51A, With the MacroWinkler Oxygen Determination

(U. S. Navy Oceanographic Office, 1968)

The values do not include the results of the daily studies in August, 1971 (Event 14) and January, 1972 (Event 17).

Vertical distribution. There was no significant difference ("t" test) between the surface and bottom except in the summer for section C.

Section analysis. There was no significant difference between sections B, C, and D over all seasons. However, section A was significantly different from sections B and C in the fall of 1970 and 1971.

Seasonal analysis. Although there was no significant difference in sections A, B, and C between winter and spring there was a significant difference in both sections A and B between fall and winter and in section B between spring and summer.

Oxygen per cent saturation seldom reached critical values of 57% (Klein. 1959; State of Virginia. 1971) in the Lafayette River. Section B appeared to have two distinct oxygen levels, these being 80% saturation for the summer and fall and 100% saturation for the winter and spring. Section C had essentially the same oxygen values for all the seasons sampled.

Temperature. The range of temperature was from 0°C to 27.7 $^{\circ}$ C. There was no significant difference ("t" test) between the surface temperature values of all sections over the sampling period nor between the various sections in the same season. The mean temperature for all sections

FIGURE 3

Seasonal Values of Oxygen Saturation Expressed as Percentages, for Sections A(......), B(.......),

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 $C(-,-,-)$ and $D(X---X)$ Through 1970-1971.

Sectional oxygen values are combined averages of surface am\ bottom samples •. A+ on the line between **seasons** indicates a significant differenoe in the values. A on the line indicates that there is no significant difference in the values. A dotted rectangle indicates that there is no significant difference in the oxygen values for sections for that season.

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by season is given in Table XI. There appears to be a temperature difference between fall and winter.

Salinity. The range of salinity was from $11:0$ to 24.9 parts per thousand. There was no significant difference (^{"t"} test) between surface and bottom salinity values nor **between** the various sections at the same season, therefore the mean salinity values for all sections were used (Table XI). The salinity appears to be higher in the fall and lower in the spring.

Nitrate. The method for determination of nitrate was found to be too variable and imprecise to be of any actual use in this study. The range was from 0 to 18 microgramatoms nitrate nitrogen per liter. The largest values **were** in the summer and fall and lowest in the spring. The values obtained are shown in Appendix A but no further use **will be made of the data for nitrates in this paper.**

Nitrite. The value for nitrites ranged from 0 to 4 microgram-atoms nitrite nitrogen per liter. The higher values were generally found in the fall although the maximum nitrite was in the winter at section C. The lowest values were always in the spring (Appendix A).

Tidal cycle. On May 18, 1971 (Event 9), water samples were collected at the Norfolk X&oht Club pier (station B-16) over a six and one half hour period. Data for nitrates,

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TABLE·XI

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 $\omega = \omega_{\rm{eff}}/\omega_{\rm{eff}}$

Seasonal Salinities, in Parts Per Thousand, **and water** Temperature, in Degrees Centigrade, tor the Compesite . Section $A + B + C + D$ for the Period 1970-1972.

The values are composite means for all four sections by **seasons.,** It two values are shown the first is the surface and the second is the bottom value.

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nitrites, phosphates, and oxygen was collected (Table XII and Appendix A). On November 13, 1971, a 12 hour study (Event 16) was conducted over a wide area to detect any differences in concentrations or dissolved inorganic phosphate. Three stations were chosen so as to span the Lafa7ette River at the Hampton Boulevard Bridge. Data on nitrates, nitrites, phosphates, oxygen and temperature was collected (Appendix A). Data of phosphates, oxygen, and temperature for this event are shown in Table XIII. When these values were examined statistically, no significant difference was found either between the surface and **bottom** values for phosphate at each station or between **stations.**

DailY results. A clail7 study was made on August *4-S,* 1971 (Event 14) **and on** January 12-13, 1972 (Event 17). Event 14 was done at three different sites; these being stations B-18, c-4, and D-10. Stations c-4 and D-10 are located near the Lamberts Point and Army Base sewage plant outfalls respectively (Appendix E and A). The January daily samples were collected at site B-16, where data of nitrates, nitrites, dissolved inorganic phosphate, oxygen, salinity, and temperature was analyzed (Appendix E and A).

Oxygen. The mean saturation of oxygen for both August, 1971, and January, 1972, ranged from 74-133 per cent. The saturation values of oxygen for both events were essentially the same.

TABLE XII

Dissolved Inorganic Phosphate, in Microgram-atoms Phosphate Phosphorous Per Liter, Oxygen, as Per Cent Saturation, and Tide Stage for the Lafayette River Station B-16 on May 18, 1971 (Event 9) Over a Six and One Half Hour Period

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TABLE XIII

Dissolved Inorganic Phosphate, in Microgram-atoms Phosphate
Phosphorous Per Liter, Temperature in Degrees
Centigrade, Oxygen, as Per Cent Saturation,
and Tide Stage, for the Lafayette River,
Stations B-15, B-16, and B-17 o

P is expressed at the greater than 0.05 confidence limits.

Phosphate. No significant difference was found between surface and bottom values of dissolved incrganic phosphate for either August, 1971 or January, 1972. For the remainder of the discussion the mean of the surface and bottom values will apply. No significant difference existed between the mean values of section B and C, August, 1971. Therefore, the combined means for the same time period were used (Appendix E). The values of stations B-16 and C-4 were combined because the difference in sampling times and the distance between stations were insignificant. (Appendix E). There was a significant difference in the values between stations B-18 and D-10 (Appendix E&A). Values for dissolved inorganic phosphate for these time periods in August, 1971 and January, 1972 are given (Figures 4 and 5, and Appendix E).

Seasonal cycle of phosphate. The levels of dissolved inorganic phosphate, water temperature, rainfall, and wind direction for the sampling period are shown in Appendix F. The data was expressed as the means of the combined sections A plus B plus C. These three sections comprise the Lafayette River. The wind directions was expressed as cosine theta (page 5, this thesis). The Elizabeth River, section D, with the same information, excepting cosine theta, are shown in Appendix F. These same parameters were then further combined into seasons for the composite section $A + B + C$ comprising the Lafayette River and are shown in Appendix G.

FIGUBE 4

Dissolved Inorganic Phosphate, in Microgram-atoms Phosphate Phosphorous Per Liter for August 4-5, 1971 Over a 24 Hour

> Period (E.D.S.T.) at Two Sampling-sites $B-18 + C-4$ ($\leftarrow\bullet$) and $D-10$ ($\leftarrow\bullet\bullet\bullet$)

Tidal stages are shown and are coied 1 tor beginning flood tide and 2 for beginning ebb tide. All of the dissolved inorganic phosphate values are composite means for the surface and bottom values. The values for Stations $(B-18 + C-4)$ are composite means of the two stations for each sampling time.

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 $\frac{1}{2}$

FIGURE 5

Dissolved Inorganic Phosphate, in Microgram-atoms Phosphate Phosphorous Per Liter Over a 24 Hour Period (E.S.T.) for January 12-13, 1972, at Station B-16

Tidal stages are shown and are coded 1 for beginning flood tide and 2 for beginning ebb tide. The dissolved inorganic phosphate values are composite averages of the surface and bottom values.

Ill. PROPOSED PREDICTIVE MODELS FOR PHOSPHATE Daily models. A linear regression model was proposed for the dissolved inorganic phosphate in the combined stations B-18 and C-4 for August, 1971. The same model was proposed for January, 1912, station B-16. The predicted dissolved inorganic phosphate is expressed as the logarithm to the base 10. This form was found to give the best tit when the following independent variables were used in the regression: tidal stage, wind component (page 5, this thesis), and the rate of dissolved inorganic phosphate, in kg/hr, from the sewage outfall. This rate of flow of phosphate from the Lamberts Point Plant was determined using the data in Appendix D. The mean daily sewage pugping rates for August, 1971 (Appendix C) and January, 1972 (Appendix C), and the mean daily sewage pumping rates for March, 1972 (Appendix D) were not found to be signifioantly different. It was assumed that- the levels of dissolved inorganic phosphate in the final effluent of the Lamberts Point Plant tor August, 1971 and January, 1972 were not significantly different from the levels of phosphate found in March, 1912. Therefore, the rate of flow of phosphate on March, 1972 was used to compute the levels of dissolved inorganic phosphate in the final **sewage** effluent for the August, 1971 and January, 1972 sampling periods. The concentration of dissolved inorganic phosphate, tidal stage, rate of phosphate from the sewage outfall, wind

component and sampling **t1ae ls** abown. for August, 1971 and January, 1972 (Appendix E). The resulting linear regression models computed from theae variables are shon in Table XIV, formulas IV-2 through IV-5. The observed and predicted concentrations of phosphate are given for August, 1971 (Figure 6) and January, 1972 (Figure?).

seasonal models. Using the observed dissolved inorganic phosphate from the sampllng period 1970 to 1972 for combined sections A plus B plus C **(Appendix** F and G), an attempt was made to form a linear regression model tor the dissolved inorganic phosphate in these three sections for that period. Thia seasonal model utilized the following independent variables: water temperature, rainfall, and wind direction, expressed as the cosine of the angle the resultant wind makes relative to the Lafayette River Channel at the mouth. The summary of these resultant models are disclosed in fable XV, formulas IV-6 and IV-7, and the observed and predicted levels of dissolved inorganic phosphate are shown in Figures 8 and $9.$

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TABLE XIV

Results of the Daily Dissolved Inorganic Phosphate Prediction Models for August 4-5, 1971 and
January 12-13, 1972 for the
Lafayette River

The models are for Ebb or Flood tides. The estimated dependent variable, P_2 , is the ordinate expressed as log₁₀ of dissolved inorganic phosphate in microgram-atoms/liter.

Independent variables (X) Code:

- indicates the stage of the tide either abbing or ·T flooding.
- indicates the rate of phosphate phosphorous from S. sewage effluent in kilograms per hour interpolated from March, 1972 data.
- indicates the wind component computed by taking the W. cosine of the angle of the wind relative to the Lafayette River channel at 280 True and multiplying this times the wind speed in knots.

FIGURE 6

Observed (.-.,) and Predicted (X..X) Values of Dissolved Inorganic Phosphate in Microgram-atoms Phosphate Phosphorous, for August $4-5$, 1971, Over a 24 Hour Period

The regression model equations from Table XIV and the data from Appendix E were used. Note the break in the ordinate. The two observed values shown for each sampling time are the values from station B-18 and C_{-4} .

FIGURE 7

Observed (....) and Predicted (X--X) Values of Dissolved Inorganic Phosphate, in Microgram-atoms Phosphate Phosphorous Per Liter, for January 12-13, 1972 Over a 24 Hour Period (E.S.T.) at Station B-16

The regression equations from Table XIV-and the data in Appendix E were used.

TABLE XV

Annual and Seasonal Predictive Model for Dissolved Inorganic

Phosphate for the Combined Lafayette River

Sections A Plus B Plus C

Predictive model for dissolved inorganic phosphate over the sampling period 1970 to 1972

 $\widehat{D_6I_6P_6} = 1.04 + 0.2(^{0}C) - 0.05(R) - 0.87$ (Cos e) equation $(TV-6)$

Significance level of the regression equation, P greater than 0.10

 $R^2 = \frac{30.3}{47.37} = 67\%$

Predictive model for seasonal dissolved inorganic phosphate over the sampling period 1970 to 1972

$$
\overline{D_{\bullet}I_{\bullet}P_{\bullet}} = 1.1 + 0.19(^{0}C) + 2.2 \text{ (Cos 4)}
$$

equation $(TV-7)$

Significance level of the regression equation. P greater t han 0.10

 $R^2 = \frac{17.8}{20.6} = 86%$

Code

FIGURE 8

Observed and Predicted **Levels** *ot* Dissolved Inorganic Phosphate, in Microgram-atoms Phosphate Phosphorous Per Liter for the Lafayette River (Sections A+B+C) tor the Sampling Period 1970-1972.

Predicted values were obtained using regression model equations from Table xv. The observed values are combined averages *tor* Section A, B, and C tor the months during which the samples were collected.

J:--:f Observed values and p greater than *0.05* confidence limits.

Predicted values.

A + between months indicates that a significant difference existed between these two values. A - between months indicates that there was no significant difference.

FIGURE 9

of Dissolved Inorganic Phosphate in Microgram-atoms Phosphate Phosphorous Per Liter for the Lafayette River (Section A+B+C) for the Sampling Period 1970-1972.

Predicted values were obtained using the regression model equations from Table XV. The observed values are combined means for Sections A, B, and C for the seasons during which samples were collected. The P greater than 0.05 confidence limits for the observed values are shown for the observed values.
CHAPTER V

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DISCUSSION OF RESULTS

LIMITATIONS OF THE COLLECTED DATA I.

Discussion of the data gathered over the sampling period must be considered within the restrictions of the sampling method, i.e., the samples are consecutive and not synoptic, and therefore, there is a possibility that nutrient levels could be affected by the tidal stage or the time of day. Also, the sampling dates and times chosen for the sampling period could bias the data. Another factor to be considered is that the analytical methods could not detect nutrient values below one microgram-atom dissolved inorganic phosphate phosphorous per liter.

II. DISCUSSION OF THE CIRCULATION OF THE LAFAYETTE RIVER

In general there was no difference in the surface and bottom values of temperature, oxygen, salinity and nutrients over the sampling period. This indicates that the Lafayette River is thoroughly mixed in the vertical direction. This is probably due to its shallow depth and the turbulent diffusion produced by tidal currents. Pritchard (1960) states that vertical diffusion is most intense in layers having vertical homogeneity. The role of tidal movements

and mixing, in vertically homogenious estuaries is also very large as compared to the water motion and stability produced by inflowing fresh water (Pritchard, 1960).

III. DATA FOR OXYGEN. NITRATE. AND NITRITE

Except in the fall of 1970 and 1971, there was no significant difference between the saturation values of oxygen in the sampling sections A, B, C, or D. In the fall of 1970 and 1971 oxygen saturation values 1n section A of 69 per cent were significantly lower than those of section Bat 82 per cent. Section B levels of oxygen were also significantly lower, at 80 per cent saturation in the fall and summer of 1970 and 1971, as compared to 100 per cent saturation 1n the winter and spring of 1970 and 1971 (Appendix H). The difference between sections A and B in the fall of 1970 and 1971 could be due to higher heterotrophic activity, and to the increased organic load of the higher phytoplankton densities in this section (T. Purcell, personal communication). This could also indicate that the circulation of the Lafayette River is sluggish, especially in the warm dry months when the water movement in the river - . is dependent'on tidal exchange only.

The method for nitrate used was too imprecise to yield any valid results. The values of nitrites ranged from one to four microgram-atoms nitrite nitrogen per liter and appeared to be inversely related to the levels of oxygen **i.e., higher in the fall and summer of 1970 and 1971 when** \cdot the level of oxygen was lowest (Figure 3).

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IV. DISSOLVED INORGANIC PHOSPHATE LEVELS OVER , • *:* • " ·THE ,SAMPLING PERIOD

Vertical and horizontal distribution. There was no observable difference in the surface to bottom concentration of dissolved inorganic phosphate concentration at any section over the complete sampling period. The lack of any observed lateral difference in the dissolved inorganic phosphate in November, 1971 at stations B-15, B-16 and B-17 over a 12 hour period (Table XIII, page 48) was the reason for the assumption that although the level of dissolved inorganic phosphate may vary from the head of the river to the mouth and at one station over time, there is probably no lateral difference in dissolved inorganic phosphate 1n the Lafayette River. This lends further weight to the contention that the river is dominated by tidal influence rather than fresh water influx.

Possible mechanisms for the levels of phosphate ln the Lafayette River. The level of dissolved inorganic phosphate over the sampling period exceeded the upper limit value of 3.3 microgram-atoms per liter, as suggested by Pritchard (1969), in all the months sampled (Appendix F) $\mathcal{D} = \{ \mathcal{D} \mid \mathcal{D} \in \mathcal{D} \}$. In the set of the except December, 1970, January, 1971 and March, 1971. The levels of phosphate seem to depend on water temperature. This can be shown by comparing the January, 1972 (Section B) mean water temperature of 11ºC and the mean concentration of phosphate of 5.8 microgram-atoms per liter with the January, (New York Book Life Line) 2013年(本部581) An

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1971 (Section B) mean water temperature of 2⁰C and mean level of phosphate of 2.4 microgram-atoms per liter. **The** water temperature is 9⁰C higher in 1972 and dissolved inorganic phosphate in 1972 is double that of the 1971 concentration of phosphate. This appears to agree with the general statement that for an increase of 10°C in the temperature the chemical reaction rate is doubled (Briscoe, 1949). The fact that levels of phosphate in estuaries increase with temperature is further supported by Pomeroy (1960). Pomeroy (1960) showed that the concentration of dissolved inorganic phosphate increased from 3 to 5.5 microgram-atoms dissolved incrganic phosphate phosphorous per liter when the water temperature rose from 15^oC to 27^0 C. As well as a direct relationship between phosphate and temperature. there was an increase in phosphate turnover time from 2.0 to 4.0 milligrams phosphate phosphorous per subic meter per hour. The influence of temperature on the level of dissolved inorganic phosphate of the Lafayette River is best shown by the results of the annual and seasonal models for dissolved inorganic phosphate. (Table XV, page 58, equation IV-6 and IV-7). The model using the composite mean of the dissolved inorganic phosphate for the months sampled is referred to as the annual model. This annual model has a positive regression coefficient for temperature and negative regression coef. ficients for rain and wind direction. This annual model has a constant value of approximately one. The seasonal model

of dissolved inorganic phosphate in the Lafayette River. has a constant of one and positive regression coefficients for temperature and wind direction. The seasonal model accounts for approximately 86 per cent and the annual model 65 per cent of the variance in the dissolved inorganic phosphate level. The prediction of a constant level of one microgram-atom dissolved inorganic phosphate phosphorous per liter in both models, which can be obtained by setting the independent variables to zero in the regression equations, agrees with the value which Pomeroy et al., (1965) states is the equilibrium value for an estuarine system. This system (Pomeroy, 1965) consists of a two step ion exchange between clay minerals and water, and interstitial microorganisms and water. This system maintains a concentration of dissolved inorganic phosphate of one microgramatom phosphate phosphorous per liter. Pomeroy's hypothesis could explain the fact that there were yery few times when dissolved inorganic phosphate was not found in the Lafayette River over this sampling period (Appendix A). The regression of dissolved inorganic phosphate with temperature suggests a possible biological mechanism for the high levels of phosphate found in the Lafayette River. Few of the murely physical or chemical models for phosphate in estumetes (Rochford, 1951; Carritt and Goodgal, 1954; Jitts. 1959; Pomeroy, et al., 1965; Reimold, 1965; Young. 1968), appear to be capable of the high levels of phosphate

found in the Lafayette River. Pomeroy postulates a model for a Georgia salt marsh estuary that is very similar to the Lafayette River in many physical aspects but dissimilar in three main categories. which are:

1. Concentration of phosphate in the Lafayette River ranged from 1.9 to 8.6 microgram-atoms per liter whereas the Duplin River ranged from 1.0 to 4.0 microgram-atoms phosphate phosphorous per liter.

2. The Duplin River was dominated by Spartina type marsh grasses. Whereas the Lafayette River has comparatively few marshes.

3. The Duplin River area is not urbanized or polluted while the Lafayette River is surrounded by the City of Norfolk whose sewage outfalls deposit primary treated sewage effluent at the mouth of the river.

Pomeroy's model uses the Spartina marsh grass as the controlling mechanism for the level of phosphate. If this same general model is appropriate for this area, then the small amount of marsh grass in the Lafayette River could cause the Spartina-sediment equilibrium to shift and release higher quantities of phosphate to the waters of the Lafayette River. This shifting of the Spartinasediment system, with an increase in phosphate from 1 to 10 microgram-atoms phosphate phosphorous per liter, has been noted by Pomeroy in the Georgia salt marsh. Pomeroy's model reveals that the level of phosphate in the Duplin

River is directly related to water temperature and inversely related to rainfall. The annual and seasonal models show that similar results were found in the Lafayette River (Table XV, page 58, this thesis). It would appear that the Lafayette River's level of dissolved inorganic phosphate is controlled primarily by metabolic processes of the organisms in the sediment or water rather than the marsh grass as in Pomeroy's model. If this is so, then it is possible that the level of dissolved inorganic phosphate could result from the metabolic activities of zooplankton or other organisms in the water (Rigler, 1956, 1964; Smayda, 1957; Hayes, 1963; Raymont, 1963; Martin, 1965; Satami. and Pomeroy, 1965; McKellar, 1971), or in the sediment (Zobell and Feltham, 1948; Teal and Kanwisher, 1961; Oppenheimer and Ward, 1963; Wood, 1965; Aurand, 1968; Gooch, 1968; Pomeroy, et al., 1972). The high values of loosely bound phosphate found in estuarine sediments (Noore, 1929; Rochford, 1951; Young, 1968), lends strength to the belief that the primary control of the levels of dissolved inorganic phosphate in the Lafayette River is determined by the sediment-water system.

The inverse relationship of rainfall to the level of \mathbb{R}^2 dissolved imorganic phosphate in the Lafayette River suggests that the rainfall either dilutes the concentration of phosphate in the water thereby reducing the level of phosphate or causes a body of more saline water with a lower value of

phosphate to enter the Lafayette River. This. water deficient in phosphate could be water from the Hampton Roads area which has been shown to contain lower concentrations of phosphate (Stroup and Wood, 1966). The concentration of phosphate in storm runoff for similar areas can range from 3.5 to 29 microgram-atoms phosphate per liter (Fruh, 1968 . The values of phosphate for rainwater can vary from 0.13 to 3.2 microgram-atoms phosphate phosphorous per liter (Fruh, 1968). As the magnitude of the concentration of phosphate 1n rainwater and storm runoff could cause the concentration of phosphate in the Lafayette River to·increaae rather than decrease. it appears that the influx of waters lower in phosphate from Hampton Roads may better explain the diluting effect of rainwater on the content of phosphate in the Lafayette River.

The direct relation of a northerly or a southerly wind to levels of phosphate in the seasonal predictive and which model for phosphate seems to tie in with the seasonal shift in winds in the Nerfolk area from a northeasterly direction in the winter to a southwesterly direction in the summer . (Table XV, page '58). A northeasterly wind could cause a wind induced flow from the Lafayette River at the surface along with a bottom flow into the Lafayette River of Hampton Roads 'water, which 'is lower in dissolved inorganic phosphate. A southeasterly wind could cause just the opposite 第1 号单 三十六 result,• 解除性 とう 网络小头 人名德布雷特 化二氧化氢 医单细胞的

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Discussion of the daily fluctuation of phosphate. The daily cycle of dissolved inorganic phosphate for August. 1971 appears to be controlled by tide and the rate of flow of phosphate in the sewage effluent. from the Lamberts Point Sewage Plant outfall. The regression coefficients in the daily model (Table XIV, page 55, this thesis) reveal that on a flood tide a unit increase in tide stage has three times the effect as a unit increase in the rate of flow of phosphate from the sewage outfall. However, on the ebb tide the coefficients have equal weight. The level of phosphate in the Lafayette River decreases as the tidal stage changes from slack to flood and increases as the tide progresses from slack to ebb. At the same time there is a positive regression coefficient for the rate of flow of phosphate from the sewage plant outfall during the flood tide and a negative regression coefficient for this variable on the ebb tide. In August the size of the tidal regression coefficients seems to indicate that the tidal effect is more important than the flux of phosphate from the sewage plant outfall. The positive signs for the tidal regression coefficient in the August. 1971 daily model could indicate $\mathcal{W} \subseteq \mathcal{W} \cap T$ $\mathcal{L}(\mathcal{L})$ ತಿರಿ the following:

"1. The source of dissolved inorganic phosphate for the Lafayette River is upstream (Section A) from the daily sampling stations (Section B and C).

Firm 2. The ebbing waters of the Elizabeth River, along with its high load of dissolved inorganic phosphate from

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the sewage outfall, forms an eddy of water which enters the Lafayette River.

The model is wrong and the regression equation $3.$ results purely by chance.

The B_nX_n values (page 3, this thesis) are more 4. important in the regression than the variables entered into the model.

5. The flood waters coming from the Hampton Roads area. where the values of dissolved inorganic phosphate are lower. could dilute the waters of the Lafayette River.

Of these five alternatives, it is not possible to dispute numbers three and four with the small amount of data presently available. The first alternative, that the source of phosphate is upstream (Section A) does not appear to be valid as it was very seldom that concentrations of phosphate were higher upstream (Appendix A, Section A). The second alternative appears more likely but the daily model for concentration of phosphate on the ebb tide also contains a negative regression coefficient for the rate of flow of phosphate from the Lamberts Point sewage outfall. This indicates that if there is an eddy at ebb tide, it is not bringing water with a high content of phosphate from the Elizabeth River into the Lafayette River. The August, 1971 daily prediction model for phosphate seems to show that the phosphate from the sewage plant on the Elizabeth River does affect the levels of phosphate in the Lafayette River on the flood tide. The concentration of phosphate

in the Lafayette River increases as the flow of phosphate In the effluent from the Lamberts Point sewage plant increases. However this is true only on the flood tide when the Elizabeth River water moves into the Lafayette River. The daily model for January, 1972 is entirely different from the August, 1971 daily prediction model for phosphate, especially in these aspects:

1. The water temperature in August, 1971 was approximately 25°C whereas in January, 1972 it was approximately 10[°]C.

2. The overall range of concentrations of phosphate in August. 1971 was from 5-16 microgram-atoms phosphate per liter as compared to 5-7 microgram-atoms phosphate per liter for January, 1972.

3. The mean concentration of phosphate for August. 1971 was 8.6 as compared to 5.8 microgram-atoms phosphate per liter for the January, 1972 daily study. . The differences in concentration of phosphate for the two studies could be due to the following:

1. The August, 1971 or the January, 1972 values of phosphate resulted totally from chance and were not typical of that sampling period.

Phill 2. The levels of phosphate in the Lafayette River are the result of a biological-sediment-water regeneration of phosphate, where colder temperatures would depress the release of phosphates from the sediment to the water. have ັນສາມາດເມີດເປັນຫຼາຍ **ເຮັດໃນລະ**ຫຼາຍຂ່າວສອງ ການ ການ ການ ການ ການ ກ່ຽວ. ຄັ້ນ **ຫຼວຍເຂັ້ນຂ່າ**ຍ ກັນສາ 12.000

-The daily fluctuations of phosphate are the result **or a** clllution of the higher level of dissolved inorganic phosphate in the waters of the Lafayette River by the lower content of phosphate in the flooding waters of Baapton Roads. There is then less production of phosphate in the waters of the Lafayette River in the winter. Therefore. when the level of phosphate in the Lafayette River is diluted by the waters deficient in phosphate from Hampton Roads, there is no noticeable effect because the level of phosphate is already low in the Lafayette River. There is greater production of phosphate in the Lafayette River in the summer. When the summer level of phosphate in the Lafayette River is diluted by the waters deficient in phosphate from Hampton Roads, there is a noticeable differenoe, for the Lafayette River has a higher concentration of phosphate at this time.

Discussion of the "atypical" cycle of phosphate in the **Lafayette River 11s** compared to other **estuaries.** It has been noted by many researchers (Newcombe, et al., 1939, 1940; Rochford, 1951; Smayda, 1957; Pomeroy, et al., 1972) that estuaries have an "atypical" cycle of phosphate, i.e., high values of phosphate in the summer and low values of phosphate in the winter. This cycle is in general just the opposite of that in the open ocean (Sverdrup, et al., 1942: Moore. 1958). The Lafayette River has the same type of •atypical• cycle of' phosphate. The Lafayette River has levels of phosphate similar to those in the polluted Rew York

Harbor (Howells, et al., 1970). However, the values are far less than those of a Delaware salt marsh (Reimold, 1965). The Lafayette River has much higher values of phosphate then either Hampton Roads, lower Chesapeake Bay, or the York River in the lower Chesapeake Bay. The levels of phosphate for other estuaries (Table III, pages 1J and 14, this thesis) appear to dispute the statement by Pritchard (1969) that J.J microgram-atoms phosphate phosphorous per liter is the upper limit for estuarine waters before the deleterious effects of eutrophication occur. The values for salt marshes and rivers bordering salt marshes (Reimold, 1965; Pomeroy, et al., 1972) are from two to ten times the value stated by Pritchard (1969). Although phosphate can be used as an index and tracer of pollution (Ketchum, 1967), it can not be used a priori to define pollution. There are environments which normally contain concentrations of phosphate much greater than J.J microgram-atoms phosphate '['] phosphorous per liter.

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CHAPTER VT

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CONCLUSION

The Lafayette River is a shallow, turbid, urban estuary in Norfolk, Virginia. Water movement is controlled mainly by the tide rather than fresh water influx. Oxygen, temperature and salinity values are vertioally and laterally homogenious in the Lafayette River. Temperature and oxygen are also horizontally homogenious except during the warm. dry months when the oxygen values at the head of the river were lower than those at the mouth. There is usually a small horizontal salinity gradient from the mouth to the head of the **river.**

The Lafa7ette River has an •atypioal• phosphate **oyole.** The values of phosphate are higher in the summer and lower in the winter. The values of phosphate ranged. from one to ,., twenty four microgram-atoms per liter.

The mean values of phosphate in the Lafayette River for the winter $(1970-1971$ and $1972)$ ranged from 2.4 to 5.8 microgram-atoms per liter and for the summer of 1971 , 8.0 ld.crogram-&toms pe; liter. • • $\mathcal{L}^{\text{max}}_{\text{max}}$. The set of \mathcal{L}^{max} . The set of \mathcal{L}^{max} is the set of \mathcal{L}^{max}

The concentration of phosphate in the Lafayette River is much higher than that of the Hampton Roads and Chesapeake Bay area. The Lafayette River contains from two to four どうししれく (動物)

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times as much phosphate as other estuaries and rivers in the **Chesapeake Bay area,** the Elizabeth River being the 'one exception with values of phosphate comparable to the Lafayette River. The levels of phosphate over the sampling period were in general higher than the value of 3.3 microgram-atoms per liter, set by Pritchard (1969) as the upper level for concentration of phosphate beyond which large algal blooms occur.

Multiple linear regression models were prepared and attempted to relate the daily changes in phosphate (\hat{P}) to: tide stage (T) , wind component (W) , rate of phosphate (kg/hr) from the Lamberts Point sewer outfall (S).

of flow of phosphate from the sewage effluent (S) on the ebbing tide and ia equally as important aa the. rate of flow of phosphate from the sewage effluent on the flooding tide.

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The daily variations in phosphate are more noticeable in the summer because of the higher concentrations of phosphate in the Lafayette River during this season. The increase of phosphate on the ebb tide and the decrease on the flood tide over a.dally. cycle was attributed to a dilution of the waters of the Lafayette River by the water from Hampton Roads. The water from Hampton Roads contains from o.8 to 1.0 microgramatoms of phosphate per liter.

The predictive multiple regression model for phosphate (D.I.P.) over the sampling period 1970-1972 is found to be a function of water temperature (^0C) , rainfall (R) , and wind direction (cos θ), The predictive model for seasonal ¹ concentration of phosphate was a function of water temperature and wind direction.

Annual Model

 $D_0I_0P_0 = 1.0 + 0.2(^{0}C) - 0.05(R) - 0.87(\cos \theta)$ (equation IV-6) Seasonal Model

 $\widehat{\mathbf{D}_\bullet \mathbf{I}_\bullet \mathbf{P}_\bullet} = \mathbf{1}_\bullet \mathbf{1} + \mathbf{0}_\bullet \mathbf{1} \mathbf{9} (\mathbf{O} \mathbf{C}) + 2_\bullet \mathbf{2} (\cos \theta)$

The direct relation of water temperature to content of phosphate was Attributed to the increased biochemical activities of the microorganisms in the sediment-water **system.** The inverse relation of rain to concentration of phosphate was due to a dilution of the Lafayette River water by inflowing, more saline Hampton Roads water and its lower concentration of phosphate.

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APPENDIX

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APPENDIX A - RAW DATA

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The phosphate values are expressed as microgram-atoms phosphate phosphorous per liter. The nitrate as microgram-
atoms nitrate nitrogen per liter and nitrite as microgramatoms nitrite nitrogen per liter. The oxygen is in
milliliters of oxygen per liter, temperature as degrees
Centigrade and salinity in parts per thousand. If there are two values at one station the first value is the surface sample and second is the bottom sample. The tide stage is coded E for ebb and F for flood.

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APPENDIX B

Mean monthly rainfall, in inches, and the mean monthly sewage pumping rate for the Lamberts Point Plant and the Army Base Plant (Hampton Roads Sanitation District, Norfolk, Virginia) for the sampling period 1970-1972. The sewage pumping rate is expressed as million gallons per day.

Sewage pumping rate fluctuations, in million gallons
per day, over a twenty-four hour period, August 4-5,
1971 and January 12-13, 1972 for the Lamberts Point
Sewage Plant (Hampton Roads Sanitation District, Norfolk,
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APPENDIX D

Concentration of dissolved inorganic phosphate, in
microgram-atoms per liter, in the final, primary treated
sewage effluent, the sewage pumping rate, in million
gallons per day, and the rate of flow of phosphate from
the o on March 30, 1972.

APPENDIX E

Processed observed data for the 24 hour stations.
Dissolved inorganic phosphate, in microgram-atoms per
liter, tidal stage, expressed as 1 to less than 2 for flood
and 2 up to, but not including 3, for ebb, computed rate o wind component (p. this thesis) and time for August 45, 1971, combined stations (B-18⁺ C-4) and January 12-13,
1972, sstation (B-16).

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APPENDIX F

'Combined Values for Dissolved Inorganic Phosphate, Rainfall, Water Temperature, and Wind Direction, Expressed as Cosine Theta, for the Combined Sections $(A + B + C)$ Comprising the
Lafayette River and Section D, the Elizabeth River, During
the Sampling Interval, 1970-1972

Statistical values for phosphate (microgram-atoms per liter) and water (degrees Centigrade) are listed in the following sequence: mean, standard deviation, number of measurements, and range.

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APPENDIX G

Seasonal Dissolved Inorganic Phosphate, Water Temperature, in Degrees Centigrade, Rain, and Wind Direction for the Lafayette River for 1970 to 1972.

The values are the composite means of the values in Sections A, B, and C. Mean dissolved phosphate (microgramatoms per liter) and mean water temperature in degrees Centigrade are listed with their standard deviations. number of samples, and ranges of values.

No data available, assumed same as Fall, 1970. a_{\bullet} No data available, assumed same as Winter, 1970-71. b_{\bullet}

APPENDIX H

Seasonal Oxygen Saturation Values for Sections A, B, C, and D

For 1970-1971

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