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Michigan State University, Ph.D., 1972
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THE INTERACTION OF LINEAR PHOSPHATES
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IN THE
THUNDER BAY, ALPENA, MICHIGAN

BY

Richard Barnaba Moreau

A THESIS

Submitted to
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ABSTRACT

THE INTERACTION OF LINEAR PHOSPHATES
WITH
SOLUBLE AND PARTICULATE CALCIUM
AND
NATURAL COLORED ORGANIC ACIDS
IN THE
THUNDER BAY, ALPENA, MICHIGAN

BY

Richard Barnaba Moreau

The Thunder Bay Watershed has been found to have a relatively high water quality, with much of the 1250-square-mile drainage basin still in its natural state. The regional inventory of the watershed showed domestic, agricultural, and industrial influences on the quality of the water, character of the watershed resources, and aquatic species composition.

The local sewage plant effluent contained a high level of the simple linear phosphates: ortho, pyro, and tripoly. These forms would be involved in phosphorus availability and contribute to eutrophication of Thunder Bay.

Calcareous particles from natural limestone sources and calcinated cement dust can serve as adsorption sites for the soluble linear phosphate forms. The removal of ortho, pyro, and tripolyphosphates from standard solutions and phosphorus from composite sewage samples by the cement dust indicated a probable uptake of phosphates in the bay by dust particles.

Oxidation of natural water samples showed that there exists an interaction between calcium and natural organic matter. The colored materials had an acidic nature and were recovered in sufficient concentration to determine metal-organic acid-phosphate interactions. The interaction of phosphate linear forms with this natural complex was determined in standard calcium-phosphate solutions using calcium and hydrogen electrodes.

The milliequivalence response of the calcium-phosphate mixtures was reduced in the presence of concentrated colored organic acids from the watershed. The values of association constants for the mixtures were increased by involvement of these natural organic acids. The phosphates in the calcium complexes may occur as $P_xO_y^{n-}$ bonded through soluble calcium to the acidic groups of the organic matter in natural waters.

In the Thunder Bay Watershed, the adsorption of phosphates on calcareous sediments and the formation of a soluble complex between the calcium-phosphate system and natural organic acids, will certainly influence the movement and availability of phosphorus in the Thunder Bay ecosystem.

ACKNOWLEDGMENTS

To God: It is our duty to glory in the cross of our Lord. He saves us and sets us free; through Him we find salvation, life, and resurrection.

I wish to thank my major professor, Dr. Frank M. D'Itri, for his guidance and encouragement throughout this research. I would also like to acknowledge the support of the National Science Foundation through a Science Faculty Fellowship for an academic year. As well, the assistance and suggestions of Dr. Niles R. Kevern, Dr. Clifford R. Humphrys, Dr. Andrew Timnick, Jack E. Petoskey, Charles S. Annett, Thomas E. Mears, numerous technical students and local industrial personnel have been essential to the completion of this project.

To my family and parents, may I say, that without your support and prayers, this task would never have been accomplished.

To Joyce, my wife, for her typing skill and whose devotion and encouragement sustained me in my many moments of frustration.

Be praised, O Lord, through our sister Mother Earth,
For she sustains and guides our life,
And yields us divers fruits, with tinted flowers and grass,
Praise and bless my Lord, and thank him too,
And serve him all, in great humility.

St. Francis of Assisi

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INTRODUCTION

This project has been developed within the frame of reference of the far-sweeping recommendations of the American Chemical Society (ACS) Committee on Chemistry and Public Affairs (1969). This thesis concerns natural water, particularly from a chemical point of view, in order to upgrade man's knowledge of his environment and the means whereby it may be controlled.

The ACS Committee emphasized that extensive fundamental research is required to elevate man's understanding of the environmental system around him. It was evident that there was a need for an initiation of such research on the resources of the Thunder Bay Watershed in Northeastern Michigan's Lower Peninsula.

The survey-analysis program was developed for the purpose of obtaining physical and chemical data on the quality of the waters flowing into the Thunder Bay River and Thunder Bay. The physical and chemical characteristics of the natural water of the Thunder Bay Watershed were determined under different seasonal conditions and over a four year period. From results of these investigations, the degree of eutrophication and the amounts of nutrients contributed from watershed drainage as well as domestic or industrial sources can be evaluated.

The ACS Committee recommended that basic data should be gathered systematically to delineate the presence and relative importance of agricultural and domestic sources of compounds of nitrogen and phosphorus in surface waters. The study of the interaction of soluble calcium from natural limestone sources with phosphorus nutrients, in the form of ortho-, pyro-, and tripolyphosphates discharged from domestic sewage effluents, would reflect phosphorus availability.

The water quality of our aquatic environment is related to the water sources feeding the system, and the resultant effect which the composition of these sources has on the components of the aquatic system. The constant increasing water requirements of our society has resulted in a growing concern about the presence of nutrients in surface waters. The productivity of a given body of water has been found to depend on solar radiation, temperature, and the concentration of plant nutrients which are available to these organisms in the water (Lee, 1970).

Nitrogen and phosphorus nutrients and some trace metals are often considered to be significant in limiting the growth of aquatic plants in surface water. Mackenthun (1968) reviewing the phosphorus problem in natural water concluded that when phosphorus is present in excess of a critical concentration, and when other environmental conditions are favorable, it can stimulate aquatic plant growths which will produce scums and odors, remove oxygen and destroy water uses. The lower limit of optimum growth has been reported to occur when available phosphorus concentrations reaches a level of 0.02 mg/l in the water (Fitzgerald, 1970).

Another concern of the ACS Committee was the investigation of naturally occurring and pollutant particles in water as to their size, charge, composition and adsorptive properties. A prevalent source of pollutant particles in Thunder Bay is an industrial cement dust discharge into the atmosphere over the bay. The second phase of this study was to establish the possible involvement of the dust in phosphate adsorption relative to its composition and assimulation in water.

The presence of large amounts of suspended solids can influence aquatic plant production by limiting light penetration and providing adsorption sites for phosphorus forms. Lake nutrient-budget studies have shown that the sediments of an eutrophic lake are greatly enriched in phosphorus (Frink, 1967). Keup (1968) has indicated that suspended particles may have a key role in phosphorus movement in natural water. He concluded that significant quantities of phosphorus may pass downstream unmeasured as bed-loads or with floating materials.

Uptake or release of dissolved inorganic phosphate by sediments has been considered to be pH and redox dependent. The phosphate released to a soluble form from an adsorption complex in the sediments results from an equilibrium exchange. Much soluble phosphorus may be available for algal growth when the sediment is somehow physically mixed with the overlying water. Natural flow of water over sediments, stirring action of currents and organisms, movement of sediments by wind action, diffusion processes, and gas formation and release from mud can all re-suspend the upper layer of sediment into overlying water.

The ACS Committee considered research on specific chemical compounds, particularly organic compounds, which are present in both waste and natural waters, as being essential to the knowledge of a regional inventory. The major phase of this research project was concerned with the organic soluble materials of the area waters and the cultural effluents and their interaction with domestic phosphate discharge in Thunder Bay at Alpena, Michigan.

With respect to the phosphorus balance in a given water system, the interactions of complex physical and chemical factors involving the equilibria present in natural systems influences the seasonal utilization of phosphorus. Chemical complexation by metal ions and soluble organic matter can play an important role in affecting the phosphorus concentration in a water environment. The availability of phosphate forms, from natural, agricultural, and sewage sources in Thunder Bay waters has been determined in view of their involvement in a possible chemical complexation with soluble calcium and natural yellow organic acids, and physical adsorption on calcareous particles.

A comprehensive review of the literature has been accomplished and is presented in Appendix I.

OBJECTIVES

The areas of this study were selected to determine the forms of phosphorus prevalent and available for ecological utilization in Thunder Bay natural waters. Their involvement in three means of phosphorus fixation above the bottom sediments (mud-water interface) was measured.

(1) The interaction of calcium ions with the phosphorus forms (ortho-, pyro-, and tripolyphosphate) was followed by potentiometric (mv) titration of the calcium in the presence of the phosphates. The pH titration of the phosphates in the presence of calcium was also carried out. The field studies on calcium complexation were done in the Thunder Bay Watershed where limestone deposits are prevalent. Calcium was considered as an important part of the phosphorus cycle in the river and bay.

(2) The second area of study was concerned with the suspended solids which may provide adsorption sites for the phosphorus forms. The solids could be important in the consideration of the movement of phosphorus in the Thunder Bay natural systems. The possible adsorption of ortho-, pyro-, and tripolyphosphates and any variation in the fixation was measured by sediment extraction methods. Substantial amounts of phosphorus may be temporarily stored in stream-bottom deposits that can be subsequently scoured from the channel and rapidly discharged into the aquatic ecosystem.

Bed-load transport of solids may be a significant mode of transporting of nutrients incorporated with the solids. The Thunder Bay field studies concerned the calcareous particles from natural sources and from the industrial cement operation in Alpena, Michigan.

(3) The laboratory and field testing of the interaction of soluble organic matter with the phosphorus forms (ortho, pyro, and tripoly) in the presence of calcium, were followed by the same procedures used in the calcium-phosphate complexation determination. The organic material was primarily the yellow organic acids of natural colored water extracted from the Thunder Bay River and its tributaries.

The foregoing three studies were all conducted in the laboratory by two methods. The first part of each one was the determination of the direct interaction of species dissolved in double-deionized water of appropriate ionic strength. The second part was performed with Thunder Bay natural waters.

The parameter composition of the artificial waters used in these experiments to maintain comparable ionic strengths was based upon results which Kramer (1964) obtained from Great Lakes water. Kramer's model was a good approximation for fresh water because it allows the calculation of:

(a) upper limits for fresh water composition due entirely to natural processes;

(b) degree of pollution from comparison of the actual composition with the natural process calculation;

(c) absolute concentration limits because of natural sources and pollution additives.

METHODS OF STUDY

This study involved the complexation reactions of the three phosphate forms with the soluble constituents (calcium and natural organic acids) and adsorption on cement dust particles. These reactions were studied relative to the composition of the natural water, sewage discharge, and suspended materials.

With respect to a phosphorus balance in a given water system, complex physical and chemical interactions involving equilibria present in natural systems produce seasonal fluctuations of aquatic phosphorus. There are two basic physical conditions and two chemical reaction systems that influence phosphorus concentration in a water environment. The physical adsorption of phosphorus compounds on bottom sediments and suspended solids would affect the amount of available phosphorus. Chemical complexation by metal ions and soluble organic matter have an important involvement in phosphate availability.

The purpose of the adsorption investigation was to measure the availability of the phosphate forms fixed on suspended calcareous sediments. The calcareous suspended particles entering the bay come from two sources: natural particles from limestone deposits in the area and from the emission, over the bay, of calcinated dust from the local cement plant. The stability of the bound phosphorus on the sediments was determined by soil extraction methods.

A major source of phosphorus in Thunder Bay is a domestic sewage discharge. The sewage was analyzed for the three phosphate forms by chromatographic anion-exchange separation. The phosphate content was determined by colorimetric methods.

The phosphate fixation with soluble components was measured in two ways. The effect of calcium ion on the prevalent phosphorus forms such as ortho-, pyro-, tripolyphosphates, was determined by use of a Corning Calcium Select-ion electrode. The association constants of calcium ions and phosphate forms involved in complexation can be calculated by the measurement of the free calcium-ion activity in the presence of the phosphate ions using the electrode. When the constants have been determined, the influence on these constants of the organic acids from three selected tributaries were measured.

The interaction of soluble organic matter with phosphates and calcium ions was also studied using pH titration, in order to determine the change in the weak acid function of the phosphates identified by Odajiri and Nickerson (1964). This phosphate function, which occurs before precipitation, was followed by measurement for the phosphate forms using sodium hydroxide and calcium hydroxide. Sodium hydroxide was also used in the presence of calcium chloride to titrate the function. Finally, sodium hydroxide and calcium hydroxide were used in the presence of the organic acids, with, and without, soluble calcium. The results were compared with Visser (1962) who followed a similar procedure with casein. The organic material was primarily the fulvic acid portions of natural colored water recovered from the Thunder Bay Watershed.

The current interaction of the organic matter with calcium and phosphorus was determined by oxidation of river and bay samples. The potentiometric titration of natural samples and measurement of calcium-ion activity determined the extent of the metal ion - organic acid and phosphate interactions.

Hutchinson and Bowen (1947) described the phosphorus cycle in natural water as involving several areas in stratified lakes. These include:

(1) liberation of the phosphorus into the epilimnion from the decay of littoral vegetation;

(2) uptake of liberated phosphorus by bacteria, phytoplankton and vegetation;

(3) loss of phosphorus as a soluble compound from the phytoplankton with possible slow regeneration of ionic phosphate;

(4) sedimentation of phytoplankton and other phosphorus containing seston;

(5) liberation of phosphorus from sediments and at the mud-water interface in the hypolimnion;

(6) diffusion of phosphorus from the sediments into the water at those depths at which the superficial layer of the mud lacks an oxidized microzone.

This research project was concerned primarily with phosphorus as a nutrient in the Thunder Bay Watershed - soluble phosphate, the phosphate adsorbed on suspended solids, and phosphorus complexed by natural soluble calcium and organic matter. The results of the study will give additional information about the water quality in Thunder Bay and movement of phosphorus throughout the watershed.

A thorough survey of the resources and regional inventory of the water quality of the Thunder Bay Watershed have been conducted and are presented in Appendix II.

METHODS OF ANALYSIS

SAMPLING STATIONS

Sampling stations are particular sites where water samples are collected systematically over a period of time for use in measurement of water quality. There were eighteen sampling stations established in the Thunder Bay Watershed. Stations were located as close as possible to the mouths of all major tributaries of the Thunder Bay River and below all possible sources of cultural discharges on the main branch of the river.

Samples for physical and chemical analysis were collected during each season. The measurement of discharge was done at least once at each station (Appendix III). Data representing the measured flow was also obtained from the nearest U. S. Geological gaging station and from Alpena Power Company records at the hydroelectric dams.

The description of tributaries in the Thunder Bay Basin are given in Table 1. The location and descriptions of sampling stations and geographic sites are given in Appendix III. These descriptions concern width and depth of water course, bottom materials and vegetation, and other pertinent resources unique for the season. The lake shore classification of Thunder Bay was considered primarily low-wet swamp with marl and boulders,

Table 1

Description of the Tributaries of the Thunder Bay River

Water Course	County	Length (mi.)	Elevation (feet)	Description
Hunt Creek	Montmorency	8.5	800-1100	Flows through woods and brushwood
Miller Creek	Montmorency	10.0	920-1000	Brushwood and cleared areas
	Alpena	1.5	780-860	
Crooked Creek	Montmorency	5.5	860-1000	Brushwood and cleared areas
Crooked Lake	" "		880	Headwaters at Avery Lake
Sheridan Creek	Montmorency	5.0	1000-1250	Flows through woods and brushwood into McCormick Lake
Gilchrist Creek	Montmorency	8.0	780-900	Woods and brushland
	Oscoda	4.0	1000	
Brush Creek	Montmorency	6.5	900-1000	Woods and brushwood
	Alpena	5.5	760-840	Forestland
Beaver Creek	Alpena	6.4	750-875	Brushwood and marshes emitting from Beaver Lake
Wolf Creek	Alpena	13.5	725-750	Brushwood and forest land along with marsh and swampland into cleared, farmed areas above Lower So. Branch
	Alcona	6.5	750-900	
Bean Creek	Alpena	9.0	750	Marsh and swamp land
North Branch	Montmorency	8.5	875	Woodlands and swamp areas from Rush Lake
	Presque Isle	7.0	750-850	Marshland and clear areas
	Alpena	22.0	725-820	Variety of land areas
Lower So. Branch	Alpena	17.5	680-780	Forestland and marshland with farmed land below Hubbard Lake
	Alcona	8.5	750-1000	Swamp lands and brushwood
Upper So. Branch	Oscoda	8.5	900-1000	Woods and brushland from Shamrock Lake
	Montmorency	6.5	750-900	Brushwood and marshland up to Fletcher
	Alpena	4.0	750	Pond and woodland below the pond

marsh and low-sand plain with wet sand, and small amounts of beach ridge with sand.

All samples were collected according to prescribed methods taken from Standard Methods (1965) procedures. The samples were collected in brown acid-washed polypropylene bottles, preserved (chloroform or mercuric chloride) and stored in an insulated box until refrigerated. Subsequent analyses were made as soon as feasible. At the stations: temperature, dissolved oxygen, discharge, alkalinity, hardness, and chloride measurements were conducted prior to preservation. Samples were subjected to further analysis for hydrogen ion concentration (pH), suspended and total solids, ammonia, nitrate, phosphates, iron, calcium, magnesium, sulfate, chlorine, color, and detergents. These chemical and physical determinations were made at the Alpena Community College quantitative laboratory.

EQUIPMENT AND REAGENTS

Equipment included a Millipore Filtering apparatus, Bausch & Lomb Spectronic 20 colorimeter, Sargent-Welch NX digital meter, Corning Calcium Select-ion electrode, Turner Fluorometer, Heath pH Recording Electrometer, Friden 1162 Electronic Calculator, H & L Infrared Spectrometer, and portable meters (Dissolved Oxygen, pH, and Temperature). The chromatographic set-up includes a small plastic column (2.5 x 25 cm) packed with strong-base anion-exchange resin in chloride form, Dowex 1-X8.

Water samples from the river and bay as well as the watershed samples were collected and stored in the polypropylene bottles, preserved and refrigerated. The dust samples were obtained from stack emission precipitators of the cement plant. After collection, the sample was well-mixed and stored in a moisture-proof plastic container. Composite samples from the sewage plant were obtained for 24-hour periods and kept refrigerated until analysis. The field kit for organic acid separation consisted of a support container, five-gallon plastic bottles, resin columns, battery-operated water pump, anion resin, and a 12-volt storage battery.

Standard solutions were prepared from American Chemical Society reagents with double de-ionized water. Phosphate concentration in natural Thunder Bay water was found to be 0.10 to 0.30 mg/1 so complexation concentrations were from 0.001M to 0.01M. The alkali metal salts of orthophosphate, pyrophosphate and tripolyphosphate were used to prepare solutions. The solutions were refrigerated until use and checked regularly for hydrolysis.

The phosphate solutions were standardized by preparing the acid form of the phosphate by passing the solutions through a column of Dowex 50W-X2 cation-exchange resin (100-200 mesh). As the acid form was eluted from the column with water, it was titrated immediately under nitrogen gas with standard solution of $(CH_3)_4NOH$. The titration was carried out at 25C using a combination pH electrode at a specific depth and constant stirring. The $(CH_3)_4NOH$ solution contained the same concentration of phosphate salt as the phosphate solutions to eliminate dilution effect.

The calcium solutions were prepared in concentrations of 1×10^{-2} to 1×10^{-5} M, depending on artificial and natural environmental conditions. Reagent grade calcium chloride was used to make up the standard solutions and diluted with double de-ionized water to any desired concentration. The calcium solutions were standardized by passing the solution through a 20 cm column of Dowex 50W-X2 (100-200 mesh) in hydrogen form. The eluate was titrated with standard NaOH and $(CH_3)_4NOH$. The calcium electrode was calibrated with the standard $CaCl_2$ solutions, assuming $CaCl_2$ was completely dissociated at a constant ionic strength.

ANALYTICAL PROCEDURES

Temperature

The temperature was measured, either using the temperature probe of the oxygen analyzer or a centigrade (Celcius) thermometer, at various depths and sites in the streams or bay. The temperature values are reported as a profile at selected depths or as the mean value for the water course.

Dissolved Oxygen (D. O.)

The dissolved oxygen was measured in the field with a Precision Galvanic Cell Oxygen Analyzer (No. 68850) manufactured by Precision Scientific Company. The dissolved oxygen values were determined from appropriate calibration tables. The probe was standardized by Winkler method using azide-modification. When the meter was not used, the modified azide technique was followed (Standard Methods, 1965).

Hydrogen-Ion Concentration (pH)

The pH of the solutions was measured instrumentally with a Beckman Zeromatic pH meter or a Heath Recording pH meter as soon as possible after collection. A Sargent-Welch portable pH meter was used at selected stations in the watershed.

Suspended (Filterable) Solids

The watershed, river and bay samples were measured for suspended solids following FWQA (1970) procedures. A glass fiber filter disc (Reeve Angel Type 934AH, 2.1 cm) was prepared by insertion into the bottom of a suitable Gooch crucible. While vacuum is applied, the disc is washed with three successive 20 ml volumes of de-ionized water. After last traces of water were removed by suction, the crucible and filter were dried in an oven at 105C for one hour, removed, cooled in a desiccator and weighed.

The filtering apparatus and crucible were assembled and suction begun. The sample was shaken vigorously and 100 ml were rapidly transferred to the funnel. The sample was filtered and vacuum continued for three minutes after filtration was complete to remove the last traces of water. The crucible was placed in a drying oven and dried at 105C to a constant weight. The increase in weight times ten results in the suspended solids reported as mg/l.

Dissolved Solids

The sample filtrate recovered after filtration for suspended solids was evaporated at 110C for one hour. The evaporation was continued until constant weight was attained for the dish. The dissolved solids in mg/l were calculated from the weight measured and selected volume (25 ml) used.

Maximum Suspended Cement Dust

The maximum suspendable cement dust in solutions was determined by mixing dust samples (1 to 20 mg) with de-ionized water and river water. The maximum limit of suspended cement dust in the water was found by mixing weighed dust samples in 1000 ml of de-ionized water and allowing the mixture to stand for four hours. A measured volume of water was decanted and filtered through a washed, weighed Millipore filter (0.45u). The milligrams of suspended material per measured volume of decanted sample was converted to mg/l of maximum suspended dust.

Discharge

The velocity of the streams was measured with a Gurley current meter at a minimum of three sites equidistant apart across the stream. The speed in feet per second was found at a position of 0.6 depth or as the mean velocity for 0.2 and 0.8 depths where stream was deep enough.

The discharge of each equivalent section was found as the product of distance (b), average depth (d), and velocity (V).

$$Q = \frac{b(d_1 + d_2)}{2} V$$

The total discharge is then the sum of the discharges for each section of the stream selected.

Color (Tannin)

The total organic color (tannin and lignin) were originally measured by Tyrosine method. Hach tyrosine reagent is added to the sample and de-ionized water. Hach sodium carbonate solution for tannin was added to each mixture and allowed to stand for ten minutes. The blue color of the organic-tyrosine complex was measured colorimetrically at 700 mu.

Organic Acids Color

The fluorescent response of the natural organic colored material was used initially to determine the presence and concentration of organic acids in the Thunder Bay Watershed samples.

For colored water from a variety of sources, Christman and Ghassemi (1966) found a maximum excitation wavelength at 361 mu with maximum fluorescence at 490 mu. A Turner Fluorometer was used with primary filter #7-60 to give an excitation wavelength of 365 mu. The Thunder Bay organic concentrate was found to give a maximum fluorescence response at 470 mu using a secondary filter #2A+48.

The units were calibrated in mg/1 by evaporation of sample selected to find actual concentration in volume. The conversion factor of 27 units/mg/100 ml was determined. A log plot of F units vs. mg of organic acids gave a linear curve (Figure 1). The fluorescence reading was fairly constant in a temperature range of OC to 40C. This allowed for adaptation of the fluorescence method in the field.

The spectrophometric method for determination of humic acids (Semenov, _et_ _al._, 1963) was evaluated with a Beckman DK-2 Spectrophotometer. There were absorbence peaks at 325 mu and in the 400 to 450 mu range, as well as in the infrared range of 1010 to 1880 mu. The excitation absorbence at 340 mu and transmittance at 440 mu using a Bausch & Lomb Spectronic 20 colorimeter gave results, as Organic Carbon (Humic Acid) in mg/1, comparable with the fluorometer results. This spectrophotometric method was used for field testing of color concentration in the Thunder Bay Watershed.

Nitrogen-Ammonia

The ammonia-nitrogen in the samples was measured by direct Nesslerization method from Standard Methods (1965). Selected

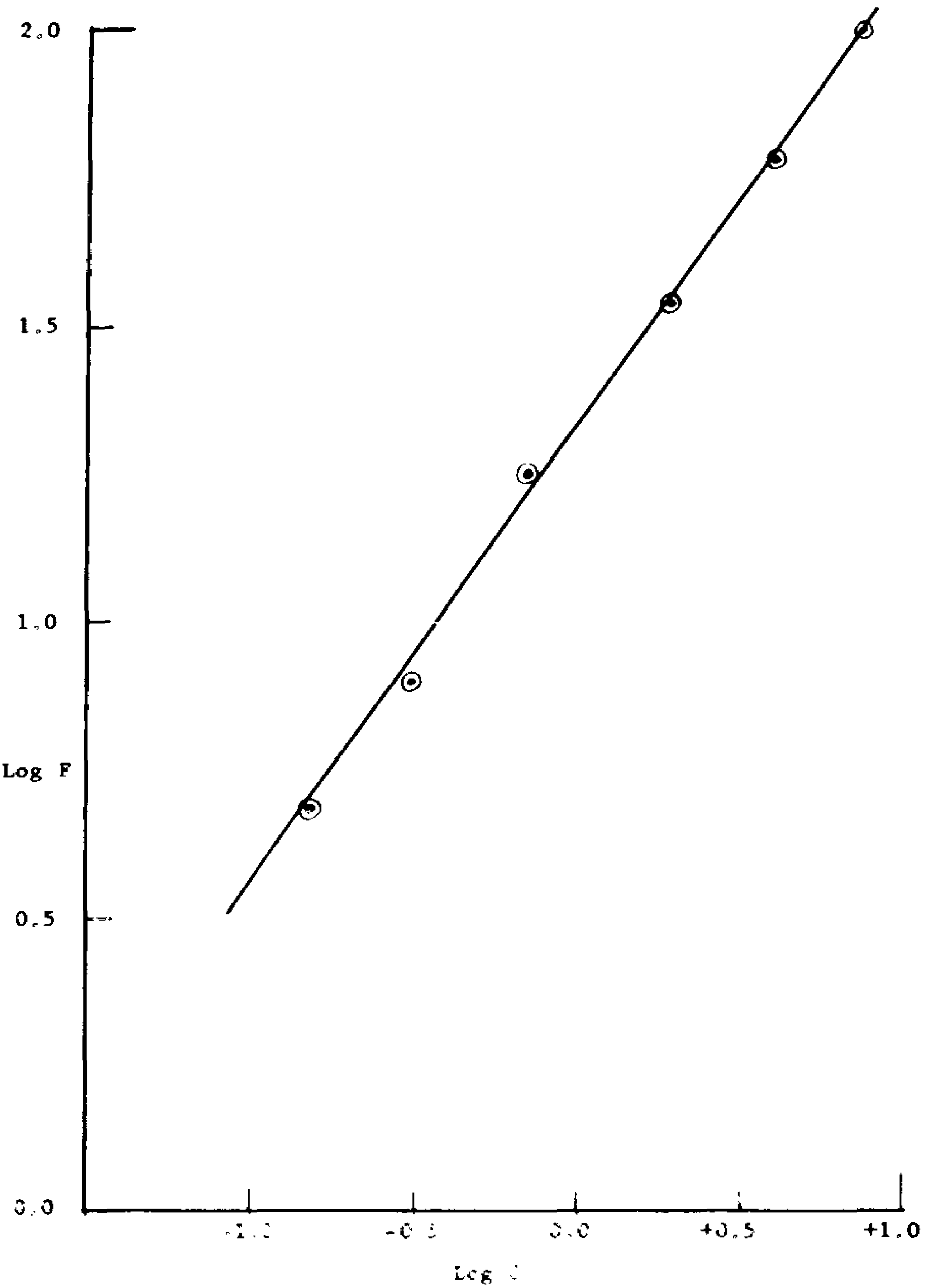


Figure 1 Fluorescence vs Organic Acids Concentration

samples were measured for ammonia-nitrogen using Standard Methods (1965) distillation procedure. The results were comparable with the direct Nesslerization method used.

Nitrogen-Nitrate

The method was based upon the reaction of the nitrate ion with brucine sulfate with sulfanilic acid in strong sulfuric acid solution at a temperature of 100C. The yellow color of the resulting complex was measured at 410 mu. The nitrate concentration (mg/l) was determined from a standard curve. The curve was prepared with samples and standards analyzed simultaneously.

Phosphate (Soluble and Total)

The soluble (ortho) and total phosphate in sewage samples and watershed or bay samples were measured by Standard Methods (1965) procedures. A Bausch & Lomb Spectronic 20 colorimeter was used for measurement of absorbence of the stannous chloride-blue complex at 690 mu. Dilution with de-ionized water was necessary for the composite sewage samples.

Phosphate Form Separation and Concentration

The composition and concentration of phosphate forms present in the composite sewage samples were determined by ion-exchange chromatography. Anion-exchange resins have been used by Peters and Rieman (1956) and Grande and Beukenkamp (1956) for analysis of mixtures of condensed phosphates. They used buffered potassium chloride solutions as eluants. In this study, a strong base anion-exchanger in chloride form, Dowex 1-X8, 50-100 mesh, was used following procedures modified from Puchkova and Mironova (1967) and Herold (1967), to separate standard mixtures and domestic sewage samples.

The rate of elution was four to six ml/min on a resin column 2 x 15 cm. The eluate fractions separated were recovered according to the following sequence:

1. Ortho - 50 ml 0.5N KCl + 50 ml 0.001N HCl (pH - 3.60)
2. Pyro - 75 ml 0.5N KCl + 75 ml 0.001N HCl (pH - 3.40)
3. Tripoly - 75 ml 1.0N KCl + 75 ml 0.010N HCl (ph - 3.00)
4. Remain - 150 ml 1.0N KCl + 150 ml 0.100N HCl (ph - 2.00)

The total phosphorus in each eluted fraction was determined according to standard Methods (1965) digestion procedures for total phosphate.

Detergents

The methyl green method was used to measure the detergent in the water sample by extraction with toluene. Ten milliliters of Hach sulfate buffer was added to 300 ml sample and de-ionized water blank along with methyl green powder. The methyl green-detergent complex was extracted with toluene. Toluene is added to the blank and separated for use in standardizing the colorimeter at 100%. The blue color of the detergent complex in toluene is measured at 615 mu.

Sulfate

The sample was measured by the turbidity developed with soluble barium chloride and suspended with conditioning agent (Standard Methods, 1965). The sulfate ion concentration was determined by comparison of the percent transmittance with a standard curve.

Total Hardness

Disodium magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and other cations in the sample to form a more stable EDTA chelate than magnesium. The free magnesium reacts with Eriochrome Black at a buffered pH of 10 to give a red-violet complex.

The EDTA was standardized with calcium carbonate at 1.0 mg/1.0 ml (1000 mg/1). The selected volume (25 ml) of sample was titrated with EDTA and mg/1 of hardness expressed as $CaCO_3$ was determined.

Total Alkalinity

Methyl orange was used as the indicator in this method because its pH range is in the same range as the equivalence point for total alkalinity. The indicator was added to a specific volume of sample (25 ml) and the solution titrated with standard HCl solution (0.2N). The volume of acid used was converted to total alkalinity (methyl orange) as mg/1 $CaCO_3$.

Iron

Total iron in the samples was determined with 1,10-phenanthroline. Twenty-five milliliters of sample were mixed with Hach 1,10-phenanthroline powder or solution. The orange color was allowed to develop for several minutes. The iron-phenanthroline complex color was measured at 500 mu.

Chloride

The chloride ion in solution was measured with standard mercuric chloride using an acidified (HNO_3) indicator of

S-diphenyl carbazone and xylene cyanol. The amount of chloride in the sample was found for a 100 ml sample as: 5 (volume of titrant).

The argentometric method (Standard Methods, 1965) was used from 1967 to 1969.

Chlorine

The Hach method measured the total available chlorine in water. The reaction procedure uses Hach orthotolidine in solution or powder form combined with 25 ml of sample. The yellow color which develops was measured colorimetrically at 440 mu after 3 to 5 minutes. The original sample was used to set the colorimeter at 100%.

Coliform

Multiple-tube fermentation test gives an actual coliform count per 100 ml. The membrane filter technique for coliform determination (multiple-tube densities) gives 'most probable number' (MPN) per 100 ml of sample.

Coliform count per 100 ml has been measured in the Thunder Bay area by the membrane filter technique to give a result of MPN/100 ml for multiple-tube coliform densities. The analyses have been conducted by Michigan Department of Public Health.

Calcium (Soluble)

The Corning Calcium Select-Ion electrode was used with a Sargent-Welch NX Digital meter for the measurement of the free calcium in solution.

The calcium electrode of the liquid-ion exchange type is subject to pH influence. The sample's pH should be adjusted to at least 2 pH units higher than the sample's equivalent pCa++ and not higher than pH 10. Ross (1967) found the potential response of the electrode to be linear for pH 5 to 10, which is within the normal range of natural water systems. $(CH_3)_4NOH$ and HCl were used when needed to adjust the pH of standard solutions to the desired pH range.

The electrode functions by the movement of the exchanger, so the response is influenced by temperature. The range of temperature for a reproducible response was measured. The samples were allowed to come to room temperature before measurement so as to be within the range found.

The lower limit of detection of the electrode is usually determined by the solubility of the liquid ion-exchanger. The upper limit of detection for liquid membrane electrodes is determined by the level at which there is an appreciable solubility of the ions from the sample into the ion exchange phase. The natural range selected for the standard solutions of $CaCl_2$ was 1×10^{-2} to 1×10^{-5} M.

Calcium Complexation with Natural Organic Matter (Oxidizable Calcium)

The determination of existing calcium-organic-phosphate interactions in the Thunder Bay waters was done by oxidation of the water samples from the bay and river with concentrated nitric acid. The calcium concentration in sample before oxidation was determined with the calcium electrode. The oxidized residue was dissolved and increase in free calcium measured with the electrode. Any change in phosphate level (fixed) was measured in the pre- and post-oxidized solutions.

Organic Acid Separation

The extraction of the organic acids from selected Thunder Bay natural water sources in the field was best accomplished by use of anion-exchange chromatography. Ten to fifteen grams of Dowex 1-X8 anion resin in the chloride form (50-100 mesh) was pre-soaked in 0.001N HCl before being placed on the plastic column. The resin is rinsed with de-ionized water until acid is washed off column (neutral). The water sample (5 gallons) was passed through the column until the exchange capacity of the resin was attained. This capacity was indicated by a deep brown color on the yellow resin solid.

The resin was removed from the column and combined with a solution composed of 50 ml of 2M NaCl and 50 ml of 1M NaOH. The mixture was allowed to stand for two hours. The colored solution was decanted and solid treated with additional 100 ml of the extractant and left overnight. The decantates were combined and treated with HCl until the orange solution turned yellow (pH - 5). The solution was evaporated to dryness.

Ninety-five percent alcohol was added to the solid residue to extract soluble polar-acids. The solution was decanted and alcohol added to remaining residue and subsequent recoveries done until brown color was removed. Alcohol extracts were combined. A measured portion was dried at 105C to obtain the concentration (mg/ml) of acids in the extracted solution.

Naturally Available Adsorbed Phosphate and Calcium in Cement Dust

The available phosphate and calcium extractable from the cement dust were measured from collected sample. For the measurement of phosphate adsorption on dust, 10 to 100 mg of dust was used. The separation of calcium phosphate forms from cement dust was done by soil extraction methods using dilute mineral acids. The differential dissolution technique for acid-extractable calcium phosphate forms developed by Chang and Juo (1965) and Williams et al. (1967) was used.

The dust samples after contact with water for two hours were filtered through a washed 0.45u Millipore filter paper. The residue solid and paper were digested for one hour with 50 ml of 0.5M HCl. The acid-dust mixture was refiltered through the Millipore paper, and the filtrate separated.

The total phosphate was determined in the original filtrate and in the acid filtrate. The analysis for phosphate was done by stannous chloride procedure (Standard Methods 1965). The dust and paper were re-digested for an additional two hours with 1.0M HCl and the filtrate checked for additional phosphate. Calcium was measured in all solutions by use of calcium selection electrode.

Extractable Phosphate from Natural Suspended Solids

The total phosphate on suspended solids was extracted with hydrochloric acid (0.5N). The net phosphate recovered from each river and bay sediment samples was found as the difference between the total phosphate extracted with acid and the background phosphate. The background phosphate was found with a de-ionized water blank using the acid and a fiberglass filter disc. The suspended solids and extracted phosphate represent the total suspended material and adsorbed phosphorus in 100 ml and 500 ml of samples taken at the various sites in the bay and river.

Adsorbed Phosphates on Cement Dust

For the measurement of phosphate adsorption on dust, the amount of dust used was varied from 5 to 100 mg. Standard solutions (100 ml) of the three phosphate forms were mixed with the dust and the mixtures allowed to equilibrate for two hours at room temperature. There was no apparent change in the capacity of the settled dust to adsorb phosphate after two hours, so this interval was assumed sufficient to attain an equilibrium exchange. De-ionized water and natural water from the river were used as the dilution water. The resulting pH was not altered appreciably in the solution process. The amount of phosphate extracted from the standard solution and adsorbed on the dust was determined per gram of dust.

The cement dust-phosphate solutions were filtered through a Millipore filter (0.45u). The total phosphate concentration of the filtrate was determined by Standard Methods (1965). This value was compared with the original phosphate concentration and was considered the phosphate removed by cement dust.

The total phosphate of the dust and filter was extracted with 0.5N HCl by digestion for one hour. The net phosphate adsorbed on the cement dust was found as the difference between the total phosphate extracted by acid and the background phosphate measured as a blank for cement dust, filter paper, and acid.

River and Bay Characteristics

The river and bay were analyzed for phosphate and other sewage effluent constituents at selected sites in the bay area (Figure 2). The plume of the river was followed by measurement of phosphate concentrations at the selected sites. The phosphorus, chloride, and nitrogen compounds were being contributed mainly from the sewage plant, industrial wood-products discharge, and natural river discharge.

The discharge of the river and tributaries were found by direct measurement on streams. The on-stream measurements are included in the seasonal summaries. Discharge data from Alpena Power Company (1971) records and U. S. Geological Survey (1966+ 1967) gaging stations are given in Appendix II.

Organic Acid Identification

The identification of the important functional groups present in the colored organic acids isolated from natural water sources has been done by infrared spectrometry, Midwood and Felbeck (1968), Black and Christman (1963), and Steelink (1963) have used different infrared instruments and natural water from different sources to establish the organic nature of these groups.

A Hilger-Watts Infragraph H1200 (Wilks Scientific) was used to identify the similarity between the organic acids from Thunder Bay waters and that characterized above. The acids are in ethyl alcohol solution, so the C-H, O-H, and C-C bands of an aliphatic alcohol will be present in spectra.

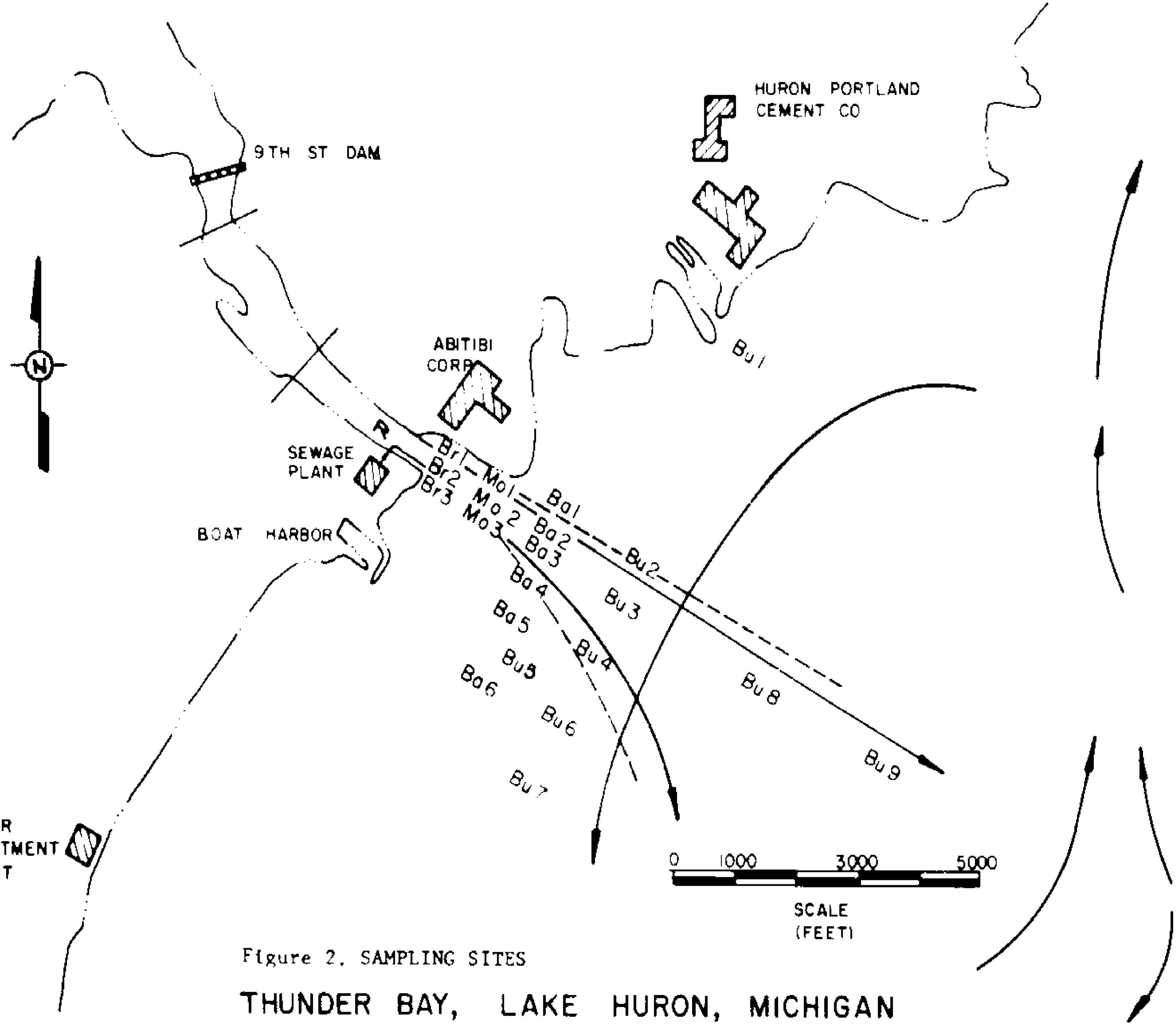


Figure 2. SAMPLING SITES

THUNDER BAY, LAKE HURON, MICHIGAN

Complexation Measurement

The determination of the extent of complexation between soluble calcium with phosphates and organic acids, using potential measurements with the calcium electrode, was done by two methods.

In the potential comparison method (Rechnitz and Zamochnick, 1964), the potential of a standard calcium ion solution is measured. The electrode is transferred to another solution which contains a known analytical concentration of the test phosphate. Increments of a known calcium solution are added to the sample solution until the potential of the sample solution equals that of the initial standard (reference) solution. At this point, the activity of calcium in the two solutions must be the same. Since the concentrations of calcium in the standard solution, total metal ion in the sample solution, and phosphate in the sample solution are all known, the complex association constant can be readily calculated. The point of identity was approached from both the direction of excess phosphate and of excess calcium. Constants were determined with and without natural organic acid present. This method largely eliminates electrode drift. Variation in solution composition would be negligible.

In the titration method (Rechnitz and Bauner, 1964), a plot of electrode potential vs. -Log(calcium ion) is prepared as a calibration curve in the absence of complexing phosphate forms. A known initial concentration of calcium chloride is titrated with a standard solution of phosphate. From the calibration curve, apparent concentration of free calcium is determined at selected volume increments. With appropriate correction for dilution effects, the complex association constant can be calculated from the original ion concentration, the amount of complexing phosphate added, and the measured decrease in metal ion concentration at the specific volumes used. Constants were measured with and without the organic acids added to the calcium solution.

The other method for evaluation of interactions was based on the pH measurement of the change in the weak acid function of the phosphate forms in the presence of calcium and natural organic acids (Odagiri and Nickerson, 1964). The standard solutions of ortho, pyro, and tripoly-phosphate are adjusted to a pH of 2.5 with HCl and titrated with standard solutions of NaOH and $Ca(OH)_2$.

The plot of pH vs. volume gives an S curve which can be evaluated as a weak acid equivalence of the phosphate forms. The weak-acid hydrogen has been found to come from the terminal PO_4 groups of polyphosphate molecules (VanWazer and Campanella, 1950). The only type of complex formation that can affect the strength of the weak-acid function must involve the terminal groups. The milliquivalence of the organic acids and $CaCl_2$ solutions used were determined from the pH titration with a standard base.

The titrations with $Ca(OH)_2$ were conducted at fast and slow rates to note precipitation present at the concentrations used in this study. As well, known increments of $CaCl_2$ were added to phosphate solutions and titrated with NaOH. The organic acids were extracted from three tributaries: North Branch Thunder Bay River, Bean Creek, and Wolf Creek, as well as the main branch at the bay. These concentrated extracts were added to phosphate solutions before titration with $Ca(OH)_2$ and along with $CaCl_2$ before titration with NaOH. The decrease in the weak-acid equivalence of the phosphate forms theoretically would indicate a change in the availability of the phosphate ionic sites for reaction because of complexation with calcium, with or without the involvement of organic acids.

RESULTS

Both the river and the sewage plant effluent are contributing phosphorus and nitrogen containing nutrients to the natural waters of Thunder Bay. The amount of total phosphates from the sewage plant discharged into the river had a daily mean of 25 to 30 mg/l. The average total phosphate level of the river was 0.15 to 0.20 mg/l. In addition, the wood-products discharge gave an apparent high total phosphate result.

The raw materials used in cement production are composed of minerals (Table 2) which when emitted as dust can either physically or chemically affect the availability of phosphate forms in the natural waters of Thunder Bay. The dust used from the cement plant in this study had 5.75 mg of acid-extractable phosphate per gram of dust and an aqueous solubility of 0.06 mg of phosphate in de-ionized water (Table 3). These levels of phosphate were considered as background in studies involving the cement dust.

A monthly mass-balance between the river flow and phosphate discharge from sewage plant effluent showed a direct, stable relation between added phosphates and river flow. The yearly mass-balance between river and sewage flow showed a gradual increased relationship between the flows (Table 4). The comparison of phosphate concentration in the sewage effluent and the river discharge showed the dilution effect of the river water (Figure 3).

Table 2

Composition of Natural Constituents Used in Cement Production

(Mean Weight Percentages, Dow, 1971)

Limestone Analysis

$CaCO_3$ - 90.32

$MgCO_3$ - 2.64

CaO - 50.56
MgO - 1.33
SiO_2 - 4.84
Al_2O_3 - 1.28
Fe_2O_3 - 0.14
K_2O - 0.24
SO_3 - 0.46

Shale Analysis

CaO - 2.02

SiO_2 - 57.76

Al_2O_3 - 15.22

Fe_2O_3 - 6.18

MgO - 2.75

K_2O - 3.52

SO_3 - 7.24

Table 3

Characteristics of Cement Dust

Phosphate Available from Dust

Wt. Dust (mg)	Water-Soluble PO_4 (mg/l)	Acid-Extractable PO_4 (mg/l)
24.0	0.03	0.13
55.0	0.07	0.36
62.5	0.15	0.40
106.5	0.18	0.62
147.5	0.24	0.83
Mean	1.53 ± 0.26 mg/g	5.66 ± 0.62 mg/g

Comparison by Acid-Extraction

Wt. Dust (mg)	Phosphate Extracted (mg/l)	Phosphate Available (mg PO_4/g dust)
10.2	0.56	
50.3	0.80	6.00
14.5	0.36	
63.0	0.69	6.80
31.6	0.500	
53.3	0.625	5.10
51.6	0.55	
101.4	0.80	5.05
100.4	0.80	
152.2	1.10	5.80

Mean - 5.75 ± 0.81 mg/g

Table 4

MASS-BALANCE RELATIONSHIPS

River Flow	1967	1968	1969	1970	1971	Mean
Average CFS	1222	995	1180	886	1215	1071
Total Flow CF x 10^9	39.5	31.4	37.2	27.8	38.4	34.0
Gallon x 10^9	296	236	278	208	287	261
Sewage Flow						
Average MGD	2.56	2.23	2.69	2.52	3.01	2.50
Total-Gallon x 10^9	0.936	0.818	0.983	0.922	1.102	0.952
Dilution Factor						
$\frac{\text{Total Sew. Gal.}}{\text{Total Riv. Gal.}} 10^{-3}$	3.16	3.46	3.54	4.43	3.82	3.65

River Flow	1/71	2/71	3/71	4/71	5/71	6/71
Average CFS	881	987	1563	3709	1282	1083
Mean MGD	571	637	1008	2393	827	700
Sewage Flow						
Mean MGD	1.98	2.36	3.98	4.54	3.69	3.47
Total PO_4 (mg/l)	24	24	19	12	17	14
Kg/day	182	215	288	207	243	185
$\frac{\text{Daily Sewage } PO_4}{\text{Mean River Flow}}$ (mg PO_4/liter)	0.100	0.090	0.077	0.024	0.077	0.067

River Flow	7/71	8/71	9/71	10/71	11/71	12/71
Average CFS	1004	663	583	575	701	1536
Mean MGD	648	427	388	373	452	991
Sewage Flow						
Mean MGD	3.39	3.07	2.67	2.01	1.87	3.07
Total PO_4 (mg/l)	20	10	22	21	29	13
Kg/day	259	117	223	160	138	152
$\frac{\text{Daily Sewage } PO_4}{\text{Mean River Flow}}$ (mg PO_4/liter)	0.106	0.072	0.150	0.114	0.082	0.040

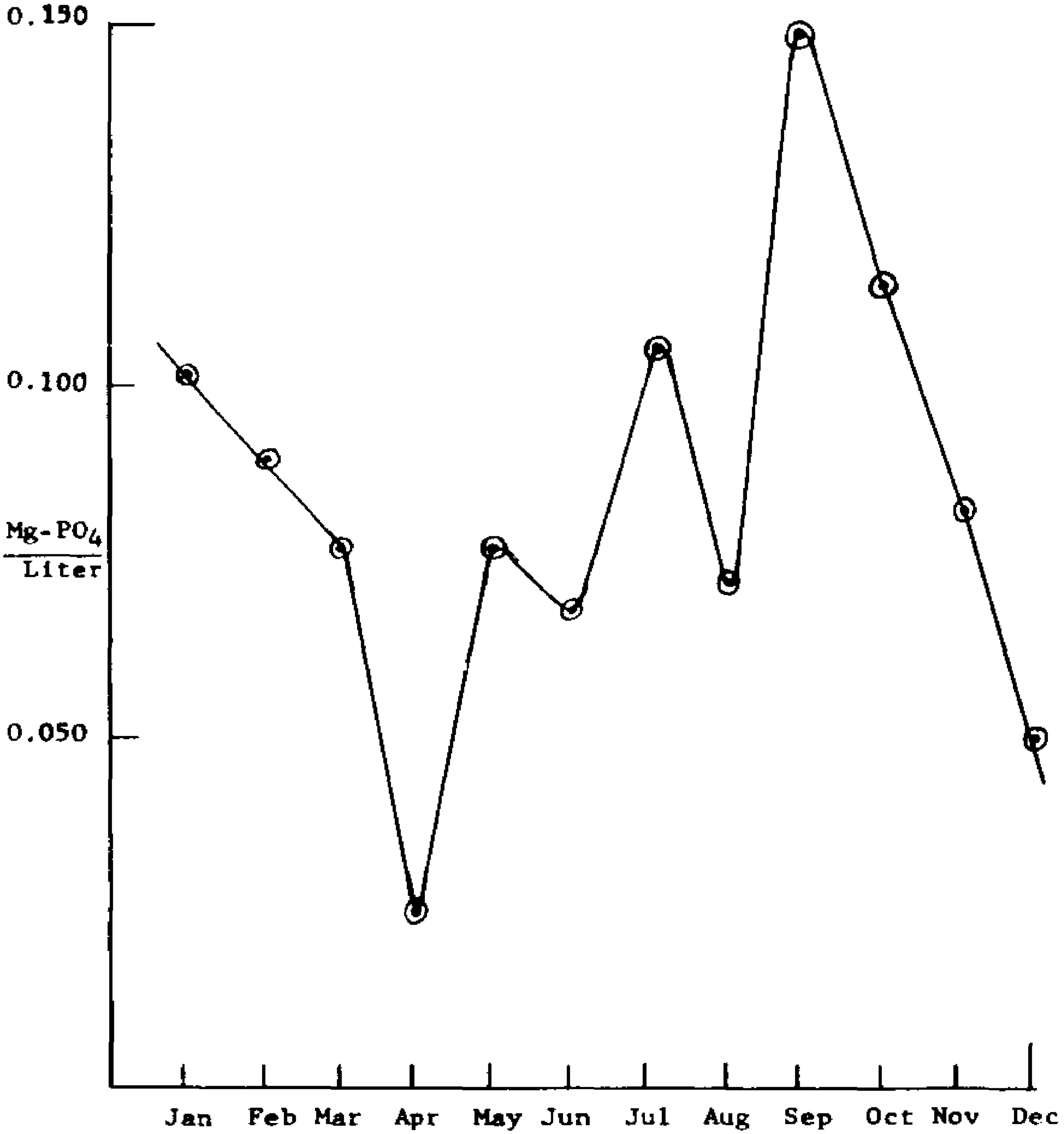


Figure 3. Monthly Dilution Relationship for 1971 Sewage Phosphate Discharge and River Flow

The sewage plant's primary treatment operation achieves removal of organic nutrient materials (BOD) and suspended solids (Table 5). The sewage plant has been estimated to achieve up to 20 percent removal of phosphates from the effluent during the primary treatment (LaMarre, 1970). This will be increased to 90 percent removal on completion of a proposed secondary treatment facility with chemical phosphate removal.

The chromatographic separation of the sewage samples by anion-exchange chromatography indicated that three basic linear phosphate forms are present in the effluent. Approximately 80 percent of the sewage effluent (Table 6) being added to the Thunder Bay system consists of the simpler phosphate forms (ortho, pyro, and tripoly) as measured by the anion-exchange separation (Figure 4). These forms were selected for this study concerning phosphate availability in the bay.

The percentages for phosphate recovered in chromatographic analysis of sewage effluent indicated a continual variation in the phosphate composition of the effluent. The extent of hydrolysis of polyphosphates would be related to the physical conditions existing during treatment of the sewage. The presence of organic phosphorus could influence the separation and removal of phosphates from the column through fouling.

Condensed phosphates as pyrophosphate and tripolyphosphate make up over 90 percent of detergent phosphorus. In sewage, Finstein and Hunter (1967) found condensed phosphates generally have a half-life in excess of one day, while in surface waters they may persist for weeks or months. Pomeroy (1960) found that residence time of

Table 5

Characteristics of Sewage Plant Effluent
(LaMarre, 1971)

Year	River Flow at 9th St. Dam	Raw Sewage Flow	
	Total Gallons	Total Gallons	Mean MGD
1967	2.96×10^{11}	9.36×10^{8}	2.56
1968	2.36×10^{11}	8.17×10^{8}	2.23
1969	2.78×10^{11}	9.83×10^{8}	2.69
1970	2.08×10^{11}	9.22×10^{8}	2.52
1971	2.87×10^{11}	11.02×10^{8}	3.01
Mean	2.61×10^{11}	9.52×10^{8}	2.60

Year	Mean BOD (lbs/month)			Suspended Solids (lbs/month)			Phosphates (mg PO_4)		
	In	Out	Remvd.	In	Out	Remvd.	Monthly Soluble	Monthly Total	Est. Remvd.
1967	1546	1090	28%	2383	1313	50%	6.5	26.5	20%
1968	1518	1090	28%	1926	1032	47%	9.0	26.0	20%
1969	1914	1250	34%	2680	1343	46%	14.0	29.0	15%
1970	1881	1352	28%	2066	1006	52%	12.0	24.0	15%
1971	1650	1170	29%	1810	950	48%	12.5	25.0	20%
Mean	1704	1170	30%	2173	1130	48%	11.0	26.1	18%

Table 6

Anion-Exchange Chromatographic Analysis
of
Phosphate Mixtures and Sewage Samples

1. **Analysis of Prepared Phosphate (mg/1) Mixtures**

		Found						
Phosphate Form	Taken	1	2	3	4	Mean	Taken	Found
Ortho - Na_3PO_4	4.4	4.5	4.6	4.8	4.4	4.6 ± 0.2	22.4	22.6 ± 0.2
Pyro - $Na_4P_2O_7$	6.4	6.4	6.8	6.8	6.6	6.6 ± 0.2	32.7	32.8 ± 0.2
Tripoly - $Na_5P_3O_{10}$	8.8	9.2	8.8	9.2	8.2	8.9 ± 0.5	44.9	44.3 ± 0.5
								99.7 ± 0.3%

2. **Analysis of Sewage Effluent (mg/1)**

					Total Recovery	
Total P	Ortho	Pyro	Tripoly	Remainder	Amt.	Percent
4.43	1.77 (48.1%)	0.56 (15.2%)	0.59 (16.0%)	0.76 (20.7%)	3.68 -	85.0%
3.67	1.75 (47.0%)	0.75 (20.0%)	0.73 (19.6%)	0.50 (13.4%)	3.72 -	102%
3.00	1.15 (34.4%)	0.56 (16.8%)	0.88 (26.3%)	0.75 (22.5%)	3.34 -	111%
7.50	2.50 (35.7%)	1.50 (21.4%)	1.40 (20.0%)	1.60 (22.9%)	7.00 -	93.0%
7.33	2.60 (33.3%)	1.70 (21.8%)	2.20 (28.2%)	1.30 (16.7%)	7.80 -	106%
6.00	2.20 (39.3%)	1.00 (17.9%)	1.10 (19.6%)	1.30 (23.3%)	5.60 -	93.0%
	39.6±6.5%	18.9±2.2%	21.6±4.6%	19.9±4.1%	98.5±11.1%	

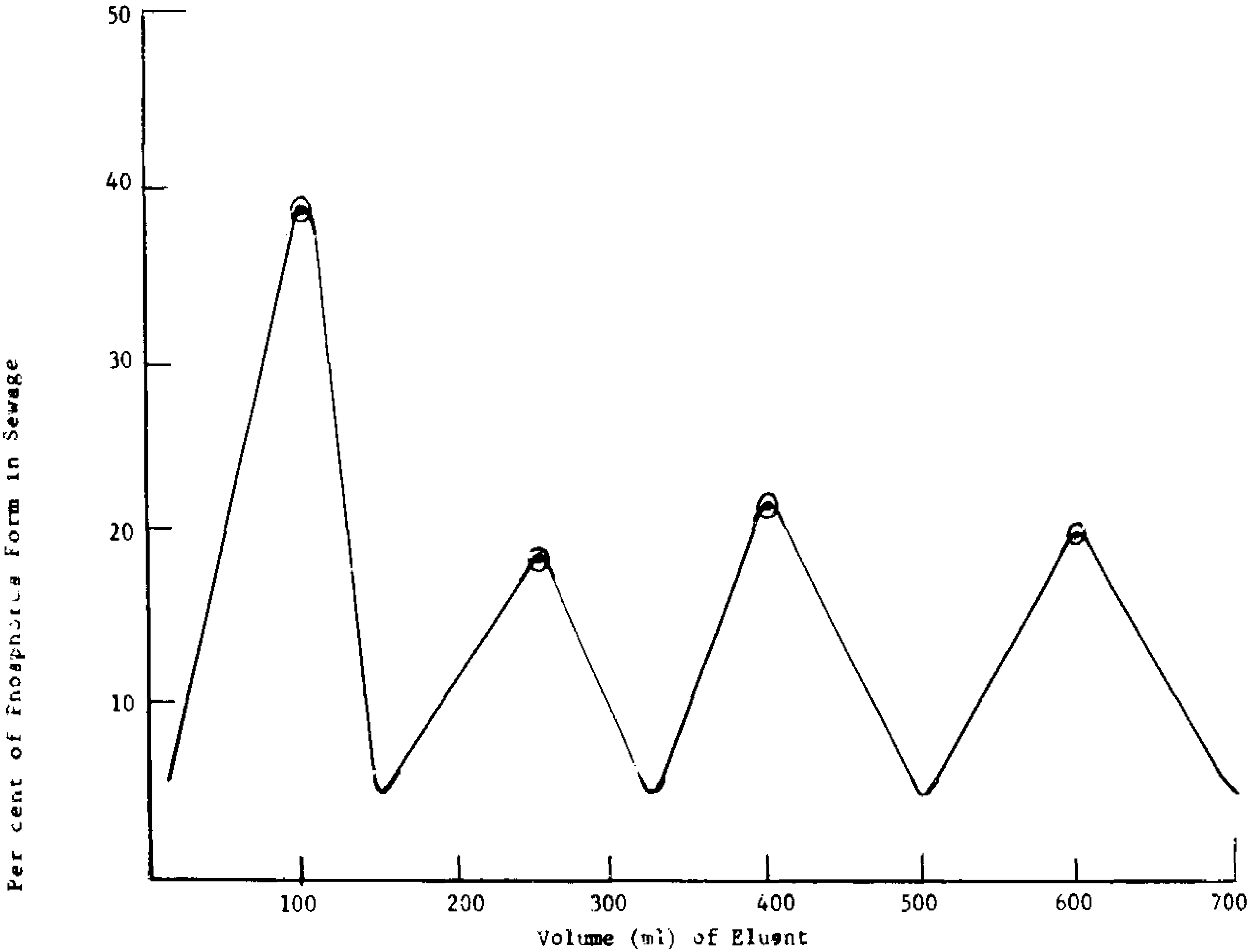


Figure 4. Separation of Sewage Effluent by Anion Chromatography

dissolved phosphates in natural water varies from approximately 0.5 to 200 hours. The turn-over rate of phosphate was between 0.01 and 1.0 milligram of phosphorus per cubic meter per hour

A rapid flux of phosphate would be typical of a highly productive system. The phosphate forms from sewage plant are available in Thunder Bay to produce biologically active systems. This has only recently become apparent in the form of floating plankton blooms off bay beaches.

The sewage discharge for 1970 was 922 million gallons and for 1971 was 1172 million gallons. The total river flow during 1970 was 27.84 billion cubic feet (208 billion gallons) and for 1971 was 38.36 billion cubic feet (287 billion gallons). The contribution of total phosphate from the sewage discharge for 1970-1971 at 30 mg/l for 2.50 million gallons per day is 500 lb/day. The average 1970-1971 daily river contribution of phosphate at 0.20 mg/l for 575 million gallons daily discharge at Ninth Street Dam is approximately 960 lb/day.

The sampling of the area near the river mouth and inner bay indicated that the sewage effluent moved from the south (right) side of the river to the center of the river being diluted by the river flow. As the river reaches the bay with the natural, wood-products, and sewage discharges, the plume moves out into the shipping channel and swings to the right. The extent of drift is dependent on the wind and influencing currents in the bay.

The wind direction is predominantly west-northwest for eight months of the year. For approximately 250 days, the dust from the cement plant is moving primarily out over the bay. This would give an estimated suspended material of 25,000 to 50,000 tons annually.

PHOSPHATE ADSORPTION ON CEMENT DUST

The dust in the bay waters would be available as suspended particles for complexation to a limited extent (Table 7). The cement dust sample produced an average suspended solids of 1.4 mg/l in test solutions. Most of these solids would eventually settle to the bottom of the bay. The dust particles would contain an inherent phosphate concentration of approximately 5.75 mg/g (55.7 lb/ton) and adsorbed phosphates from natural and domestic sources.

The suspended solids in the bay ranged from 4 to 10 mg/l with a mean of 7 mg/l. The acid-extractable phosphate of these suspended solids had a mean of 0.24 mg/l. This would indicate that some phosphorus is being tied up by the suspended particles prevalent in the river and bay.

In sewage treatment, phosphate precipitation with sodium aluminate (alum) and similar chemicals has been found to be pH dependent. The cement dust when placed in de-ionized water showed a definite change in the pH of the water up to a maximum level (Table 8).

As well, these substances have been used in eutrophic lakes to remove phosphates. When alum has been applied to the top two feet of water in a Wisconsin lake (Anon, 1971), particles of it settled, apparently taking phosphates along. Water clarity improved, winter fish kills were eliminated, and there were no blue-green algae blooms during the summer. Calculations indicated that about 110 pounds of phosphorus were removed by 11 tons of alum. The cement dust contains water-soluble and acid-extractable calcium along with the other com-

Table 7

Characteristics of Cement Dust

Cement Dust as Suspended Solids in Natural Systems

Wt. Dust Added to Water	Suspended (Filterable) Solids
1.5 mg	1.2 mg/l
3.5	1.4
6.0	1.2
13.0	1.7
16.0	1.5
25.0	1.2
50.0	1.6
100.0	1.6
	Mean - 1.4 ± 0.25 mg/l

Table 8

Characteristics of Cement Dust

pH of Aqueous Solutions with Cement Dust

Wt. Dust (mg)	pH	pH Difference/g-Dust
-	6.54	-
53.5	7.70	21.7
99.0	9.30	16.8
164.0	10.40	23.5
211.0	10.70	19.7
		20.9 ± 3.0
1000	11.40	4.87

ponents. These may be a factor involved in the absorption process occurring in the bay (Table 9).

When a standard orthophosphate solution was used, the amount of removal (adsorption) of phosphate from solution for a specific weight of dust showed a mean of 23.2 mg/g (46.2 lb PO_4/ton of dust). For standard pyrophosphate solution, the mean removal was 28.4 mg/g (56.5 lb PO_4/ton of dust). For standard tripolyphosphate, a mean 58.4 mg/g (116.8 lb PO_4/ton of dust) were removed from solution (Table 10).

The phosphates of the composite sewage samples were removed by cement dust (Table 11). The adsorption of phosphates was lower in river water, indicating a possible involvement of other factors present in natural river water. One of these factors could be soluble organic substances such as natural yellow acids since twenty-five per cent of the natural waters of the Thunder Bay River system is discharged from tributaries that have high organic colored materials (Anon, 1963).

The potentiometric titration (pH) of the phosphate-dust interactions indicated that there is a saturation limit for the dust. A definite amount of phosphorus can be accomodated by a specific quantity of solid. The titration method of Dollman (1968) seemed adequate to measure higher amounts of phosphate adsorbed together with the reactive sites on the dust (Table 12).

The phosphate adsorption by cement dust in both de-ionized water and natural river water varied with the water source, amount of dust used, the type of phosphate form, and its respective concentration. Up to the saturation point of the dust, there would be a definite influence of the calcinated material on the availability of phosphorus

Table 9

Phosphate and Calcium Inherent in Cement Dust

Water-Soluble

Wt. Dust	Phosphate	PO_4/Dust	Calcium	Ca/Dust
24.0 mg	0.06	2.5	10.8	450
53.5	0.14	2.7	20.8	388
58.6	0.16	2.7	29.7	507
99.0	0.46	4.6	30.5	308
107.6	0.56	5.2	71.1	661
160.2	1.04	6.5	86.4	539
164.0	0.99	6.0	42.9	262
211.0	1.12	5.3	62.9	298
280.7	1.19	4.2	102.9	367
		4.4 ± 1.4 mg/g		420 ± 131 mg/g

Acid-Extractable

Wt. Dust	Phosphate	PO_4/Dust	Calcium	Ca/Dust
20.0 mg	0.10	5.0	17	850
56.0	0.25	4.5	55	982
82.3	0.40	4.8	80	850
97.5	0.62	6.4	78	800
106.5	0.62	5.8	118	751
164.0	1.44	8.8	134	817
		5.9 ± 1.6 mg/g		842 ± 78 mg/g

Table 10, 11 and 12 Headings

Wt. Dust - Amount of dust used

Total PO_4 - Amount of phosphate in original solution

PO_4 Filtrate - Total phosphate in filtrate after separation of solids from mixture

PO_4 Residue - Total phosphate in residue by acid extraction with hydrochloric acid

Total Recv. - Sum of filtered and residue phosphate

Dust PO_4 - Amount of phosphate extractable from dust with acid

Total PO_4 Add - Milligrams of total phosphate in standard solution used, dust phosphate (5.75 mg/g), and phosphate measured in Millipore filter paper (0.13 mg/l) and reagents used (0.26 mg/l)

PO_4 Removed - Amount of phosphate removed from the phosphate added by dust used measured in milligrams per gram

PO_4 Adsorbed - Amount of phosphate recovered from the dust as milligram of phosphate per gram of dust used

Table 10

The Phosphate Adsorption (mg/l) on Cement Dust in Aqueous Systems

Sample	Wt. Dust (mg)	PO_4 Filtrate (mg/l)	PO_4 Residue (mg/l)	Total Recv. (mg/l)	PO_4 Removed (mg/g)	PO_4 Adsorbed (mg/g)
Na_3PO_4	15.6	0.61	0.75	1.36	31.4	25.6
	23.2	0.80	0.65	1.45	31.0	11.2
	23.3	0.70	0.36	1.06	17.2	15.5
1.10 mg/l	32.7	0.22	0.85	1.07	26.9	12.2
	38.4	0.33	1.20	1.53	20.0	18.8
	50.0	0.01	1.30	1.31	22.0	17.0
	60.4	0.08	1.55	1.63	17.0	15.5
	63.0	0.18	1.30	1.48	15.0	13.5
	81.8	0.01	1.65	1.66	13.4	11.2
	89.0	0.14	2.50	2.64	23.2	19.3
					21.7±6.4	16.0±4.2
Na_3PO_4	31.0	1.21	0.65	1.86	32.1	21.1
2.20 mg/l	63.0	0.65	1.19	1.84	24.6	19.0
	89.0	0.14	1.72	1.86	23.2	19.3
Na_3PO_4	78.6	0.62	2.86	3.48	32.8	36.4
3.4 mg/l	102.2	0.38	3.12	3.50	29.5	30.7
	151.2	0.13	3.40	3.53	21.6	22.5
$Na_4P_2O_7$	22.0	1.30	1.15	2.45	22.7	25.8
	30.0	2.30	1.05	3.35	30.0	34.0
	62.0	0.95	1.30	2.25	23.4	29.2
3.20 mg/l	63.5	1.55	2.40	3.95	26.0	27.8
	81.5	1.15	2.10	3.25	26.5	30.8
	93.0	0.74	2.90	3.64	26.4	22.6
	102.0	0.13	4.40	4.53	31.8	39.0
					26.9±3.3	29.9±5.4
$Na_5P_3O_{10}$	13.5	2.96	0.94	3.90	76.5	70.0
	26.7	1.95	1.96	3.91	76.8	73.4
	50.0	0.83	3.50	4.33	76.7	66.3
4.0 mg/l	54.3	1.14	3.05	4.19	52.7	56.2
	100.0	0.37	3.83	4.20	46.3	42.3
	109.6	0.62	3.53	4.15	30.8	32.2
					60.0±19.6	56.7±16.5

Table 11

Phosphate Adsorption on Cement Dust in Natural and Domestic Sewage Samples

Wt. Dust (mg)	Sample	Total PO_4 (mg/l)	Filtr. PO_4 (mg/l)	Residue PO_4 (mg/l)	Dust PO_4 (mg)	PO_4 Removed (mg/g)	PO_4 Adsorb. (mg/g)
47.0	9th St.	0.145	0.075	0.70	0.30	1.50	1.59
54.7		0.330	0.280	0.75	0.35	0.91	1.37
70.0	Dam	0.440	0.330	0.80	0.43	1.57	1.14
112.0		0.145	0.020	0.90	0.68	1.28	1.30
						1.32±0.31	1.35±0.18
18.0	9th St.	1.250	1.05	0.70	0.10	11.1	18.8
40.0	Dam		0.40	1.35	0.23	21.2	21.1
64.5	+		0.03	2.55	0.37	19.0	30.0
81.7	Na_3PO_4		0.10	3.40	0.47	13.0	34.6
						16.1±4.8	26.3±7.4
41.0	9th St.	22.4	12.0	12.2	0.24	25.4	24.5
44.0	Dam +		13.0	11.5	0.28	21.4	24.0
62.0	$Na_4P_2O_7$		9.5	13.0	0.46	20.8	20.0
						22.5±2.5	24.2±2.4
66.4	Composite	2.42	0.82	-	0.38	24.2	33.9
146.0	Sewage		0.29	-	0.94	14.6	22.7
210.0	(Dil.)		0.12	-	1.21	11.0	17.9
						16.7±6.9	24.7±7.9
53.7	Composite	2.86	1.92	-	0.31	17.5	27.9
100.0	Sewage		0.52	-	0.58	23.4	29.2
144.1	(Dil.)		0.46	-	0.93	16.7	26.2
200.0			0.42	-	1.16	12.2	18.0
						17.5±5.6	25.4±5.8
68.0	Sewage	2.51	1.17	-	0.43	20.0	30.0
140.0	In		0.69	-	0.81	13.1	20.7
55.0	Sewage	2.20	1.21	-	0.32	18.0	28.4
150.0	Out		0.37	-	0.87	13.1	19.7
356.0			0.26	-	2.05	5.5	11.9

Table 12

High Phosphate Adsorption on Cement Dust in De-Ionized Water

Wt. Dust (mg)	Sample (mg/l)	PO_4 Filtr. (mg/l)	PO_4 Residue (mg/l)	Dust PO_4 (mg)	Total Recv. (mg/l)	PO_4 Removed (mg/l)	PO_4 Adsorb. (mg/l)
50.0	Na_3PO_4	8.50	18.75	0.29	27.25	290	364
106.0	23.0	2.35	22.00	0.61	24.35	195	199
205.0		1.75	19.00	1.09	20.75	104	86
						196±92	216±108
12.3	Na_3PO_4	7.3	2.65	0.07	9.95	203	187
34.8		4.0	4.3	0.20	8.30	167	110
54.0	9.8	3.2	4.4	0.31	7.60	193	71
109.6		2.1	6.5	0.64	8.60	61	51
						156±65	105±40
26.8	Na_3PO_4	4.10	2.60	0.16	6.70	106	81
41.0		3.40	4.80	0.24	8.20	93	106
50.0	7.2	2.60	5.70	0.29	8.30	92	103
86.2		0.22	7.20	0.50	7.42	81	78
						93±10	92±15
78.6	Na_3PO_4	0.62	2.86	0.48	3.48	33	36
102.2	3.4	0.38	3.12	0.59	3.50	30	31
151.2		0.13	3.40	0.82	3.53	22	23
						28.3±5.1	30.0±6.6
31.0	Na_3PO_4	0.65	1.70	0.18	2.35	50	40.7
63.0		0.18	2.30	0.37	2.48	32	26.5
61.7	2.2	0.10	2.35	0.36	2.45	34	28.0
89.0		0.14	2.50	0.51	2.64	23	19.4
						34.8±11.2	28.7±8.9
Mean	Na_3PO_4	1.10 mg/l				21.7±6.4	16.0±4.2

in the waters of the bay. The extent of this involvement was indicated by the adsorptive removal of phosphate for a definite amount of dust present. Based on the amount of dust added, the difference in amounts of phosphate left in the filtrate compared to the amount of phosphate originally taken, substantiated the extent of adsorption.

USE OF CALCIUM SELECT-ION ELECTRODE

In most cases where phosphorus compounds are added to natural systems, the presence of calcium ions results in greater fixation of phosphorus in soils or complexation in water. Calcium ions in solution are involved in the phosphate uptake or release in natural water. The calcium select-ion electrode can be used in the pH range of natural water for the study of the formation of soluble calcium-phosphorus complexes by potentiometric titration (mv).

The standard solutions for the electrode were prepared from $CaCl_2$ and the potentiometric response (millivolts) of the solutions was measured on a digital pH meter for concentrations from 1×10^{-2} to 1×10^{-5} M. The potentiometric (mv) response for these standard solutions are given in Table 13. The plot of concentration vs. millivolts resulted in a linear curve (Figure 5).

Ionic Strength and Millivolts

The ionic strengths of the solutions were maintained between 0.01 and 0.001 molar and the millivolt variation did not exceed four millivolts for the ten-fold change in the ionic strength. The measurement of millivolt response for diluted standard solutions and solutions with constant ionic strength gave a uniform change for the electrode (Table 13). The ionic strengths and pH values were maintained by using $(CH_3)_4NOH$, HCl, and $(CH_3)_4NCl$ were required.

Table 13

Calcium Ion Electrode Standard Values

Original Electrode		New Electrode	
$CaCl_2$	mv	$CaCl_2$	mv
9.12×10^{-3}M	- 42	1.0×10^{-2}M	+14
9.12×10^{-4}	- 66	1.0×10^{-3}	- 6
9.12×10^{-5}	- 90	1.0×10^{-4}	-24
9.12×10^{-6}	-105	1.0×10^{-5}	-42

Ionic Strength and MV

$CaCl_2$	mv (Stan. Soln.)	mv ($\mu = 0.01$)
0.01 M	- 62	- 61
0.005	- 68	- 67
0.001	- 85	- 83
0.0005	- 93	- 91
0.0001	-111	-110
0.00005	-118	-117
0.00001	-133	-130

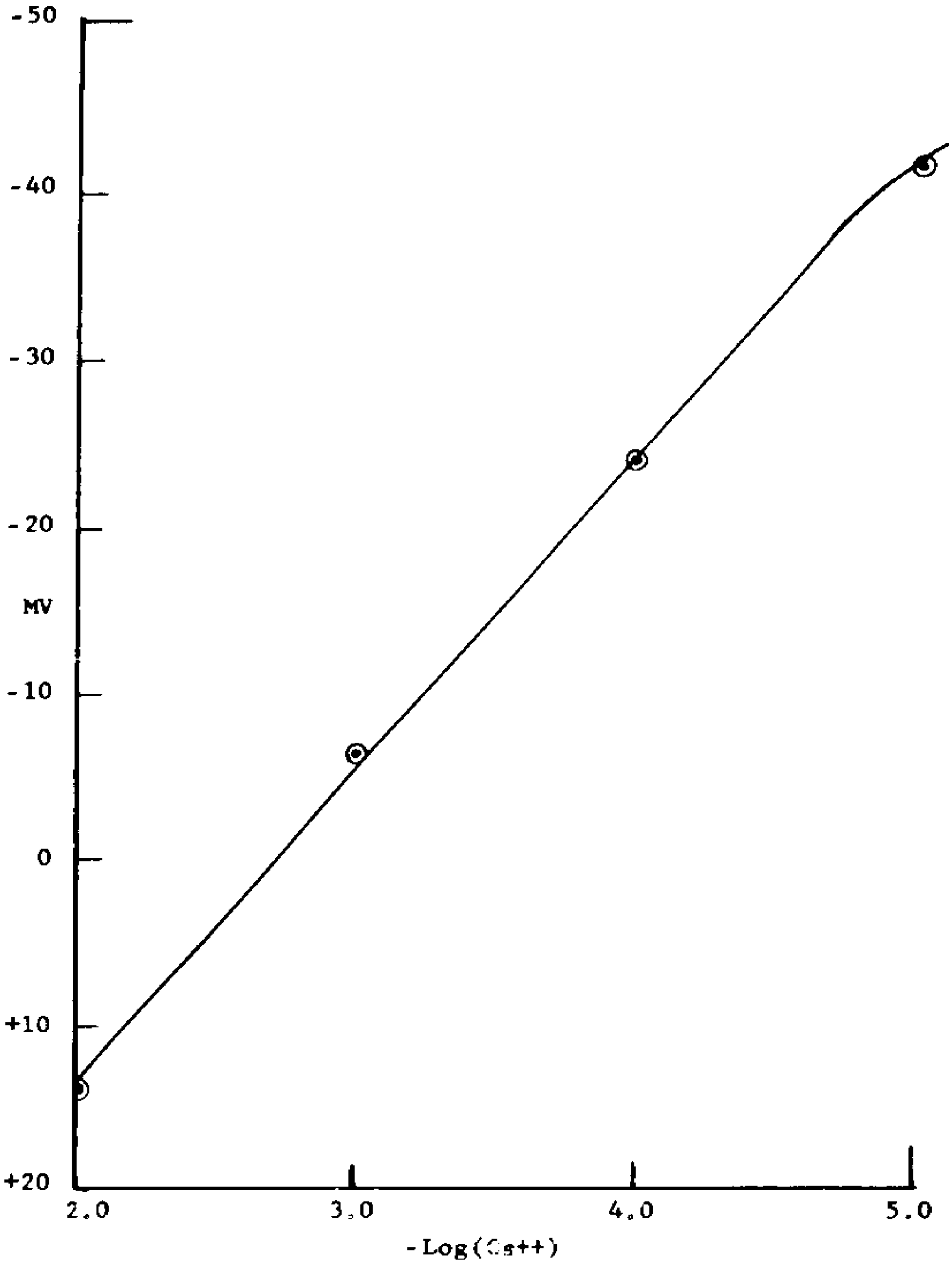


Figure 5. Standard Calcium Curve

pH vs. millivolts

The influence of hydrogen ion on the millivolt response of the standard $CaCl_2$ solutions was measured for the three solutions most representative of calcium levels of natural water systems (1×10^{-2} to 1×10^{-4} M). The results are given in Table 14 and represented in Figure 6. This plot of mv vs. pH indicated the extent of usability of the electrode as the linear portion of the curve for each concentration.

Temperature and millivolts

The temperature of the $CaCl_2$ solutions was varied in the range of the normal natural water temperatures. The results for the three standard solutions showed a definite temperature relationship with the potential of the solutions, especially the more concentrated, as indicated in Table 15.

Measurement of Organic Acids in Water

Initially, the fluorescent response of the natural colored material was used to determine the concentration of organic acids in the Thunder Bay Watershed samples. At an excitation wavelength of 365 mu, the fluorescence was measured at 470 mu in fluorescent units taken from the Turner Fluorometer. The fluorescent reading was related to organic mass by evaporation of a known volume of the concentrated extracts in alcohol. A conversion factor of 27 units/mg/100 ml was determined. A log plot of F vs. log mg of organic matter gave a linear curve.

The following specific results were found by fluorescent measurement using the fluorometer:

Sep/69 - Thunder Bay River at the Breakwall = 42 mg/l
Sep/69 - Wolf Creek (Hubbard Lake Road) = 54 mg/l

Table 14

Effect of pH on Calcium Ion Electrode Potential (mv)

Solution	pH	mv	Solution	pH	mv	Solution	pH	mv
$CaCl_2$	3.2	- 8	$CaCl_2$	3.0	-43	$CaCl_2$	3.1	-14
	3.5	25		3.4	51		3.3	26
1.02×10^{-2}	3.9	41	9.12×10^{-4}	3.8	57	1.0×10^{-4}	3.5	30
	4.2	43		4.6	59		3.7	36
-43 mv	4.8	43	-61 mv	5.4	61	-81 mv	3.8	45
	5.8	43		6.2	61		4.0	48
(pH-6.78)	6.4	43	(pH-6.35)	6.6	61	(pH-6.82)	4.2	65
	6.9	43		7.0	62		4.6	75
	7.7	43		7.3	62		4.8	78
	8.2	43		8.0	63		5.2	80
	9.1	43		8.5	64		6.0	80
	10.0	43		8.9	65		6.2	81
	10.2	43		9.5	66		6.6	81
	10.5	44		10.8	68		7.3	81
	11.0	45		11.0	70		7.8	81
	12.0	48		11.5	71		8.6	81
				12.0	75		9.2	82
							9.6	86
							10.0	89
							10.4	93
							11.0	96

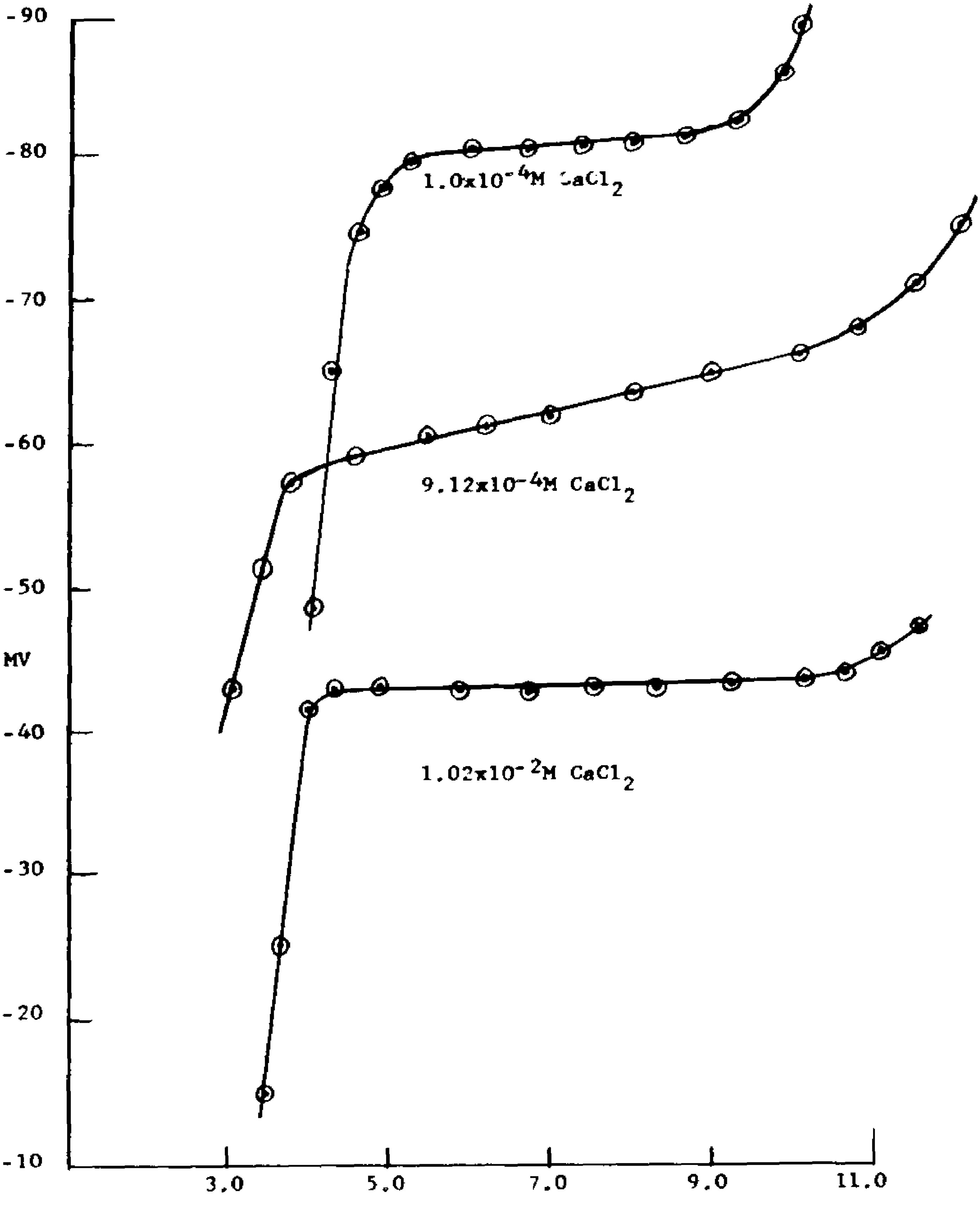


Figure 6. Effect of pH on Calcium Ion Electrode Potential

Table 15

Temperature (C) and Calcium Ion Electrode Potential (mv)

Solution	Temp	mv	Solution	Temp	mv	Solution	Temp	mv
	11	-10		12	-42		12	-64
	13	12		13	45		13	66
$CaCl_2$	15	14	$CaCl_2$	14	47	$CaCl_2$	14	68
	17	16		16	48		15	69
1×10^{-2}	18	18	1×10^{-3}	17	49	1×10^{-4}	16	70
	19	20		19	50		18	69
-26 mv	20	22	-50 mv	20	50	-69 mv	20	69
	22	23		21	51		22	69
	24	24		22	51		24	69
	25	25		23	52		25	70
	26	26		24	52		26	70
	28	27		25	53		27	71
	30	28		27	53		28	72
	32	28		28	53		29	73
	33	28		30	54		30	74
	35	28		31	55		32	75
	36	28		32	56		33	76
	38	29		35	58		34	78
	40	30		37	60		35	80
	42	30		38	61		38	83
	45	32		40	65		42	86

The fluorescence readings were fairly constant in a temperature range of 0C to 40C which would be adaptable to field measurements.

The spectrophotometric method for determination of humic acids (Semenov, et al., 1963) was checked using a Beckman DK-2 Spectrophotometer. There were absorbance peaks at 325 mu and in 400 to 450 mu range and in the infrared area of the spectrum. The excitation absorbance at 340 mu and transmittance at 440 mu gave comparible results as Organic Carbon (Humic acid) in mg/l with that of the fluorescent method. This spectrophotometric procedure was used for subsequent field measurement of color concentration in the Thunder Bay Watershed. The results of watershed sampling where significant amounts of organic color were found are given in Table 16.

The infrared spectrums for three sources were run on the Hilger-Watts Infrared spectrophotometer. The spectral curve for organic extract from the Main Branch of Thunder Bay River (in ethyl alcohol) is given in Figure 7. The assignment of functional groups to the observed peaks were taken from VanderMaas (1969) and are given in Table 17.

Organic Acid Separation

The water samples when passed through the anion-exchange resin, turned the resin from yellow to brown as the exchange proceeded down the column until its capacity (saturation) was attained. The material was removed from the column and fresh resin put on until the five gallon sample was used. On mixing with NaCl and NaOH, the resin and attached anionic organic material lightened in color and the solution became orange-brown. The filtrate from solids on treatment with HCl also lightens and effervescence occurred. The residue on evaporation gave a brown solution in ethyl alcohol. These alcohol solutions had

Table 16

Organic Color Measurement in Thunder Bay Watershed

Season	Date	Sample Location	mg/l
Fall	8/19/70	Bean Creek	58.0
"	8/22/70	Wolf Creek	15.5
"	8/26/70	Upper So. Bran. Thunder Bay	11.3
"	8/26/70	Main Branch at Breakwall	7.2
"	8/30/70	No. Bran. Thunder Bay	10.5
Winter	11/8/70	Bean Creek	56.0
"	11/8/70	Upper So. Bran. Thunder Bay	22.0
"	11/23/70	Wolf Creek	25.3
"	11/23/70	No. Bran. Thunder Bay	53.8
"	12/3/70	Main Branch - Atlanta	26.3
"	12/3/70	Main Branch - 9th St. Dam	50.0
"	12/3/70	Main Branch at Breakwall	21.9
Spring	5/13/71	No. Bran. Thunder Bay	55.0
"	5/15/71	Wolf Creek	18.8
"	5/23/71	Main Branch - 4-mile Dam	36.0
"	5/23/71	Main Branch - 9th St. Dam	29.0
"	5/23/71	Main Branch at Breakwall	35.6
"	5/31/71	Bean Creek	59.0
Summer	6/27/71	Brush Creek	32.6
"	6/26/71	Main Branch - Hillman	31.4
"	6/27/71	Main Branch at M-32	39.0
"	7/22/71	Main Branch at Breakwall (Bridge Construction)	94.0
"	8/2/71	Main Branch at Breakwall	81.0

INFRARED SPECTRUM
OF
THUNDER BAY NATURAL ORGANIC ACIDS

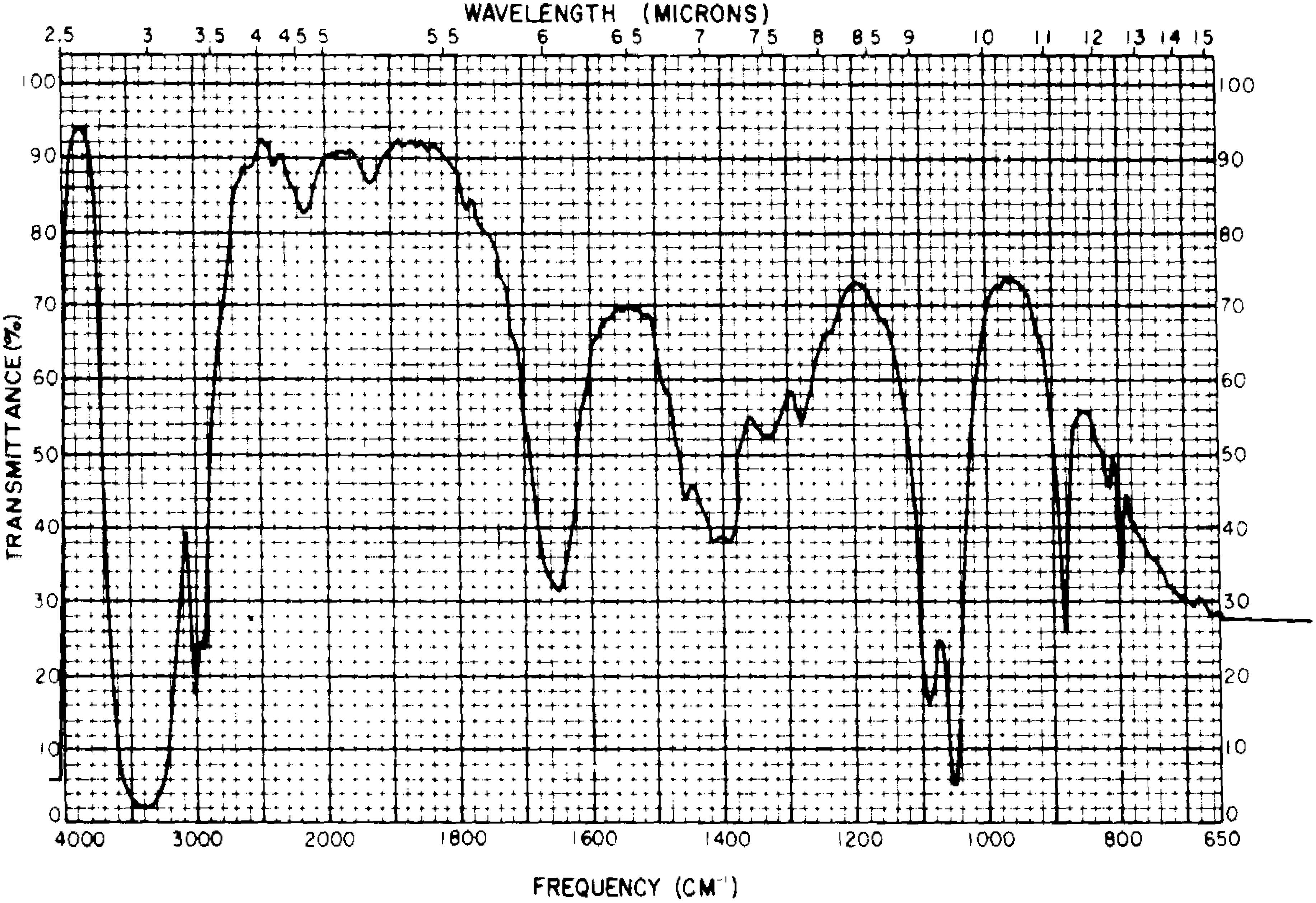


Table 17

The Infra-Red Assignment of Bands for Organic Functional Groups
(Vander Maas, 1969)

Source	Strong		Moderate	
	cm^{-1}	Group	cm^{-1}	Group
Thunder Bay River	3200-	-OH	1460	R-O-
	3600	-COOH		
	2950-	C-H	1330	Ø-OH
Main Branch	3020			
	1650-70	Ø	1280	Ø-O-R
+	1390-	$-CH_3$		
	1420	-OH	805	Ø-X_n
North Branch	1090	-C-OH		
	1050	Ø-X		
	880	Ø-X_2	(Phenyl - Ø)	
Wolf Creek	3200-	-OH	1710-20	-COOH
	3600	-COOH		
	2900-	C-H	1640-50	Ø
	3000			
	1460	R-O-	1280	Ø-O-R
	1390-	-OH		
	1410		1200	Ø-OH
	1040-90	Ø-X		
	890	Ø-X_2	805	Ø-X_n
Bean Creek	3200-	-OH		
	3550	-COOH	1650	-COOH
	2900-			
	3000	C-H	1580	$-COO^-$
	1390-	-OH	1460	R-O-
	1410		1330	Ø-OH
	1090	-C-OH	1280	Ø-O-R
	1050	Ø-X	805	Ø-X_n
	880	Ø-X_2		

organic acid concentrations in a range of 1 to 3 mg/ml. For a Thunder Bay River sample with 80 mg of Organic Carbon (Humic acid) per liter, the amount of organic acids recovered was 2.5 mg/ml. For a Wolf Creek sample with 50 mg of carbon per liter, the extraction procedure gave 1.5 mg/ml of organic acids.

The determination of available and fixed calcium was done at the sampling sites in the river and bay. The change in concentration of soluble calcium has been attributed to the complexation with oxidizable, anionic organic-substances (Hoffman and Ehrlich, 1970). The possible involvement of phosphates in this complexation was a major portion of this study.

The measurement of these interactions was established from changes in the weak-acid function (milliequivalence) of the phosphate forms and increases in association constants of calcium-phosphate complexes in the presence of organic acids.

The potential comparison method used the potential response (mv) of a known concentration of calcium to compare the original free calcium with that of complexed calcium. The reactions assuming unimolecular exchange at a pH of 4.5 to 7.0 would be:

$$Ca^{++} + H_2PO_4^{-} = CaH_2PO_4^{+}$$

while at a pH of 7.5 to 9.0:

$$Ca^{++} + HPO_4^{=} = CaHPO_4$$

and at a pH of 9.0 to 10.5:

$$3Ca^{++} + 2PO_4^{-3} = CaPO_4^{-} + Ca_2PO_4^{+}$$

When the pH is maintained below 9.0, precipitation is avoided.

In these equilibria, the concentration of the soluble ions would be found according to:

$(Ca^{++})_c$ - Complexed calcium ion

$(Ca^{++})_t$ - Original calcium solution

$(Ca^{++})_e$ - Free calcium at equilibrium

$(P)_t$ - Original phosphate solution

$(P)_e$ - Free phosphate at equilibrium

so that after correction for dilution:

$(Ca\text{-}P)_c$ - Concentration of calcium-phosphate complex

$$(Ca\text{-}P)_c = (Ca^{++})_c = (Ca^{++})_t - (Ca^{++})_e$$

$$(P)_e = (P)_t - (Ca^{++})_c$$

and the association constant (K_f) would be found from:

$$K_f = \frac{(Ca\text{-}P)_c}{(Ca^{++})_e \cdot (P)_e}$$

Sample calculation for K_f:

Phosphate solution - $Na_3PO_4 = 1.02 \times 10^{-3}$ M (50 ml)

Calcium titrant - $CaCl_2 = 1.00 \times 10^{-2}$ M (9.8 ml)

$(Ca^{++})_e = 1.00 \times 10^{-3}$ M (-91 mv)

$(PO_4^{-3})_t = 1.02 \times 10^{-3} \cdot (50/59.8) = 8.53 \times 10^{-4}$ M

$(Ca^{++})_t = 1.00 \times 10^{-2} \cdot (9.8/59.8) = 1.64 \times 10^{-3}$ M

$(Ca^{++})_c = (Ca\text{-}PO_4)_c = (1.64\text{-}1.00) \times 10^{-3} = 6.4 \times 10^{-4}$ M

$(PO_4)_e = (8.53\text{-}6.4) \times 10^{-4} = 2.13 \times 10^{-4}$ M

$$K_f = \frac{(6.4 \times 10^{-4})}{(1 \times 10^{-3})(2.13 \times 10^{-4})} = 3000$$

The association constants found by the Potential Comparison method for the three phosphate solutions at selected pH values are given in Table 18.

The effect of natural organic acids on the association constants found above for the calcium-phosphate mixtures was measured under identical conditions of pH, temperature, and ionic strength. The

Table 18

Association Constant by Potential Comparison

$(Ca^{++})_e$		Phosphate Sample		Ca Titrant		
Conc	mv	Conc	Vol (ml)	Conc	Vol (ml)	K_f
pH - 9.0-10.5		Na_3PO_4				
$1.0x10^{-3}$	- 26	$1.17x10^{-2}$	10	$1.10x10^{-4}$	100	$1.63x10^4$
$1.0x10^{-4}$	- 37	$1.17x10^{-3}$	120	$1.00x10^{-3}$	100	$1.25x10^4$
$9.3x10^{-5}$	- 89	$1.02x10^{-4}$	50	$9.27x10^{-4}$	8.5	$1.02x10^4$
$9.3x10^{-5}$	- 87	$1.02x10^{-4}$	50	$9.27x10^{-5}$	100	$1.10x10^4$
						$1.25x10^4 \pm 0.27$
pH - 8.5-10.0		Na_3PO_4				
$1.0x10^{-3}$	- 91	$1.02x10^{-3}$	50	$1.0x10^{-2}$	9.8	$3.0x10^3$
$1.0x10^{-3}$	- 25	$1.17x10^{-3}$	100	$1.0x10^{-3}$	22.0	$4.9x10^3$
$9.3x10^{-5}$	- 87	$1.02x10^{-4}$	100	$9.3x10^{-4}$	14.7	$4.5x10^3$
$9.3x10^{-5}$	-107	$1.02x10^{-4}$	100	$9.3x10^{-4}$	15.2	$5.4x10^3$
						$4.5x10^3 \pm 1.0$
		$Na_4P_2O_7$				
$9.3x10^{-5}$	-108	$1.16x10^{-4}$	50	$9.3x10^{-3}$	11.2	$4.8x10^4$
$9.3x10^{-5}$	-108	$1.16x10^{-4}$	100	$9.3x10^{-4}$	21.2	$2.9x10^4$
		$Na_5P_2O_{10}$				
$9.3x10^{-5}$	-102	$1.25x10^{-4}$	50	$9.3x10^{-4}$	14.4	$3.2x10^3$
$9.3x10^{-5}$	-101	$1.25x10^{-4}$	100	$9.3x10^{-4}$	30.4	$5.1x10^3$
pH - 6.5-7.5		Na_3PO_4				
$1.0x10^{-3}$	- 11	$1.17x10^{-3}$	100	$1.0x10^{-2}$	15.0	417
$1.0x10^{-3}$	- 11	$1.17x10^{-3}$	50	$1.0x10^{-2}$	8.0	656
$1.0x10^{-3}$	- 14	$1.17x10^{-3}$	150	$1.0x10^{-2}$	23.0	448
						507 ± 130
		$Na_4P_2O_7$				
$1.0x10^{-3}$	- 17	$1.06x10^{-3}$	100	$1.0x10^{-2}$	15.0	482
$1.0x10^{-3}$	- 16	$1.06x10^{-3}$	100	$1.0x10^{-2}$	16.0	710
		$Na_5P_3O_{10}$				
$1.0x10^{-3}$	- 17	$1.13x10^{-3}$	100	$1.0x10^{-2}$	15.0	440
$1.0x10^{-3}$	- 16	$1.13x10^{-3}$	100	$1.0x10^{-2}$	15.5	874

organic acids were extracted from the Thunder Bay system. The results for these measurements are given in Table 19.

Potential-Titration Method

The calibration curve was prepared witn standard solutions of $CaCl_2$ with pH adjusted to 6.5 to 8.0. The sample of standard calcium was titrated with a known concentration of the phosphate solutions. This procedure was reversed and a standard phosphate solution was titrated with known calcium solutions. The potential (mv) was measured after each addition of selected volumes of titrant. The apparent (Ca^{++}) for the millivolt reading can be obtained from the curve. This method was used to determine the extent of calcium-phosphate complexation and extended to include interaction of organic acid concentrates.

After appropriate dilution correction, the association constants (K_f) were calculated according to: $K_f = \frac{(Ca\text{-}P)_c}{(Ca^{++})_e \cdot (P)_e}$

with:

$$(Ca^{++})_t = 9.27 \times 10^{-5}(100/150) = 6.18 \times 10^{-5}\ M$$

$$(PO_4)_t = 1.02 \times 10^{-4}(50/150) = 3.40 \times 10^{-5}\ M$$

$$(Ca^{++})_e = 5.25 \times 10^{-5}\ M$$

$$(Ca^{++})_c = (6.18-5.25) \times 10^{-5} = 0.93 \times 10^{-5}\ M = (Ca\text{-}P)_c$$

$$(PO_4)_e = (3.40-0.93) \times 10^{-5} = 2.47 \times 10^{-5}\ M$$

$$K_f = \frac{(9.3 \times 10^{-6})}{(5.25 \times 10^{-5})(2.47 \times 10^{-5})} = 7200$$

Precipitation was noted when the concentration of the phosphate solution approached a 2 to 1 ratio of calcium to phosphate. When the pH of the solution was above 9.0, the reaction mixture was cloudy. However, when pH was above 10.0, a white precipitate settled out on standing. The association constants determined by Potential-Titration method were done at different pH values comparible to those used in

Table 19

Association Constant by Potential Comparison in the Presence of Natural Organic Acids

$(Ca^{++})_e$		Phosphate Sample			Ca Titrant		
Conc	mv	Soln	Conc	Vol (ml)	Conc	Vol (ml)	K_f
			pH - 9.0-10.5				
9.27×10^{-5}	-107	Na_3PO_4	1.02×10^{-4}	100	9.27×10^{-4}	15.2	5400
9.27×10^{-5}	-109	Na_3PO_4 + Org acid	1.02×10^{-4}	100	9.27×10^{-4}	15.5	6000
9.27×10^{-5}	-108	$Na_4P_2O_7$	1.16×10^{-4}	100	9.27×10^{-4}	21.2	2.9×10^4
9.27×10^{-5}	-108	$Na_4P_2O_7$ + Org acid	1.16×10^{-4}	100	9.27×10^{-4}	22.3	4.4×10^4
9.27×10^{-5}	-101	$Na_5P_3O_{10}$	1.25×10^{-4}	100	9.27×10^{-4}	30.4	5100
9.27×10^{-5}	-108	$Na_5P_3O_{10}$ + Org acid	1.25×10^{-4}	100	9.27×10^{-4}	31.9	7500
			pH - 6.5-7.5				
1.0×10^{-3}	- 16	Na_3PO_4	1.17×10^{-3}	100	1.0×10^{-2}	15.0	417
1.0×10^{-3}	- 16	Na_3PO_4 + Org acid	1.17×10^{-3}	100	1.0×10^{-2}	16.0	601
1.0×10^{-3}	- 16	$Na_4P_2O_7$	1.06×10^{-3}	100	1.0×10^{-2}	16.0	710
1.0×10^{-3}	- 16	$Na_4P_2O_7$ + Org acid	1.06×10^{-3}	100	1.0×10^{-2}	17.0	1000
1.0×10^{-3}	- 16	$Na_5P_3O_{10}$	1.13×10^{-3}	100	1.0×10^{-2}	15.5	874
1.0×10^{-3}	- 16	$Na_5P_3O_{10}$ + Org acid	1.13×10^{-3}	100	1.0×10^{-2}	18.0	1212

Potential Comparison method. The association constants found in the Potential-Titration method are given in Table 20.

From the potential (mv) titration of Na_3PO_4 with soluble calcium, increased precipitation occurred at higher pH values (above nine with $Ca(OH)_2$)(Figure 8). As well, an indication of additional calcium ion complexation with orthophosphate was apparent when the amount of Ca^{++} was increased.

In the pH range of natural waters, no precipitation occurred and a smooth curve resulted with some indication of structural changes in the calcium-phosphate complex indicated. When Na_3PO_4 was used as a titrant, precipitation occurred at pH values greater than nine. The curve (Figure 9) for this titration showed apparent areas of calcium removal from solution as complexes or insoluble forms were formed.

Comparable results also occurred with the pyro and tripolyphosphates at these higher pH values. The curves (Figure 10) were somewhat similar but again showed areas different for each calcium complex phosphate species.

Next, the titration procedure was reversed and the three phosphate solutions were titrated with $CaCl_2$. The change in potential (mv) was followed during the addition. The results of this procedure and the association constants determined from the results are given in Table 21.

The potentiometric (mv) titration of the phosphate solutions with $CaCl_2$ was repeated in the presence of the Thunder Bay natural organic acids. The same conditions were maintained during all of the titrations. The effect of these acids on the association constants measured at pH values for natural water (6.5 to 7.5) are

Table 20

Association Constant by Potential-Titration Using Calcium

Calcium		Phosphate Sample			Equilibrium		
Conc	mv	Soln	Conc	Vol (ml)	mv	$(Ca^{++})_e$ (10^{-5})	K_f
pH = 9.5-10.5							
$1.0x10^{-3}$	-14	Na_3PO_4	$1.17x10^{-3}$	70	-30	38.8	$2.06x10^4$
"	-14	"	"	100	-35	12.0	$1.20x10^4$
"	-14	"	"	140	-39	8.33	$1.14x10^4$
							$1.47x10^4 \pm 0.52$
pH = 8.5-9.0							
$9.27x10^{-5}$	-90	Na_3PO_4	$1.02x10^{-4}$	50	-93	5.25	7200
"	-87	"	"	30	-89	2.82	5600
"	-108	"	"	25	-111	7.10	4800
$1.00x10^{-4}$	-42	Na_3PO_4	$1.17x10^{-3}$	10	-44	6.30	2700
"	-43	"	"	20	-46	6.30	3400
$1.00x10^{-3}$	-26	"	"	5	-34	25.0	4500
"	-20	"	"	50	-25	44.0	3400
							4500 ± 1540
$1.0x10^{-4}$	-20	$Na_4P_2O_7$	$1.06x10^{-3}$	6	-28	4.80	$4.0x10^4$
"	-20	"	"	15	-29	3.80	$1.8x10^4$
$1.0x10^{-4}$	-30	$Na_5P_3O_{10}$	$1.13x10^{-3}$	10	-37	4.50	$1.8x10^4$
"	-30	"	"	15	-38	3.80	$1.3x10^4$
"	-30	"	"	25	-41	2.80	$1.0x10^4$
							$1.4x10^4 \pm 0.40$
pH = 6.5-7.5							
$1.0x10^{-3}$	-11	Na_3PO_4	$1.17x10^{-3}$	25	-12	4.60	345
"	-11	"	"	50	-14	3.70	354
$1.0x10^{-4}$	-30	"	"	18	-32	0.52	410
"	-28	"	"	50	-35	4.50	430
							385 ± 42
$1.0x10^{-3}$	-2	$Na_4P_2O_7$	$1.06x10^{-2}$	3	-4	85.0	810
"	-4	"	"	5	-6	74.0	725
"	-4	"	"	6	-20	72.0	787
"	-4	"	"	12	-32	55.0	786
							777 ± 36
$1.0x10^{-3}$	-16	$Na_5P_3O_{10}$	$1.13x10^{-3}$	10	-20	72.0	840
"	-16	"	"	15	-17	110	870

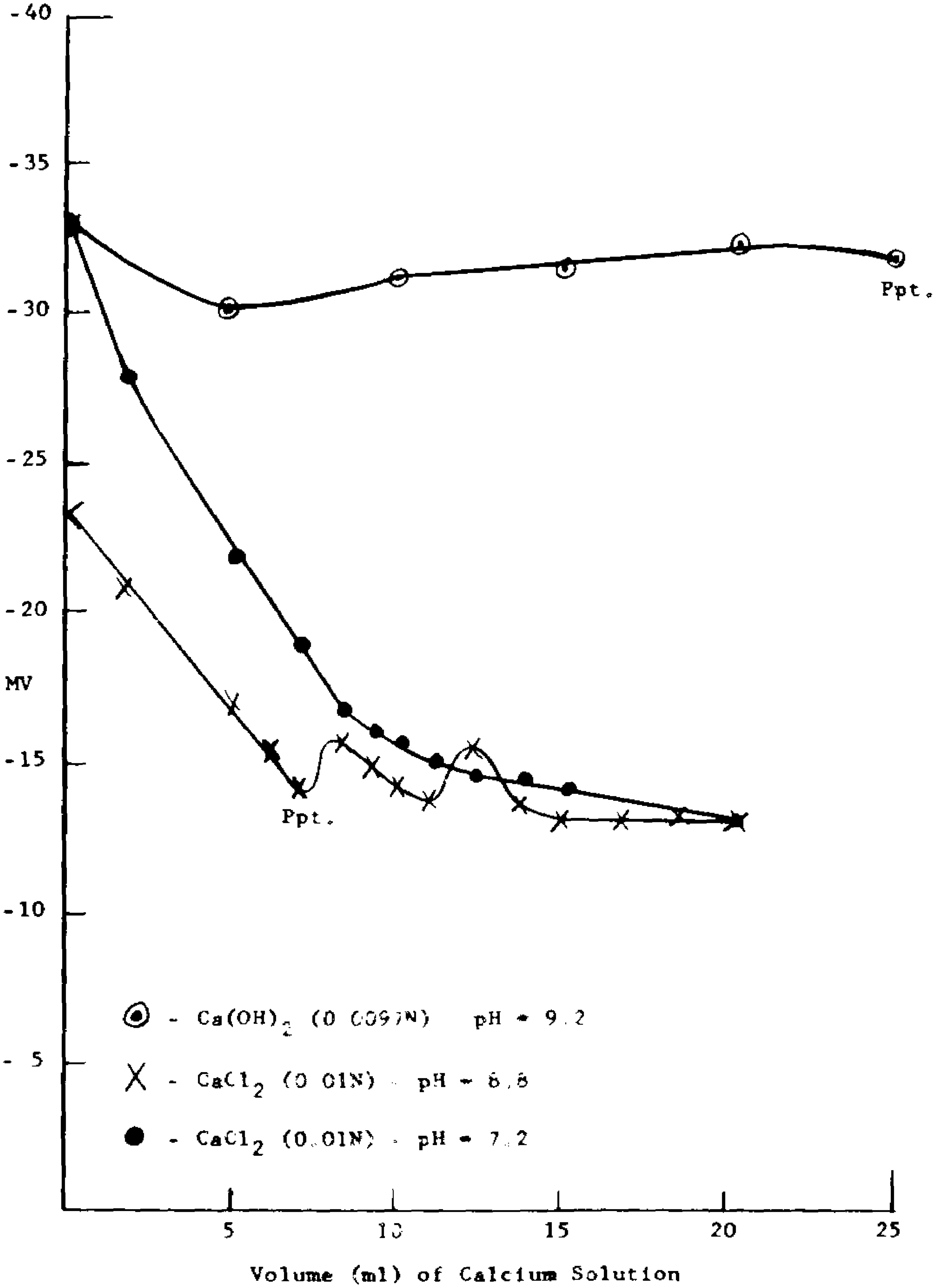


Figure 8. Titration of Na_3PO_4 (1.17×10^{-3}M) with Calcium at Variable pH

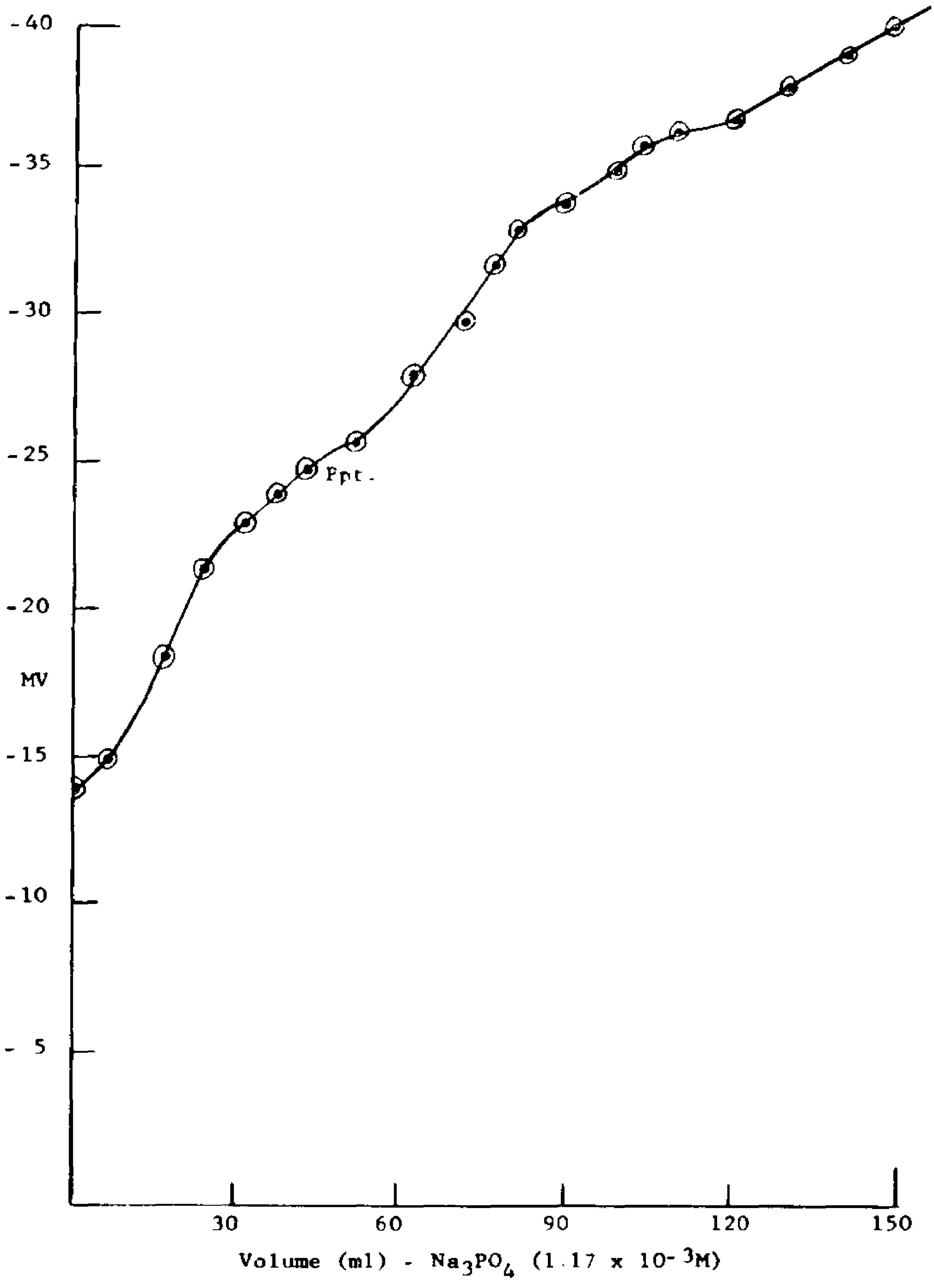


Figure 9. Titration of $CaCl_2$ ($1.0 \times 10^{-3}M$) with Na_3PO_4

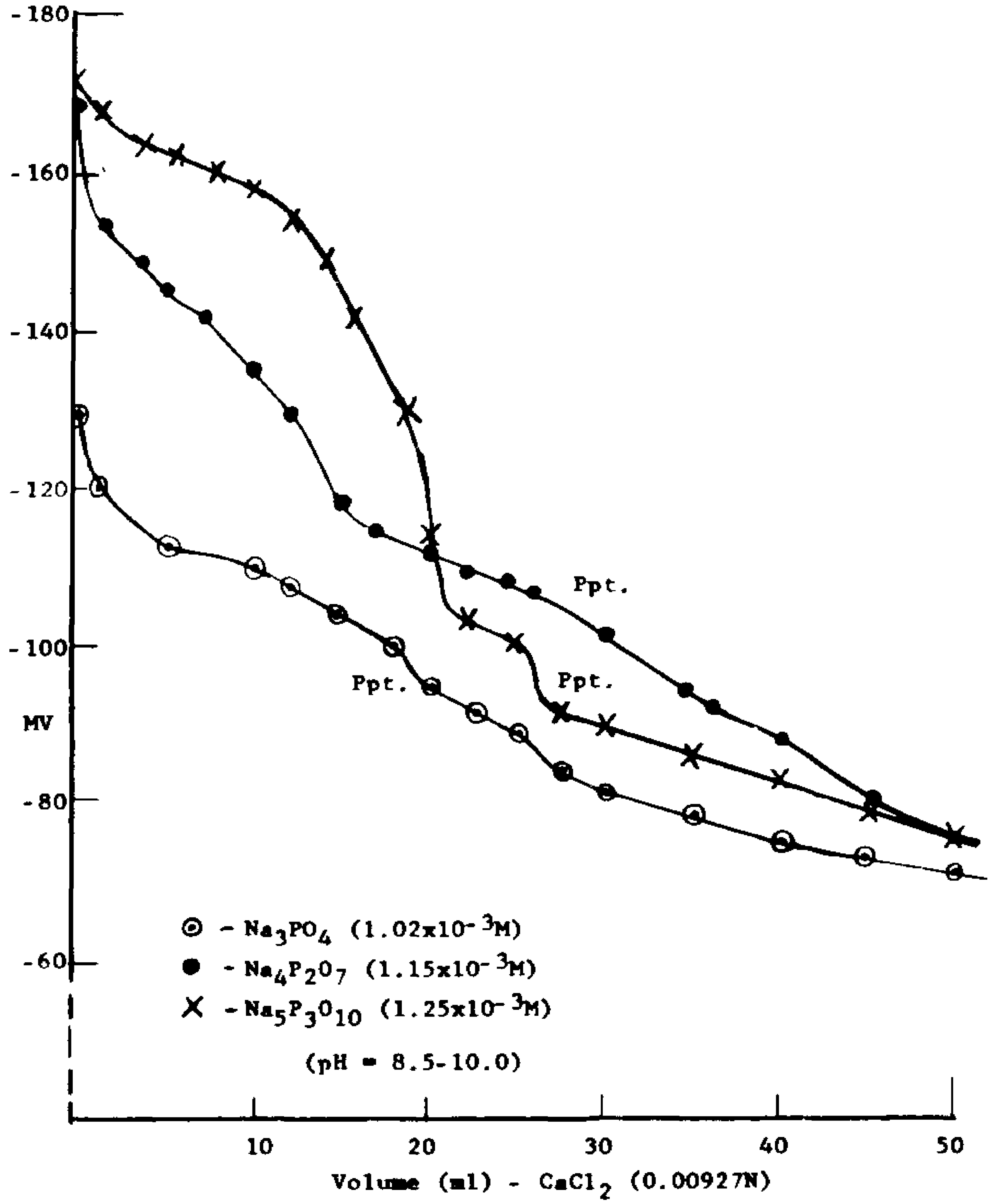


Figure 10. Titration of Linear Phosphate Forms with $CaCl_2$

Table 21

Association Constant by Potential-Titration Using Phosphates

Phosphate		Calcium Sample				
Soln	Conc	Conc	Vol (ml)	mv	$(Ca\text{-}F)_c$	K_f
pH - 10.0-10.5						
Na_3PO_4	$1.02x10^{-3}$	$9.27x10^{-3}$	5	-12	$3.80x10^{-5}$	$1.85x10^{4}$
Na_3PO_4	$1.17x10^{-3}$	$9.27x10^{-3}$	10	-10	$4.60x10^{-5}$	$1.20x10^{4}$
pH - 6.5-7.0						
Na_3PO_4	$1.17x10^{-3}$	$1.0x10^{-3}$	23	-39	$3.50x10^{-4}$	646
Na_3PO_4	$1.17x10^{-2}$	$1.0x10^{-3}$	25	-38	$3.80x10^{-4}$	645
Na_3PO_4	$1.17x10^{-2}$	$1.0x10^{-3}$	30	-36	$4.00x10^{-4}$	750
+						
Org acid						
$Na_4P_2O_7$	$1.06x10^{-3}$	$1.0x10^{-2}$	8	-22	$1.90x10^{-4}$	437
"	" "	" "	12	-19	$2.58x10^{-4}$	461
"	" "	" "	15	-17	$3.00x10^{-4}$	482
"	" "	" "	16	-16	$3.80x10^{-4}$	610
						498 ± 76
$Na_4P_2O_7$	$1.06x10^{-3}$	$1.0x10^{-2}$	10	-21	$2.78x10^{-4}$	642
+	" "	" "	12.5	-19	$2.58x10^{-4}$	461
Wolf Creek	" "	" "	14	-18	$2.95x10^{-4}$	502
	" "	" "	17	-16	$4.53x10^{-4}$	996
						650 ± 211
$Na_5P_3O_{10}$	$1.13x10^{-3}$	$1.0x10^{-2}$	12.5	-19	$2.98x10^{-4}$	460
"	" "	" "	15	-17	$3.00x10^{-4}$	540
"	" "	" "	15.5	-16	$3.40x10^{-4}$	774
						591 ± 163
$Na_5P_3O_{10}$	$1.13x10^{-3}$	$1.0x10^{-2}$	10	-20	$1.84x10^{-4}$	840
+	" "	" "	15	-17	$3.00x10^{-4}$	640
Wolf Creek	" "	" "	18	-16	$5.30x10^{-4}$	1010
						830 ± 185

given in Table 22. These results again showed that these natural organic acids are involved in the complexation of calcium and the phosphate species.

In the presence of natural organic acids, the complexation areas shifted slightly (Figure 11) showing involvement of acids in the interaction, while the apparent soluble calcium used in the reaction system increased. The association constants determined by potential comparison methods increased when the organic acids were present, as did the constants determined by potential-titration methods.

In all cases, the amount of calcium involved in the calcium-phosphate complexation was increased by the presence of the concentrated natural-organic-acid extract from the Thunder Bay Watershed.

When three milligrams of Wolf Creek organic acid concentrate were added directly to a $CaCl_2$ and Na_3PO_4 mixture and allowed to stand, the initial free-calcium concentration was lowered on an average, 8.8 mg/l. This calcium would be fixed in addition to the calcium already complexed by the orthophosphate.

Potentiometric (pH) Titration of Natural Organic Acids

After adjustment of the solution pH to 2.5, the pure organic acids were titrated with NaOH and $Ca(OH)_2$ to obtain the equivalence of their anionic solution. The samples used were both in salt form and in pure acidic form. The measurement of acid nature of the organic acids from various sources is given in Table 23.

The resulting representative curves for the pH titration of the organic acids with NaOH and $Ca(OH)_2$ are given in Figures 12 and 13. The titration curve, between 2.5 and 11.0, represents the alkali consumption of the organic material by neutralization of the carboxylic and phenolic groups.

Table 22

Association Constant by Potential-Titration in the Presence of Natural Organic Acids

(pH - 6.5-7.5)

Phosphate Sample			Calcium Titrant			
Soln	Conc	Vol	Conc	Vol	(Ca-P)	K_f
Na_3PO_4 +	$1.17x10^{-3}$	100ml	$1.0x10^{-2}$	15.0ml	$3.00x10^{-4}$	418
Org acid	$1.17x10^{-3}$	150	$1.0x10^{-2}$	23	$3.29x10^{-4}$	448
Na_3PO_4 +	$1.17x10^{-3}$	100	$1.0x10^{-2}$	20	$4.67x10^{-4}$	765
Org acid	$1.17x10^{-3}$	150	$1.0x10^{-2}$	30	$4.67x10^{-4}$	964
$Na_4P_2O_7$ +	$1.06x10^{-3}$	100	$1.0x10^{-2}$	16	$3.80x10^{-4}$	710
Org acid	$1.06x10^{-3}$	100	$1.0x10^{-2}$	17	$4.53x10^{-4}$	1000
$Na_5P_3O_{10}$ +	$1.13x10^{-3}$	100	$1.0x10^{-2}$	15.5	$3.40x10^{-4}$	874
Org acid	$1.13x10^{-3}$	100	$1.0x10^{-2}$	18.0	$5.30x10^{-4}$	1240

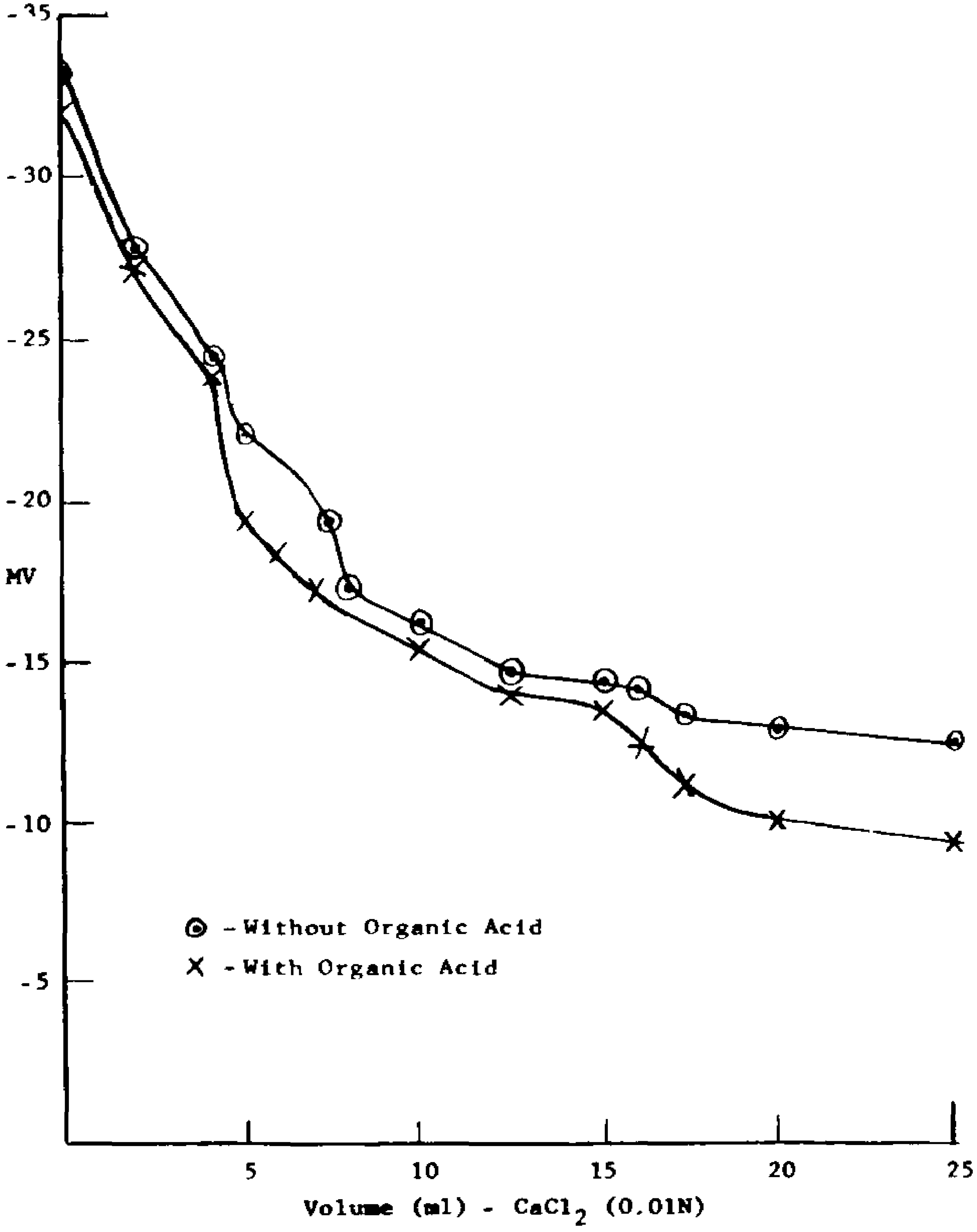


Figure 11. Titration of Na_3PO_4 (1.17×10^{-3}, pH-7.2) with $CaCl_2$ in the Presence of Thunder Bay Organic Acids

Table 23

pH Measurements of Natural Organic Acids with Base

Sample Source	Organic Conc.	Titrant	Base Conc	Base Vol	f_a - meq
Main Branch Organic Salts	-	NaOH	0.0912	2.45 ml	0.223
		NaOH	0.0886	3.10	0.275
		NaOH	0.0886	2.50	0.222
Main Branch Org Salts	-	$Ca(OH)_2$	0.0263	8.00	0.210
		$Ca(OH)_2$	0.0100	28.0	0.280
North Branch Org Salts	-	NaOH	0.0886	3.10	0.275
		NaOH	0.0886	2.40	0.213
		NaOH	0.0886	1.95	0.173
North Branch Org Acids	1 mg/l	NaOH	0.0911	1.80	0.314
Wolf Creek Org Acids	3 mg/l	NaOH	0.0911	34.0	3.040
Bean Creek	0.5 mg/l	$Ca(OH)_2$	0.0060	14.0	0.084

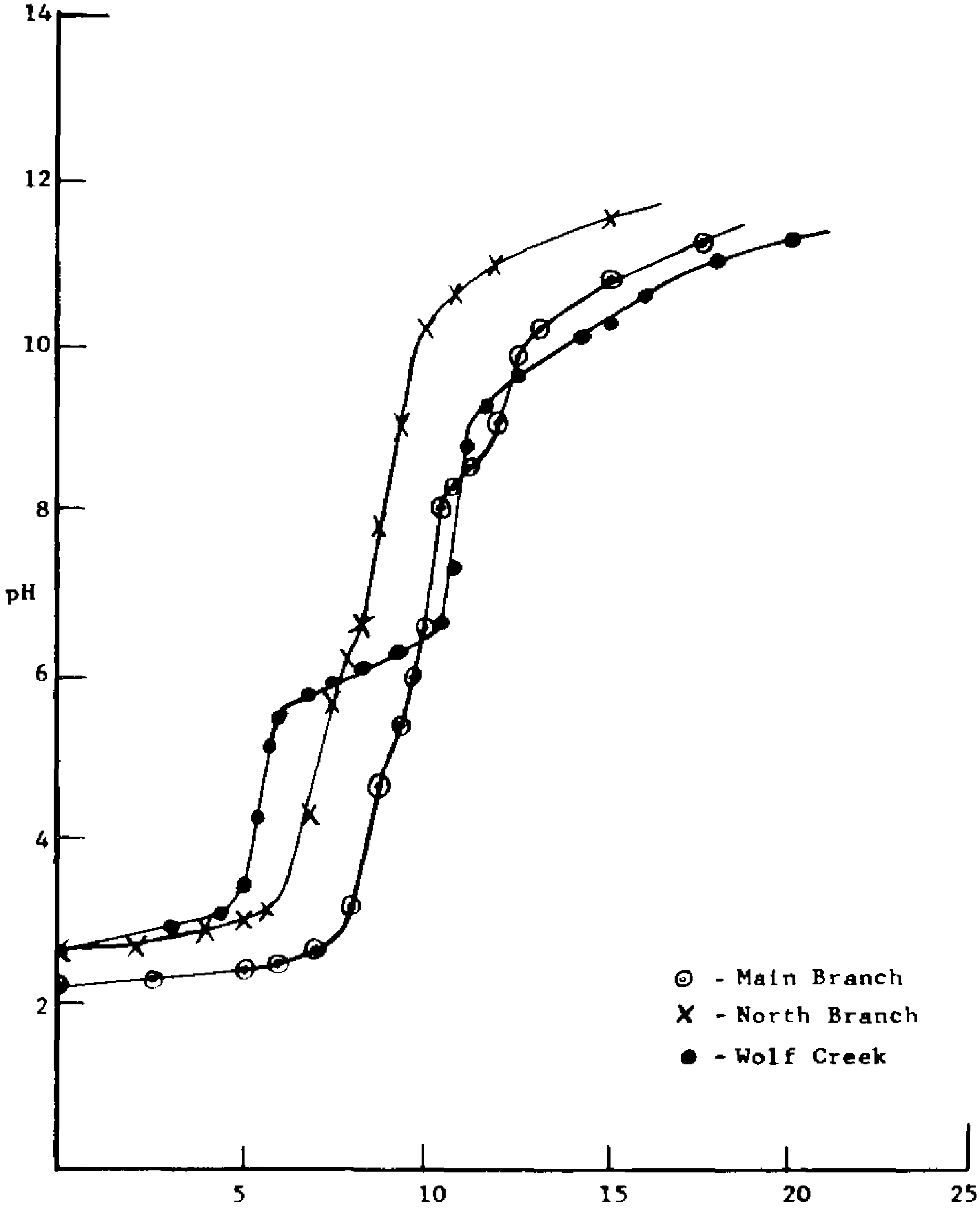


Figure 12. Titration of Organic Acids with NaOH

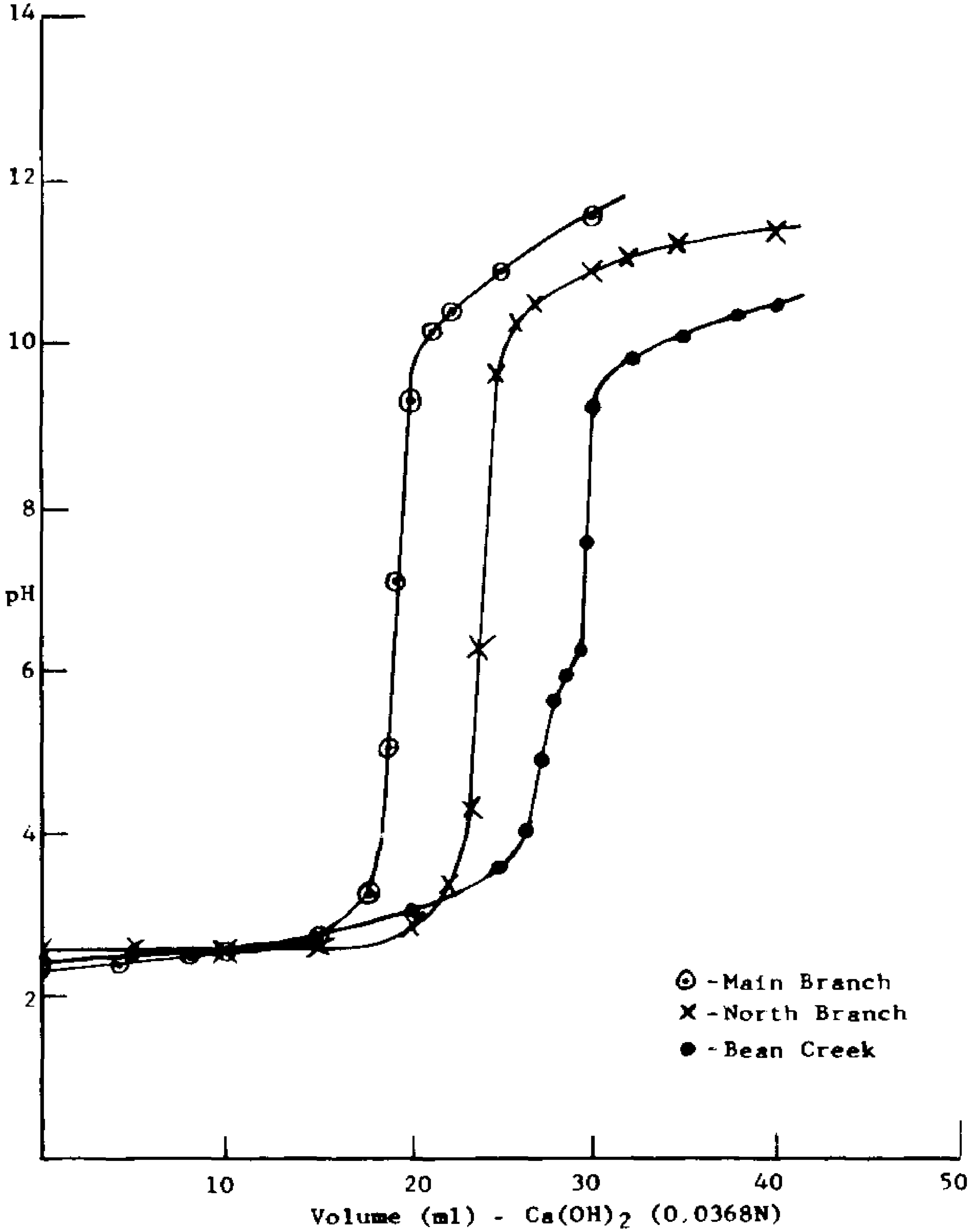


Figure 13. Titration of Organic Acids with $Ca(OH)_2$

Potentiometric (pH) Titration of Phosphates

In Figure 14, the change in pH for solutions of the three phosphate forms titrated with NaOH is shown. The formation of the mono and disodium phosphates are observed in the typical S curve described by Odajiri and Nickerson (1964). The titration of the phosphates with base between pH 2.5 and 11.0 represents the weak-acid consumption of the phosphates by neutralization.

The titration of Na_3PO_4 was done at two rates to compare the effect of rate of titration with $Ca(OH)_2$ on the formation of Ca-PO_4 complexes. The curves are shown in figure 15. The titration of the poly-forms with $Ca(OH)_2$ is shown in Figure 16. The presence of precipitation and a decrease in pH indicated the formation of insoluble phosphate forms. On further addition of alkali, only a small change in pH occurred. The results of complete titration of the phosphate forms are given in Tables 24 and 25.

The influence of calcium on the titration of the phosphate forms was followed by adding $CaCl_2$ to the solutions before neutralization with NaOH (Figure 17). In this way, the involvement of calcium ion in possible calcium-phosphate-organic acid complexation could be measured from two directions with calcium. In all cases, the presence of $CaCl_2$ in the phosphate solutions resulted in an increase in the amount of NaOH needed to reach the weak-acid function equivalency. This was more pronounced for orthophosphate where the solubility of dicalcium phosphate formed was depressed by the calcium present in the solution.

When the phosphate forms were titrated with NaOH in the presence of $CaCl_2$, the formation of insoluble calcium phosphate occurred above pH of 6. When natural organic acid concentrates were added to

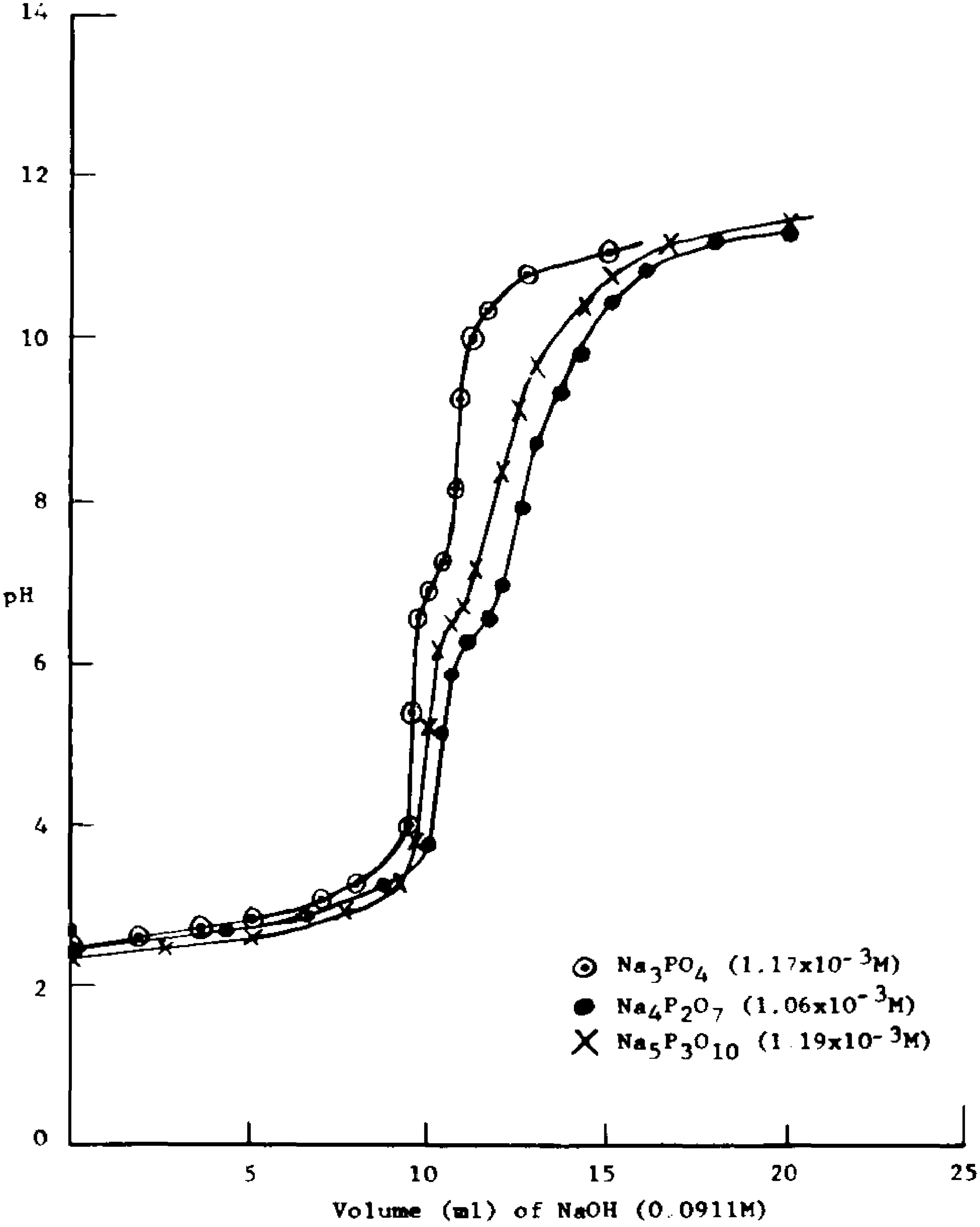


Figure 14. Titration of Linear Phosphate Forms with NaOH

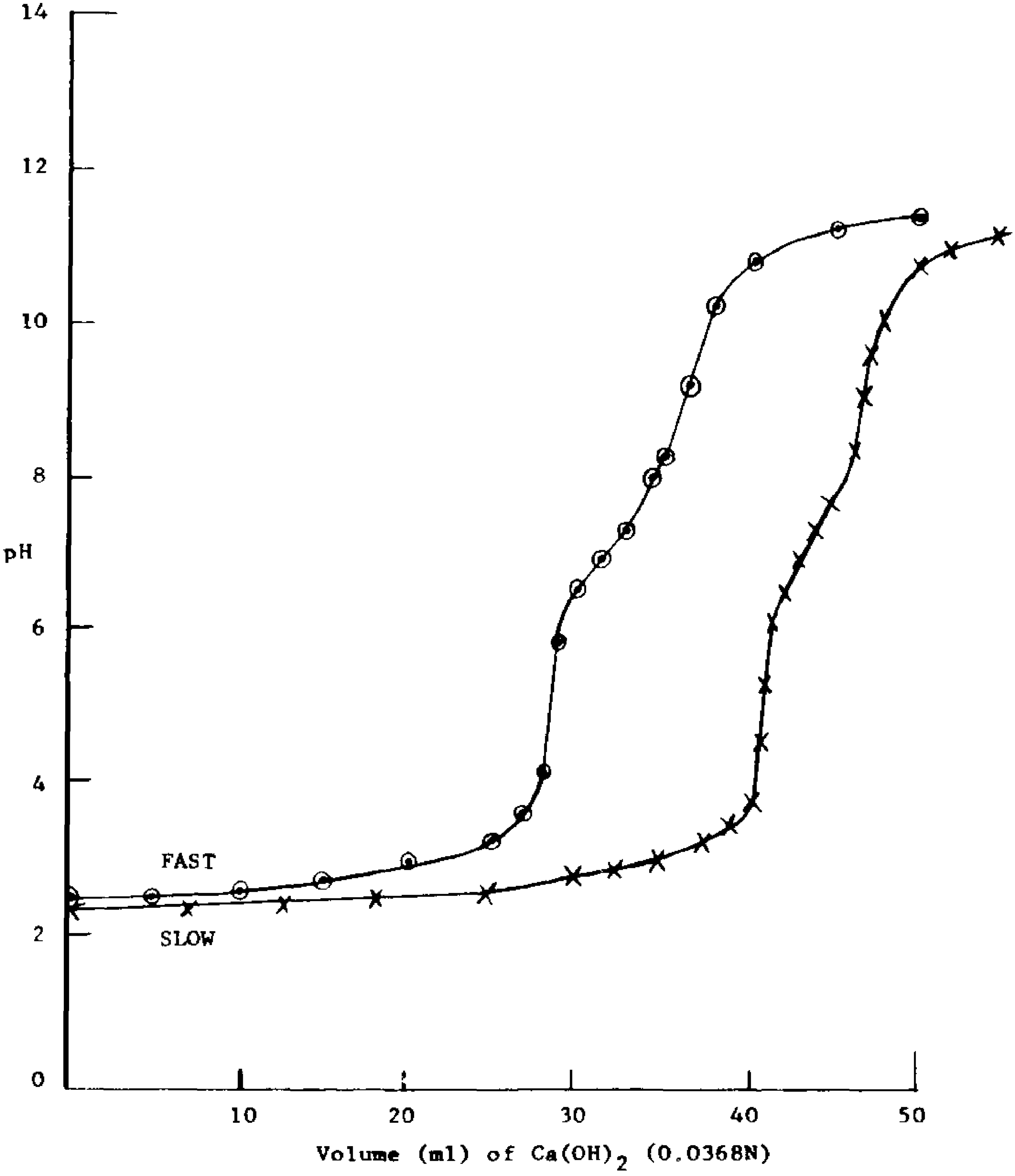


Figure 15. Titration of Na_3PO_4 with $Ca(OH)_2$ at Variable Rates

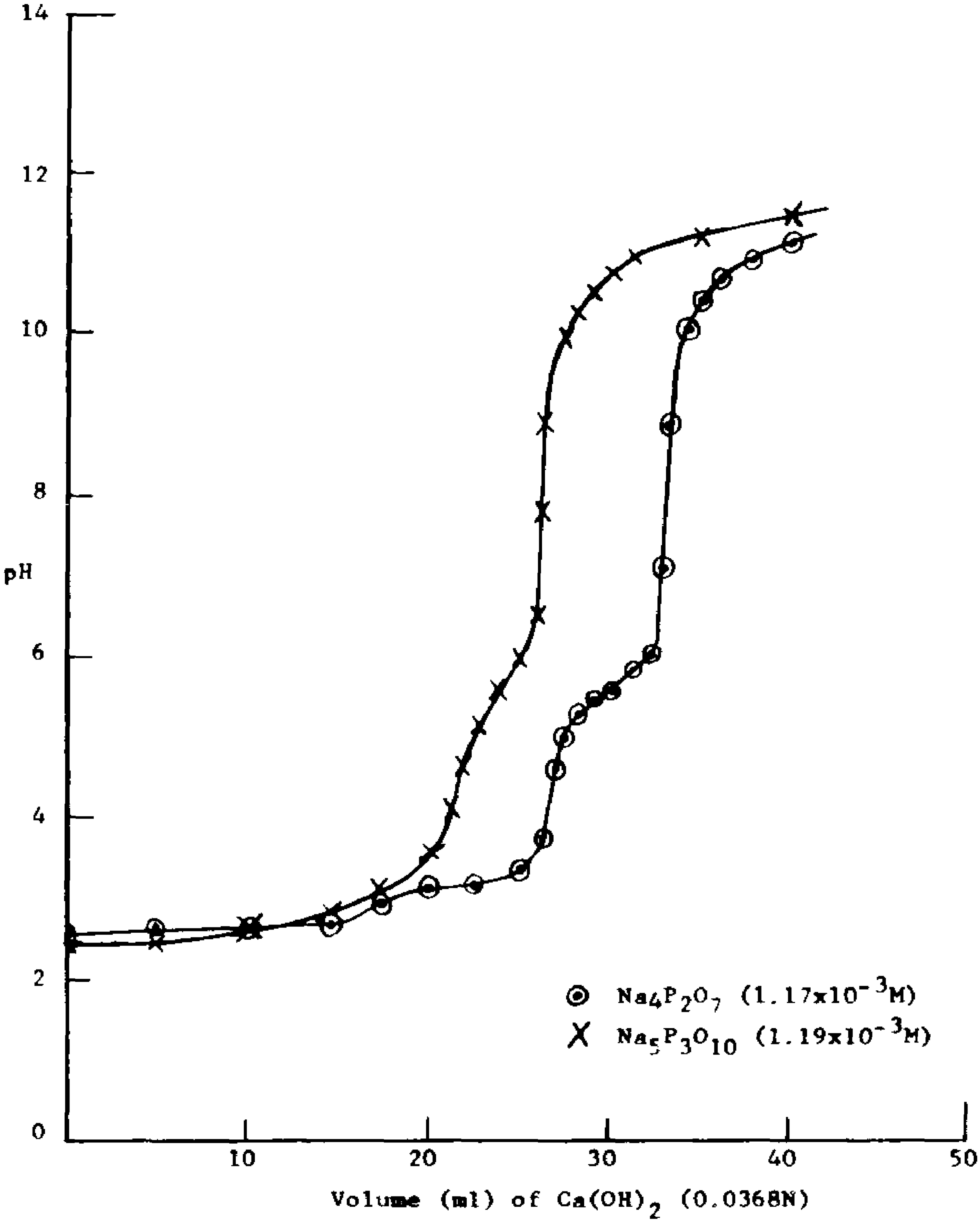


Figure 16. Titration of Pyrophosphate and Tripolyphosphate with $Ca(OH)_2$

Table 24

The pH Measurements ot Phosphates with NaOH

Sample	Conc.	(NaOH)	Vol_{NaOH}	f_s - meq
Na_3PO_4	1.02×10^{-3}	0.0912	2.2 ml	0.201
	1.02×10^{-5}	0.0886	2.2	0.195
	1.02×10^{-5}	0.0886	2.7	0.248
	1.02×10^{-4}	0.1000	1.95	0.225
	1.02×10^{-2}	0.0994	1.9	0.189
	1.17×10^{-3}	0.0911	2.4	0.218
	1.17×10^{-3}	0.0911	2.6	0.237
				0.216 ± 0.022
$Na_4P_2O_7$	1.155×10^{-2}	0.0994	1.8	0.179
	1.06×10^{-3}	0.0911	2.5	0.215
$Na_5P_3O_{10}$	1.25×10^{-2}	0.0994	1.6	0.159
	1.13×10^{-3}	0.0911	2.8	0.226

Table 25

pH Measurements of Phosphates with $Ca(OH)_2$

Sample	Conc.	$(Ca(OH)_2)$	Vol Ca(OH)2	f_a - meq
Na_3PO_4	$1.02x10^{-3}$	.0263N	7.2 ml	0.189
	$1.02x10^{-3}$	.0263	7.5	0.197
	$1.02x10^{-2}$	.0263	8.7	0.230
	$1.02x10^{-2}$	.0097	25.0	0.243
				0.215 ± 0.026
Na_3PO_4 fast	$1.02x10^{-3}$	.0263	8.6	0.224
	$1.17x10^{-3}$	.0368	8.0	0.294
Na_3PO_4 slow	$1.02x10^{-3}$	.0263	5.75	0.151
	$1.17x10^{-3}$	.0368	6.6	0.242
$Na_4P_2O_7$	$1.155x10^{-2}$	.0097	23.5	0.141
	$1.06x10^{-3}$	.0368	6.3	0.232
$Na_5P_3O_{10}$	$1.25x10^{-2}$	.0097	23.5	o.141
	$1.13x10^{-3}$	.0368	5.4	0.200

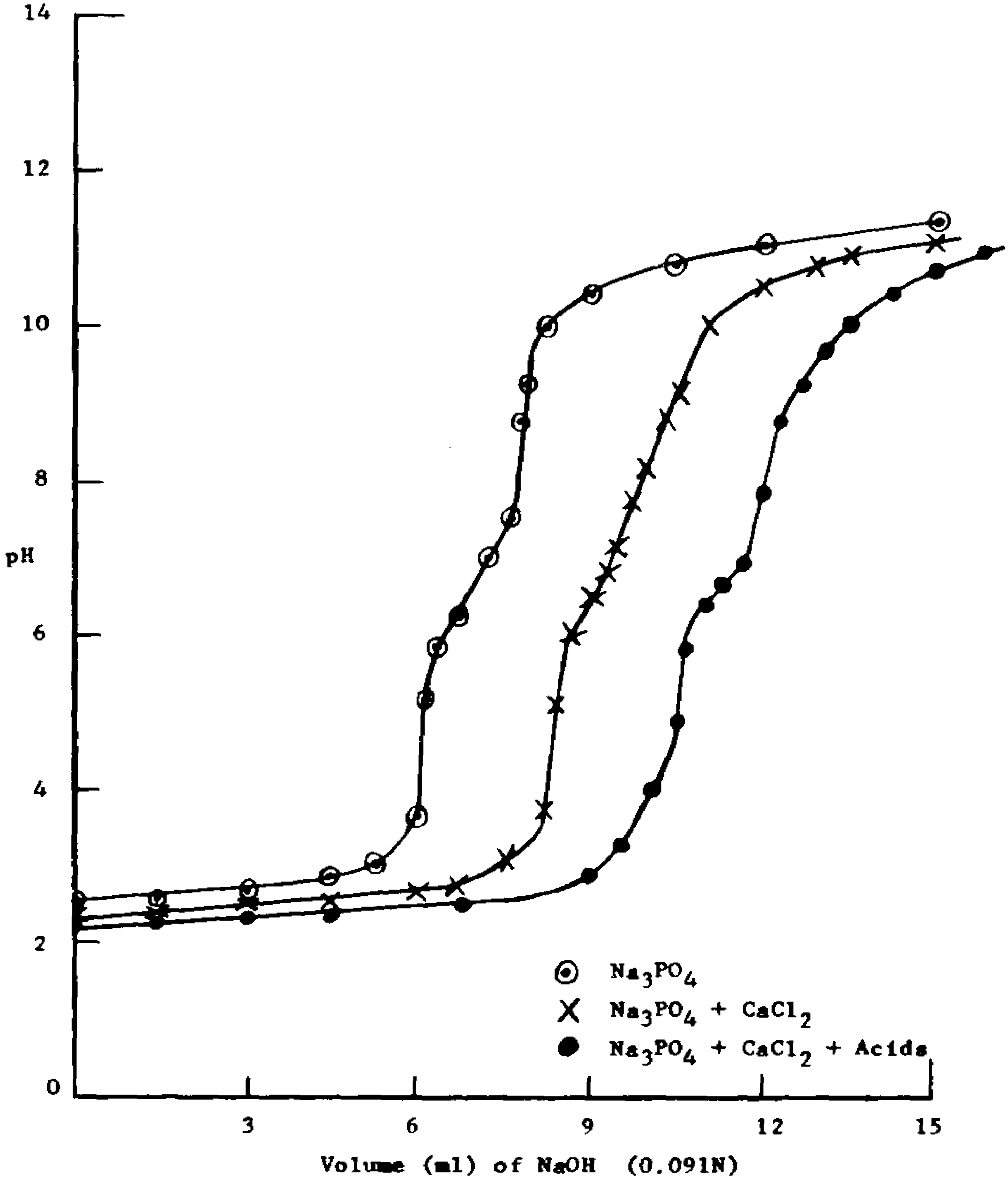


Figure 17. Titration of Na_3PO_4, $CaCl_2$ and Main Branch Organic Acids with NaOH

the mixtures, the cloudiness was reduced, dependent upon the quantity of organic material added to the mixture.

The comparison of the milliequivalence of the weak-acid function for the phosphate expected from the mixture of calcium chloride and phosphates with organic acids and that actually measured is given in Table 26.

Potentiometric (pH) Titration of Organic Acid-Phosphate Mixtures

When the titrations of phosphate forms were carried out in the presence of both calcium and natural organic acids, less volume of NaOH was needed to attain curves similar to that of the pure phosphate (Figure 17). The equivalent amount of base used was reduced and the precipitation of calcium phosphates was inhibited and sometimes eliminated. The maximum effect of the organic acids on the formation of insoluble calcium phosphates would depend on the number of acid groups which can be neutralized on the organic colloid. These interactions are shown in Figures 18 and 19. The influence on complexation of organic acids from different sources is shown in Figures 20 and 21.

The determination of the amount of anticipated milliequivalence for phosphate-organic acid mixtures also resulted in a reduction of the equivalent values when $Ca(OH)_2$ was used. The orthophosphate showed the greatest difference and the most noticeable reduction in cloudiness of the calcium phosphate mixtures with organic acids (Figure 22). With main branch organic extract (Figure 23) and with tripolyphosphate (Table 27), the volume of base used was greater. There was a general trend in the increase in the amount of base needed as the number of phosphorus atoms increased. Additional milliequivalence titration results are given in Table 28.

Table 26

Mean Equivalent Measurements of Phosphate Mixtures with NaOH

Organic Acid		Phosphates		Measured Meq	Total	Measured Meq	Meq
Source	Meq	Soln.	Meq	P + $CaCl_2$	Meq	P + $CaCl_2$ + Org Acid	Change
North Branch	0.246	Na_3PO_4	0.221	0.321	0.567	0.416	0.151
	0.164	Na_3PO_4	0.213	0.263	0.427	0.292	0.135
	0.096	Na_3PO_4	0.228	0.356	0.452	0.292	0.160
Main Branch	0.223	Na_3PO_4	0.201	0.305	0.528	0.337	0.191
	0.249	Na_3PO_4	0.221	0.313	0.562	0.426	0.136
Wolf Creek	0.304	Na_3PO_4	0.201	0.250	0.554	0.421	0.133
North Branch	0.164	$Na_4P_2O_7$	0.196	0.209	0.373	0.337	0.036
North Branch	0.164	$Na_5P_3O_{10}$	0.202	0.237	0.366	0.337	0.029

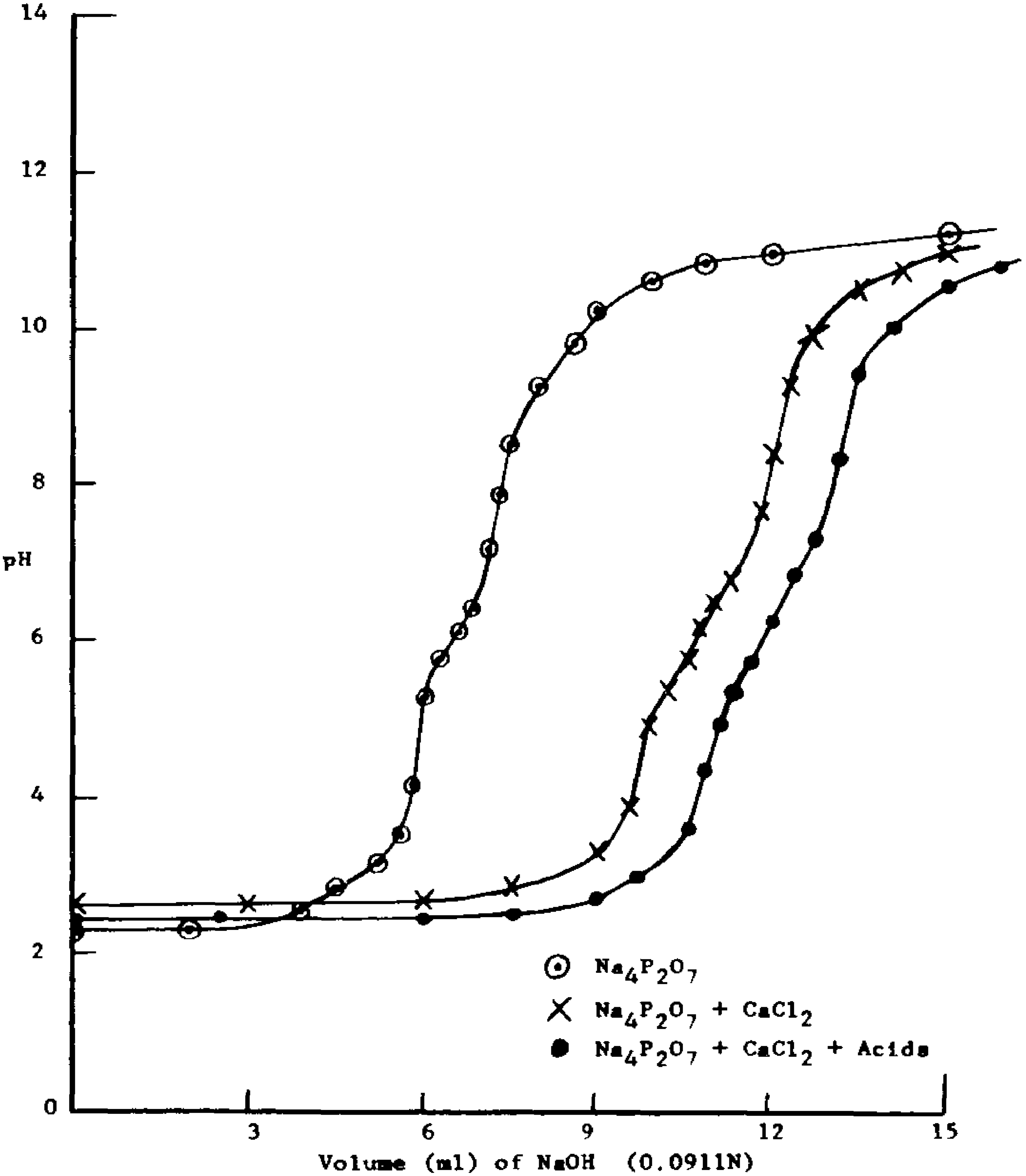


Figure 18. Titration of $Na_4P_2O_7$, $CaCl_2$ and Main Branch Organic Acids with NaOH

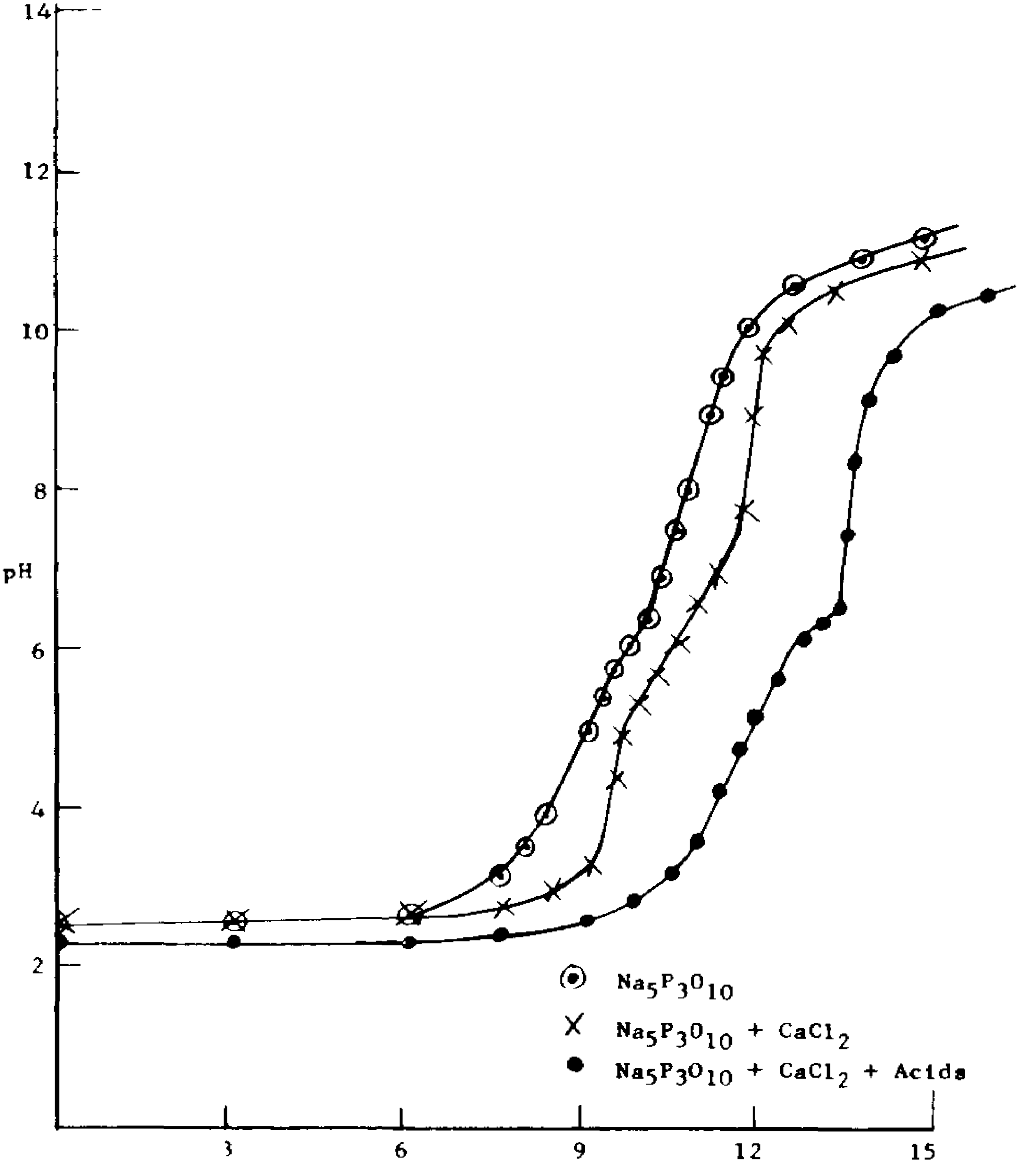


Figure 19. Titration of $Na_5P_3O_{10}$, $CaCl_2$ and Main Branch Organic Acids with NaOH

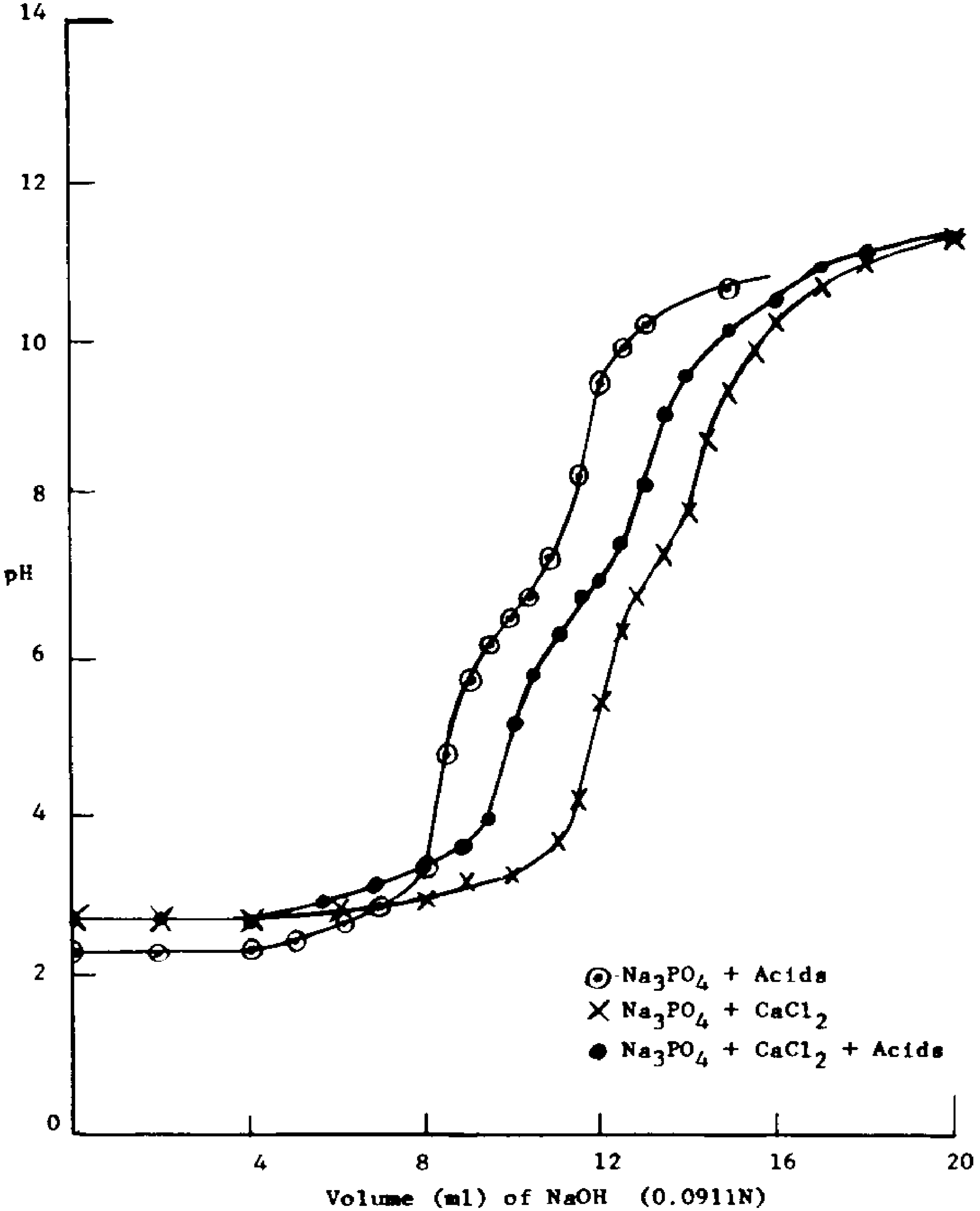


Figure 20. Titration of Na_3PO_4, $CaCl_2$ and North Branch Organic Acids with NaOH

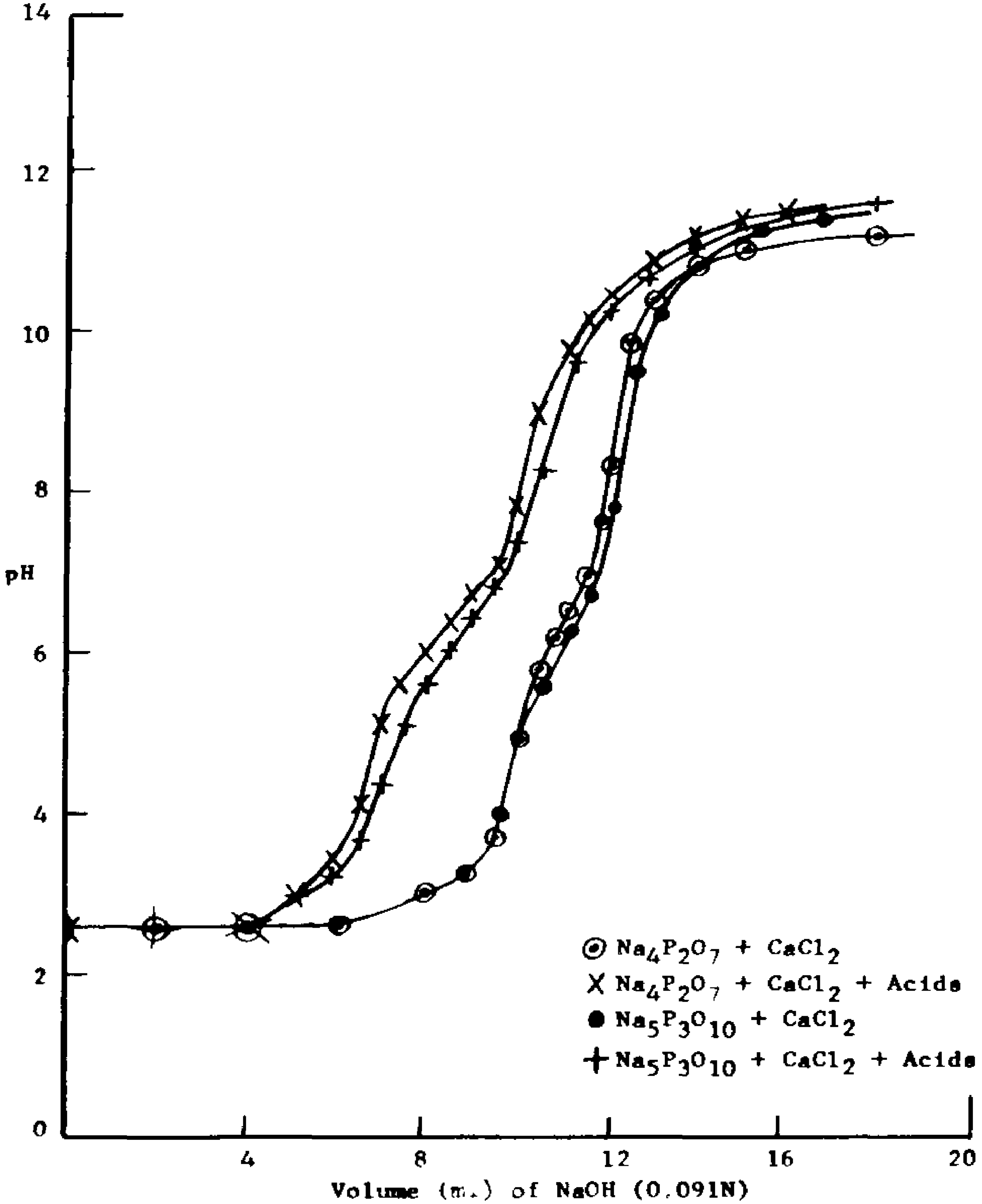


Figure 21. Titration of $Na_4P_2O_7$ and $Na_5P_3O_{10}$ with $CaCl_2$ and North Branch Organic Acids Using NaOH

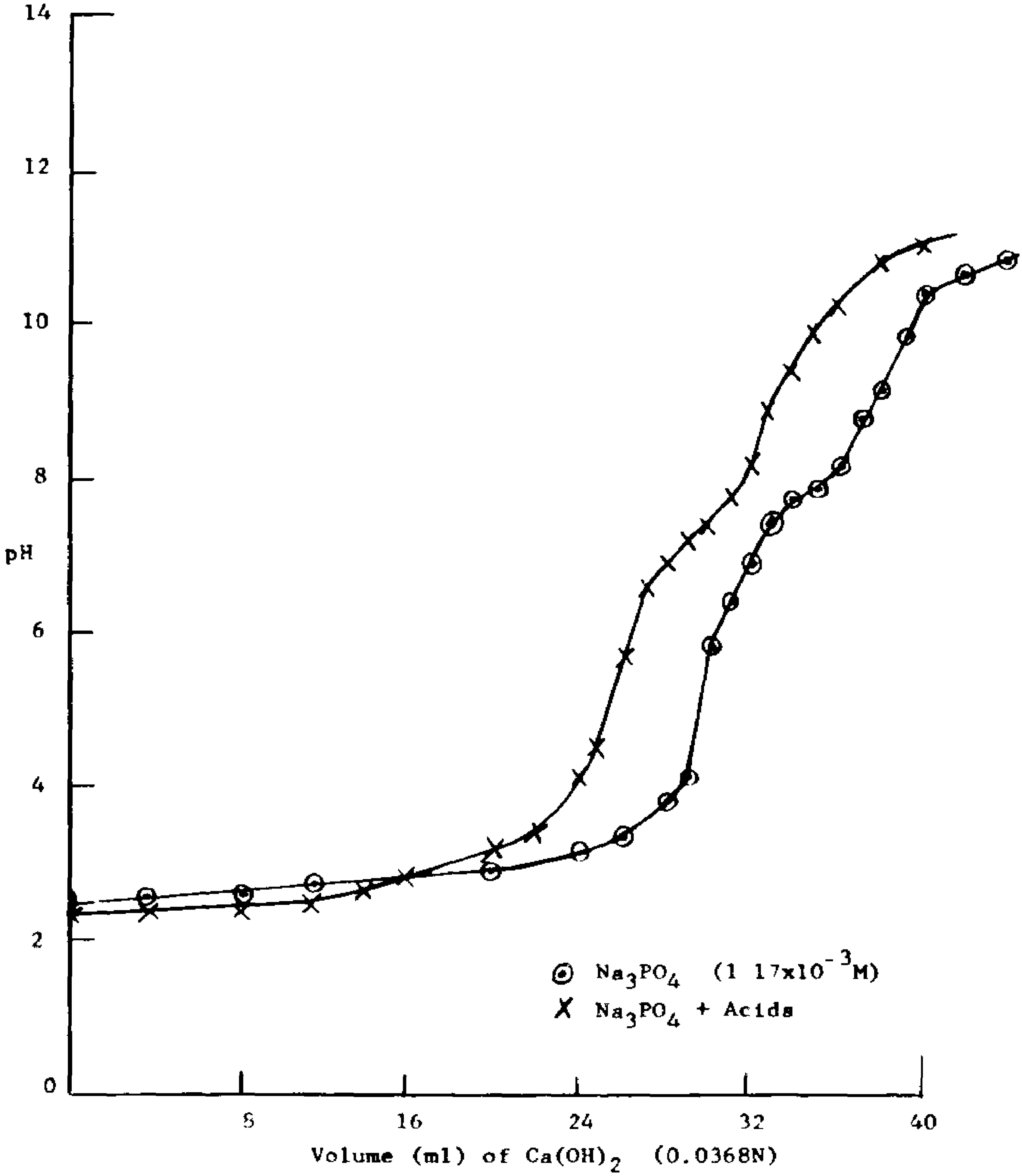


Figure 22. Titration of Na_3PO_4 and North Branch Organic Acids with $Ca(OH)_2$

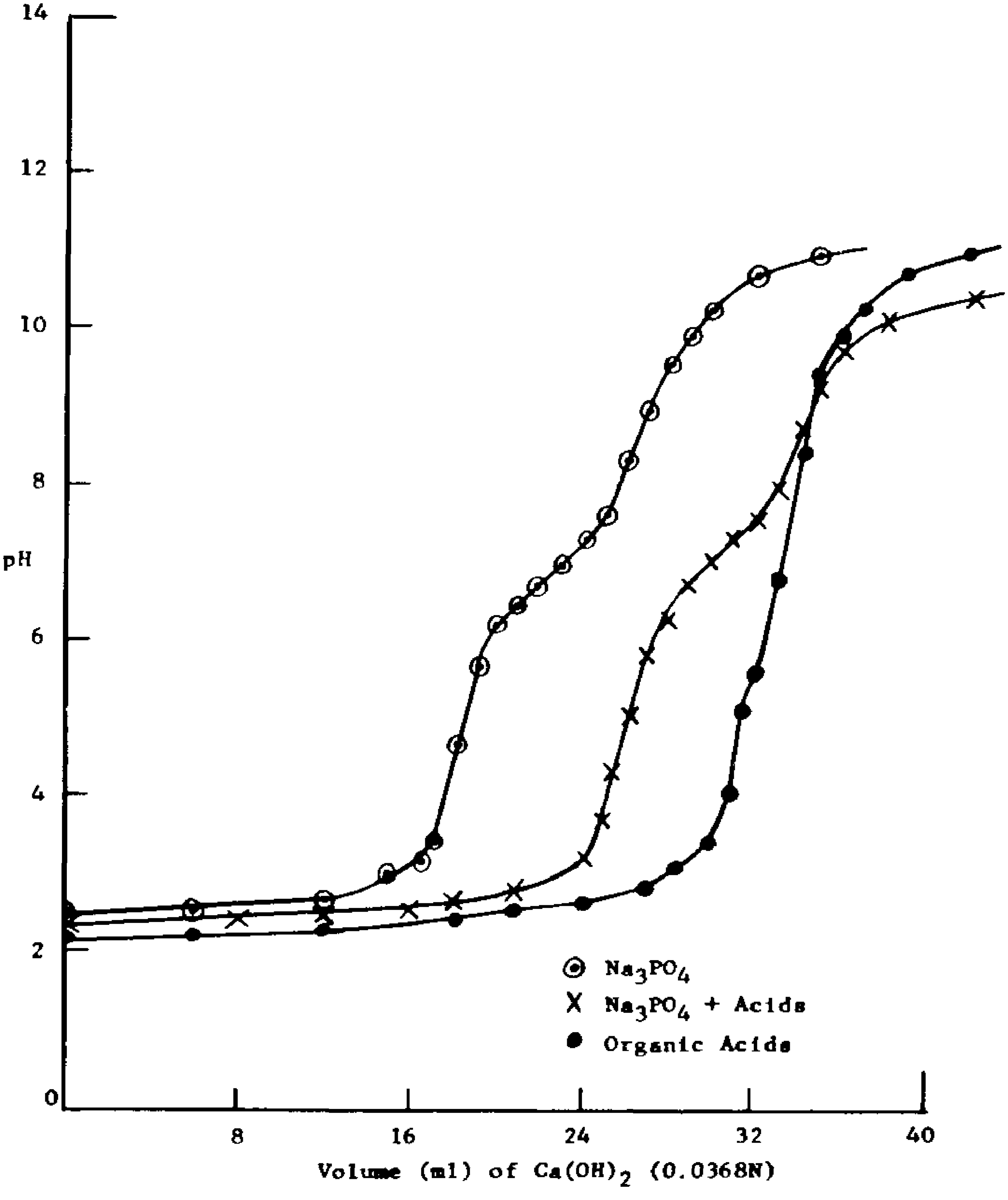


Figure 23. Titration of Na_3PO_4 and Main Branch Organic Acids with $Ca(OH)_2$

Table 27

Mean Equivalent Measurements of Phosphate Mixtures with $Ca(OH)_2$

Organic Acids		Phosphates		Total Meq	Measured Meq	Meq
Source	Meq	Soln.	Meq	P + Org Acid	P + Org Acid	Change
North Branch	0.280	Na_3PO_4	0.227	0.507	0.361	0.146
	0.096	Na_3PO_4	0.290	0.386	0.250	0.136
Main Branch	0.210	Na_3PO_4	0.189	0.399	0.284	0.115
	0.140	Na_3PO_4	0.232	0.328	0.242	0.131
North Branch	0.096	$Na_4P_2O_7$	0.232	0.328	0.294	0.032
North Branch	0.096	$Na_5P_3O_{10}$	0.170	0.266	0.302	+0.036

Table 28

The Phosphate-Ca-Organic Acid Interactions by pH Measurement

Sample	Conc.	Titrant	Conc.	Volume	Meq
Na_3PO_4	1.02×10^{-3}	NaOH	0.0912	2.20ml	0.201
	1.02×10^{-5}	NaOH	0.0886	2.20	0.195
	1.02×10^{-5}	NaOH	0.0886	2.50	0.222
					0.206 ± 0.014
Na_3PO_4 + $CaCl_2$	1.02×10^{-3}	NaOH	0.0912	3.35	0.305
Na_3PO_4 + $CaCl_2$ + Organic acids	1.02×10^{-3}	NaOH	0.0912	3.70	0.337
Na_3PO_4 + $CaCl_2$	1.02×10^{-3}	NaOH	0.0911	2.75	0.250
Na_3PO_4 + North Branch Org. acids	1.02×10^{-3}	NaOH	0.0886	4.80	0.426
Na_3PO_4 + $CaCl_2$ + No. Bran. Org. acids	1.02×10^{-3}	NaOH	0.0911	3.20	0.291
Na_3PO_4	1.02×10^{-3}	$Ca(OH)_2$	0.0263	7.20	0.189
	"		0.0263	8.50	0.224
	"		0.0263	8.70	0.230
	"		0.0283	7.50	0.197
					0.210 ± 0.020
Na_3PO_4	1.02×10^{-3}	$Ca(OH)_2$ (slow)	0.0263	5.75	0.151
Na_3PO_4 + Organic salts	1.02×10^{-3}	$Ca(OH)_2$	0.0263	10.8	0.284
Na_3PO_4 + North Branch Organic acids	1.02×10^{-3}	$Ca(OH)_2$	0.0286	9.50	0.250

The natural colored organic acids generally appear to be stable and remain in apparent solution for considerable periods of time. On standing, there was a color change, as additional complex non-volatile acids may result from polymerization in the alcohol solution. Polymeric non-volatile carboxylic acids predominate in the mixture of the organic acids that occur naturally in colored waters and behave like negatively charged colloids.

The usual mineral analysis of naturally colored waters frequently has shown an excess of cations over anions of less than 0.2 equivalent per million (Lamar and Goerlitz, 1966). The nature of this imbalance can be interpreted by the fact that these high molecular weight colored polymeric substances may exist in water as a colloidal sol which has complexed or adsorbed cations.

The increase in the amount of soluble calcium phosphates in the presence of natural organic acids and the decrease in amount of base necessary to neutralize available anionic sites on the phosphates and acids is related to the combined occurrance of both a colloidal adsorbance of phosphate on the organic molecule and the complexation of one or more chemically active groups with calcium. In the phosphate titration with $Ca(OH)_2$, the formation of soluble calcium phosphates results from the presence of both a colloidal substance and free carboxyl or phenolic groups.

Visser (1962) found between pH 5 and 12 that calcium caseinate and orthophosphate occur together in a solution mixture as a soluble chemical complex. The formation of this complex would be possible between the organic colloid with free carboxyl groups and the tricalcium phosphate.

The acidic nature of the anionic groups (carboxylic and phenolic) of the natural color molecule would be comparable to that of the cationic resin used by Levesque and Schnitzer (1967) to show phosphate bonding through the calcium ion to the acid group. Ogner and Schnitzer (1970) suggested that when the -COOH groups are close enough on the organic acid chain, the divalent calcium can act as an ionic-bridge between the anionic portions of the acid and the phosphates.

Humic and fulvic acids can then form a soluble complex with the calcium ions and phosphates. This phenomenon could be of importance in the transport and immobilization (binding) of calcium phosphates in organic soils and natural waters.

DISCUSSION

WATER QUALITY OF THE BASIN

The quality of the water resources of the Thunder Bay River is, generally, of a natural state in the upstream portions which originate in Oscoda and Montmorency Counties. As the drainage basin progresses Northeast towards Thunder Bay, the waters acquire increasing concentrations of nutrients. A slight decline in dissolved oxygen occurs in the agricultural areas and population centers of the watershed, together with an increase in temperature. Other physical and chemical parameters show relatively constant values with only slight seasonal fluctuations in the quantities measured.

The industrial and domestic waste-water of the population areas of the watershed contribute to the increase of synthetic additives in the drainage area. In the Hillman area streams, ammonia, nitrate, and phosphate levels were above the mean recorded in watershed samples, suggesting the presence of domestic discharge. The influence of agricultural areas was observed in significant ammonia levels of Wolf Creek, Bean Creek, and North Branch Thunder Bay.

Industrial wood-product effluents have influenced the quality of Thunder Bay through increased turbidity and addition of organic materials. These discharges are considered to have caused a definite change in the benthic invertebrate populations in portions of the river and bay (Fetterlof, et al., 1968).

The Alpena sewage-treatment plant introduces a large concentration of nutrients into the main stream and contributes to the enrichment of the bay. All cultural discharges had a lower dissolved-oxygen content and a higher temperature than the river or bay natural water.

The project measurements of water quality compared favorably with water quality data compiled by the Michigan Water Resources Commission from selected sampling sites on the bay, river, and main tributaries. The water quality of the Thunder Bay Watershed in relation to the water quality standards for Michigan intrastate waters as adopted by the Michigan Water Resources Commission in January, 1968, showed that the majority of the natural waters in the basin are within acceptable quality limits.

The sampling at the river mouth and in Thunder Bay gave an indication of the presence and availability of nutrients in the waters. The relation of these quantities to the living organisms in the bay would provide an indication of the nutrient cycle prevalent in the ecosystem of the bay. Since the phosphate level is above that which is indicated as necessary for the support of living systems, there should be growth of aquatic vegetation and algae. Only recently have these growths become visually apparent.

The phosphate level in the bay exceeds even the maximum limit of phosphorus needed for aquatic production, varying from

0.14 mg/l in the river in 1970 to 4.84 mg/l in 1971 below the woods-product effluent. The average phosphate concentration at the river mouth was 0.40 mg/l in 1970 and 0.46 mg/l in 1971. In the bay, the phosphate average was 0.29 mg/l in 1970 and 0.56 mg/l in 1971. Farther out in the bay, in the vicinity of the shipping channel, the 1970 average total phosphate concentration was 0.28 mg/l and in 1971 the average was 0.39 mg/l.

The presence of suspended solids and extractable phosphate from these solids reflect the apparent adsorption occurring naturally. The existence of organics in the water was indicated by the measurement of color in the river and bay together with visual and photographic observation of the river plume.

The interaction of calcium with this material was evident from the measurement of oxidized water samples. The other parameters measured at selected times and sites showed both the influence of the sewage-effluent, wood-products discharge, and natural run-off from forest areas and agricultural operations.

The quality of the watershed and the bay represent that of a natural discharge. In some instances, there is evidence of domestic, agricultural, and industrial effluents from population and rural areas. This is indicated by increased turbidity and suspended solids and abundant amounts of aquatic vegetation especially in the backwaters of the dams where the materials concentrate in the reservoirs.

The Thunder Bay Basin can be considered a relatively unpopulated area over the majority of its 1250-square-mile drainage area which will undoubtedly experience an increased demand for water for domestic, agricultural, and industrial uses. The quality of water and the character of stream resources needs to be continually evaluated through regional inventories and regulated at a level which will not allow further degradation of the resources.

HYDROLYSIS OF COMPLEX PHOSPHATES

The tripolyphosphate and pyrophosphate will ultimately hydrolyze to orthophosphate in waste treatment facilities and natural waters. The rates of hydrolysis of these compounds in natural waters are controlled by biochemical reactions depending on the types and numbers of micro-organisms present, temperature, and pH. The rate of hydrolysis of pyrophosphate and tripolyphosphate has been found to be greater in natural water than in distilled water (Shannon and Lee, 1966). The polyphosphates from the sewage plant which are prevalent in the effluent need to be considered in the nutrient budget of Thunder Bay.

CULTURAL ADDITIVES

In the area of domestic and industrial discharges, the evaluation of the effect of their addition, and the determination of the contributions to the over-all water quality, and eutrophication of the watershed, was done with three major constituents: (1) the interactions of cement dust, (2) natural organics from the watershed and industrial effluents, and (3) phosphates from the sewage plant and natural sources.

The relationship between phosphate discharge from the sewage plant and the river flow showed a direct dilution effect. The annual river flow is 275 times as great as the sewage flow which facilitate this dilution (0.12 mg of phosphate per liter of river water). The chromatographic separation of the sewage samples indicated that eighty percent of the primary-treatment effluents consist of the three simplest linear phosphate forms (ortho, pyro, tripoly).

When the diluted sewage effluent and other sources of phosphate of the river reaches the bay, the plume moves out into the channel and swings to the South. The extent of this movement depends upon the wind direction and currents.

The wind carries a significant quantity of dust over the bay and a minor portion of these particles are suspended in the water. The suspended particles in the bay have extractable phosphate, indicating that domestic and natural phosphorus is being adsorbed on these solids.

PHOSPHATE ADSORPTION ON CEMENT DUST

The cement dust has a mineral composition which can physically and chemically affect the availability of phosphorus in the natural waters of Thunder Bay. The adsorption of the three linear phosphate forms by the cement dust in de-ionized water and natural river water, varied with the type of phosphate form used, water source, and amount of dust. There is a definite influence of the calcinated material on the availability of phosphorus in the waters of the bay, based on the concentration of phosphate taken to the point of dust saturation. Once the phosphates are adsorbed on the dust, there is a possibility of a reversible exchange taking place and some of this phosphorus being returned to soluble state in the water.

CALCIUM MEASUREMENT

The influence by calcium in natural waters can be followed by the use of the Calcium Select-Ion electrode. The potential values for the standard solutions varied with the age of the electrode, the amount of exchanger, and the physical and chemical conditions of the reaction systems.

In all cases, the ten-fold concentration difference resulted in at least a 20 millivolt change. From 1.0×10^{-4} to 1.0×10^{-5} molar calcium ion, the difference was sometimes below 20 mv, resulting in a non-linear portion to the curve. This region was not used in this study. Therefore, a linear portion was present in all determinations of calcium concentrations from the curve, within the natural range of soluble calcium. Once the electrode was operational, the potential response realized, was comparable in values to that of Corning (1968).

The effect of pH on the potential readings was apparent at mild acid and basic strengths. The more dilute the calcium solutions were, the more subject, they were to the effect of hydrogen-ion change. The pH range for reproducible potential was 4.5 to 9.5. These results compared favorably with Ross (1967) and Rechnitz and Hseu (1969).

In the case of ionic strength, solutions in the normal range (0.01 to 0.001) for natural Great Lakes waters (Kramer, 1964), showed a millivolt variation of approximately 6 mv. The ionic strength of solutions were kept similar and within this range, to avoid interferences with ionic strength differences or variation between test solutions.

The temperature effect on potential response showed that the movement of exchanger measuring the calcium activity is sensitive to definite temperature fluctuations. The range of temperatures that gave a reproducible response was from 15C to 35C. The more dilute solutions were more constant. This normal, natural range occurs part of the year. In other cases, the samples were allowed to come to room temperature.

POTENTIAL-COMPARISON METHODS

From the potential-comparison results, the association-constant values increased with the pH value which would indicate the involvement of precipitation in the reduction of the free calcium ions. This precipitation was indicated by the appearance of cloudiness in the solutions at high pH with a more negative potential. Also evident is the increased complexation by the more condensed phosphates because of the increased number of negative sites in the chain.

In the pH range of natural water systems, the Na_3PO_4 complexation with $CaCl_2$ was comparable with Chughtai _et_ _al_. (1968) from pH values of 6.5 to 7.5. The association-constants found by titration from either direction were nearly reproducible:

at 9.0 to 10.5 pH, K_f had a mean value of $1.50 \times 10^{+4}$ while at 6.5 to 7.5 pH, K_f averaged 485. The influence of natural organic acid on the complexation was indicated by an increase in the amount of free calcium apparently removed from the solution and an increase in the constant at pH 6.5 to 7.5 to an average of 688.

In the case of pyro- and tripolyphosphates, the association-constant again increased with pH value as precipitation occurred to also reduce the free calcium in solution. In the pH range of 8.5 to 10.0, the precipitation was reduced and the results were comparable to those found by Watters and Lambert (1959). In the natural pH range of 6.5 to 7.5, the constant was lower than that found by Irani and Callis (1960) by a factor of 10, however, their ionic strength was higher. In the presence of organic acids, the effect on the association-constants again showed an increase. The change was greater than that for orthophosphate.

POTENTIAL-TITRATION METHODS

The potential-titration results compared favorably with those found by potential-comparison. There was a definite relationship between the pH of the solution and the association-constant. A comparison of the means of the results is given in Table 29.

The specific reduction of free calcium in orthophosphate complex mixtures by the addition of Wolf Creek acid averaged

Table 29

Association-Constant Means for Potential-Comparison and Potential-Titration Methods

		— K_f —			
pH	Phosphates	Pot. Comp.	Pot. Titr.	Organic Acid Source	— K_f —
9.5-10.5	Na_3PO_4	$1.24x10^4$	$1.49x10^4$	Main Branch	$6.0x10^3$
8.5- 9.5	Na_3PO_4	$4.50x10^3$	$4.50x10^3$	Main Branch	$6.0x10^3$
8.5- 9.5	$Na_4P_2O_7$	$3.80x10^4$	$2.90x10^4$	Main Branch	$4.4x10^4$
8.5- 9.5	$Na_5P_3O_{10}$	$4.10x10^3$	$9.50x10^3$	Main Branch	$7.5x10^3$
6.5- 7.5	Na_3PO_4	507	515	Main Branch	613
6.5- 7.5	$Na_4P_2O_7$	596	650	Main Branch	1000
				Wolf Creek	680
6.7- 7.5	$Na_5P_3O_{10}$	657	720	Main Branch	1212
				Wolf Creek	830

8.8 mg/l. This change in association-constant and the decrease in apparent free calcium in solution showed that the organic acids were becoming involved in calcium complexation either separately or with the phosphate. The pH-titration method attempted to resolve this.

In the natural water samples, there was apparently some calcium fixation by oxidizible matter in the samples. The bay and river samples taken at selected sites showed a rather irregular amount of calcium being involved, ranging from 1 to 65 mg of calcium, with the average calcium released by oxidation being 13.5 mg.

This again shows that all the calcium in the natural waters of Thunder Bay is not free, but complexed in an organic and phosphate system.

NATURAL COLORED ORGANIC ACIDS

The extraction of the organic acids from the natural samples was one on four streams of highest fluorescence response. The concentration process was somewhat time-consuming, especially in removing the last traces of salt crystals.

In selected cases, purification was not carried out completely when potentiometric titration by pH was done. In the case of potential (mv) measurement of calcium, it was essential that the sodium concentration be reduced to a minimal amount. In these cases, satisfactory samples were obtained after repeated evaporation and dissolution in alcohol.

The identification and characteristics of the natural organic acids was accomplished by fluorescence response and infrared absorbance. The natural water samples showed a fluorescent excitation and emission at wave lengths similar to that observed by Christman and Ghassemi (1966) and Packham (1969) who used similar extraction procedures.

The main-branch water continued to increase in the amount (mg/l) of organic carbon throughout the study. Bean Creek and the North Branch of Thunder Bay River also showed high values throughout the investigation, with Wolf Creek showing medium-range values.

IDENTIFICATION OF NATURAL ORGANIC ACIDS

Organic color in natural water has its origin in the multitude of organic molecules comprising the forest vegetation and varies in composition and amount with season and source. This color could arise from the aqueous extraction of living woody substances, the solution of degradation products in decaying wood, and the solution of organic soil matter.

The infrared spectrum for the Thunder Bay River natural-organic-concentrate in alcohol was similar to that recorded by Black and Christman (1963) and by Midwood and Felbesk (1968). Infrared spectra for the Thunder Bay organic fractions showed carboxylic acid and hydroxy absorption maxima in the 2.5 to 3.5 micron range. A strong absorption band was located at 6.0 micron which is the region characteristic of carbonyl-group stretching-frequency and the double-bounded carbons in conjugated phenyl groups. Absorption in the 3.5 to 7.0 micron range in the samples was probably due to alkane groups and alkyl branches. The broad absorption regions between 7.0 and 8.0 micron, 9.0 and 10.0 micron are possibly due to combination of C-C and C-O stretching frequencies. The strong bands at 9 to 10 micron and 11 to 12 micron indicate the C-H out-of-plane deformation frequencies of free hydrogen atoms on substituted benzene rings in a polymer chain.

The functional groups identified (Table 17) were R-OH, C-H, -COOH, Ar-OH, Ar-X, Ar-X_n, and R-O-Ar. Black and Christman (1963) found peaks in fulvic acid samples which were characteristic of carboxyl groups, -OH, C-H, conjugated phenyl groups, and substituted phenyl groups. Midwood and Felbest (1968) found that most of the spectra of organic fractions show peaks of alcoholic and phenolic -OH groups, CH_3- and -CH_2- groups, C-C, -COO^-, and -COOH.

The natural colored organic materials extracted from the waters of Thunder Bay Watershed have a definite acid nature. The adjustment of the pH of their solutions with hydrogen ion results in a conjugate base that can be neutralized with standard hydroxide. The neutralization was somewhat lower for $Ca(OH)_2$ indicating a possible complexation of the divalent metal ion by neighboring negative groups.

The measurement of the equivalence reaction of the phosphate forms gives a definite weak-acid fraction that could be used to indicate the effect of organic acids on the neutralization process. The milliequivalence found was directly related to the concentration of the phosphate solution used. Titration seemed to be an accurate measurement of anionic phosphate available for cationic interaction (hydrogen or calcium).

The calcium ion is involved in reaction with the phosphate forms in precipitation that can occur at alkaline pH values according to the equation:

$$Ca(H_2PO_4)_2 + Ca^{++} \rightarrow 2CaHPO_4 + 2H^+$$

and slow conversion of precipitated dicalcium phosphate into tertiary salt, Ca_3PO_4. These calcium reactions with the phosphates also occurred when calcium was added separately as $CaCl_2$ and titration carried out with NaOH.

The maximum quantity of soluble calcium phosphates formed depends on the number of acid groups (anionic) which can be neutralized on the organic molecule. The apparent reduction in weak-acid equivalent reaction by the addition of natural organic acids to the calcium-phosphate reaction solution was shown by the presence of a reduction in the milliequivalents. The reduction was measured in the mixtures by the summation of the anticipated equivalence found for separate reactants. The formation of apparent soluble calcium phosphate could also involve a chemical complexation as a result of certain chemically active groups present in the organic molecule.

The soluble calcium phosphates could be formed as a result of the colloidal properties of the organic matter. The overall phenomena of this interaction could be possibly allied with the combined occurrence of both a colloid and one or more chemically active anionic groups. In the absence of metal, only a slight reaction took place between the phosphates and natural organic acids used.

POTENTIOMETRIC (pH) TITRATION METHOD

The concentrated organic acids from the Main Branch and North Branch of Thunder Bay River were titrated potentiometrically with NaOH and $Ca(OH)_2$. The curve with NaOH showed two equivalence points, one at acidic pH and the other at slight basic conditions. The titration curves, between pH 2.5 and 11.0, represent the actual alkali consumption by the anionic colored material through neutralization of acidic sites.

In the case of $Ca(OH)_2$, the curve was a simple neutralization curve with no indication of the presence of more than one type of acidic group. The titration process has indicated that anionic sites are available for reaction with cations in a basic solution. The inflections on the curve using NaOH would seem to reflect the presence of more than one type of functional group.

After the salt solution of the standard phosphate forms were acidified to a pH of 2.5, titration was carried out with NaOH and $Ca(OH)_2$. The formation of mono- and di-metallic salts were indicated by the S curve obtained in the neutralization process. The tertiary salt can exist only in such a strong alkaline environment that its formation below pH of 11.0 does not occur in any measurable amounts.

In the titration of the phosphate forms with $Ca(OH)_2$, starting at pH 2.5, there is a similarity in curves up to the monophosphate stage at pH 6. After addition of more $Ca(OH)_2$, there was a slight non-linear change at pH of 7.0 possibly because of the presence ot a secondary calcium phosphate along with partial precipitation. Above a pH of 8.0, secondary calcium phosphate was converted into the insoluble tertiary salt.

The presence of calcium ions seem to influence the course of the pH change. The titration of the phosphate forms with NaOH in the presence of a known and constant amount of $CaCl_2$, showed a drop in pH after the formation of monocalcium phosphate is apparent. The calcium concentration seems to depress the solubility of the dicalcium phosphate to such an extent that the transformation into tricalcium phosphate was not observed initially but did occur with time as precipitation increased in the calcium-phosphate solutions.

The titration of the phosphate in the presence of $CaCl_2$ and organic acids with NaOH was conducted under identical conditions as previous reactions. When the phosphate forms were combined with $CaCl_2$, the dicalcium phosphates were formed. The formation of soluble tricalcium phosphates took place when the organic acid was present. The precipitate which was noticed above pH of 7.0 in the phosphate solutions was reduced when the organic acids were present. When the amount of reacting species was increased, the formation of the precipitate was noticed at pH values above 8.0. Therefore, the amount of tricalcium phosphate which can be formed in solution depends on the quantity of organic acid present in the system.

When $Ca(OH)_2$ was used as the titrant, the dicalcium phosphate precipitate again formed above a pH of 6.0 as a non-linear portion of the curve at pH of 7.0. While, above pH 8.0, in the presence of organic acids, the precipitates seemed to decrease in quantity. In addition, the amount of base used to reach pH of 11.0 was greater than that for NaOH. The influence of organic carbon on this amount of base was more pronounced than the effect during NaOH titration. In the phosphate titration with $Ca(OH)_2$, the presence of the free carboxyl and phenolic groups is necessary for the formation of the soluble tricalcium phosphate as long as the phosphate originally was in solution.

In all cases of titration with base, the pH of the phosphate-calcium-organic acid reaction system decreased for the three phosphate forms from 1 to 2 pH units on standing. This would seem to indicate that on continual contact the calcium is replacing the hydrogen ions on the acidic groups by ion-exchange and serving as a bridging site for the phosphate forms in solution.

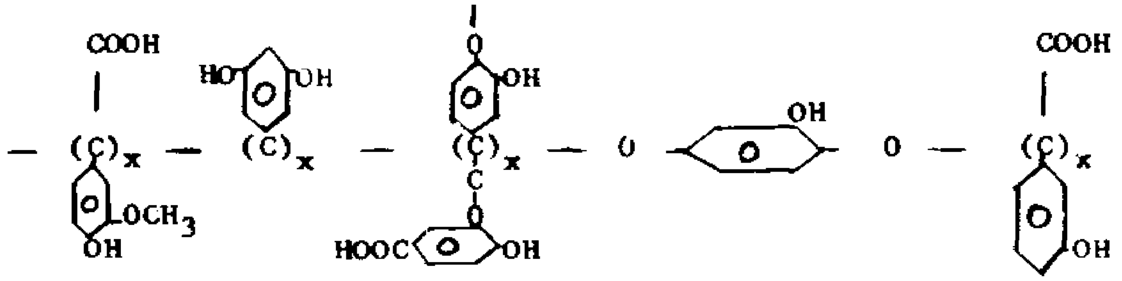
In evaluating the equivalent reaction ability of the phosphate forms, the pH of the sodium phosphate solution was adjusted to 2.5 with HCl. The pH readings per unit volume of added standard alkali were plotted to obtain a phosphate titration curve. Hydrolysis was avoided by conducting the reaction at room temperature and as rapidly as possible. The distance between the two equivalence points was considered equivalent to the weak acid function (f_w) of Odagiri and Nickerson (1964).

In the case of titration of orthophosphate with NaOH, both the presence of $CaCl_2$ and Main Branch organic acids adds to the equivalence of the phosphate solution. When the three components were combined only a slight decrease in the milliequivalency was observed. When $Ca(OH)_2$ was used as the titrant, the reduction was much more pronounced which would be attributable to involvement of the divalent calcium in an ionic reaction other than neutralization.

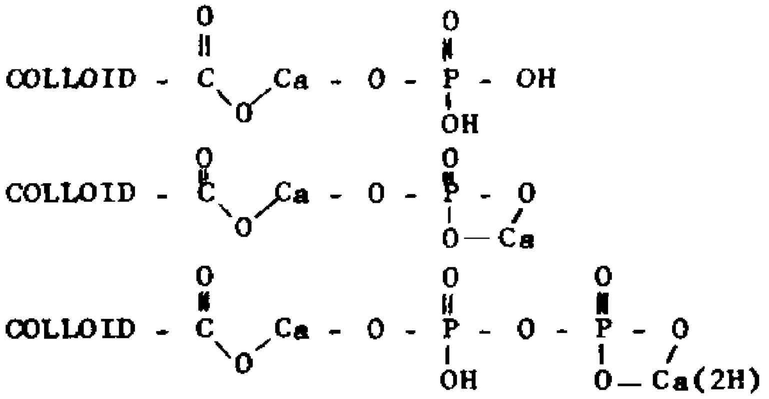
After chemically blocking the acid groups in casein, Visser (1962) concluded that where the organic material does not possess free carboxylic groups, it has no influence on the course of normal phosphate titration in the presence of calcium. This would indicate that the maximum quantities of soluble tricalcium orthophosphate formed depends on the number of acidic groups which can be neutralized on the natural organic acid molecule. According to Visser, the formation of the calcium orthophosphate is probably related to the combined occurrence of both a colloid and one or more chemically active groups.

In the pH range used, the primary ions present in the calcium-phosphate mixtures would be $CaH_2PO_4^+$, $CaH_3P_2O_7^+$, $Ca_2HPO_4^+$ and $Ca_2H_2P_3O_{10}^+$. The phosphates in the metal complexes could be bonded through the calcium to the acidic groups of the organic matter. When the amount of calcium increases as in the titration with $Ca(OH)_2$, a considerable amount of the phosphate could occur as calcium phosphates which are physically mixed with the organic acid-metal phosphates.

Visser (1962) proposed that the humic acid of organic soils would be a major factor in the transport of calcium phosphates by involving the colloidal matrix and the carboxyl groups should both be present in the one substance. The general structural formula for the acids according to Christman and Ghassemi (1966) involves:



These structures could be part of a natural complex as:



$$\text{COLLOID}-\overset{O}{\overset{\|}{C}}\underset{O}{\smile}Ca-O-\overset{O}{\overset{\|}{\underset{OH}{\underset{|}{P}}}}-OH$$

$$\text{COLLOID}-\overset{O}{\overset{\|}{C}}\underset{O}{\smile}Ca-O-\overset{O}{\overset{\|}{\underset{O-Ca}{\underset{|}{P}}}}-O$$

$$\text{COLLOID}-\overset{O}{\overset{\|}{C}}\underset{O}{\smile}Ca-O-\overset{O}{\overset{\|}{\underset{OH}{\underset{|}{P}}}}-O-\overset{O}{\overset{\|}{\underset{O-Ca(2H)}{\underset{|}{P}}}}-O$$

The phenol groups in the molecule may be involved as well in this complexation. In either case, the interaction makes possible the movement of calcium phosphates in soils and natural water as a calcium-phosphate-organic acid complex.

The phosphorus cycle in a natural water environment can be influenced by chemical complexation with calcium ions and soluble organic matter. Moreover, the physical occulsion of phosphates on natural colloidal organic material could involve calcium. Potentiometric titration by either millivolt or pH response showed a definite involvement of organic material extracted from the Thunder Bay waters in the complexation of the three phosphate forms by calcium through the acidic sites on the natural organic polymer molecule.

SUMMARY

The water quality of the Thunder Bay Watershed has been found to be relatively high. Much of the 1250 square mile drainage basin is still in its natural state. The regional inventory of this watershed showed instances of domestic, agricultural, and industrial influences on the quality of the water, character of the watershed resources and composition of aquatic species.

Both the sewage effluent and the discharges from wood-products industries contain significant organic materials. Eighty per cent of the local primary-treatment sewage effluent was determined to be composed of the simple linear phosphates: ortho, pyro, and tripoly. These phosphates are involved in the phosphorus cycle of Thunder Bay and associated with accelerated eutrophication of natural waters when temperature, light, and other necessary nutrients are present.

Suspended and settleable solids can serve as adsorption sites for linear phosphate forms in natural waters. In the Thunder Bay at Alpena, Michigan, calcareous particles are present from natural limestone sources and as cement dust emitted from a local industry.

The composition of the cement dust and the domestic sewage effluent entering the bay indicates that constituents for possible interaction are available. The suspended solids level in Thunder Bay water along with total and acid-extractable phosphates from solids were measured to determine the extent of the fixation occurring in waters of the bay. In the removal of phosphorus from standard phosphate solutions, cement dust showed a definite uptake of ortho, pyro, and tripolyphosphate forms. In river water, the adsorption of orthophosphate was lower, indicating the possible involvement of soluble natural organic acids and metal ions in the complexation.

Chemical oxidation of natural samples showed that in Thunder Bay, an interaction exists between calcium and natural organic material. The colored organic materials are acidic in nature and were recovered in sufficient concentration to determine metal-organic acid-phosphate interactions.

The three linear forms of phosphorus were combined with the organic acids extracted from the natural colored water of selected tributaries of the Thunder Bay system in the presence of soluble calcium. In the presence of the concentrated organic colored material, there was a reduction in the milliequivalence of calcium-phosphate mixtures. In identical solution mixtures, increases in the association constants for calcium-phosphate complexes indicated involvement of the phosphates with calcium and natural organic acids. Calcium and hydrogen electrodes were adequate for following this complexation in natural waters by potentiometric titration.

It has been shown that the natural organic material of the Thunder Bay Watershed form soluble complexes with the calcium-phosphate systems and the suspended calcareous particles adsorbing phosphates. These phenomena are important factors in the transport and availability of phosphorus in the Thunder Bay aquatic ecosystem.

RECOMMENDATIONS FOR CEMENT DUST

If the dust from the cement operation has a fairly consistent composition during its production and dispersion over the bay, it could serve as an agent to fix phosphates in the natural eutrophic water system. Hynes and Greiv (1970) showed that preventing the release of nutrient ions from the mud-surface can cause the water above sediments to be a less suitable medium for the growth of algae.

The use of cement dust as a phosphorus adsorbing material in an eutrophic system could lead to interruption of the phosphorus cycle, thereby slowing the release of nutrients so that undesirable algals blooms do not occur or cease to re-occur. The reversibility (phosphate-release) of the dust-phosphate particles has been found to average 7.0 mg/g above the original phosphorus in the solution.

Moreover, phosphorus could be removed in sewage oxidation lagoons by applying the appropriate amount of dust to reduce the phosphate level to the desired value. In their work on sewage lagoons, Buzzell and Sawyer (1967) found that lime-treatment of raw wastewater can effect a 97% removal of soluble inorganic phosphorus forms. The lime requirement is independent of the phosphorus content and can be estimated in terms of the alkalinity (controlled by pH). Since the lime treatment of wastewater produces effluents with N:P ratios of 30 or above, it appears that properly managed stabilization ponds could provide very suitable secondary treatment of sewage with the dust.

Another specialized application of the dust in the sewage area could be as a substitute for lime in the chemical treatment of the domestic sewage. To institute this proposal, adequate equipment would be needed to remove the moist dust material by sedimentation and sludge draw-off in the final clarifers. O'Farrell (1969) found that the treatment of the secondary effluent from a modified aeration plant can consist of single or two-stage lime precipitation and filtration. In the two-stage high lime process, lime is added to a pH of 11.5 in the first stage and then is recarbonated to a pH of 9.5 to 10.0 with flocculating additives in the second stage. The two-stage process with flocculants has maintained ninety per cent removals of phosphorus.

The chemical phosphate removal techniques can be accomplished by conversion of soluble phosphates to an insoluble form by either precipitation or adsorption with the metallic salts added to wastewater. The pH of the water is usually increased with lime to permit the formation of insoluble metal phosphate salts. The cement dust has been found to cause a 0.02 pH change for each milligram of dust used, with a maximum of 10.70. With an excess of cement dust, higher values can be reached up to 12.00 pH.

Wirkasch (1968) has found these suspended metallic phosphates are fine and well-dispersed in submicron-micron size. The precipitates can be flocculated with organic polyelectrolytes, coalescing into large quickly-settling flocs. The cement dust could be an economical precipitating agent, especially with small amounts of ferric ion added as a coagulant aid. Moreover, the dust could be discarded along with the adsorbed nutrients which would involve removal and disposal without reclamation.

CONCLUSIONS

The water quality of the Thunder Bay River and its tributaries is at high levels above the population centers. As the drainage basin progresses toward Lake Huron, the water accumulates increasing concentration of pollutants especially nutrients from agricultural and domestic sources. The industrial and domestic waste-waters discharged into the watershed are contributing synthetic additives to Thunder Bay and lead to degradation of the bay waters. The quality of the basin waters and the character of the stream resources need to be regulated at a level which will not allow further degradation of the system to occur.

Highly diversified benthic communities containing many clean water forms have been found in substantial areas of Thunder Bay near shore (Fetterolf, _et_ _al_., 1968). Only in the areas near discharge of wood-products operations is a highly degraded ecosystem existing under the prevailing sewage conditions and presence of cement dust.

The wind directions, current patterns, and the movement of the river flow into the bay aid in the distribution of the high phosphate contribution of the sewage plant. The presence of cement dust in the natural water environment of Thunder Bay has an influence on the availability of phosphorus to the ecosystem of the bay through its adsorption and subsequent sedimentation.

The calcium ions in Thunder Bay waters interact with phosphates and this interaction is influenced by the presence of natural organic acids. The involvement of the organic acids in the complexation is directly related to the anionic nature of the colloidal polymer. The carboxylic groups in the natural colored organic acids form stable metal-organic complexes as well as water soluble multi-dentate chelates with calcium.

In the watershed, the organic color observed in selected tributaries was high enough to acquire a sufficient amount of concentrated extract. In the case of the measurement of the amount of soluble calcium fixed by oxidizable organic material, a mean value of 15 mg/l was measured. This indicated that there is an interaction between calcium and the natural organic acids occurring in Thunder Bay system.

The Thunder Bay River and its branches have been found to contain significant organic color. With the natural organic acids of the Thunder Bay Watershed forming a soluble complex in the calcium-phosphate system, this phenomenon will most certainly be of importance in the transport and availability of calcium phosphates in the bay aquatic environment. The apparent reduction in milliequivalence of calcium-phosphate mixtures by the presence of the organic acids supports this involvement. The increase in association constants for calcium-phosphate complexes when organic acids are added further substantiates this conclusion.

The interactions of the calcium constituents (soluble and solids) with phosphorus and natural organic acids should be considered as controlling factors in the over-all equilibria in the Thunder Bay system. Evaluation of other physical and chemical complexation systems that may exist should be done in order to attain a more complete picture of the eco-processes operating in Thunder Bay. The Thunder Bay water system is a vital part of the natural resources of Northeastern Michigan and should be protected for use and enjoyment of present and future generations.

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APPENDICES

Appendix I. Historical Review

APPENDIX I

HISTORICAL REVIEW

The amounts and forms of nutrients in natural waters are determined by their relative rates of input into, and loss from, the water body. As well, the nutrient levels can be regulated by biochemical, chemical, and physical processes occurring within the aquatic system.

Within a body of water, the primary regulatory processes are assimilation of inorganic forms (NH_4^+, NO_3^-, $H_2PO_4^-$, and $HPO_4^{=}$) by microorganisms and aquatic plants, mineralization or organic forms by microorganisms, and uptake and release by sediments. Transformations of condensed, inorganic phosphorus forms appear to be restricted to the chemical and biochemical hydrolysis of these phosphates to orthophosphate.

The forms and amounts of phosphorus in waters have been described by Jenkins (1968), according to analytically defined fractions, namely: (1) particulate phosphorus (retained by 0.45 micron filter), (2) dissolved phosphorus - orthophosphate (reactive in reduced phosphomolybdate colorimetric procedure) and condensed phosphate (contains P-O-P linkages hydrolyzed by mild acid), and (3) dissolved organic phosphorus (contains P-O-C and P-C linkages degraded to orthophosphate by acid digestion).

The biological productivity of a body of water has been directly related to the degree of fertilization by plant nutrients, especially phosphorus. Phosphorus enters surface waters primarily from land-run-off, percolation through soil, and waste waters. Frink (1967) found that an isolated lake which supported a large population of rooted aquatic and planktonic algae had a high inorganic nitrogen and phosphorus concentration coming from land drainage.

Engelbrecht and Morgan (1961) considered the source of phosphorus in Illinois surface waters from land-drainage to be in the form of simple orthophosphate or as soluble, hydrolyzable forms of phosphate. These phosphates could be adsorbed on clay particles which enter water during erosion. Engelbrecht and Morgan (1959) found the phosphorus present in natural waters from surface drainage amounted to 0.036 mg/l as orthophosphate and 0.081 mg/l as total phosphates (P_2O_5). Samples from streams with significant amounts of treated and untreated wastes had an average of 0.411 mg/l orthophosphate and a maximum inorganic-condensed-hydrolyzable-phosphate concentration equal to 0.657 mg/l. They found that a sewage plant, with activated-sludge treatment, had an average 18 mg/l as P_2O_5 in the effluent.

Missingham (1967) found that the phosphorus content of domestic sewage is four times what it was before the advent of synthetic detergents. These detergents are composed of 30 to 50 percent phosphate builders (primarily polyphosphates). Herold (1967) found that the phosphate builders in detergents, such as Tide, were composed of 5%-ortho, 25%-pyro, and 70%-tripolyphosphates.

In his discussion of the overall picture of eutrophication, Fruh (1967) proposed that the type and intensity of the eutrophication problem depends on the frequency of algal blooms (5×10^5 cells/liter). The frequency is related to the respective genera and species of algae present and phosphate concentration.

Shapiro (1967) has indicated that there are either ionic or organic reactions systems involved in phosphate uptake which should be measured in the evaluation of eutrophication of natural water by phosphorus.

The high phosphorus concentrations are associated with accelerated eutrophication of waters when other factors such as: temperature, sunlight, size and shape of water body, type of stratification, and level of other nutrients are adequate to support aquatic growth. To prevent production of biological nuisances, Mackenthun (1968) suggested that total phosphorus concentration should not exceed 0.10 mg/l at any point within a flowing stream and should not exceed 0.05 mg/l in a lake or reservoir.

Rigler (1964) indicated that phosphorus concentration in a water body depends on a dynamic equilibrium between the bacteria and plants and the solution phases. Natural amounts of total phosphorus are commonly less than 0.05 to 0.10 mg/l and usually not greater than 0.50 mg/l. The particulate phosphorus usually exceeds dissolved phosphorus. The dissolved organic phosphorus is about 15 to 30 percent, and, the dissolved orthophosphate is about 10 percent of the total phosphorus in natural waters.

The availability of phosphorus in natural systems from man's activities depends upon the conversion of polyphosphates to biologically assimilable phosphorus forms by hydrolysis. The structures of the polyphosphate ions and their respective hydrolysis to orthophosphate have been studied to determine the rates of decomposition. Karl-Kroupa, et al. (1957) found sterilized aqueous solutions that the condensed phosphates have half-lives of several months at pH 7 and 20C, and are eventually hydrolyzed at the slow rate to orthophosphate. Factors Karl-Kroupa found that affect hydrolytic degradation were: pH, temperature, enzymes, colloidal gels, concentration of phosphates, and the solution's ionic state.

Shannon and Lee (1966) studied the rates of hydrolysis of pyrophosphate and tripolyphosphate into orthophosphate under laboratory conditions using various natural waters. They showed that the rates of hydrolysis of pyrophosphate was 0.08 mg P/l per 500 hours at 4C and varied from 0.23 to 0.47 mg P/l per 500 hours at 20C. Tripolyphosphate averaged 0.15 mg P/l per 500 hours at 4C and varied from 0.34 to 0.50 mg P/l per 500 hours at 20C. Studies in a natural stream showed the presence of an apparently natural condensed phosphate that hydrolyzed at approximately the same rate as tripolyphosphate did under laboratory conditions.

Clesceri and Lee (1965) found the hydrolysis degradation of all chain and ring phosphates is affected by increasing hydrogen ion concentration, as well as, the amount of certain metal ions, and the presence of specific enzymes. In general, divalent cations (Ca, Mg) were found to have a pronounced effect on the enzymatic hydrolysis of P-O-P linkages. Van Wazer, et al. (1952) studying hydrolysis of pyro and tripolyphosphates found that the presence of calcium ions increased the hydrolysis rates. Biologic systems (bacteria, algae) definitely influence the rate of degradation of the condensed phosphates, with tripolyphosphate degrading at a more rapid rate than pyrophosphate.

Crowther and Weston (1953) have determined that the hydrolysis of the pyrophosphate anion is a first-order reaction at constant hydrogen-ion concentration. The rate-constant at pH 6.0 was 1.25×10^{-4}, while at pH 9.3, the rate-constant was 1.00×10^{-5}. First-order rate-constants for the hydrolysis of the tripolyphosphate anion depended upon the initial phosphate concentration. The rate-constant at pH 5.0 was 2.9×10^{-4} and at pH 9.3, it was 1.50×10^{-5}.

Aquatic plants generally utilize inorganic phosphate and show little tendency to assimilate organic phosphorus. Zooplankton and higher invertebrates can obtain phosphorus through digestion of particulate matter but do not appear to assimilate soluble inorganic or organic phosphorus directly from natural water (Phillips, 1964). The transformations of organic phosphorus to inorganic phosphorus can be carried out by bacteria in the mineralization process. Stumm and Morgan (1962) have shown with laboratory algal studies that phosphorus may be the key element in the fertilization of natural bodies of water.

Studies involving the addition of artificial fertilizers to natural systems, Tanner (1960), McIntire and Bond (1962), and Hooper and Ball (1964 and 1966). The results of these studies indicate a definite relationship between the aquatic life of a body of water and the amounts of nutrients added. Hepner (1958) studying the dynamics of phosphorus added to fishponds in Isreal, found a direct relationship between the alkalinity and the amount of added phosphate that was removed from the water. These findings were related to both the calcium concentration in the water, as well as that found in the bottom muds.

Pomeroy et al. (1965) have suggested that the amount of phosphate involved in adsorptive chemical exchanges between sediments and water is large enough to be significant in regulating biological processes. Fruh (1967) in his discussion on the overall picture of eutrophication proposed that, depending on the type of sediment fixation prevalent, the recycling of available nutrients within a lake might be sufficient to sustain highly productive conditions over a period of years.

In the case of soils and land areas, phosphorus is removed more by erosion than by leaching, because phosphorus is usually fixed and held by the soil in some form of a metal-phosphorus compound. Bailey (1968) established that inorganic and organic phosphorus compounds are retained largely by the calcium, iron, and aluminum components of soils. The iron and aluminum phosphates predominate in acid soils and the calcium phosphates in alkaline soils. Hortenstine (1966) found that liming can be effective in increasing phosphorus fixation on sandy soils.

The release or uptake of phosphates by sediments from land and water sources is dependent on pH, aerobic conditions, temperature and the movement of overlying water. The properties of the sediments that affect this exchange of phosphorus have been considered from various aspects. Sommers et al. (1970) found that the phosphorus retention capacity of a sediment is largely determined by its mineral composition. Calcareous and non-calcareous sediments differ in phosphorus retention, with the retention property related to the amorphous iron and aluminum components and the calcareous carbonate fraction. Malquori and Radcielli (1967) studied the influence of calcium compounds on reaction of polyphosphates with soil particles and found that limestone fixed the simple linear phosphates to a greater degree than the complex ones.

The sediments of an eutrophic lake may have a high nutrient concentration which becomes available to planktonic algae on lake destratification. Sedimentation and phosphorus-release, at the bottom, influence the soluble phosphorus content of water and control the nature and rate of biological growth when phosphorus is less than the 0.10 mg/l limiting concentration (Mackenthum, 1964).

Mortimer (1941 and 1942) has done the basic study of exchange between mud and waters in lakes which showed a definite relationship between the rate of supply of nutrients and seasonal changes. Holden (1959) studied the location of the phosphate in the deposits at the bottom of lakes and found most of the adsorbed phosphate remained in the upper aerobic zone of the mud and may be converted to non-usable organic forms. These may be released during periods of temporary anaerobic conditions. With high phosphate concentration, the penetration in mud is up to fifteen centimeters. Sylvester and Anderson (1964) indicated that adsorption of phosphate proceeds during degradation and oxidation. Under reducing conditions, phosphate solutes are released to overlying water. Therefore, it appears that redox conditions are involved in phosphate adsorption on the suspended and settleable particles.

Harter (1968) found that there may be two types of adsorption on sediments. One is a strong, chemically-bonded mechanism while the other is of a more loosely-bonded nature when high amounts of phosphorus were present. Pomeroy _et al_. (1965) also identified two adsorption reactions which occurred at different rates. He suggested that the more rapid process is an initial surface adsorption. The slower process may be a secondary combination of phosphate into the crystal lattice of clay. The effectiveness of the adsorption process would depend on:

1. The exchange capacity of the sediments;
2. the exchange rate between water and sediments;
3. the rapidity of vertical mixing (flushing) in the water.

Suspended solids can provide adsorption sites for phosphate forms and thereby are an important consideration in the movement of phosphorus in natural ecosystems. The extent to which sediments will regulate nutrient levels in natural waters is partially dependent on the process controlling nutrient-transport to and from the sediment-water interface, in particular, water movement and physical settling of particulate material. Chemical diffusion plays a minor role.

Lee (1970) found that sediments can serve as a buffer for phosphorus, with the net flux of phosphorus from lake water to the sediments. The determination of the mixing process and a better understanding of the hydrodynamics of water bodies will give an indication of the relative flux of phosphorus from the sediments.

A thorough understanding of the water circulation patterns in a lake is essential in determining the influence of water-sediment interactions. With sediments acting as a major 'sink' for nutrients entering the Great Lakes, the success of efforts to reverse eutrophication by controlling nutrient sources will depend in particular on the extent of nutrient re-supply by the sediments (Harlow, 1966).

The influence of calcium compounds on the phosphate adsorption is of concern in areas that have limestone and calcareous materials. Studies by Hasler (1957) and Misra (1963) indicate that the application of lime to water or sediments, reduces the amount of soluble phosphorus released. This release is dependent on both pH and the amount of circulation in the water. Williams _et al_. (1969) suggested that the phosphorus retention capacity of a sediment is an important factor in determining the levels of phosphorus which accumulate in lake sediments under natural conditions.

In summary, McKee _et al_. (1969) have reached the following conclusions concerning sediment-water nutrient relationships:

1. A portion of the nutrients, soluble and insoluble, in a water body are ultimately destined to become part of the sediments. The extent of deposition depends upon the nature of the particle and its role in the aquatic system.

2. The initial area of deposition may be only temporary, the nutrient containing sediments or may be physically transported or the nutrient re-dissolved.

3. Wind-induced currents are a major factor that determines the rate and area of final deposition and the contact time between suspended sediments and water.

4. Suspension of sediments increases their effect on the overlying water.

5. The sediments act as reservoirs of nutrients for the overlying water.

6. The rapidness of sediment build-up will affect the degree of influence on the overlying water. Deeper sediments exhibit very little influence on the water.

The role of the sediments in the phosphate cycle in natural waters is a full study in itself, so this study will only evaluate the influence of suspended calcareous solids from a cement-dust discharge and natural sources. The phosphate-sediment adsorption considered in this study will be that of three phosphate forms with the calcareous cement dust as suspended material in water.

The identification of these phosphate forms (ortho, pyro, and tripoly) can be accomplished by chromatographic separation. Both paper and column chromatography have been used to separate polyphosphates into identifiable fractions. Ion-exchange chromatography has developed as a method for recoverable separation of the various phosphate species by the use of proper elution solutions and rates. Grande and Beukenkamp (1956) and Shiraishi and Iba (1964) have used various buffered potassium chloride combinations as eluants for the separation of polyphosphates. Matsuura et al. (1967) have separated the three phosphate forms being considered in this project by elution with KCl-buffered solutions, and their procedure was used in this study.

Herold (1967) used Dowex-1-X8 anion resin in the chloride form to determine the phosphate components in detergents. Specific volumes of a KCl-buffered solution were used to separate the phosphates. The eluants were acidified and the phosphorus concentrations determined colorimetrically. The method was adequate to separate milligram quantities of detergents. Peters and Rieman (1956) found that the ion-exchange methods require less time and yield more accurate results.

The analytical procedures used in this study for measuring interactions of suspended-calcium compounds with these phosphates have been primarily taken from soil-analysis methods. Wentz and

Lee (1969) have described procedures for determining sedimentary phosphorus in lake cores. They used a dilute HCl-H_2SO_4 extraction procedure for the removal of 'available' phosphorus from lake sediments. The sediment sample size, pH of the sediment-extractant mixture and sample pre-treatment effects the amount of phosphorus removed. They measured the rate of available phosphorus deposition and found it to be constant in the marl sediments. The deposition reached a maximum at about 30 centimeters below the water-sediment interface and increased proportionately as the sediments change from marl to sludge. The available phosphorus appears to be associated with the carbonate portion of the sediments studied.

Livingstone and Boykin (1962) examined bottom-sediment cores by extraction with acid-digestion. They concluded that the ionic activity of the water would be directly proportional to the ion-exchange capacity of the sediments. Biological productivity would be inversely proportionate to the adsorptive capacity of the sediments.

Williams _et al_. (1967) found that one-hour extraction with 0.5N acid will completely dissolve samples of pure apatite identified by Chang and Jackson (1957) as 'first HCl-P'. A second extraction with acid was found to remove additional amounts of phosphate from soils high in first HCl-P. The phosphate in both HCl extracts seemed to originate from apatite. The summation of the first HCl-P and second HCl-P was denoted by the expression, 'acid-extractable Ca-P'. During the total fractionation process no appreciable dissolution of apatite occurred prior to the determination of acid-extractable Ca-P. This fraction would not contain any aluminum or iron-bound phosphate.

A practical application of these complexations and adsorption have been applied to phosphorus removal from waste water. The classical objectives of primary and secondary wastewater treatment are the removal of oxygen-demanding material and suspended matter. Phosphorus removal by primary sedimentation is influenced by particulate matter, as well as, by the presence of metal ions that form insoluble salts with ortho and polyphosphates. The addition of sufficient amounts of lime serves the dual purpose of providing calcium ions, as well as, increasing the pH to facilitate precipitation. The final concentrations of soluble orthophosphate in secondary sewage effluent has been postulated by Jenkins and Menar (1968) as a combination of:

1. Biological incorporation into activated sludge cells;
2. collodial precipitation with calcium similar to $CaHPO_4$ ($K_{sp} = 2.2 \times 10^{-7}$) followed by adsorption on the sludge floc.

Most of the research on phosphate precipitation has been concerned with the fundamental mechanisms of cation-phosphate reactions and with the evaluation of the effects of pH and cation concentration on the extent of phosphate removal. Buzzell and Sawyer (1967) suggested a pH-controlled-lime addition could reduce phosphate in sewage by 80 to 90 per cent. Berg *et al*. (1970) removed phosphorus and suspended solids from secondary effluent of conventional water-treatment system by clarification with lime. Sufficient lime was added to maintain a pH of 9.5. Dickerson and Farrell (1969) found lime (CaO) most effective in reducing phosphate in waste water of a Michigan flour industry. In a pilot plant operation, 1340 mg/l lime as CaO were required to reduce the phosphate level in a primary effluent from 295 mg/l to 5.6 mg/l at a pH of 9.5. The suspended solids level was reduced from 3740 mg/l to a mean of 193 mg/l.

Rebhum and Manka (1971) found that the effect and behavior of organic matter from secondary sewage effluents which has undergone chemical treatment to be similar to that of humic compounds in natural waters and soil. Forty to fifty per cent of the organic composition of these effluents was reported to be humic substances (humic, fulvic and hymatomelanic acids). The use of calcium for phosphorus removal from natural water and sewage would be influenced by this organic material.

Harter (1969) has found that organic matter may be important in the initial bonding of phosphorus by soils. Phosphorus is initially bonded to anion exchange sites of organic as well as inorganic matter and subsequently transformed into less soluble metal phosphates. Anderson (1967) suggested that some mineral soils normally contain in the range of 1000 ppm total phosphorus of which approximately thirty to seventy per cent is associated with organic material. Scharpenseel (1967) used humic and fulvic acids together with $Ca(OH)_2$ to show that particles from clay soils can form a metal-acid complex. The calcium can act as a bridge ion between organic acids and clay material. Therefore, the total picture of phosphate fixation must include these organic materials.

Many surface waters have a characteristic, yellow-brown color which is caused by the presence of complex organic compounds of natural origin. The organic compounds producing color in water, fall within a broad category collectively termed humic substances.

The general origin of colored organic molecules is from soil run-off and the decomposition of vegetable material. The formation of humic acid is a result of polymerization of polyphenolic units derived either from bacterial synthesis or the break-down of lignin residues formed during the plant decomposition.

Origin of organic matter may be allochthonous from decomposing terrestial vegetation and soil-humus material. The second source is autochthonous organics which are released from aquatic vegetation decomposition and extraction from bottom sediments of lakes. The concentration of organic acids in lakes has been found higher nearer the bottom, and below any thermocline that may be present (Buck, 1968).

Steelink (1953) found that the structure of humic acid has a molecular weight range of 20,000 to 50,000. The macromolecule contains an easily hydrolyzable protein and carbohydrate fraction attached to a highly condensed 'core'. This core is partly aromatic, with structural elements derived from lignin phenols and resorcinol phenols. In addition, alcohol, carboxyl, and carbonyl groups are present together with heterocyclic nitrogen structures.

In the molecular structure of the chemical components which contribute to natural color, the structural units are probably linked through C-C alkyl-aryl and aryl-aryl bonds and through ether bridges. Packham (1969) showed that humic substances in water are in true solution, but a proportion of the molecules are large enough to exhibit colloidal properties in the natural water.

Midwood and Felbest (1968) found that the structural units in humic acids and fulvic acids are similar, although fulvic acid is of lower molecular weight and has more reactive groups than humic acid. Black (1963) identified fulvic acid as the most water-soluble fraction of natural soil humus. This acid would be expected to be found in colored, natural waters in higher concentrations than either humic or hymatomelanic acids. Low BOD results indicated that these organic substances normally considered responsible for color in water are apparently in their final state of microbiologic decomposition.

The humic substances present in water would be expected to be confined to humic, hymatomelanic, and fulvic acids, with properties:

Humic acid - Soluble in sodium hydroxide, insoluble in mineral acid and alcohol.

Hymatomelanic acid - Soluble in sodium hydroxide and alcohol, insoluble in mineral acid.

Fulvic acid - Soluble in sodium hydroxide, mineral acid, and alcohol.

In these natural organic acids, Wagner and Stevenson (1965) found one-third of the total -COOH groups were close enough to form cyclic anhydrides, and two-thirds of the total -OH groups were phenolic: a definite ionic environment suitable for complexation of metal ions.

Analysis by Black and Christman (1963) characterized fulvic acids as polymeric-hydroxy-methoxy-carboxylic-aromatic acids with the negative charges of the color particles because of the ionization of the carboxyl and aromatic hydroxyl groups. The groups characterized as fulvic acids have equivalent weights of 89 to 133 together with strong indications of unsaturation and aromacity.

The fulvic acids, as water-soluble, relatively low molecular weight humic substances, can form stable complexes with metal ions and hydrous oxides (Ogner and Schnitzer, 1970). Fulvic acid was found to be a chemically and biologically stable polyelectrolyte with a number-average molecular weight of 951 and 9.1 milliequivalence for -COOH with 6.9 milliequivalence of total phenolic -OH. Therefore, fulvic acid, in an aquatic environment, may act as a vehicle for the mobilization, transport, and complexation of natural organic and inorganic compounds.

Shapiro (1958) has done work on the complexation of iron by yellow organic acids in lake water and found that the humins of organic matter in lakes cause color and stimulate the growth of certain limnetic algae.

Prakash and Rashid (1968) indicated that the yellow soluble organic material in natural waters is of interest because of its influence on photosynthesis by the reduction of available light and its share in the biochemical oxygen demand. Its capacity for binding cations and phosphate has a specific influence on growth of aquatic vegetation.

Buck (1968) found that the addition of yellow organic acids to natural waters in Northern Michigan ponds, produced changes in pH, conductivity, alkalinity, and color intensity of water. The first three may be explained by a hypothetical union between these acids and calcium carbonate. The change in color absorbance may be a result of the change in pH.

Wilson (1959) found the absorbance of light by the organic color increased when the wave length of light passed through the sample, decreased from 350 to 250 mu. This response has been used for measurement of the level of colored organic matter in natural waters.

Packham (1969) found an optical density (absorbance) response for the colored water at 350 and 450 mu. Christman and Ghassemi (1966) noted a fluorescence excitation in natural colored water at 361 mu. Semenov _et_ _al_. (1963) have measured the humic acid content of surface waters in milligrams of carbon per liter, by the difference in fluorescence absorbance at 340 and 440 mu respectively.

The two common solvents that have been used for the elution and concentration of these colored organics from natural water are chloroform and ethyl alcohol. With these solvents, Sproul and Ryckman (1961) found that the organic compounds extracted into the chloroform fraction were more odorous than those extracted into the polar, alcohol fraction.

Daniels _et_ _al_. (1963) sampled organic compounds in waters of Lake Huron by adsorption on activated carbon and extraction with chloroform and ethanol. The choice of solvents, and the order of use, was based primarily upon the polarity of the adsorbed materials. The eluates were evaporated and the chloroform extracts were assumed to represent less polar compounds from industrial sources. The alcohol extracts were associated with the more polar varieties of natural origin. Comparison of the organic material extracted by chloroform and alcohol eluates appeared to be useful in judging water quality.

From these data of Daniels _et_ _al_. (1963), the waters of Northern Lake Huron were found relatively free from pollution. Moreover, their data indicated that the ratio of extracts fluctuated seasonally, since the alcohol to chloroform ratio was 3.77 for the summer and 3.70 in winter. The periodicity of the fluctuations in the ratio was related to those of lake level, temperature and sampling location.

The actual composition of this organic matter has been studied by various procedures and in different natural locations. Gjessing and Lee (1967) fractionated moderately-colored creek water using Sephadex columns by gel-permeation procedures. Various streams showed different organic carbon elution patterns. Moed (1971) used the adsorption of soluble organic yellow material on aluminum oxide to separate organics by the elution of yellow material with buffers of varying molar strengths. The procedure allows the concentration of yellow material without exposure to the action of organic solvents and acids.

In the demineralization of water by ion-exchange, Packham (1969) found that humic substances can create considerable difficulties by fouling the anion-exchange resin. The strongly-basic anion exchangers have a high-chemical affinity for organic acids together with an open structure in the resin bed (Wilson, 1959). The organic matter was removed when the resin was regenerated with sodium chloride.

Christman and Ghassemi (1966) identified the sources of natural organic color as the aqueous extraction of living woody substances, as well as, the dissolution of degradation products in decaying vegetation. They isolated the organic matter by ion-exchange separation and elution of the colored material from the anion resin with 2M NaCl and extraction with normal-butanol.

Buck (1968) has adapted an anion-exchange procedure for the separation of yellow organic acids from Michigan ponds by elution from the resin with sodium hydroxide. In the use of these macroporous resins, the ion-exchange procedure may not be quantitative. It does permit relatively large quantities of the various natural organic-acid fractions to be isolated readily even from waters of low color.

Packham (1969) found that more complete recovery could be obtained using 2M sodium chloride with 1M sodium hydroxide solution as regenerant, at a slow rate of diffusion within the resin. The acid filtrate from the humic acid separation contained a high concentration of salts and a fulvic acid fraction. The aqueous solutions were extracted with alcohol or acetone and the extract filtered and evaporated to dryness. The solid residue of fulvic acid recovered can be stored or dissolved in alcohol.

The involvement of these anionic-acidic organic structures with metals in natural waters results in the formation of soluble metallo-organic complexes (Khanna and Stevenson, 1962). They suggested that the retention of micronutrients added to soil as fertilizers may be due, in part, to the formation of stable complexes with the polycarboxylic and hydroxy sites of the organic matter. Phosphate binding to the natural organic acid material has been found by Gupta (1967) not to be a simple adsorption phenomenon but one related to the amount of humic acid present and the type of soil (calcareous or non-calcareous).

Khanna and Bajwa (1967) used potentiometric titration of humic acid from two soils to measure the formation of stable metal-organic complexes. The humic acid was found to have two definite carboxylic groups per-molecular-weight in the calcium complex.

Weir and Soper (1963) studying the reactions of phosphates and iron with the active groups of ion-exchange resins found that only small amounts of phosphate held by the complex were releasable. Chemical analysis showed that the complexes can exist as PO_4^{-3} bonded through the metal of the acid group on the cationic resin.

There may be two types of binding between the humic acids and the anion resins. The normal electrovalent bonding between the humic acid carboxylate groups and the functional groups of the ion-exchange resins would be present. A second type of bonding appears to be dependent on the pH of the solution: the bonding is much weaker in alkaline solution than in acid solution, possibly due to van derWaal forces or dipole interactions of the very large, essentially aromatic molecules.

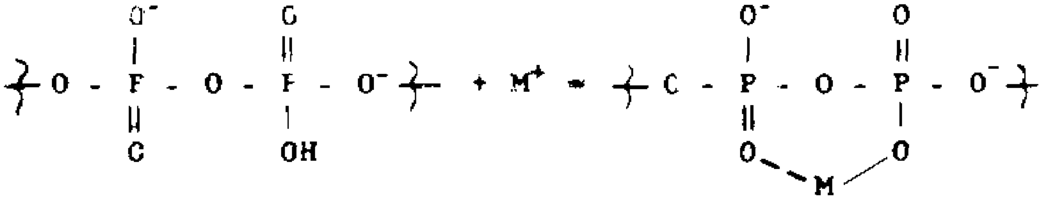
The involvement of calcium in these complexes was studied in clay soils by D'yakonova (1964) who found that with humic acids extracted from clay-humus complexes, an indirect relationship existed between the calcium content and the organic matter. In selected, molecular metal-to-fulvic ratios prepared by Levesque and Schnitzer (1967), it was found that in the absence of metal, no reaction can take place between added phosphates and fulvic acid.

Visser (1962) studied the interaction of the different ionic states of orthophosphate with calcium and organic matter (proteins, polysaccharides, and organic acids). He found that between pH values of 5 and 12, calcium caseinate and tricalcium phosphate will occur together as a soluble chemical complex. The formation of this complex was thought possible between colloids which have free carboxyl groups present within the organic structure and the calcium phosphate.

Shapiro (1964) found that the yellow organic acids were capable of chelating iron and keeping it in solution up to a pH of 9.5. He determined that the color was suspended in a colloidal form in direct proportion to the iron concentration. The coagulation and reactions of colored material involved colloids with an average diameter between 3.5 and 10 mu.

The formation of soluble calcium-phosphate-organic acid complexes would influence the transport and deposit of these components in soils and natural waters -- the major area of study in this project.

The complexing ability of the linear polyphosphates would be due to the formation of chelate rings. On consideration of the structure of chains of interlinked phosphate tetrahedra, it appeared that a chelate ring might be completed between any two adjacent PO_4 tetrahedra (Van Wazer and Campanella, 1950). The complexing ability of a linear phosphate would be proportional to the total number of phosphorus atoms in the polyphosphate structure:



$$\left\{ O - \underset{\underset{O}{\|}}{\overset{\overset{O^-}{|}}{P}} - O - \underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}} - O^- \right\} + M^+ = \left\{ O - \underset{\underset{O \diagdown}{\|}}{\overset{\overset{O^-}{|}}{P}} - O - \underset{\underset{\diagup O}{|}}{\overset{\overset{O}{\|}}{P}} - O^- \right\}_{M}$$

The total number of positions along the chain where a metal ion can form a complex, could be one less than the number of phosphorus atoms in the chain. Since the weakly-acid hydrogen is associated with the terminal PO_4 groups of polyphosphate molecules, the only type of complex formation that can effect the strength of the weak-acid function must involve these terminal groups. Watters and Lambert (1959) measured the stabilities of calcium complexes formed with pyrophosphate and tripolyphosphate ions by means of the neutralization reactions involving titration of the salts with hydrogen ion.

Irani and Callis (1960) studied the effect of pH, temperature, ionic strength, and length of phosphate chain on the calcium complexes. The tetramethyl ammonium polyphosphates were prepared by ion-exchange reaction of the sodium salts with the hydrogen form of Dowex 50W-X2, followed by neutralization of the resulting acids with tetramethyl ammonium hydroxide at 25C and pH of 12. Under varying conditions, they found a direct relationship between the length of the phosphate chain and the stability of calcium complexes.

In aqueous solutions, numerous studies have been conducted investigating the interactions between calcium and phosphorus under natural water conditions. Schnofield (1964) indicated that the normal precipitation of calcium from water as $CaCO_3$ at a pH of 12 was inhibited by the presence of as little as 1.0 to 1.5 ppm ortho or pyrophosphate. Balba (1966) measuring the concentration of the three forms of orthophosphate ions by titration of phosphoric acid with calcium hydroxide found that $H_2PO_4^-$ was the ion in greatest abundance in a pH range of 2.4 to 12.0 and would form $CaH_2PO_4^+$ with calcium.

An evaluation of natural interactions can be based on the pH measurement of the change in the weak-acid function (Odagiri and Nickerson, 1964) of the phosphate forms in the presence of calcium and natural organic acids. In order to measure possible complexation between calcium and anionic organic colloids, Visser (1962) used different forms of orthophosphate. These forms were determined by titrating phosphoric acid with alkali in the presence of calcium and observing complexes resulting with selected organic substances.

Machen (1967) studied magnesium and calcium tetraphosphate complexes as a function of pH lowering. Part of the increase in stability of the tetraphosphate ion complexes may be attributed to a metal ion first forming a single bond with any terminal oxygen before rearranging into a chelating position to form a ring with phosphorus, oxygen, and metal ions.

The calcium select-ion electrode was used to measure the activity of the free calcium ion. This activity can be applied to the ligands forming a soluble compound. Cation-sensitive glass electrodes offer the possibility of specificity and make possible activity measurement in the presence of other cations and anions (Eisenman, 1967). This means that ion-association studies can be carried out conventiently in multi-component systems. In the past few years, the development of a calcium select-ion electrode has resulted in the measurement of calcium ion rapidly and reproducible in the pH range of 3.5 to 10.0 (Schultz, et al., 1968).

For example, Rechnitz and Hseu (1969) have demonstrated that a solid-membrance calcium select-ion electrode gives a satisfactory response with respect to changes in calcium ion concentration. They found the electrode was suitable for indicating the course of potentiometric titration involving the Ca^{++} ion. Through direct selective measurement of the free calcium activity at equilibrium, the stability constants of calcium complexes with polycarboxylic acids were determined.

The select-ion calcium electrodes measure the single ion activity of the calcium ion in solution, rather than the concentration of the ion. Since, activity of the calcium ion in solution is the measure of the reactivity of the ion, the extent and rate to which the calcium ion takes part in a chemical reaction can be established. In dilute solution, the activity of the calcium ion approaches calcium ion concentration. Therefore, in these cases, the activity is proportional to the concentration, and the electrode can be calibrated with respect to concentration.

The activity of the Ca^{++} ion is measured by the potential developed across the liquid-liquid junction of the electrode's exchanger fluid and test solution. The integrity of the junction is maintained by a ceramic plug through which the exchanger in the electrode fluid flows. The silver-silver chloride internal electrode element provides a stable potential between all inner electrode interfaces, assuring that variations in potential are related only to changes in ionic activities of the test solution. The water-immiscible organic phase in the electrode forms a liquid ion-exchange 'membrane' whose ion-exchange properties for cations are similar to mechanisms to liquid ion-exchanger concentration cells. The electrode is insensitive to chemically-bound or unionized calcium.

The transport number of calcium ions across the organic phase has been found to be unity (Corning, 1968). Under these conditions, the equilibrium potential across the membrane is described by the following form of the Nernst Equation:

$$E = E^{o} + 2.303 \frac{RT}{2F} \text{Log } (a_{Ca^{++}})$$

The activity (a) of an ion can be related to its concentration (c) by the activity coefficient (γCa^{++}). The Nernst equation at 25C for Ca^{++} can be rewritten using the activity coefficients and concentrations of Ca^{++} instead of activity as:

$$E = E^{o} + 29.6 \text{ Log } (c_{Ca^{++}}) + 29.6 \text{ Log } (\gamma \, Ca^{++})$$

When the activity coefficient is a constant over the concentration range of interest (small ionic strength change), the potential of the electrode would be a function of the calcium concentration.

When the ionic activity increases, the electrode potential response becomes more positive for the select-ion electrode. The 29.6 mv term is the theoretical slope of the E(mv) vs. Log (Ca^{++}) plot for the electrode. At 25C, for every tenfold change in concentration (moles per liter), there should be a 29.6 mv change in potential for a theoretical operating electrode system. Additionally, the standard solution used should bracket the concentration range of the unknowns and contain the same ionic composition as the test solutions. Otherwise, correction for change in total ionic strength is necessary to determine the mean ionic activity.

All specific-ion electrodes may be subject to interferences from other ions. Divalent cations other than Ca^{++} affect electrode readings to some extent; both changing the total ionic strength of the solution and by selectively competing with Ca^{++} ions. An apparent selectivity constant (K) can be related by:

$$E = E^{o} + 29.6 \text{ Log } (a_{Ca^{++}} + K_{a_{M^{+n}}})$$

The selectivity constant specifies the interference from competing ions. For K greater than one, the electrode is more sensitive to the competing ion than to Ca^{++}. For K less than one, the electrode is more sensitive to Ca^{++} than to the competing ion. Listed below are selectivity constants for divalent cations expressed as the ratio of electrode response to the interfering cation to the electrode response to calcium ion (Orion, 1969):

Cation (M^{++})	-K-
Zn	3.2
Ca	1.0
Fe	0.8
Pb	0.63
Ba	0.016
Mg	0.014

Only magnesium is present in significant quantities in an aquatic system, but the selectivity constant value is low enough to neglect this interference. Sodium and potassium interfere only if the level of these ions is high (more than 1000 times), in relation to the calcium level. This type of electrode will be used for the measurement of the interaction of calcium ions with the three common phosphorus forms in Thunder Bay natural waters. Furthermore, it will be used to measure the role calcium plays in the calcium-phosphate-organic acid complexation in natural systems.

Rechnitz and Hseu (1969) used an immobilized matrix type calcium ion-selective-membrane electrode, for direct potentiometric titrations in the study of three calcium complexes of biological significance. The electrode was shown to have a reduced selectivity for the hydrogen ion while selectivity for calcium over common interfering univalent and divalent cations is satisfactory for most practical measurements.

Rechnitz and Brauner (1964) have used a titration method for the study of alkali metal complexes. A plot of select-ion electrode potential vs. log sodium ion concentration was prepared as a calibration curve in the absence of complexing ligand. A known initial concentration of sodium chloride was then titrated using a standard solution of malic acid. A plot of potential vs. log of the apparent concentration of free sodium was prepared to determine concentrations of uncomplexed sodium and organic acid.

Rechnitz and Zamochnick (1964) devised a potential comparison method which largely eliminates sources of error, such as electrode drift and variation in solution composition, yet retained the advantages gained by the use of the cation-sensitive electrodes. Any possible errors from electrode drift or temperature effects would be of no consequence. The method does not even require that the electrode show Nernstian behavior. Moreover, dilution errors and ionic-strength changes were reduced to a minimum by the use of concentrated titrants and high-buffer concentrations.

The accuracy with which formation constants can be determined depends primarily on the limitations of the titrimetric technique employed. The potential comparison method can be used to determine formation constants of any weak complex of metal cations with organic acids, providing that proper precautions are taken to eliminate interfering species, to control pH, and to maintain ionic strength. For example, Rechnitz and Lin (1968) used the electrode to measure complexation reactions of Ca^{++} with organic acids by potentiometry.

Therefore, the quantitative measurement of the stability of complexes formed between Ca^{++} and a series of carboxylic acids or linear phosphate forms can be studied by the use of the technique which permits the direct selective measurement of the free calcium activity at equilibrium with the calcium selective-membrane electrode.

Appendix II. Thunder Bay Drainage Basin

APPENDIX II

THUNDER BAY DRAINAGE BASIN

The Thunder Bay River Basin comprises a drainage area of approximately 1250 square miles. The watershed lies in the Northeastern portion of Michigan's Lower Peninsula extending over parts of Presque Isle, Montmorency, Oscoda, Alcona, and Alpena Counties (Figure 24). The basin has an irregular shape and is forty miles in length and thirty-four miles across, measured at the longest and widest points (Velz and Gannon, 1960). The Thunder Bay River flows generally easterly to its mouth in Thunder Bay, an arm of Lake Huron.

The largest city in the watershed is Alpena (15,000 population) which is located on Thunder Bay at the mouth of the Thunder Bay River. Other population centers are at the villages of Hillman and Atlanta in Montmorency County, both of which are on the main branch of the river.

The major tributaries of Thunder Bay River are the North Branch, draining the northern area of the watershed, and the Upper and Lower South Branches together with Wolf Creek which drain the southern portion of the basin (Figure 25).

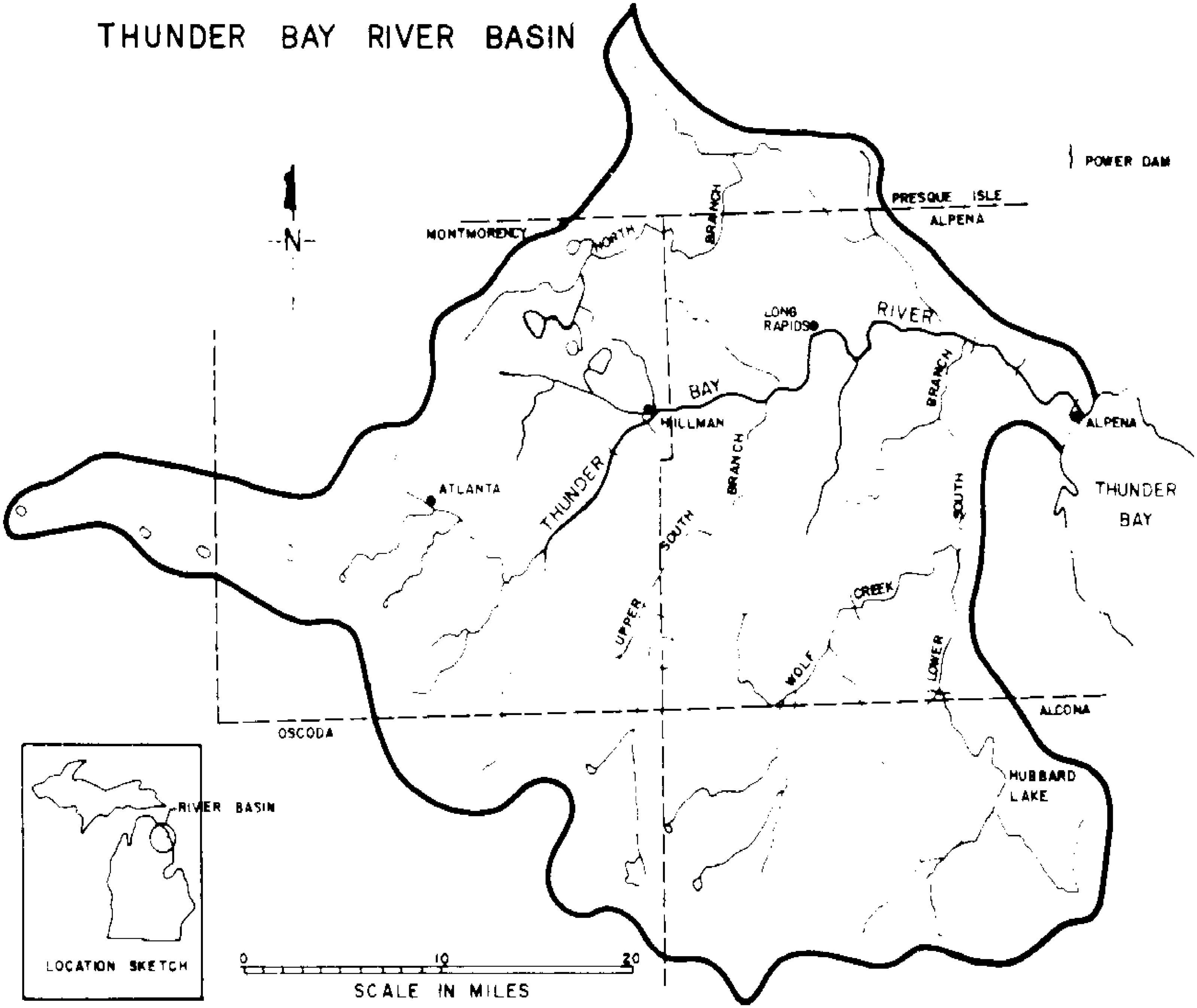
The Thunder Bay River system drains fully three-fourths of Alpena County and about 850 square miles of the adjoining counties before it reaches Lake Huron. The drainage that flows from the moraine region in the southwest to the main branch is

FIGURE 24.

NORTHERN LAKE MICHIGAN AND LAKE HURON DRAINAGE AREA, LOWER PENINSULA

FIGURE 25.

THUNDER BAY RIVER BASIN



from springs and spring-fed lakes. The creeks and streams that drain the northwest and southeast parts of the county have their source in swamps and lakes. Several run-of-the-river type hydroelectric dams with storage capacity such as impoundments or natural lakes, are scattered throughout the watershed. These dams supply a portion of the electric power to the region.

The four hydroelectric power dams (Ninth Street, Four-Mile, Norway, and Hillman) deliver about 2.34×10^7 KWH during an average year. The dams operate at an over-all 60 percent efficiency (Alpena Power Co., 1970). The reservoir at Hillman covers 100 acres. The reservoir (7-mile pond) at the Norway Dam covers 1530 acres. The reservoir at the Four-Mile Dam covers 98 acres. The Oxbow reservoir together with Besser Lake located behind the Ninth Street Dam in the city of Alpena covers 392 acres.

Other reservoirs, used to maintain water levels, are the headwaters of the North Branch of the Thunder Bay River at Rush Lake which covers 355 acres and the Fletcher Floodwaters on the Upper South Branch of the Thunder Bay River. The Floodwaters cover 3660 acres in Montmorency County and 1650 acres in Alpena County (Soil Conservation Service, 1970). There is also a water-level-controlling dam on Hubbard Lake in Alcona County flowing into the Lower South Branch of the Thunder Bay River. The operation of the dams and maintenance of reservoir levels induce diurnal fluctuations in the flow during the hours of the day and throughout the week, and have control over flooding conditions.

GEOLOGY

The oldest geologic bedrock formations in Lower Michigan occur at the northern tip of the Lower Peninsula. They were formed during the Devonian era and consist primarily of limestone. Limestone outcrops are found in Alpena and Presque Isle Counties. Lying in a wide band across the northern portion of the watershed is an undifferentiated bedrock composed of gray-blue limestone and calcareous shale. Antrim shale, the oldest of the Mississippian-era rock, is exposed in Alpena and Presque Isle Counties.

The geology of the Thunder Bay River Watershed was developed during the Devonian and Mississippian Periods with the underlying rock being limestone and shale. The northern area has the generally undivided sub-surface limestones of the Traverse Group — Alpena, Thunder Bay, and Petoskey (Martin, 1936). The central portion of the watershed flows over Antrim and Sunbury shale. In the southern area, Berea sandstone and Coldwater shale of the early Mississippian Period are found. In the lower portion of the watershed; sandstones, beds of gypsum and some dolomitic limestone are present together with Coldwater shale (Water Resources Commission, 1968).

The series succession of bedrock consist of the Middle and Upper Devonian at the lower end of the watershed. Lower Mississippian and Mississippian with Devonian lie in the upper reaches of the watershed as indicated in Figure 26 and identified in Table 30 (Kelley, 1968).

In Alpena County, the limestone and shale, underlying the County are several thousand feet thick. They are in layers which were once sediments in the bottom of the oceans covering Michigan. The limestone rock is filled with old shells and coral. At a depth of about 1250 feet, there is a bed of solid rock salt lying below the County.

The Thunder Bay basin is underlain primarily by three different geological formations. The northern area is underlain by crystalline-type, hard Alpena limestone. The main branch is underlain by the

FIGURE 26.

BEDROCK OF MICHIGAN

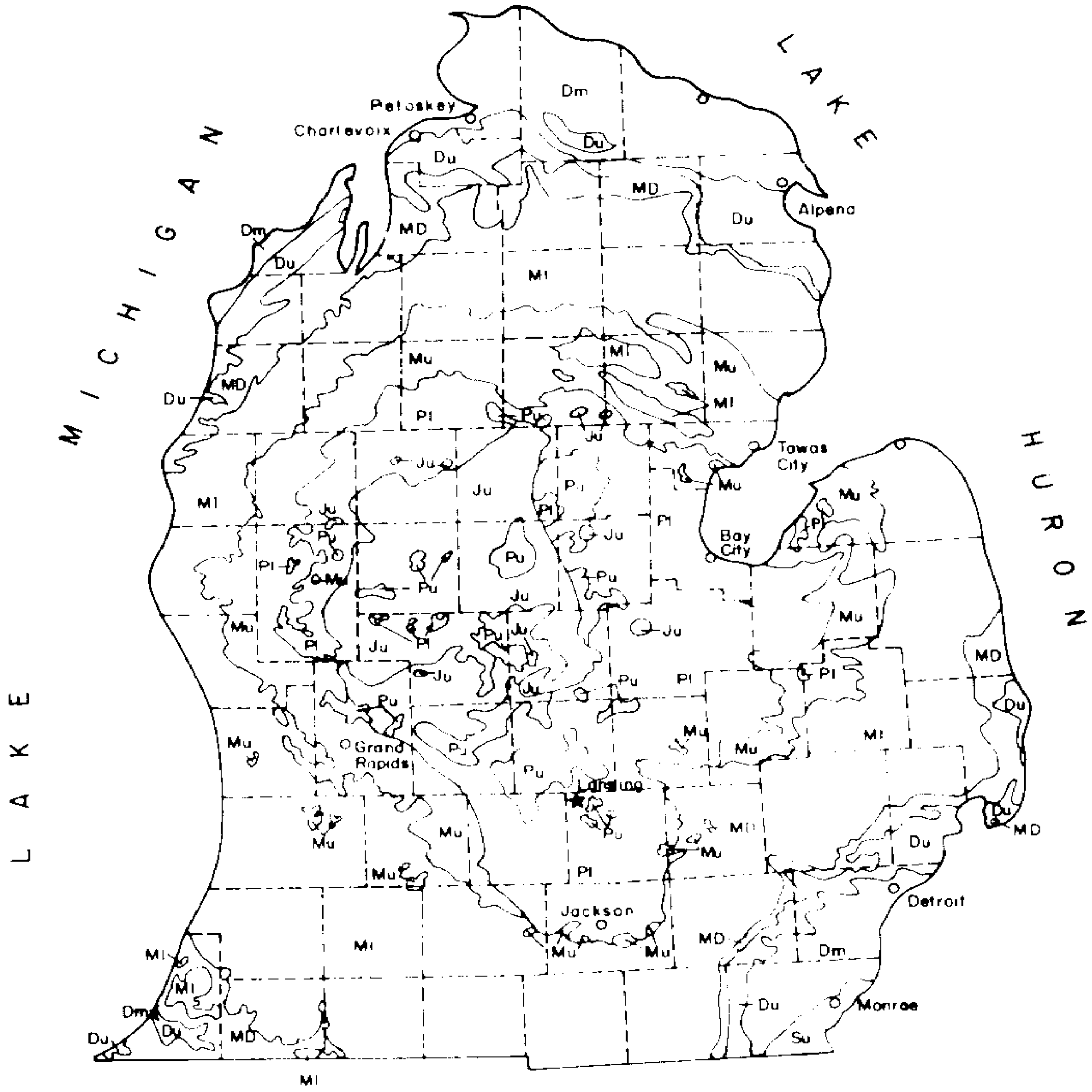


Table 30

Stratigraphic Units of Michigan Bedrock
(Kelley, 1968)

Era	Symbol	Series
Mesozoic	Ju	Upper Jurassic
Paleozoic	Pu	Upper Pennsylvanian
	Pl	Lower Pennsylvanian
	Mu	Upper Mississippian
	Ml	Lower Mississippian
	MD	Mississippian and/or Devonian
	Du	Upper Devonian
	Dm	Middle Devonian
	Su	Upper Silurian

Thunder Bay rock formations, which are alternating layers of various types of limestones and shales, with limestone comprising the upper thirty feet of the bedrock. The southern area of the basin is underlain by the dense sedimentary rock, Antrim shale (Figure 27)(VerWeibe, 1927).

The Thunder Bay basin has an area of great glacial accumulation with extensive moraines, till plains, and broad outwash aprons. The latter constitutes sand plains, found throughout the Thunder Bay River drainage basin. These glacial moraines, till plains, and outwash plains occur with frequency and apparent magnitude (Scott, 1921).

TOPOGRAPHY

Continental glaciers were responsible for the moraines, till plains, lake beds, and outwash plains which characterize northern Michigan topography and that of the Thunder Bay Watershed. Surface formations found in Michigan today, except for a few slight changes, were formed by the fourth and final glacier (Wisconsin) which began receding about 20,000 years ago. The glacier, as it plowed through the bed of Lake Huron, pushed up a somewhat irregular furrow on its right margin, which was a kind of ridge or lateral moraine. This moraine extends from about the middle of Alpena County, southward, more than fifty miles. A second moraine was formed west of Devil Lake and east of the Lower South Branch reaching a height of 250 feet.

Separating the moraines are areas of outwash plain and till plain. Outwash plains were formed by swift melt-water streams flowing from the melting glaciers, carrying sand and gravel from the glaciers and depositing them in a relatively flat plain. Till plains are composed of glacial material similar to that which constitutes

AERIAL GEOLOGY
OF
ALPENA COUNTY, MICHIGAN

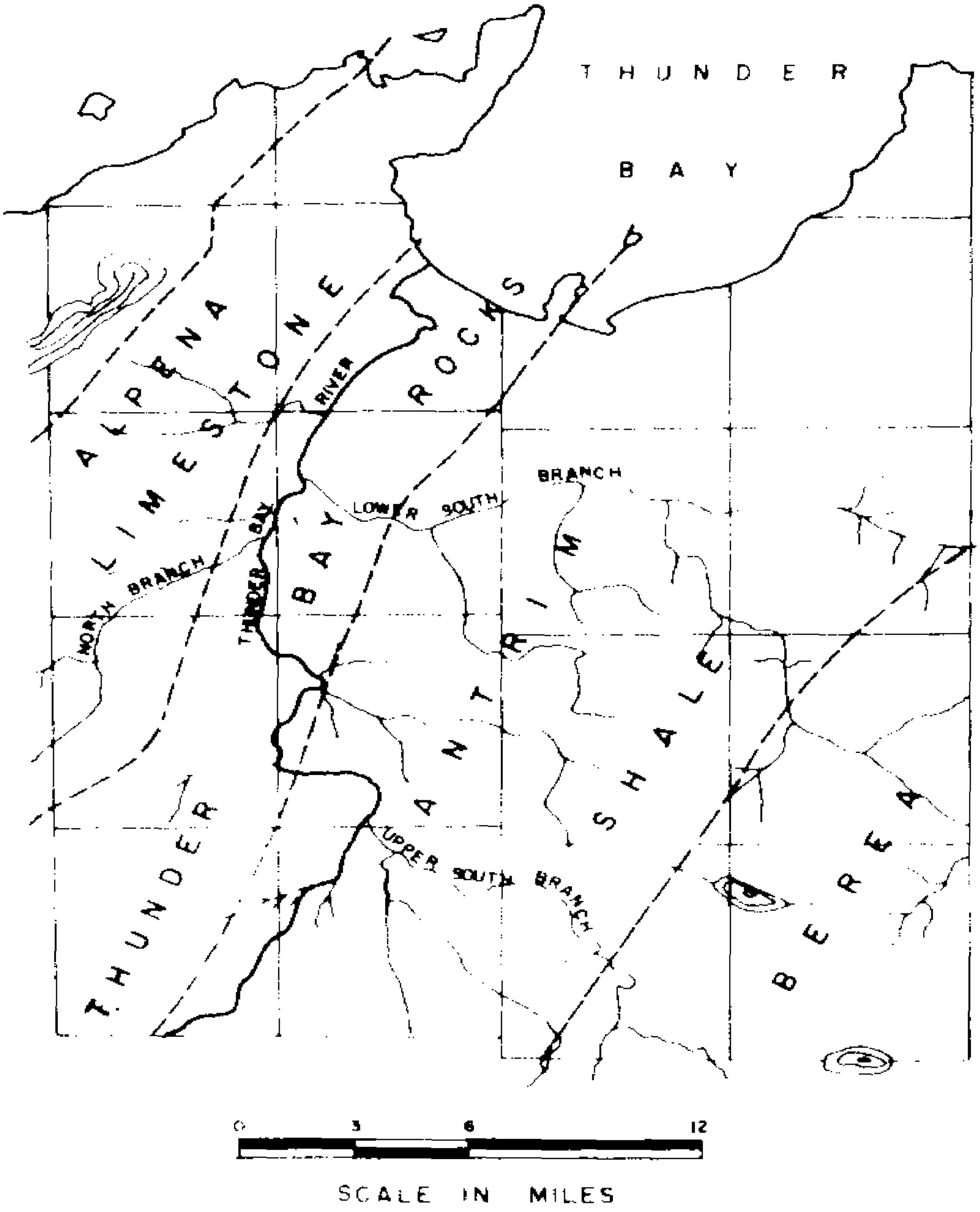


FIGURE 27.

the moraines, except that it is deposited directly from stagnant ice and forms a gently undulating surface. Hubbard Lake and the Lower South Branch of the Thunder Bay River lie in the valley between two moraines (Alpena News, 1961).

On the west of these moraines is an extensive low plain, extending from near the southern line of Alpena County, then northward, a distance of 12 to 15 miles as the bed of an accient lake which gradually escaped, as Wolf Creek cut its deep gorge through the central range of hills.

LAND RESOURCES

The land area of the Thunder Bay Watershed falls within four natural divisions: (1) Lake Plain, (2) Smooth Rolling Uplands, (3) Rolling to Hilly Uplands, and (4) Valley Lowlands.

The Lake Plain is a practically level area bordering Lake Huron and Thunder Bay. Its elevation ranges mainly between 600 and 750 feet above sea level and seldom exceeds 100 feet above Lake Huron. Northeast of the city of Alpena, it consists of shallow, stony-loam soils on limestone bedrock and a generous amount of shallow swampland. On the upland, the surface is commonly littered with thin slabs (outcrops) of limestone.

The virgin forest growth on these plains was a mixed stand of white cedar, balsam fir, spruce, maple, ash, and elm with some white pine. On the more sandy areas adjacent to the lake and bay shore, the hardwoods were more completely replaced by white and Norway pine. West and south of Alpena, the Lake Plain is prevailingly sandy instead of stony. Here, the wet lands are more variable in the depth of their swampy soils and range from wet sand with little or no mucky-surface soil to deep muck and peat swamps.

Most of the central and northern parts of the basin are occupied by the Smooth Rolling Uplands. This division includes the broadly undulating to gently rolling, fertile, well-drained loam soils of the till-plain region. General elevation is 700 to 800 feet above sea level.

The virgin forest growth was upland hardwoods with proportion of wet land to well-drained uplands with narrow strip-like areas of muck and peat swamps.

The Rolling to Hilly Uplands occupy the higher and more hilly areas on the bold and massive moraines of the southwest part of the basin. Soils are loamy sand and light sandy loam with good-to-free natural drainage. Elevation is 800 to 950 feet above sea level. Norway and white pine with a variable amount of upland hardwoods comprise the virgin forest on these sandy-loam uplands.

The Valley Lowlands occur chiefly in the western part of the basin where they occupy broad valleys and low flats associated with the Rolling and Hilly Uplands. Elevation is 750 feet. Along the central portion of the watershed, the Valley Lowlands are generally flat and have slow to poor natural drainage consisting of swamp and marsh soils and clay loams (Mich. Dept. Conservation, 1927).

The soils were composed mainly of moist-to-wet sandy lands and shallow, to deep muck, and peat swamps. The virgin forest growth on the moist, sandy soils was dominantly white pine. The wet sandy lands were occupied by a mixture of pine, swamp hardwoods and conifers, while white cedar, spruce, and tamarack cover the deep swamp soils.

SOILS

Individual soils are classified on the basis of the parent mineral material, texture and the soil profile development. The soils of the Lake Huron watersheds in Michigan are in the Podzols group. The upland northern Michigan soils were formed under a cool, moist, climate from a siliceous, glacial debris as parent material. The soil profile has a surface veneer of organic matter over a gray, leached horizon. This is underlain by another leached horizon, under which is sub-soil containing an accumulation of iron and humus matter.

The lowland hydromorphic and metamorphic soils drained by the tributaries of Lake Huron are 'dark colored', high in humus, high in level of natural fertility, durable under cultivation and not subject to serious erosion (Veatch, 1961).

Alpena and Presque Isle Counties contain in part, the more stony-clay plains. Though slopes are not steep, there are rises up to 300 feet above the adjacent valleys. Extremely course bouldery drift and bedrock at shallow depths are common. They also contain soils of the rock-plains type underlain by limestone (Water Resources Commission, 1968).

The general soil groups in the Thunder Bay Watershed consists of: the Onaway-Emmet Association which is a deep sandy loam to loam soil developed in calcareous glacial drift; the Carbondale-Roscommon Association which consists of wet sands and organic soils; and the Emmet-Posen-Longrie Association which has sandy loam with limestone bedrock often shallower than three to four feet. The major and minor soils of Alpena and Montmorency Counties are given in Tables 31 and 32 and shown in Figures 28 and 29 (Alpena and Montmorency Soil Conservation Districts, 1969).

The soils along each creek and stream that flows into the main branch of Thunder Bay River and the soils along the main river course are important contributors to the clarity and quality of the natural

Table 31

Description of Alpena County Land Resource Area Map

(Alpena Soil Conservation District, 1969)

Area Number	Acres	Slope Range	Dominant Slope	Description	Major Soils	Minor Soils
8	90,000	2-8%	6%	Mostly loam and sandy soils that are limey at shallow depths, low relief and gentle slopes. Subsurface loam to sandy clay.	Onaway Emmet Mackinaw	Selkirk
8A	25,500	0-12%	6%	Longer and slightly steeper slopes than 8, generally sandy loams.	Emmet Onaway	Leelanau Montcalm
9	19,000	0-12%	6%	Loam and sandy loam stony soils, high proportion of limestone.	Posen Longrie	Imperfect Posen
10	45,000	0-8%	5%	Loam and silt loam soils underlain by tight red clay. Low relief wet flats-shallow potholes.	Kent Selkirk	Bergland
16	12,200	0-15%	8%	Loamy sands, sandy loams and deep sands. Hilly and complex slopes.	Leelanau	Emmet Rubicon
22	21,300	all	10%	Deep sandy soil, some sandy loam surface with clay subsoils. Hilly with domed ridges and valleys.	Grayling Rubicon	Leelanau
24	8,260	0-6%	2%	Deep dry sands, low to medium in fertility. Low relief, narrow curved ridges and pit depressions.	Rubicon Augres	Roscommon
30	38,000	0-8%	6%	Shallow loams to sands over limestone bedrock. Low stony ridges.	Longrie Ruse	Alpena
35	60,000	-	-	Wet and dry sands with ridges, depressions and swales	Roscommon Rubicon	Greenwood
37	37,500	0-4%	2%	Swampy sand flats and valley lowlands and mucky loamy sands.	Carbondale Roscommon	

Table 52

Description of Montmorency Land Resource Area Map (Montmorency Soil Conservation District, 1969)

Area Number	Slope Range	Dominant Slope	Description	Major Soils	Minor Soils
8	0-16%	6%	Undulating and rolling till plains and moraines, some stones and boulders with strong influence from limestone.	Onaway Emmet	Mackinac Leelanau Angelica
10	0-5%	2%	Flat to undulating till plains and lake bed plains. Loam to silt loam surfaces underlain by tight red clay to silty clay with sandy loam.	Selkirk Bergland Kent Wester	Brimley Mackinac
16	0-18%	9%	Rolling moraines. Sandy loams to loamy sands with areas of wet sands. Swamp areas and wet sands.	Leelanau Emmet	Menominee Kalkaska
22	2-20%	12%	Moraines, hilly and undulating, small outwash areas. Deep sands with areas of loamy sands and sandy loams	Grayling Rubicon	Kalkaska Nester
24	0-6%	3%	Outwash and glacial lacustrine deposits usually flat to undulating. Soils mainly deep and dry with some dry pits and pot-hole bogs.	Rubicon Kalkaska Grayling	Saugatuck Augres Greenwood
37	0-2%	0%	Swamp flats and lowlands which are post-glacial accumulations.	Carbondale Tawas	Roscommon

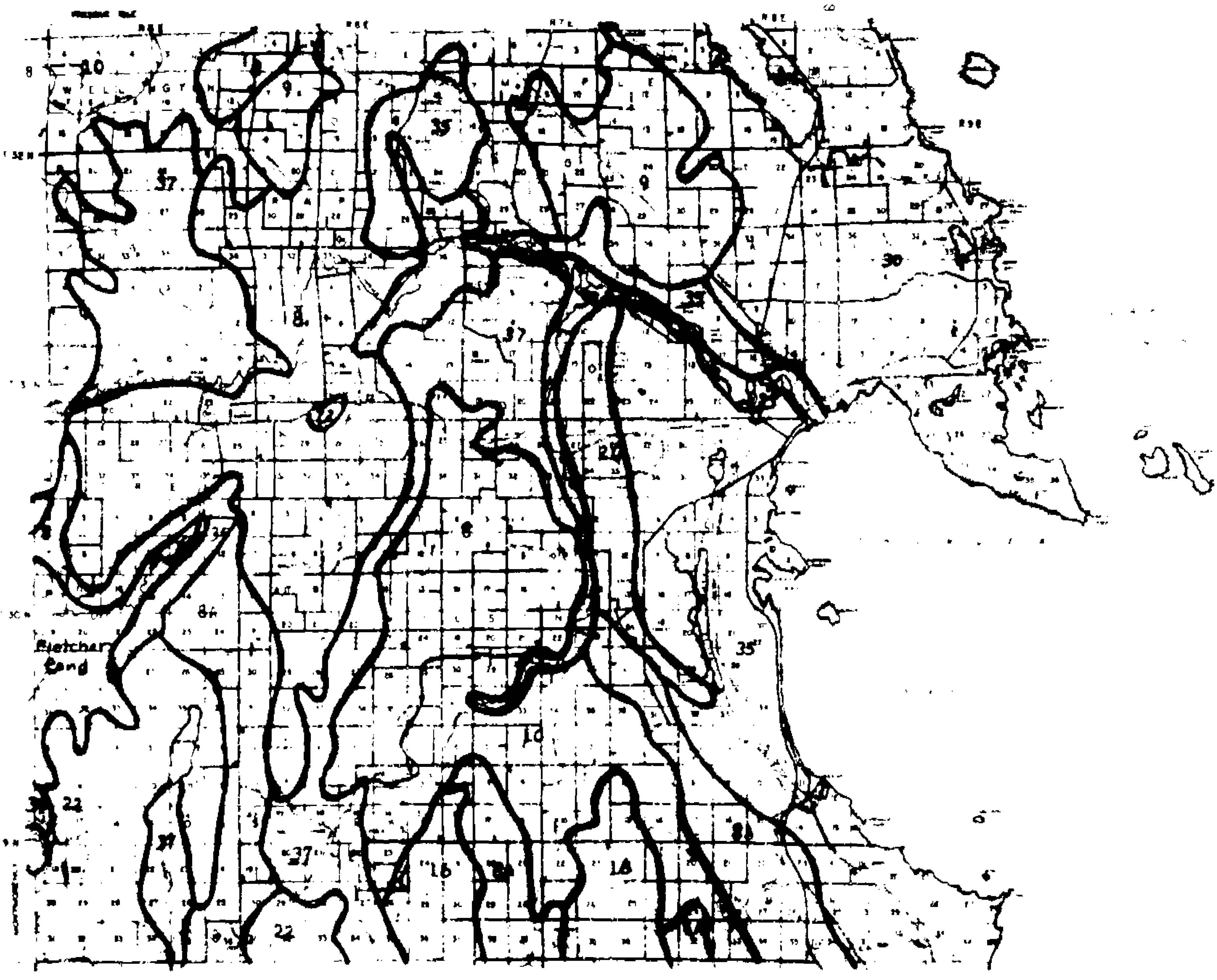


Figure 28. General Soil Map - Alpena County

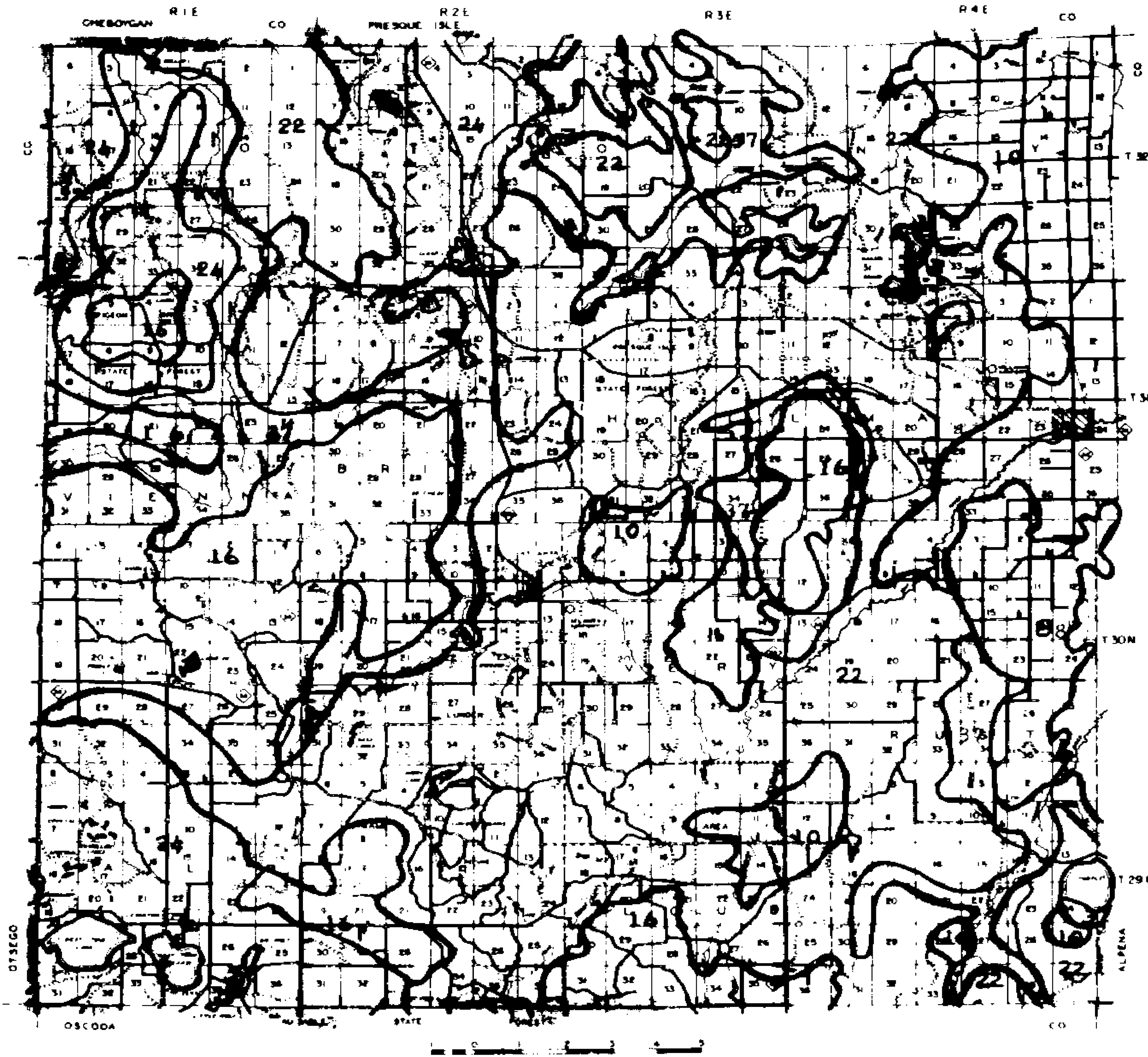


Figure 29. **General Soil Map** - Montmorency County

water. The major soil types on the main branch and the tributaries of the Thunder Bay River are given in Table 33 and described in Table 34.

The erosion of the stream banks on the main branch in most cases appears to be natural. Since most of the eroded banks are clay soils, this influences the turbidity, as the clay sediments are not soluble. In some places, sandy soils overlay clay soils and there appears to be some leaching out of the lower clay soil. The clarity of the water on the Upper and Lower South Branches is quite good with any loss of clarity being caused by siltation coming from the low banks lining the rivers.

WATERHOLDING CAPACITY

Both the behavior of water, falling on the earth's surface, and its subsequent quality is influenced by soils. The texture of the soils determines the rate at which water can flow through it. Water will percolate fairly rapidly through sand but only very slowly through clay. The rate of percolation influences surface run-off and stream flow patterns. These soil characteristics are important as far as suitability for operation of home sewage disposal systems.

The waterholding capacity of the soils in the Thunder Bay basin varies from 2.5 to 4.0 inches near the bay, to 5.0 to 8.5 inches inland. Soil infiltration rates are 1.0 to 2.0 inches per hour inland and 8.0 to 12.0 inches per hour near shore. The zones are shown in Figure 30 and described in Table 35.

WATER AVAILABILITY

From bedrock deposits along shoreland, most of the area wells in the bedrock will yield water that is too highly mineralized for

Table 33

Major Soil Types on Principal Thunder Bay Tributaries

Lower South Branch

Selkirk Loam, Ogemaw Sandy Loam, Roselawn Sandy Loam
Lupton Muck, Granby Sand, Saugatuck Sand, Roscommon Sand

Upper South Branch

Rifle Peat, Roseland Loam, Bergland Clay Loam, Onaway Loam
Emmet Sand, Mackinaw

North Branch

Ogemaw Sandy Loam, Granby Sand, Roselawn Sand, Grayling Sand
Selkirk Silt Loam, Bergland Clay Loam, Longrie Loam, Kent Loam

Wolf Creek

Rifle Peat, Roselawn Sand and Loam, Selkirk Loam, Onaway Loam
Carbondale Muck, Roscommon Sand

Bean Creek

Lupton Muck, Selkirk Loam, Onaway Loam, Bergland Clay Loam
Emmet Sand, Mackinaw

Hunt Creek

Grayling Sand, Rubicon Sand, Onaway Loam, Selkirk Loam

Gilchrist Creek

Grayling Sand, Rubicon Sand, Selkirk Loam, Emmet Sandy Loam
Bergland Clay Loam

Main Branch

Ogemaw Sandy Loam, Granby Sand, Onaway Sandy Loam, Rubicon Sand
Summerville Stony Loam, Selkirk Silt Loam, Bergland Clay Loam,
Grayling Sand, Kent Sandy Loam, Carbondale Muck

Table 34

Thunder Bay Watershed Soil Types

Light Sandy Soils

Roselawn Sand

Yellowish-brown sand on pale yellow sand, rolling to hilly, with very free natural drainage. Soil and subsoil low in lime and natural fertility. This type includes small areas which have patches and layers of reddish sandy clay in the lower subsoil.

Rubicon Sand

Deep, comparatively dry sand, well to moderately well-drained on level topography; highly acid in reaction with low fertility.

Saugatuck Sand

Wet, sandy soil characterized by a sandy hardpan or orstein layer; medium to fine sand in texture, strongly acid in reaction with low fertility. Land is flat, wet, and swampy with heavy growth of natural vegetation.

Eastport Sand

Gray sand on yellow sand, nearly level with free natural drainage. Soil and subsoil usually high in lime, never more than slightly acid. Low in natural fertility.

Granby Sand

Shallow black mucky soil on wet pale yellow or gray sand. Level to nearly level. Occupies wet sandy flats and depressions or swamp and marsh borders. Slow to poor natural drainage but better drained than the deep swamp soils. Seldom low in lime. Low to fair natural fertility.

Lake Beach

Sandy, muddy or stony lake margin which is subject to the action of storm-driven waves or ice.

Light Loam Soils

Roselawn Sandy Loam

Grayish brown (gravelly) sandy loam over reddish-brown sandy clay. Rolling to hilly. Natural drainage is good to free. Surface soil low in lime. Deep subsoil moderately high in lime. Fair natural fertility.

Ogemaw Sandy Loam

Gray-brown sandy loam over reddish sandy clay. Nearly level to level. Includes low, dry sandy mounds and small wet depressions and narrow swales. Surface soil low in lime. Clay subsoil high in lime. Natural surface drainage fair. Underdrainage is slow due to tight, clayey subsoil. Fair natural fertility.

Table 34 (Cont'd)

Emmet Sandy Loam

Well-drained soil of better grade land; light sandy in texture, underlain by gravelly or stony sand-clay mixture; reaction is acid for clay substratum Gently rolling land.

Medium Loam Soils

Onaway Loam

Gray-brown loam on compact reddish-brown pebbly sandy clay. Gentle rolling to rolling. Good natural drainage Surface soil moderately low in lime Clay subsoil high in lime Good fertility.

Posen Stony Loam

Gray-brown stony loam on limestone bedrock. Undulating to gentle rolling Good natural fertility Surface soil and subsoil high in lime Natural drainage fair to good.

Summerville Stony Loam

Shallow, brown, stony loam on limestone bedrock. Flat shelf-like outcrops of the bare limestone bedrock are common Natural drainage fair to good. Soil is high in lime. Good natural fertility

Kalkaska Loamy Sand

Lighter and deeper sandy soil of the sand plains and valley areas; possesses a dark brown layer which underlies the gray leached layer and with light cementation; not highly fertile. Moderate to strongly acid in reaction and well-drained.

Heavy Loam Soils

Selkirk Loam

Gray-brown loam on reddish-brown gritty sandy clay Undulating to smooth rolling Fair to good natural drainage. Surface soil generally low in lime Clay subsoil high in lime. Moderate to very good natural fertility

Selkirk Silt Loam

Gray-brown silt loam on heavy red clay Includes spots and narrow strips of shallow swamp soils Natural drainage slow to fair, due to nearly flat surface and heavy clay subsoil. Surface soil low in lime Clay subsoil high in lime Good natural fertility.

Stream Bottom Soils - Lupton Muck

Black or brown loamy muck; comparatively fine textured showing marked decomposition, neutral or slightly acid to high lime

Table 34 (Cont'd.)

Swamp and Marsh Border Soils

Granby Sand

Shallow black mucky soil on wet pale yellow or gray sand. Occupies wet sandy flats and depressions. Slow to poor natural drainage. Seldom low in lime. Low to fair natural fertility.

Bergland Clay Loam

Shallow black mucky soil on heavy red clay. Occupies clay flats and swales and borders. Slow to poor natural drainage. Usually high in lime. Good natural fertility.

Swamp and Marsh Soils (Rifle Peat and Lupton Muck

Brown or dark brown coarse woody material high in acid organic material underlain by fibrous material. Mineral substratum-sand and peat.

FIGURE 30.

WATERHOLDING CAPACITY IN THUNDER BAY WATERSHED

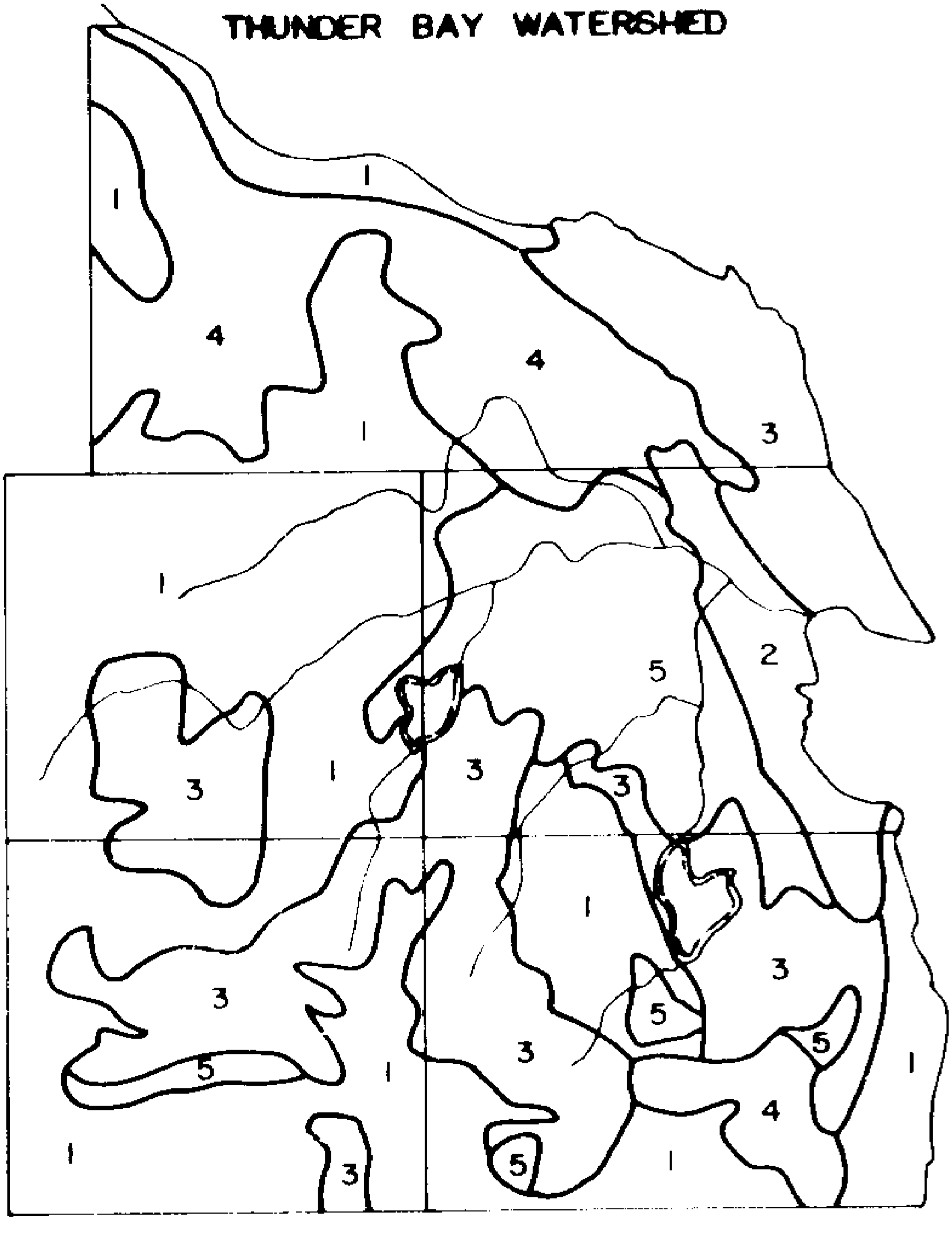


Table 35

Waterholding Capacity

Zone	Waterholding Capacity	Minimum Infiltration Rate
1	2.5 to 4.0 inches	12.0 or more inches/hour
2	3.0 to 4.5 inches	8.0 to 12.0 inches/hour
3	4.0 to 5.5 inches	4.0 to 8.0 inches/hour
4	5.0 to 6.5 inches	2.0 to 4.0 inches/hour
5	6.5 to 8.5 inches	1.0 to 2.0 inches/hour

domestic public supplies. In general, with an increase in depth, the water becomes more mineralized and dissolved solids content of more than 1000 ppm is attained. In places, especially where sand and gravel deposits occur along streams, wells will yield several hundred of gallons per minute.

From the glacial deposits throughout most of the watershed, wells six inches or more in diameter in the deposits will yield from 10 to 100 gallons per minute (GPM). Throughout the remainder of the basin, area wells in bedrock six inches or more in diameter will yield over 100 GPM. The zones are shown in Figure 31 and described in Table 36.

PRESENT FOREST RESOURCES

In the Thunder Bay Watershed, over half of the forest acreage is now of the upland forest types including: white and Norway pine, Jack pine, maples, white birch, aspen, oaks and hemlock. About 25 percent of the land is cleared farmed land, pastured land, and land that is idle.

Approximately 20 percent of the forest cover is of lowland-forest type including: elm, ash, maples, cedar, spruce, balsam fir, and tamarack. The remainder of the forest resources are of marsh and bog types, such as alder, willow, and sedges, and open wildland types which include, fire (pin) cherry, sumac and ferns.

The forest types along the major tributaries are given in Table 37. The descriptions of the major cover types is given in Table 38 (Michigan Department Conservation, 1924).

FIGURE 31.

WATER AVAILABILITY OF THUNDER BAY WATERSHED

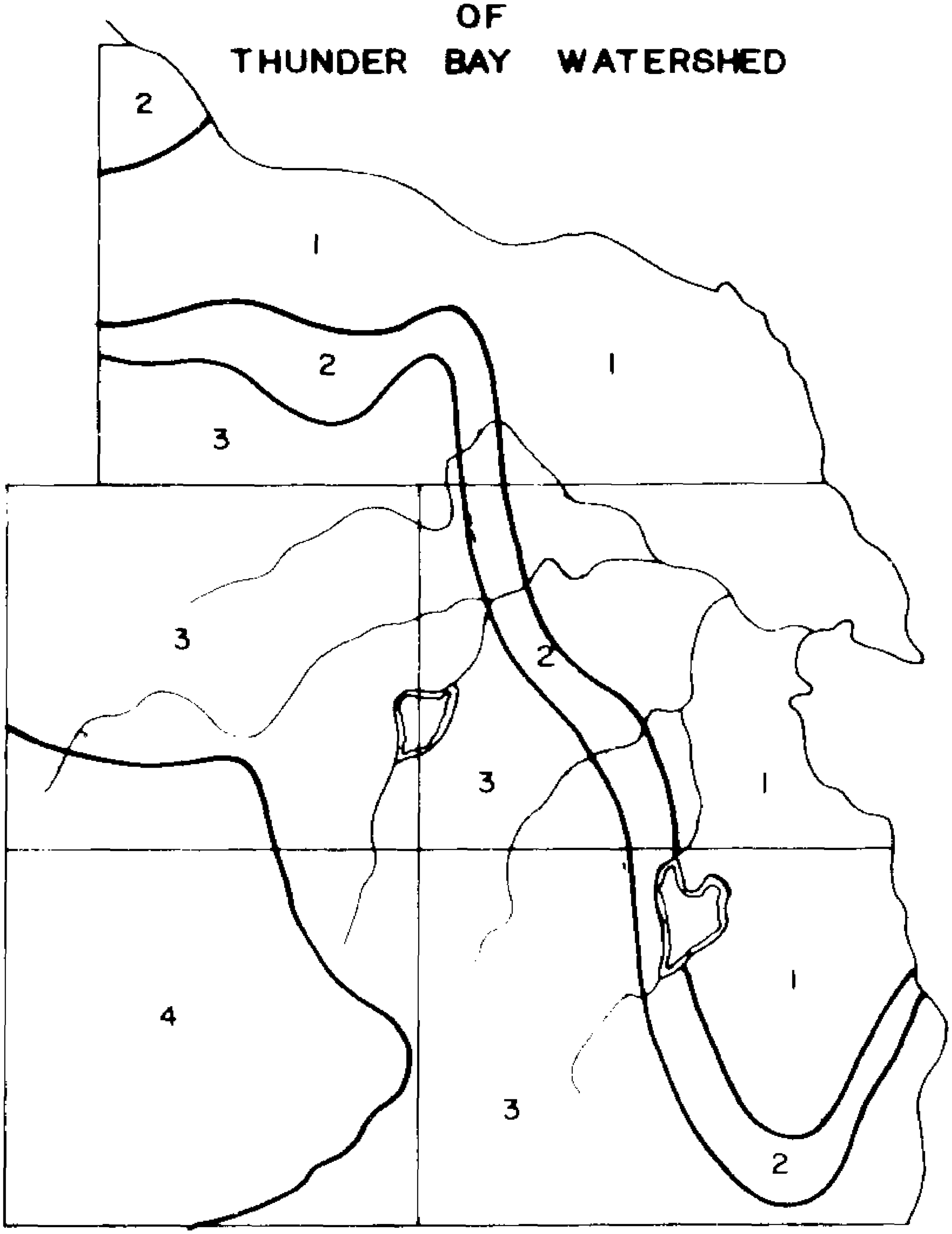


Table 36

Water Availability

Zone 1: Wells 6 inches or more in diameter will yield less than 10 gallons per minute (GPM).

Zone 2: Wells 6 inches or more in diameter will yield from 10 to 100 GPM.

Zone 3: Wells 8 inches or more in diameter will yield from 100 to 500 GPM.

Zone 4: Wells 10 inches or more in diameter will yield more than 500 GPM.

Note: In all areas where sand and gravel deposits occur along streams, the output in gallons per minute will be increased considerably.

Table 37

Forest Types along Principal Thunder Bay Streams

Lower South Branch

Lowland forest types - Maple and spruce
Stands of hardwoods - Jack Pine and white birch
Poplar (aspen) and some elms

Wolf Creek

White cedar, spruce, poplar, and white birch

Upper South Branch

Lowland forest types - Maple, cedar, and spruce

North Branch Thunder Bay

Poplar, white birch, maple, cedar, and balsam fir

Bean Creek

Poplar, white birch, maple, spruce, and cedar

Main Branch Thunder Bay River

Poplar and white birch; elm and maple, Jack Pine, balsam fir, oak, and pine. Cedar and willow

Percentages in Alpena County

(Michigan Conservation Department, 1924)

Forest Types	Per Cent
Aspen and Birch	42.3
Jack Pine	1.2
Cedar and Spruce	10.2
Maple, Hemlock, Ash	13.9
Norway and White Pine	1.0
Northern Oak	8.4
Balsam Fir	0.1
Willow	1.2
Wildland	0.5

Table 38

Forest Cover Types of Thunder Bay Watershed

Aspen(Poplar), Populus tremuloides or Populus grandidentata

The stands occur in small, even-aged clumps. Depending on site, the Aspen reaches maturity in 40-50 years. Much of it dies after that and other species take its place so that it is associated with a large number of other species. Located along the North Branch, Bean Creek and the Main Branch.

White Birch, Betula papyrifera

Species is associated with Jack Pine and Aspen. The tree matures in 60 to 75 years. When it has reached maturity, it will be replaced by other species. Located along Lower South Branch, Wolf Creek, North Branch, Bean Creek, and Main Branch.

Jack Pine, Pinus banksiana

Stands occur in small, aged clumps. Maturity is in 60 to 70 years. It is also associated with a large number of other species in drier areas. Located along Lower South Branch, and Main Branch.

Northern White Cedar, Thuja occidentalis

Species is found on wet sites in pure stand, or generally scattered under Jack Pine and Aspen. The trees mature in 100 to 110 years. Located along Wolf Creek, North Branch, Bean Creek, and Main Branch.

White Spruce, Picea glaoca

Species is found associated with fir and cedar on wet sites. It matures in 60 to 70 years. Located along Bean Creek, Hunt Creek, and Main Branch.

Red Maple, Acer rubrum

Species is generally found on wet sites as medium-age tree, maturing in 100 to 110 years. Located along Upper South Branch, Bean Creek, Gilchrist Creek, and Main Branch.

White Pine, Pinus strobus

Nearly all has been lumbered and found mixed with other species. Maturity is reached in 170 to 180 years. Some located along Main Branch.

Balsam Fir, Abies balsamea

Species is found on wet sites in limited quantities and matures in 40 to 50 years. Located on North Branch and Main Branch.

Northern Oak, Querous ellipsoidalis

This species is found in drier sites associated with many other trees. Located on Main Branch.

Table 38 (Cont'd.)

Alder, Alnus incana
Brush species.

Willow, Salix sp.
Species found as brush or small trees on wet sites scattered among other species. Alder and Willow with Sedges along most stream banks.

Open Wildland Types - Firecherry, Sumac, and Ferns

CLIMATIC CONDITIONS

The mid-continent, mid-latitude position occupied by the Great Lakes area results in varying extremes in weather conditions. The climate along the immediate Lake Huron shore is semi-maritime and lacks most of the temperature-variations shown in many cases only a few miles inland (U. S. Department of Commerce, 1967).

Temperature

The early winter temperatures are higher than are common to this latitude but, as the Great Lakes freeze, the temperature commonly approaches zero Fahrenheit. Thunder Bay and the Thunder Bay River are usually free of ice by the first week in April. The average date of the last killing frost is May 12. The growing season is 100 days. The average date of the first killing frost in autumn is October 4. The mean annual temperature is 43.6F with a high of +106F and a low of -36F over the past ten years (Table 39) (U. S. Department of Commerce, 1971).

Precipitation

Precipitation is well-distributed throughout the year. The most probable annual mean-precipitation in northern Michigan is 30.60 inches (Water Resources Commission, 1968). For the Alpena area, the annual mean-precipitation is 28.80 inches, with 16.8 inches from May to October (Velz and Gannon, 1960). The spring thaw and run-off seldom offer any flood danger because of the operation of hydroelectric dams.

The annual snow-fall averages 50 to 90 inches. The mean temperature, total precipitation, and wind direction for Thunder Bay, together with high and low yearly temperatures for duration of this study, are given in Table 40. The monthly range-and-mean

Table 39

Climatological Data for Thunder Bay Area (U. S. Department of Commerce, 1971)

Measurement	Airport	Sewage Plant	Atlanta	Rogers City
Elevation(ft)	690	585	940	1015
1966				
Mean Temp(F)	42.5	43.7	43.9	43.4
Tot Prec(in)	27.32	26.51	22.46	31.21
Temp Hi-Low	98,-15	95,-11	101,-18	96,-6
1967				
Mean Temp(F)	41.2	42.5	42.7	41.6
Tot Prec(in)	35.17	31.69	33.17	29.85
Temp Hi-Low	88,-20	88,-9	89,-24	85,-13
1968				
Mean Temp(F)	43.1	43.9	-	-
Tot Prec(in)	34.05	32.43	32.58	30.40
Temp Hi-Low	95,-21	92,-11	93,-29	93,-10
1969				
Mean Temp(F)	42.2	43.5	-	43.3
Tot Prec(in)	31.42	30.22	28.77	31.31
Temp Hi-Low	94,-10	94,-7	94,-	91,-8
1970				
Mean Temp(F)	42.6	43.8	-	-
Tot Prec(in)	27.12	25.66	26.73	32.10
Temp Hi-Low	92,-23	92,-12	91,-23	89,-18
Mean				
Mean Temp(F)	42.3	43.5	43.3	42.8
Tot Prec(in)	31.01	29.30	29.34	30.96
Temp Hi-Low	93,-18	92,-10	94,-24	91,-11

Table 40

Prevailing Weather Conditions of Thunder Bay

1960-1970

(U. S. Department of Commerce, 1971)

Month	Temperature			Mean Precipitation	Wind Direction
	Min	Mean	Max		
Jan	12.9	19.9	26.8	1.83 in	N-W
Feb	10.8	18.8	26.8	1.56	NW
Mar	18.6	26.5	34.3	1.92	NW
Apr	31.4	39.4	47.4	2.28	W
May	41.6	50.6	59.6	2.92	SE
Jun	51.6	60.9	70.1	3.03	SE
Jul	57.1	66.5	75.9	2.63	NW
Aug	55.8	64.9	73.9	2.87	SW
Sep	49.3	58.0	66.6	3.11	NW
Oct	39.6	47.4	55.2	2.70	NW
Nov	29.4	35.4	41.3	2.41	W
Dec	19.4	25.2	30.9	1.90	N-W
	34.8	42.8	50 7°F	29.16 in	W-NW (8 mo.)

Snow - 79.4 in.

for precipitation recorded at the Alpena NOAA weather station is shown in Figure 32. The monthly total discharge range-and-mean of the Thunder Bay River is shown in Figure 33.

Wind

The winds on the Great Lakes are generally from western quadrants. Across northern Michigan, west-northwest winds are prevalent. On Lake Huron, prevailing winds are from the northwest with the exception of May and June, when southeasterly winds predominate. During July and August, when lake surface temperatures are near their maximum, southeasterly winds occur during the warmest hours of the day.

Over Thunder Bay, the winds may, and often do, blow from several directions because of the frequent passage of cyclones and anti-cyclones. The wind direction is predominantly from southwest-northwest for eight months of the year. For approximately 250 days of the year, the wind is blowing off-shore over Thunder Bay (U. S. Department of Commerce, 1971). Generally, easterly winds off the bay occur during spring and late summer when temperature conditions are favorable.

CURRENT PATTERNS IN BAY

The surface circulations which exists in Lake Huron, appear to be the result of an equilibrium between the flow-through of Lake Michigan and Lake Superior waters and the wind-driven transport of surface water. The fundamental surface circulation pattern in the upper and central portions of the Lake appeared to reflect the direction and velocity of the winds of the preceding twelve years (Ayers, *et al.*, 1956).

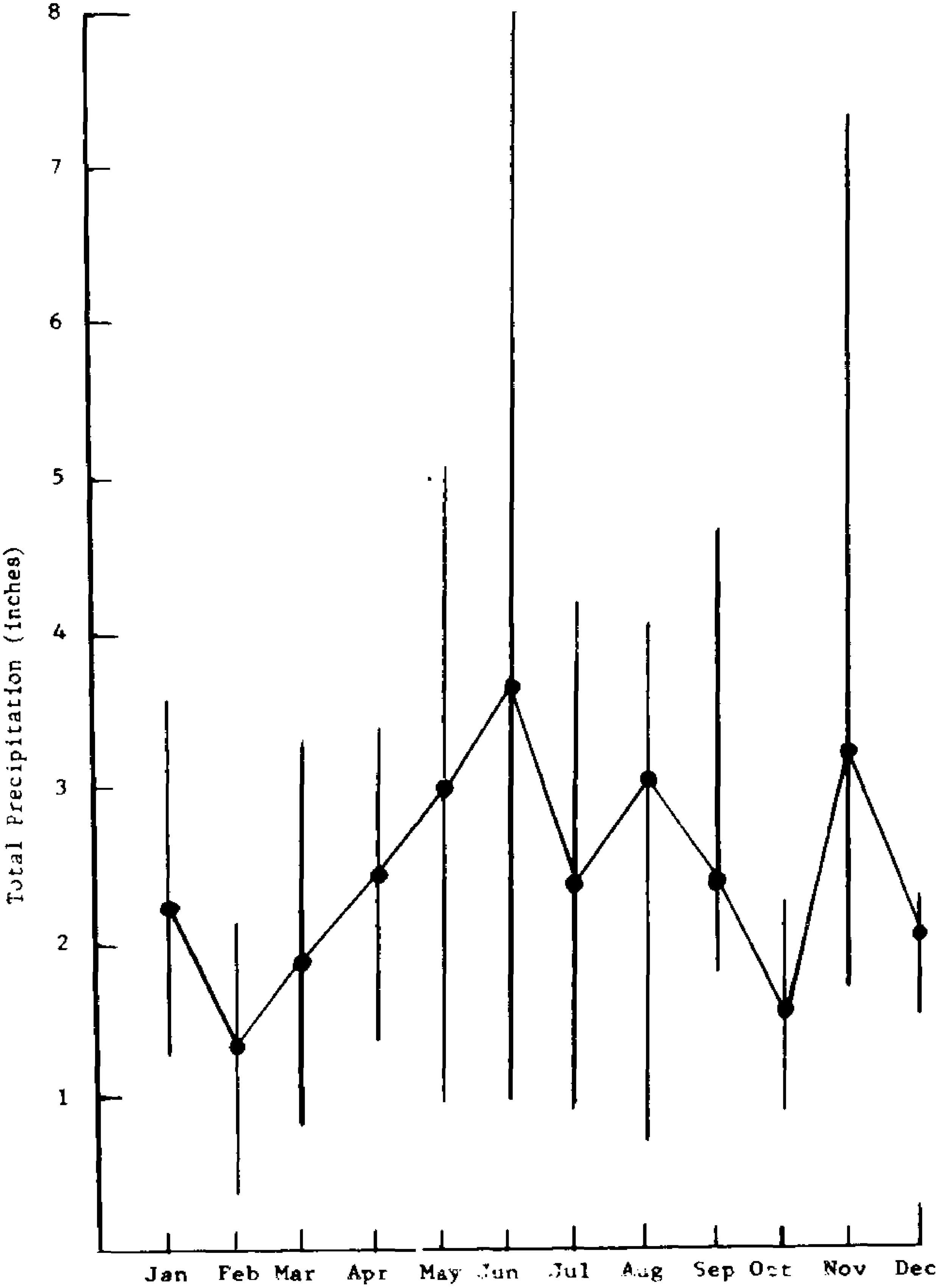


Figure 32. Monthly Precipitation for Alpena, Michigan (1960-1970)

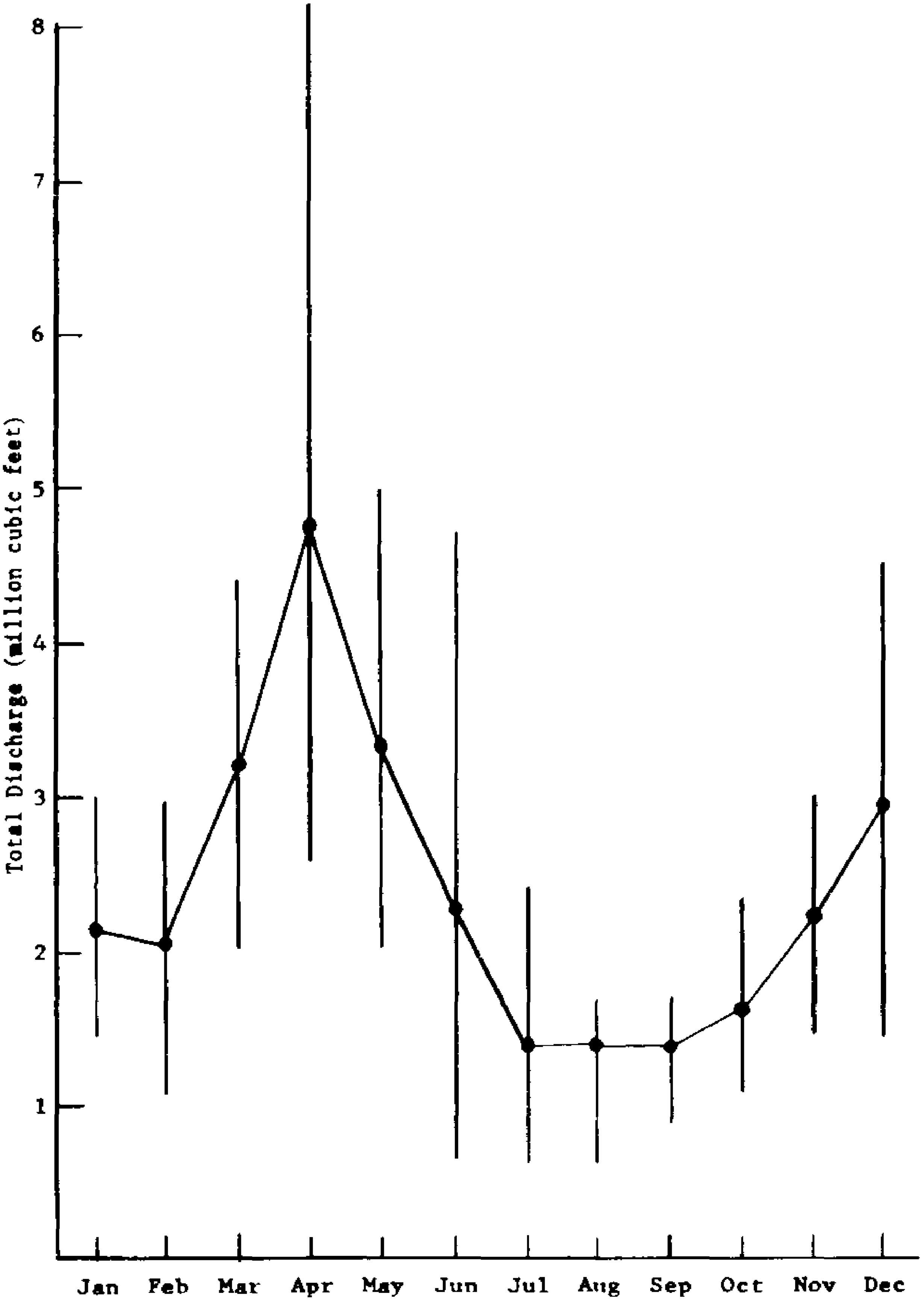


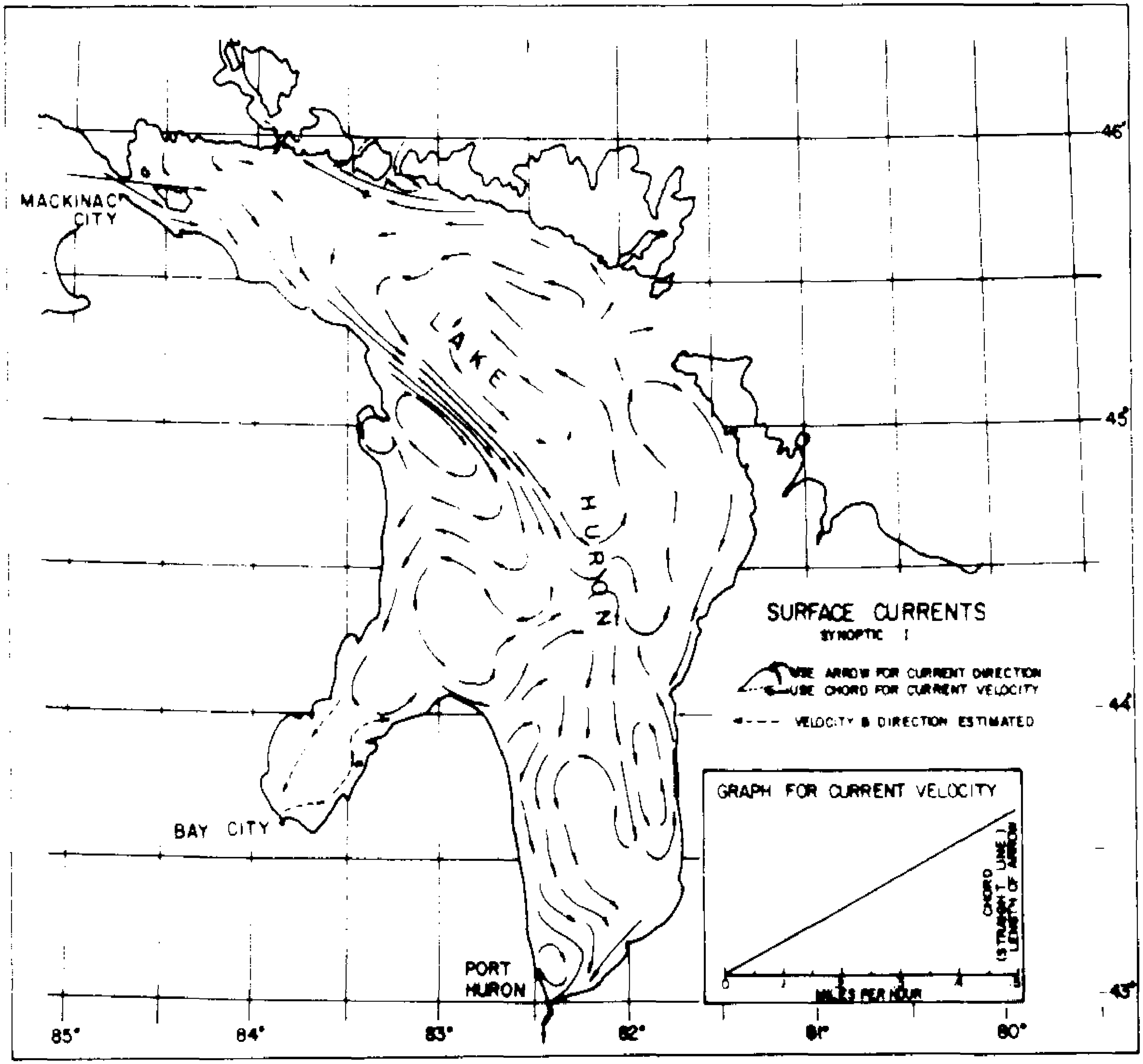
Figure 33. Monthly Total Discharge of the Thunder Bay River at the Ninth Street Dam (1960-1970)

Lake Huron has certain pseudo-oceanic characteristics. These include: (1) the tendency of the strongest currents to swing to their own right (Corioli's Force); (2) the apparent tendency of wind-direction surface water to move to the right of the wind direction; and (3) the distribution of upwelling and sinking of water on both upwind and downwind shores according to the relationship of current streamlines and the shore.

Current velocities in Lake Huron range from 0.1 m.p.h. to nearly 0.5 m.p.h. The fundamental surface circulation patterns in the upper and central portions of the Lake is counterclockwise. A counterclockwise current with a maximum velocity of 0.47 m.p.h. is located off Alpena (Figure 34). There is a smaller northern current contributing to a clockwise eddy centered off Thunder Bay. This current is apparently a simple equilibrium adjustment of the field of density, with its rotation produced by friction of the adjacent rapid current. The equilibrium eddy off Thunder Bay indicates that it acquired wind-driven, warm, surface water from close inshore, through both north and west quadrants of its center. The currents within the bay have been shown by drift bottle data to be counterclockwise because of this flow (Ayers, et al. 1956). The portion of water apparently moving northward along the Oscoda-Alpena shore appeared to be circulating around an elongated eddy and turns back south on the offshore side of the eddy. This flow averaged about 0.26 m.p.h. The thermocline was 5 to 6C at 23 feet off Alpena. A tongue of surface water with temperature greater than 20C extended southeasterly from Thunder Bay.

FIGURE 34.

SURFACE WATER CURRENTS IN LAKE HURON



THE WATERSHED CULTURAL DISCHARGES

In Alpena County, ground water pollution in limestone areas is caused by septic tanks and tile fields. Inadequate land drainage is present in the County and in Presque Isle County. Ground water and watershed management can be used to alleviate these problems.

Wood-Fiber Industry Effluents

Abitibi Corporation has an average discharge of 2.4 m.g.d. This contains organic solids (BOD - 32,000-35,000 lbs/day), suspended solids (5000 lbs/day) and elevated temperature (125F).

The Fletcher Paper Company discharges cooling water (75F) and process water. The process water contains fiber fines and additives (TiO_2, dyes, binders, etc.).

Huron Portland Cement Corporation

The local cement plant has a maximum production capacity of 18 million barrels or 3.4 million tons of cement per year. This amount is produced by three new computer-operated kilns and 16 older kilns. Ten other older kilns are on stand-by. The collection ability of the kilns is 90% efficient using precipitators and dust bags. Over 1000 tons of dust are collected daily in computerized kilns. The same amount is retained in the older kilns that are operating. The emission of dust amounts to an over-all discharge of at least 100 tons per day. This has been monitored by the company and the air pollution division of Michigan Department of Public Health (Dowd, 1971).

The composition of the cement dust used in this study contained the ranges given in Table 41 (Galer, 1970). The distribution of the material over Thunder Bay is dependent upon the direction of local

Table 41

The Mean Composition of Emitted Cement Dust Material
(Galer, 1970)

Substance		Weight Percentage Range
CaO		40-44
Al_2O_3		3.5-6.0
Fe_2O_3		1.5-3.0
K_2O		3.5-6.0
MgO		1-2
Na_2O		0.2-0.3
Silicates		20
(SiO_2	-	12)
Sulfates		18
(SO_3	-	2.5-3.0)
Phosphates		0.5-0.6

prevailing winds during the year (Table 42, U. S. NOAA Weather Bureau, 1971). Once in the water, the physical transfer of material is dependent on the hydrodynamics of the aqueous system. Mixing of sediments in the water arises primarily from wind-induced currents and flow of water from the influent streams and domestic discharges.

The cement plant generates its own power so that there is a cooling-water discharge into the plant's shipping channel. A run-off into the bay occurs from an abandoned quarry where dust from the collectors is disposed of.

Alpena Sewerage System

The sewage system handles an average of 2.5 million gallons per day serving a population of 15,000 in 3600 residential homes with a total of 4500 dwelling units. There is a combined system of sanitary and storm sewers with six lift stations. There are 72 miles of sewer lines with 60 miles combined. Since 1961, all new construction (16.7%) of sanitary and storm sewer lines has been separated.

There are four interceptors located near the river; two on the north side and two on the south side. High storm flows are diverted to the river after an initial flush of the sewage flow to the plant has occurred. The industrial plants supply only sanitary sewage and some cooling waters to the sewage system.

The plant was completed in 1958 and has a nominal capacity of three million gallons per day and a maximum of six million gallons per day to serve 18,000 persons in the city and township. Currently, a sewage plant expansion is under construction to expand service and capacity and to introduce secondary treatment together with chemical phosphate removal.

Table 42

Prevailing Mean Wind Conditions of Thunder Bay
(U. S. NOAA Weather Bureau, 1971)

Month	1960-1970 Wind Direction	1969-1970 Wind Direction	1970-1971 Wind Direction	Temperature Mean °F
Jan	NW	W	NW	19.9
Feb	NW	NW	W	18.8
Mar	NW	NW	W-NW	26.5
Apr	NW	W-SE	S-SE	39.4
May	SE	E	W-NW	50.6
Jun	SE	S-W	S-SE	60.9
Jul	NW	S-W	E-SE	66.5
Aug	NW	S-SE	S-SW	64.9
Sep	NW	SE	N-NW	58.0
Oct	NW	W	S-SW	47.4
Nov	NW	W	W	35.4
Dec	NW	SW	W-NW	25.2
Mean	W-NW(8 mo.)	S-SE(4 mo.)	SW-NW(8 Mo.)	42.8

Mean Precipitation (1960-1970) - 29.16 inches

Snow - 79.4 inches

The waste-water treatment plant how operates as a primary treatment facility with grinders and a grit chamber, sedimentation in holding tanks and bacterial digestion of the raw sewage sludge. The digester sludge is pumped onto outdoor beds several times during the year, allowed to dry, and used for soil rehabilitation.

The resulting effluent is disinfected with chlorine and discharged into the river near the bay mouth. The influent has been estimated to contain a mean total phosphate of 26 ppm (520 lbs/day) and the effluent has a mean of 18 ppm as total phosphate (365 lbs/day). The influent BOD has a mean of 1100 lbs/day while the effluent has a BOD mean of 600 lbs/day (LaMarre, 1971).

THUNDER BAY WATER QUALITY AND RESOURCES

Much of the inorganic materials and some organic matter in natural water arise from the chemical alteration of minerals; e.g. calcium and magnesium are derived from reactions involving, carbonates, feldspars and some clays. Phosphates are derived from apatites and sulfate from pyrite and gypsum. Carbon dioxide in water, dissociates to bicarbonate and carbonate depending on pH and is one of the important variables determining the alkalinity of the water.

The quality of the water in the main body of Lake Huron is excellent, as is that of its two principal sources of water, Lake Superior and Northern Lake Michigan. Since Lake Huron derives its water initially from these lakes, it is assumed much of its chemical character should be determined by the rates of mixing of Michigan and Superior waters. Lake Superior has an average discharge of 73,300 c.f.s. through St. Mary's River, while Lake Michigan has an average discharge through the Straits of Mackinaw of 55,000 c.f.s.

Lake Huron waters are low in turbidity and moderate in hardness. For the most part, the dissolved oxygen content is nearly 100 percent saturation. In northern Michigan, there has been no effective change in land use. These lands have remained for the most part forested, with second growth having replaced most of the original timber. The soils of the region have low water-holding capacity and maximum filtration rates. The streams draining this area are stable throughout the year, mostly very clear, and are low in concentrations of chemical constituents. This continues to provide a source of high quality waters to Northern Lake Huron.

Calcium, magnesium, and alkalinity account for 75 to 80 percent of the ions in Lake Huron waters. This is due directly to the approach to equilibrium of carbon dioxide from the air and $CaCO_3$ in the sediments (Kramer, 1964). Lake Huron water tends towards partial equilibrium along its length and attains a true equilibrium after passing into the Lake St. Clair system. The Lake appears to be unsaturated with respect to sodium and silica.

There is excess phosphorus in the lake compared to that which is needed to saturate apatite. Excess phosphorus increases with biological use of the lake with the difference of actual phosphate and 'hydroxy-apatite phosphate' being an empirical index of biological activity.

Hydroxyapatite, although relatively quite insoluble in aqueous medium, exists in chemical equilibrium with orthophosphate ions. If other chemical and physical environmental requirements of algae are satisfied, the utilization of orthophosphate ions by a growing algal culture can bring about the continual release of soluble phosphate from hydroxyapatite as chemical equilibrium is maintained.

Chemically 'insoluble' phosphate materials can be sources of biologically available phosphate ions. As an increasing algal population utilizes the soluble phosphate, chemical equilibrium is maintained by the release from the parent compound of additional phosphate ions into solution.

In Thunder Bay, trawling temperatures range from 10C to 20C at 5 fathoms, and 5C to 10C at 10 fathoms (60 feet). Temperature apparently does not rise above 6.5C at 15 fathoms or beyond (KAHO, 1969). Ayers et al. (1956) has found a temperature range of 5.8C to 20.0C in Thunder Bay.

Ayers et al. (1956) found a mean secchi value of 7 inches in Thunder Bay. They found a calcium mean of 22.20 mg and a magnesium mean of 6.4 mg. They found a conductivity mean of 161 micromhos/cm while Kramer (1964) measured a conductivity range of 140 to 145 in Lake Huron. Results for analysis in Thunder Bay are given in Table 43 and the results for study of Lake Huron parameters is given in Table 44.

The plume of Thunder Bay River into the bay can be seen visually and from aerial photographs over the bay as shown in Figure 35 at an altitude of 3000 feet.

Living Systems in Thunder Bay and River

Highly diversified benthic communities containing many clean water forms have been found in the majority of Thunder Bay. Mayflies, caddisflies and amphipods, common inhabitants of natural inshore populations in Lake Huron near Alpena, are widespread.

Table 43

Thunder Bay Water Quality

Study	Secchi (ft)	Current (ft/min)	Depth (ft)	Temp (C)	Ca (mg)	Mg (mg)	Cond (uohm/cm)
Ayers			0	12.4	23.50	6.6	161
I	7	-	50	11.9	23.40	6.7	162
			75	10.6	24.20	6.7	166
Ayers		NE	0	19.5	21.50	5.7	159
II	12	20	50	17.9	20.60	5.8	156
			73	16.8	20.60	6.0	157
Ayers			0	20.0	-	6.2	155
III	9	NE	50	10.0	22.45	7.6	167
			68	5.8	21.35	6.3	166

Michigan Water Resources Commission

Year	Secchi (ft)	Temp (C)	Ca (mg/1)	pH	Hard (mg/1)
1957-1965	2-12	-	-	-	-
1967	-	9.0	26.00	7.8	113

Table 44

Lake Huron Water Quality
(Kramer, 1964)

Parameter	Mean Value
Calcium	23.0 ppm
Magnesium	6.3 ppm
Sodium	2.4 ppm
Potassium	1.1 ppm
Sulfate	9.0 ppm
Alkalinity	82 ppm
Phosphorus	10 ppb
Silica	2.3 ppm
pH	8.1

Figure 35. Areal Photograph of Thunder Bay

The populations of bottom animals in the bay, around the Abitibi discharge off the river mouth, were composed almost exclusively of pollution tolerant organisms, primarily tubificids (sludgeworms) (Fetterlof, et al., 1968).

Species diversity and percent of sludgeworms in the area outside of the river influence, substantiates that environmental conditions are adequate for intolerant, clean-water forms. In the river, benthic samples, taken above the main sources of organic wastes, consistently contained normal faunal communities composed of a large variety of organisms. Certain components of these communities indicated clean-water conditions. Samples from the river, below Fletcher Paper Company waste discharge and below sewage plant discharge show a definite decline in the quality of the benthic fauna between 1957 and 1965 (Fetterlof, et al., 1968).

In the KAHO (1969) studies, a thermocline often appeared in the echo tracings. Fish concentrations were evident where the thermocline touched bottom. Yearlings and adult alewife were abundant in Thunder Bay (4000 to 9000 for 10-minute trawl catches). The spawning of alewife occurred frequently in the well-defined protected areas of the bay. Both adults and yearlings were at most depths, but were segregated spatially from one another, perhaps in schools.

Small numbers of smelt were captured in the Thunder Bay proper, but the catch increased to 1200 for a 10-minute trawl at 40 fathoms. The size of smelt increased with depth, and lakeward movement of the various size groups took place throughout the summer. Only 150 yearlings were netted, and 7500 adults were taken in deeper water.

Both fourhorn and slimy sculpins were observed, with the fourhorn species being more prevalent (434 to 145 for 10-minute trawls). The trawl catches of ninespine stickleback were extremely variable. The occasional peaks of 4000 to 7000 per 10-minute trawl were the largest catches recorded. In Thunder Bay, there appeared a distinct offshore, deeper shift of the large populations as the summer progressed. Other fish occasionally observed were spot-tail shiner (0 to 24 per 10-minute trawl) and trout perch (138 to 496 per 10-minute trawl). Individual species recovered were: bloaters (74), shortnose cisco (4), round whitefish (2), white suckers (7), and Johnny darters (19).

The Department of Natural Resources has planted Coho and Chinook salmon, rainbow trout, and brown trout in the river and in the bay during the past four years. The Fisheries Department of Alpena Community College has planted the Donaldson strain of Chinook salmon during this period. During the spring and fall for the past two years, a well-established migrational run has been occurring for both trout and salmon in the river and along bay shoreline.

Mears (1969) has studied the living systems of the Oxbow reservoir and Besser Lake waters behind the Ninth Street Dam. He found a total of nineteen genera of aquatic plants including three algae species. Thirty-four families, thirty-nine genera, and fourteen species of invertebrate animals were collected. Tendipedidae were the most commonly collected organisms, while Coenagrionidae were second in abundance. Several invertebrate taxa were collected. Freshwater sponge colonies were numerous and large in size.

The species of fish in the waters were typical of a backwaters impoundment and included: yellow perch, rockbass, red horse, carp, pumpkinseed, Northern pike, black crappie, bluegill, bowfin, bullhead (yellow and brown), smallmouth and largemouth bass, white sucker, burbot, mudminnow, northern redbelly dace, golden shiner, creek chub, banded killifish, brook stickleback, and Johnny darter. Many of these species have been caught or observed in the river, impoundments, lakes and tributaries of the Thunder Bay Basin during the course of the study. These organisms should be typical of those present throughout the watershed.

SUMMARY OF THUNDER BAY WATERSHED RESOURCES

The watershed or drainage basin of a river comprises all the land that contributes to the river's flow. The Thunder Bay Watershed has its surface water sources from both swampy land areas and groundwater springs. The groundwater flows from both limestone and shale formations, resulting in fairly hard water with significant amounts of soluble calcium. The presence of highly mineralized water from wells in the watershed adds to the hardness and alkalinity of water reaching the river.

The land resources of the watershed reflect the variety of natural and cultural development that has progressed in northern Michigan. The soils in the Thunder Bay Basin are as varied as most watersheds, ranging from porous sands to impervious clays. The loams are being used for farm purposes. These soils determine the water quality of the natural water that reaches the watershed.

Organic soils, with a fair amount of humus and low waterholding capacity, are present along several main tributaries (North Branch, Bean and Wolf Creek). With over one-fourth of the vegetation being swamp and marsh type, streams of highly colored natural water are prevalent (Table 45). There is a substantial amount of colored water reaching the main river and Thunder Bay.

Table 45

The Color of Thunder Bay Yellow Organic Natural Acids

Site	Stream	Location	Method	Fall/69	Fall/70	Win/70	Sum/71	Fall/71	Mean
1	Main Branch	Mouth	Fluor*	42.0	7.0	-	-	-	24.5
			Semen#	-	7.2	21.9	35.6	57.1	23.0
2	Main Br.	9th St.	Semen	-	3.2	50.1	29.4	10.9	23.2
4	Lo.So. Br.	M32	Semen	-	2.8	3.0	12.7	17.5	9.0
6	Wolf Cr.	Mouth	Fluor	40.0	-	21.3	-	-	30.7
			Semen	-	15.5	25.3	18.8	40.7	25.1
7	Bean Cr.	M32	Semen	44.0	58.0	56.0	59.0	48.2	53.0
8	Up.So. Br.	M32	Semen	-	11.3	22.0	10.0	14.4	14.4
10	Main Br.	Hillman	Semen	-	3.5	21.9	31.4	46.5	25.8
13	Gilchrist	M33	Semen	-	8.0	13.2	6.0	8.8	9.0
15	Main Br.	Atlanta	Semen	-	11.1	26.3	22.0	33.8	23.3
17	No. Br.	Rush Lake	Semen	-	12.0	-	65.0	14.4	30.5
18	No. Br.	Mouth	Semen	-	9.0	53.8	55.0	58.5	49.8

* Turner Fluorometer

\# Semenov, _et al._, 1963 (Color as Carbon in mg/l)

The climate of the Thunder Bay Basin is typical of northern latitudes and reflects the moderating effects of the large water masses of the Great Lakes. The precipitation is well-distributed throughout the year. The water run-off in the major streams is controlled by hydroelectric and lake-leveling dams (Table 46). The major current patterns in Thunder Bay and the river plume tend to distribute the constituents of the air and water out into the bay waters and south from the mouth of the main branch.

The cement plant emission has a significant amount of particulate matter that reaches the bay and river. The westerly wind direction carries the cement dust over Thunder Bay, the majority of the year. The high calcium composition of the cement dust contributes to the fixation ability of the particles.

The sewage effluent is a major contributor of nutrients and organic materials (Tables 47 and 48) to the river and Thunder Bay. The phosphate levels are typical of a primary treatment plant and could lead to accelerated eutrophication of the bay when available to the aquatic organisms. Both wood-products industries are currently contributing a high organic load to the river but their discharges are being corrected as to unnatural composition.

Even with these prevalent discharges, the quality of the Thunder Bay has remained fairly high except for coliform count (Table 49) and specific instances of benthos degradation near the wood-products discharges. Intolerant, clean water forms have been found above and outside of the influence of these discharges in the river and bay.

The fish populations of Thunder Bay reflect the influence of the alewife and the spawning habits of small and large lake-run species.

Table 46

Total and Mean Discharge of Thunder Bay River at Ninth Street Dam

(Alpena Power Co., 1971)

Year	Mean	River Flow (Cu.Ft.x10^6)			Mean Discharge (CFS)			Hydro KWH (10^6)
		Turbines	Spillways	Total	Turbines	Spillways	Total	
1967	Ann.	30,137	9,326	39,463	11,484	3,578	15,063	40.6
	Mon.	2,511	777	3,288	957	298	1,222	3.4
1968	Ann.	28,963	2,479	31,422	10,983	936	11,940	39.1
	Mon.	2,616	207	2,620	917	78	995	3.3
1969	Ann.	30,362	6,786	37,148	11,568	2,568	14,160	41.7
	Mon.	2,530	566	3,096	964	214	1,180	3.5
1970	Ann.	24,640	3,200	27,840	9,400	1,234	10,634	33.7
	Mon.	2,053	267	2,320	783	103	886	2.6
	Daily	67.5	8.8	76.3	26	4.0	30	0.092
1971	Ann.	27,372	10,983	38,355	10,387	4,188	14,575	37.7
	Mon.	2,280	915	3,196	866	350	1,215	3.1
	Daily	75	30	105	28.4	11.5	40	0.103

Table 47

Alpena Sewage Plant-Physical Analysis of Composite
(LaMarre, 1971)

Month	Range	Dischg. MGD	pH	BOD (mg/l)		Susp.Solid (mg/l)		Deter ppm	Type of Effluent
				In	Out	In	Out		
9/69	Mean	2.27	-	1920	1080	1030	720	-	Out
9/70	Mean	2.30	-	2150	1500	3130	1450	-	Out
10/70	Mean	1.93	-	2400	1370	-	-	-	Out
11/70	Mean	2.17	-	2650	1165	-	-	-	Out
12/70	Mean	2.56	-	1930	1220	1670	790	-	Out
1/71	Max	1.95	7.50	1840	1380	1610	870	-	Out
	Min	1.61	7.28	1650	1370	1130	540		
	Mean	1.82	7.36	1767	1377	1363	675		
2/71	Max	2.48	7.52	2260	1590	3860	2200	-	Out
	Min	1.61	7.22	1620	1220	1020	570		
	Mean	1.98	7.42	1968	1422	1766	996		
3/71	Max	5.06	-	2460	1590	4040	3380	1.20	Out
	Min	2.76		1680	740	1660	890	.73	
	Mean	3.82		2038	1216	2518	1890	.95	
4/71	Max	5.23	7.72	2090	1280	3360	1980	-	Out
	Min	3.49	7.40	910	750	690	360		
	Mean	4.64	7.59	1536	1106	2030	1175		
5/71	Max	5.06	7.50	2960	1670	10010	4400	-	Out
	Min	2.54	7.20	760	340	680	550		
	Mean	3.67	7.30	1776	1132	3402	1770		
6/71	Max	4.95	7.85	2110	1690	2100	930	-	Out
	Min	3.40	7.41	1080	930	990	370		
	Mean	4.28	7.63	1595	1310	1545	650		
6/71		-	7.50	-	-	-	-	-	In
7/71	Max	4.10	7.52	1700	1270	19460	8880	-	Out
	Min	2.84	6.70	980	600	1440	500		
	Mean	3.36	7.21	1012	945	6475	2808		
7/71		-	7.39	-	-	-	-	-	In

Table 47 (Cont'd.)

Month	Range	Dischg. MGD	pH	BOD (mg/l) In	BOD (mg/l) Out	Susp.Solid (mg/l) In	Susp.Solid (mg/l) Out	Deter ppm	Type of Effluent
8/71	Max	3.77	7.27	2330	1580	4440	2720		
	Min	2.39	7.10	1520	990	740	360	-	Out
	Mean	3.07	7.19	1930	1300	3526	1200		
8/71		-	7.10	-	-	-	-	-	In
9/71	Max	3.21	7.54			5460	2090		
	Min	2.52	7.25			1770	800	-	Out
	Mean	2.88	7.39	1180	1150	3615	1445		
9/71		-	7.20	-	-	-	-	-	In
10/71	Max	2.20	7.56	1930	1170	1760	630		
	Min	1.55	6.58	1390	770	560	370	-	Out
	Mean	1.81	7.08	1660	970	1180	520		
11/71	Max	1.92	7.10	4310	1480	1930	990		
	Min	1.56	6.80	1720	1150	950	310	-	Out
	Mean	1.73	6.96	2460	1390	1480	700		
12/71	Mean	3.34	7.00	1590	1050	1080	795	-	Out

Table 48

Alpena Sewage Plant-Chemical Analysis (mg/1) of Composite

Month	Range	Cl^-	Sol. PO_4	Tot. PO_4	NH_3	NO_3	Hard	Alk	Ca	Type of Effluent
9/69	Mean	-	-	18.0	-	-	145	-	-	Out
9/70	Max			30.0	14.0					
	Min			10.3	9.6					Out
	Mean	89	8.0	17.1	11.8	0.50	-	-	50	
10/70	Max	116	19.2	43.0						
	Min	97	14.0	21.5	-	-	-	-	-	Out
	Mean	106	17.2	31.0						
11/70	Max		15.0	32.0						
	Min	-	12.0	20.3	-	-	-	-	-	Out
	Mean		13.5	27.0						
12/70	Max		13.0	36.0	15.5	0.77				
	Min	-	5.0	11.2	4.4	0.46	-	-	-	Out
	Mean		11.9	24.7	8.7	0.59				
1/71	Max	312	15.5	31.5	13.5	0.37	204	196	52	
	Min	125	10.2	19.5	5.2	0.32	146	146	38	Out
	Mean	212	12.5	24.0	8.8	0.34	180	175	46	
2/71	Max	390	18.5	27.0	19.3	1.05	288		120	
	Min	92	12.5	19.0	14.0	0.78	229	-	76	Out
	Mean	160	16.3	23.9	16.3	0.89	264		96	
3/71	Max	255	22.0	30.0	10.5	1.05	337	240		
	Min	161	4.3	9.8	4.0	0.62	287	217	-	Out
	Mean	219	11.4	19.1	6.1	0.78	313	228		
4/71	Max	285	8.2	16.0	2.4	1.46	354	255		
	Min	170	4.5	9.2	0.5	0.90	262	222	-	Out
	Mean	206	5.8	11.7	1.5	1.12	318	234		
5/71	Max	245	11.7	20.5	6.0	2.95	353	232		
	Min	122	5.7	10.2	4.0	0.40	270	152	-	Out
	Mean	176	9.0	17.2	5.1	1.03	309	211		
5/71		121	4.7	10.2	5.8	1.18	282	242	-	In
6/71	Max	220	8.7	22.5	8.8	0.94				
	Min	130	7.5	11.4	4.5	0.12	-	-	-	In
	Mean	178	8.0	16.1	6.8	0.64				
6/71	Max	235	9.8	18.0	8.5	2.35				
	Min	140	8.1	12.4	5.2	0.90	-	-	-	Out
	Mean	190	9.0	14.3	7.1	1.52				

Table 48 (Cont'd.)

Month	Range	Cl^-	Sol.PO_4	Tot.PO_4	NH_3	NO_3	Hard	Alk	Ca	Type of Effluent
7/71	Max	120	13.7	26.4	10.0	1.07	278	238		
	Min	85	5.4	17.3	6.2	0.22	200	190	-	Out
	Mean	98	10.4	20.5	7.3	0.43	240	208		
7/71	Max	112	15.4	18.6	7.0	0.60	282			
	Min	60	5.4	13.5	6.8	0.20	272		-	In
	Mean	86	10.2	16.0	6.9	0.40	277	238		
8/71	Max	175	15.7	29.2	15.7	0.28	296	242		
	Min	85	5.0	13.2	1.6	0.07	212	177	-	Out
	Mean	134	11.4	10.3	7.7	0.18	238	206		
8/71		130	5.6	20.0	4.7	-	304	263	-	In
9/71	Max	100	8.4	24.6	8.0	0.26	222		55.2	
	Min	75	6.7	18.2	6.5	0.13	195	-	41.7	Out
	Mean	88	7.8	22.4	7.4	0.21	206		48.4	
9/71		80	8.7	29.2	8.7	0.27	220	-	45.8	In
10/71	Max	100	16.5	25.0	15.8	0.30	249			
	Min	80	12.7	16.7	13.7	0.23	244	-	-	Out
	Mean	90	14.0	20.6	15.1	0.26	247			
11/71	Max	300	20.6	32.8	11.7	1.20	310	222		
	Min	110	12.4	28.0	9.6	0.50	242	201	-	Out
	Mean	182	17.8	29.3	10.9	0.82	264	215		
12/71	Max	265	16.1	17.9	9.2	0.58	365	232		
	Min	90	4.4	5.5	1.5	0.21	233	136		Out
	Mean	161	10.4	12.8	5.5	0.42	315	206	154	

Table 49

Coliform (MPN/100 ml) in Thunder Bay

Year	Range	Swim Beach	Bay	River Mouth	River	Intake Beach
Michigan Water Resources Commission						
	Min	36	91	230	360	360
1965	Max	15,000	24,000	46,000	24,000	43,000
	Mean	2,215	5,090	23,115	4,330	4,300
	Min	100	100	360	100	360
1966	Max	1.5×10^6	820,000	300,000	500,000	250,000
	Mean	43,430	48,500	39,800	33,465	15,000
	Min					300
1967	Max	-	-	-	-	980,000
	Mean					8,400

Alpena City Health Department

Year	Range	Swim Beaches	River Mouth	River	Cemetary	Bridges
	Min			1,500	100	
1970	Max	-	-	14,500	2,300	-
	Mean			7,200	970	
	Min	100	600	800	100	80
1971	Max	100	40,000	11,000	12,000	2,700
	Mean	100	14,000	4,400	3,100	1,100

The plankton composition and fish communities of the reservoirs in basin reflect a system which has adequate nutrients and producers to provide a diverse community and extensive population of organisms. The fish species present are typical of a warm-water environment.

Sampling locations in the watershed were selected to give the most representative analysis of the discharge of each of the river systems forming the Thunder Bay Basin. Seven of the stations were on the main branch in order to monitor the effect of various cultural influences on the water quality. Only those tributaries with lengths of ten or more miles were sampled, where flow was significant (Tables 50 and 51). The variety of land, shoreline, and bottom lands of the water courses studied, were representative of various types of natural water sources, from crystal-clear spring-fed streams to slow-moving deep-colored swamp streams.

The parameters measured were defined according to Standard Methods (1965) descriptions and limnological references indicated. These parameters were selected to give an evaluation of the water quality of the streams that comprise the basin. The analytical methods were selected for the reproducibility and acceptability of the procedure, as well as, the availability of appropriate materials and instruments. These methods followed procedures taken from Standard Methods (APHA, AWWA, USPH, 1965), as well as, FWQA (1970), and Hach (1967) methods.

The physical analysis data for the station (Br3) at the river mouth, was slightly higher in values than that measured by Michigan Water Resources Commission (1971) (Tables 52 and 53). The comparisons of means were: water temperature of 11.6C and 7.7C, pH of 7.66 and 7.93, and suspended solids of 19.5 mg/l and 9.0 mg/l, respectively.

Table 50

Thunder Bay Watershed Discharge Data

(U.S. Dept. Interior, 1966-1967)

Water Course	Location	Drainage Area (sq. mi.)	Altitude (ft.)	Mean Discharge (CFS)	Max Gage Ht. (ft.)	Max-Min CFS
Main Branch	M-32	232	760	208 (1945-1967)	9.63 (5/11/63)	1380 - 98 (4/12/47-8/7/49)
Main Branch	Herron Road	588	672	438 (1945-1967)	9.99 (4/13/65)	4070 - 92 (4/13/65-9/28/55)
North Branch	Male Corners	184	675	102 (1945-1966)	7.93 (4/13/65)	2920 - 0.40 (4/13/65-10/14/55)
Upper So. Br.	Lachine	171	-	108 (8 yr. avg.)	-	450 - 0.70
Lower So. Br.	Hubbard Lake	146	-	104 (8 yr. avg.)	-	660 - 0.00

Water Course	Location	Range	Water Year 1965-1966	Water Year 1966-1967
Main Branch	M-32	Max	560 CFS	903 CFS
		Min	118	136
		Mean	199	248
		Cfsm	0.858 (11.63 in.)	1.07 (14.53 in.)
Main Branch	Herron Road (Orchard Hill Bridge)	Max	1180 CFS	3530 CFS
		Min	172	210
		Mean	403	614
North Branch	Male Corners	Max	625 CFS	-
		Min	0.70	-
		Mean	97.7	-
		Cfsm	0.531 (7.21 in.)	-

Table 51

Summary of Watershed Discharge Data

Water Course	Location	Mean Discharge (cfs)	Information Source
Main Branch	9th St. Dam	1080	Alpena Power Co.
" "	4-Mile Dam	1550	" " "
" "	7-Mile Dam	2420	" " "
" "	Hillman Dam	150	" " "
" "	" "	135	Local*
" "	Herron Rd.	438	U. S. Geol. Servic
" "	M 32	208	" " "
" "	Atlanta	63	Local
" "	Head	21	"
No. Branch	Male Corners	102	U. S. Geol. Service
" "	Head	11	Local
Up. So. Br.	M 32	108	U. S. Geol. Service
" " "	M 32	168	Local
Lo. So. Br.	Hubbard Lake	104	U. S. Geol. Service
" " "	" "	95	Local
Wolf Creek	Wolf Cr. Rd.	70	"
Bean Creek	Bean Cr. Rd.	15	"
Gilchrist Cr.	M 33	26	"
Hunt Creek	Mouth	27	"

*Local (Measured in this study)

Table 52

Water Resource Commission Water Quality Data for Thunder Bay River Watershed

Year	Range	Temp (C)	D.O. (mg/l)	Sus. Solid (mg/l)	pH	Cond (µohm/cm)	BOD$_5$ (mg/l)	COD	PO$_4$ (mg/l)	NO$_3$ (mg/l)	NH$_3$ (mg/l)	Cl$^-$ (mg/l)	Deter. (ppm)
Main Branch of Thunder Bay River at Breakwall													
	Min	-2	7.4	6	7.5	270	2.4	14	0.00	0.00	0.00	0	0.0
1965	Max	23	12.4	29	8.3	500	5.4	35	0.30	1.30	0.40	6	0.1
	Med	4	11.5	15	7.9	350	3.2	22	0.10	0.30	0.00	3	0.0
	Min	0	6.2	3	7.6	280	2.1	10	0.00	0.00	0.00	0	0.0
1966	Max	24	12.2	15	8.4	400	6.4	37	0.80	0.34	0.60	8	0.2
	Med	4	10.3	9	7.9	250	3.2	22	0.30	0.10	0.01	3	0.0
	Min	0	5.2	0.5	7.6	234	0.8	-	0.05	0.00	0.00	0	-
1967	Max	22	11.6	40.0	8.5	400	3.8	-	0.35	0.20	0.40	15	-
	Med	11	8.2	7.5	8.0	340	2.6	-	0.15	0.10	0.00	6	-

Year	Coloform	Temp	D.O.	Flow	Susp. Sld.	Ca	pH	PO$_4$	NO$_3$	NH$_3$	Cl$^-$	Hard	Alk	SO$_4$	Fe
	(MPN/100)	(C)	(mg/l)	(cfs)	(mg/l)	-	-	-(all	measured	in	mg/l)-	-	-		
North Branch Thunder Bay River															
1967	300	7	10.8	40	9.0	52	8.2	0.05	0.10	0.00	0	185	180	12	0.2
Wolf Creek															
1967	800	7	10.8	88	6.0	58	8.8	0.05	0.10	0.00	4	210	210	10	0.2

Table 53

Water Resource Commission Physical and Chemical Water Quality Data

Main Branch Thunder Bay River at Breakwall

Physical

Year	Range	Temp (C)	Turb	Cond (uohms) cm	D.O. (mg/1)	pH	Susp Sol. (mg/1)	BOD (mg/1)	Coliform
	Max	27.0			11.8	8.10	14	4.3	46,000
1968	Min	0.0	-	-	5.2	7.60	0	0.1	230
	Mean	9.9			8.4	7.93	7	[illegible].0	23,115
	Max	23.0	12	370	15.6	8.40	44	6.5	
1969	Min	0.0	1	310	7.2	7.50	0	1.4	- - -
	Mean	8.8	5	337	10.2	8.00	11	3.8	
	Max	23.0	13	470	14.0	8.30	23	6.4	40,000
1970	Min	0.0	1	210	7.2	7.80	0	1.8	600
	Mean	10.8	4.9	362	9.7	8.10	7.5	4.2	14,000
	Max	10.0	5	400	12.8	8.10	15	3.2	
1971	Min	0.0	3	270	9.8	7.70	3	1.0	- - -
	Mean	2.4	4.4	352	11.2	7.95	7	2.1	

Chemical (mg/1)

Year	Range	Alk	Org N	NH_3	NO_3	PO_4	$OrgPO_4$	Hard	Ca	Mg	Cl^-	SO_4
	Max		0.80	0.900	0.40	0.17	0.150	208	57	21	34	27
1968	Min	-	0.00	0.000	0.00	0.03	0.010	188	44	13	5	16
	Mean		0.20	0.032	0.10	0.08	0.058	200	52	17	11	20
	Max	182	0.90	0.30	1.25	0.33	0.120	488	60	15	11	34
1969	Min	153	0.20	0.02	0.00	0.02	0.010	160	46	7	2	18
	Mean	169	0.58	0.10	0.20	0.02	0.010	215	52	12	7	24
	Max	220	1.10	0.48	0.20	0.48	0.200	235	58	16	11	
1970	Min	100	0.20	0.05	0.00	0.03	0.000	120	54	12	4	
	Mean	166	0.60	0.22	0.09	0.17	0.089	182	56	15	8	20
	Max	185	0.80	0.220	0.20	0.07	0.050	200			14	
1971	Min	155	0.50	0.040	0.10	0.04	0.010	170			5	
	Mean	170	0.65	0.016	0.15	0.05	0.026	185	56	15	10	21

The mean dissolved oxygen values were similar at 10.2 ppm and 9.9 ppm. The mean BOD by the commission was 3.0 ppm and COD was 2.3 mg.

In the measurement of chemical parameters at the breakwall, phosphate, ammonia, nitrate, and chloride were similar except when samples were taken in close proximity of the sewage plant effluent discharge. Michigan Water Resources Commission measurements indicated significant levels of organic nitrogen and phosphorus at the river mouth. Their data showed higher values for alkalinity, hardness, sulfate, calcium, and magnesium. The coliform count was significant in the river and along Thunder Bay beaches (Table 54) especially when the river plume carried the domestic effluents in the southerly direction.

The Michigan Water Resources Commission (1971) has sampled the North Branch and Wolf Creek. The data for dissolved oxygen, discharge, calcium, sulfate, hardness, and alkalinity were comparable to results of this study. The nutrients (phosphates, nitrate, ammonia) levels found in the continual measurement at these stations were higher in value.

The four year seasonal study on the watershed has indicated that the natural water is of medium to high hardness, with significant soluble calcium present (Tables 55, 56 and 57). The alkalinity as calcium carbonate was more prominent than sulfate or chloride. A fairly high total solid content was found. Suspended solids were highest in the main river. There is adequate dissolved oxygen in all waters for natural clean water aquatic organisms. During the day, the nutrient levels showed only scattered instances of cultural influence. They were sufficient to support aquatic vegetation that was extensive in several locations in streams and reservoirs. Three tributaries and the lower reaches of the main river had a high natural color.

Table 54

Thunder Bay River and Bay Sampling Data
Alpena Health Department and Local Analysis

Year	Location	Range	Temp (F)	Coliform* M.F.M.	Coliform* Fecal	pH	PO_4 -	NH_3 mg/l	NO_3 mg/l	Cl^- -
Main Branch Thunder Bay River										
1970	Fish Dock	Max	78	14500	450					
		Min	67	1500	150	-	-	-	-	-
		Mean	71	7190	250					
	Cemetery Pump Station	Max	78	2500	10V					
		Min	66	100	10V	-	-	-	-	-
		Mean	71	970	10V					
1971	Fish Dock	Max	74	11000	2800	8.10	0.72	0.62	0.26	22.5
		Min	62	800	10	8.00	0.28	0.12	0.01	7.0
		Mean	67	5500	720	8.05	0.52	0.33	0.11	12.5
	Cementery Pump Station	Max	75	12000	790	8.10	0.56	0.25	0.22	15.0
		Min	62	100	10	7.88	0.30	neg	0.01	10.0
		Mean	67	3100	205	8.00	0.42	0.11	0.12	12.0
	Chisholm Bridge	Max	75	700	10V	8.14	0.68	0.17	0.17	17.5
		Min	60	80	10V	8.00	0.34	neg	0.01	6.0
		Mean	68	245	10V	8.07	0.52	0.10	0.10	11.0
	R.R. Car Bridge	Max	68	2700	60		0.64	0.60	0.30	
		Min	61	200	10V	-	0.50	0.01	0.11	-
		Mean	66	1100	30		0.57	0.30	0.20	
	Break-water	Max	69	40000	50		0.76	0.32	0.22	
		Min	62	600	10	-	0.70	0.15	0.07	-
		Mean	65	4000	30		0.73	0.23	0.14	
	Hatchery	Max	58	2800	330	7.85	0.70	0.17	0.36	8.0
		Min	49	300	10V	7.82	0.30	neg	0.02	6.0
		Mean	55	1420	30V	7.84	0.50	0.06	0.19	7.0
Thunder Bay Swimming Beaches										
1971	Starlite	Max	70			8.02	0.20	0.40	0.18	8.5
		Min	67			7.88	0.15	0.20	0.01	8.5
		Mean	68	V100	V10	7.95	0.18	0.30	0.09	8.5
	Baie View	Max	70			8.07	0.22	0.43	0.20	8
		Min	67			8.04	0.12	0.12	0.01	8
		Mean	68	V100	V10	8.06	0.17	0.28	0.11	8

* Mich. Public Health Dept. (Greer, 1971)

Table 55

1967-1968 Local Analysis (mg/l) of Thunder Bay Watershed

Site	Stream	Range	Tot Solid	pH	Hard	Ca	Mg	SO_4	Alk	Cl^-
1	Main Br.	Max	288	8.0	448	64.1	16.6	28.8	198	
		Min	234	7.1	240	61.6	8.3	1.0	145	
		Mean	254	7.5	316	62.8	12.4	11.8	174	9.0
2	Main Br.	Max	306	8.0	487			26.4	193	
		Min	196	7.1	240			1.0	147	
		Mean	253	7.5	253	95.0	44.8	9.5	166	5.0
4	Lo So. Br.	Max	612	7.9	354	96.1	51.6	24.2	191	
		Min	152	7.1	228	45.6	12.0	1.5	166	
		Mean	300	7.5	307	67.0	34.7	10.5	181	31.0
5	Lo.So. Br.	Max	216	8.1	462			31.3	166	14.2
		Min	178	7.0	204			0.2	158	7.1
		Mean	196	7.7	323	43.1	28.4	12.6	162	10.6
6	Wolf Cr.	Max	292	7.9	420			22.0	224	29.2
		Min	170	7.0	258	-	-	7.0	110	10.7
		Mean	242	7.5	332			12.7	169	20.0
7	Bean Cr.	Max	716	7.7	414			26.4	266	
		Min	166	6.8	348	-	-	6.0	152	-
		Mean	381	7.2	378			14.9	221	
8	Up.So. Br.	Max	576	7.3	522	162.4	34.2	31.3	192	
		Min	147	6.9	224	49.3	23.4	1.0	155	-
		Mean	292	7.0	323	87.4	30.1	12.7	168	
9	Up.So. Br.		392	6.9	270	54.6	23.2	3.0	189	-
10	Main Br.	Max	592	7.4	444	60.4	30.6	19.2	185	
		Min	138	6.9	192	51.0	27.4	0.8	127	
		Mean	264	7.2	343	55.7	29.0	6.5	152	3.5
11	Brush Cr.	Max	524	8.0	468			9.6	202	
		Min	196	6.8	230	-	-	1.0	135	-
		Mean	334	7.4	331			4.0	169	
13	Gilchrist	Max	334	7.8	462			19.2	208	
		Min	254	6.7	235	-	-	7.0	199	
		Mean	278	7.2	298			11.0	205	
14	Hunt Cr.	Max	318	8.0	444			21.7	194	
		Min	164	6.8	235	-	-	4.7	189	-
		Mean	231	7.3	300			9.8	192	
15	Main Br.	Max	222	7.6	409	130.7	29.6	14.7	194	
		Min	180	6.9	222	61.6	15.3	neg	163	-
		Mean	207	7.3	321	96.1	22.5	7.9	184	
16	Main Br.	Max	216	7.7	456			19.2	174	
		Min	144	6.8	228	-	-	0.5	172	-
		Mean	189	7.4	355			8.5	173	
18	No. Br.	Max	174	8.0	678			19.2	139	
		Min	68	6.9	353	-	-	neg	97	-
		Mean	121	7.4	515			9.6	118	

Table 55 (Cont'd.)

Site	Stream	Range	Sol.PO_4	Tot.PO_4	NH_3	NO_3	Fe	Tannin	Det.
1	Main Br.	Max	0.270	0.30	0.67	3.12	0.24	2.4	0.057
		Min	0.006	0.25	0.21	0.24	0.02	1.1	0.052
		Mean	0.180	0.28	0.45	1.18	0.15	1.9	0.055
2	Main Br.	Max	0.14	0.50	0.75	1.55	0.20	2.3	0.060
		Min	0.05	0.10	0.18	0.09	0.01	0.9	0.027
		Mean	0.13	0.25	0.45	0.61	0.11	1.6	0.044
4	Lo.So. Br.	Max	0.08	0.50	0.85	1.30	0.22	2.4	0.144
		Min	0.02	0.08	0.12	0.13	0.01	1.5	0.045
		Mean	0.06	0.25	0.35	0.65	0.12	1.9	0.095
5	Lo.So. Br.	Max	0.03	0.14		0.80	0.24		
		Min	neg	0.05		0.06	0.01		-
		Mean	0.02	0.08	0.08	0.43	0.12	1.3	
6	Wolf Cr.	Max	0.08	0.16	4.10	0.55	0.18	2.1	
		Min	0.01	0.15	0.05	0.11	0.01	1.8	-
		Mean	0.03	0.16	1.37	0.26	0.09	2.0	
7	Bean Cr.	Max	0.24	0.50		3.01	0.35	3.4	
		Min	0.01	0.30		0.13	0.01	3.2	-
		Mean	0.12	0.40	1.10	1.19	0.19	3.3	
8	Up.So. Br.	Max	1.00	1.28	1.10	1.17	0.40	2.4	
		Min	0.02	0.24	0.46	0.35	0.01	1.6	
		Mean	0.31	0.67	0.88	0.64	0.14	1.9	
9	Up.So. Br.	Max	neg	-	0.57	0.13	0.06	1.0	-
10	Main Br.	Max	0.15	9.40	1.77	0.69	0.24	2.2	0.177
		Min	0.01	0.16	0.13	0.16	0.01	0.7	0.006
		Mean	0.05	4.80	0.76	0.40	0.16	1.4	0.058
11	Brush Cr.	Max	0.20	2.60		1.42	0.27	1.6	
		Min	0.12	0.12		0.27	0.03	1.6	-
		Mean	0.16	1.36	0.89	0.86	0.25	1.6	
13	Gilchrist	Max	0.10	1.34	0.26	0.47	0.24	2.2	
		Min	0.07	0.30	neg	0.10	0.02	1.2	-
		Mean	0.08	0.82	0.13	0.29	0.12	1.7	
14	Hunt Cr.	Max	0.18	0.28	0.46	0.49	0.38		
		Min	neg	0.28	0.36	0.08	0.02		-
		Mean	0.05	0.28	0.42	0.22	0.14	1.5	
15	Main Br.	Max	0.26	1.54	1.03	0.27	0.31	2.0	
		Min	neg	0.20	0.11	0.07	0.02	0.4	-
		Mean	0.09	0.87	0.48	0.15	0.14	1.2	
16	Main Br.	Max	0.16	0.89	1.00	1.11	0.13	2.0	
		Min	neg	neg	0.34	0.03	0.01	1.1	-
		Mean	0.05	0.45	0.67	0.57	0.03	1.5	
18	No. Br.	Max	0.05	0.73		0.27	0.16		
		Min	neg	0.26		0.13	0.13		-
		Mean	0.03	0.50	1.12	0.20	0.14	1.1	

Table 56

1970-1971 Local Physical Data at Thunder Bay Watershed Stations

Site	Stream	Range	Air Temp (C)	H2O Temp (C)	Discharge (cfs)	Susp Solid (mg/l)	Total Solid (mg/l)	Color (mg/l)	D.O. (mg/l)
1	Main Br.	Max	22.0	16.0		37.0	348	35.6	12.3
		Min	0.5	2.0	-	7.3	217	7.2	8.2
		Mean	13.2	11.6		19.5	275	23.0	10.2
2	Main Br.	Max	26.0	21.0		13.6	382	50.1	12.1
		Min	-2.0	1.5	-	3.0	180	3.2	6.6
		Mean	13.5	11.6		6.2	310	23.2	9.6
3	Main Br.	Max	24.0	21.5		26.0	350	36.3	12.1
		Min	3.5	2.8	-	2.0	164	2.6	7.8
		Mean	14.5	12.2		10.0	264	18.9	9.8
4	Lo.So. Br.	Max	28.0	24.0		10.0	265	17.5	11.2
		Min	10.0	7.0	-	4.0	169	2.8	8.0
		Mean	17.3	14.5		8.0	234	9.0	9.6
5	Lo.So. Br.	Max	24.0	21.0	117.5	15.0	209	38.8	12.4
		Min	1.0	3.0	72.5	2.0	55	0.0	6.1
		Mean	13.3	12.7	95.0	8.7	148	12.2	9.2
6	Wolf Cr.	Max	24.5	17.5		9.0	220	40.7	12.2
		Min	2.0	6.0	-	2.0	101	15.5	10.0
		Mean	14.0	10.5		4.3	178	25.1	10.8
7	Bean Cr.	Max	22.0	25.5		32.0	453	59.0	11.3
		Min	11.0	6.0		1.5	260	44.0	6.4
		Mean	15.9	16.6	15.3	12.1	356	53.0	8.3
8	Up.So. Br.	Max	23.5	24.0		23.0	332	22.0	12.0
		Min	12.0	5.0		4.0	70	0.0	6.1
		Mean	15.8	16.0	168.0	11.2	207	11.9	9.4

Table 56 (Cont'd.)

Site	Stream	Range	Air Temp (C)	H2O Temp (C)	Discharge (cfs)	Susp.Solid (mg/l)	Total Solid (mg/l)	Color (mg/l)	D.O. (mg/l)
9	Up.So. Br.	Max	30.5	20.0		8.0	256	31.4	11.5
		Min	12.0	12.5	-	2.5	218	7.5	7.5
		Mean	22.7	17.5		4.5	241	18.0	9.4
10	Main Br.	Max	30.5	20.0		22.0	280	46.5	11.5
		Min	2.0	3.0		3.2	240	3.5	5.8
		Mean	18.2	13.8	35.0	11.0	255	25.8	8.5
11	Brush Cr.	Max	33.5	20.0		7.0	213	37.0	12.0
		Min	2.0	2.5	-	1.0	192	4.6	9.2
		Mean	18.2	13.5		3.5	204	24.2	10.6
12	Main Br.	Max	36.5	20.5		39.2	283	39.0	11.6
		Min	4.0	3.0	-	5.0	240	1.3	5.7
		Mean	20.0	13.5		17.8	270	17.0	8.9
13	Gilchrist	Max	25.0	18.0		19.0	262	13.2	12.5
		Min	4.0	2.5		2.4	224	6.0	10.0
		Mean	16.8	12.2	26.2	7.0	240	9.0	10.8
14	Hunt Cr.	Max	25.0	18.0		18.0	263	18.8	12.5
		Min	2.0	2.5		3.0	222	3.0	9.5
		Mean	15.5	11.8	27.8	6.6	246	12.2	10.6
15	Main Br.	Max	26.0	21.0	74.0	13.0	275	33.8	13.4
		Min	0.5	2.5	51.8	2.8	189	1.1	6.6
		Mean	12.6	11.9	62.9	8.5	235	20.8	10.0
16	Main Br.	Max	27.5	21.5	25.5	12.0	320	16.0	13.3
		Min	0.0	4.0	16.8	0.5	232	1.2	7.5
		Mean	12.6	12.6	21.2	4.9	272	7.9	10.6
17	No. Br.	Max	16.5	19.0		10.0	354	65.0	14.4
		Min	0.0	3.0		8.0	180	12.0	6.8
		Mean	10.5	12.2	11.0	9.0	267	30.5	11.1
18	No. Br.	Max	24.0	28.0		12.0	332	72.5	14.0
		Min	0.5	2.2	-	1.0	256	9.0	6.2
		Mean	9.6	13.8		5.3	295	49.8	10.2

Table 57

1970-1971 Local Chemical Data (mg/l) at Thunder Bay Watershed Stations

Site	Stream	Range	pH	Alk	Hard	Ca	SO_4	Cl^-	Tot. PO_4	NH_3	NO_3	Fe
1	Main Br.	Max	8.09	170	240	39.0	17.2	12.0	1.12	1.37	0.28	0.13
		Min	7.56	162	166	17.1	4.4	7.5	0.26	0.06	0.08	neg
		Mean	7.82	166	198	28.0	11.7	9.9	0.67	0.53	0.18	0.06
2	Main Br.	Max	8.35	188	235	78.0	14.3	10.3	0.33	1.04	0.40	0.13
		Min	7.92	165	169	17.1	9.0	5.5	0.22	0.20	0.05	0.03
		Mean	8.12	177	195	42.8	11.9	8.2	0.28	0.53	0.21	0.08
3	Main Br.	Max	8.36	191	235	60.0	12.5	9.0	0.31	0.48	0.36	0.16
		Min	8.14	172	187	23.1	6.0	5.0	0.19	0.46	0.05	0.025
		Mean	8.24	180	207	40.3	9.2	7.0	0.26	0.47	0.19	0.09
4	Lo.So. Br.	Max	8.10	186	222	45.0	12.2	10.3	0.56	0.06	0.30	0.05
		Min	7.08	168	170	30.5	4.4	7.2	0.15	0.04	0.01	neg
		Mean	7.76	178	200	36.8	6.9	8.4	0.30	0.05	0.11	0.02
5	Lo.So. Br.	Max	8.33	172	204	48.0	13.8	11.5	0.60	0.07	0.34	
		Min	7.13	160	154	16.0	6.4	5.4	0.06	0.01	0.06	
		Mean	7.80	168	186	29.6	9.2	7.6	0.33	0.04	0.20	neg
6	Wolf Cr.	Max	8.20	212	266	48.0	9.0	13.5	0.60	0.10	0.28	
		Min	7.26	160	208	20.0	3.2	6.3	0.08	0.0	0.08	
		Mean	7.77	195	228	34.1	6.4	10.1	0.36	0.04	0.18	0.08
7	Bean Cr.	Max	8.02	268	358	75.5	23.5	7.0	1.80	0.20	0.42	
		Min	7.71	238	237	26.0	5.0	5.0	0.21	0.10	0.01	
		Mean	7.86	255	298	51.0	13.3	5.8	0.74	0.12	0.18	0.08
8	Up.So. Br.	Max	8.12	144	187	26.8	22.0	19.2	1.36	1.60	0.15	
		Min	7.50	128	152	15.0	3.0	3.5	0.13	0.01	0.03	
		Mean	7.89	137	164	21.3	10.0	8.1	0.43	0.53	0.09	0.06
9	Up.So. Br.	Max	8.21	246	380	56.0	8.2	8.0	0.58	0.23		
		Min	8.02	197	208	34.0	7.2	5.0	0.005	0.01		
		Mean	8.14	218	260	45.0	7.4	6.1	0.29	0.12	0.17	0.11
	Truax Cr		-	-	-	-	-	3.5	1.37	(Color - 147.0)		

Table 57 (Cont'd.)

Site	Stream	Range	pH	Alk	Hard	Ca	SO_4	Cl^-	Tot.PO_4	NH_3	NO_3	Fe
10	Main Br.	Max	8.37	246	288	60.0	10.6	8.5	1.10	0.32	0.19	0.12
		Min	7.92	191	191	35.0	3.7	3.0	0.22	0.03	0.05	0.12
		Mean	8.18	208	221	43.0	7.8	5.1	0.63	0.18	0.10	0.12
11	Brush Cr.	Max	8.40	150	297	68.0	9.5	8.0	0.66	0.32	0.30	
		Min	8.12	140	148	26.0	1.2	1.0	0.01	0.09	0.07	
		Mean	8.26	148	194	45.0	6.5	3.6	0.44	0.19	0.17	0.10
12	Main Br.	Max	8.42	202	305	60.0	8.2	8.0	0.72	0.45	0.165	0.15
		Min	7.84	193	198	30.5	3.3	2.5	0.22	0.02	0.01	0.10
		Mean	8.24	198	226	43.0	6.8	4.8	0.51	0.24	0.08	0.12
13	Gilchrist	Max	8.36	272	302	62.0	8.5	6.2	0.41	0.46	0.15	
		Min	8.10	193	204	23.1	1.0	3.0	0.075	0.018	0.015	
		Mean	8.26	217	230	42.0	6.1	4.1	0.25	0.24	0.11	0.12
14	Hunt Cr.	Max	8.35	197	272	68.0	7.2	3.1	0.53	0.60	0.175	
		Min	8.22	186	196	30.5	1.0	2.5	0.15	0.033	0.008	
		Mean	8.26	193	219	51.0	4.9	2.9	0.32	0.26	0.09	0.09
15	Main Br.	Max	8.31	206	262	59.2	10.0	8.5	0.28	0.65	0.15	0.12
		Min	7.86	186	198	30.5	2.2	3.0	0.10	0.028	0.007	0.04
		Mean	8.16	196	217	45.4	7.2	4.9	0.18	0.32	0.08	0.08
16	Main Br	Max	8.34	206	267	87.5	9.8	7.6	0.23	0.40	0.13	0.10
		Min	8.06	192	200	40.0	7.2	3.5	0.08	0.028	0.005	0.03
		Mean	8.22	202	222	62.9	8.7	4.9	0.17	0.23	0.08	0.06
17	No. Br.	Max	7.96	170	200		8.0	9.4	0.30	0.32	0.16	0.13
		Min	7.80	152	183		6.5	0.2	0.10	0.005	0.034	0.008
		Mean	7.85	162	192	54.0	7.2	3.4	0.21	0.115	0.10	0.07
18	No Br.	Max	8.22	196	250	94.0	14.6	6.7	0.42	0.72	0.38	0.17
		Min	8.00	150	166	20.1	1.5	3.0	0.22	0.36	0.054	0.08
		Mean	8.10	176	203	50.5	9.2	4.0	0.31	0.51	0.205	0.12
	Devils River		8.20	-	153	30.4	-	-	0.76	(Color - 23.2)		

Analysis of specific parameters relative to the major portion of research in this study was done at selected sampling sites in the river and Thunder Bay at Alpena (Table 58). The phosphate data showed a high total phosphate level in the river below the sewage outfall (Br3) and near the discharges (Br1 and Ba2) of the wood-products plant (Tables 59 and 60). This phosphate composition is carried down to the river mouth and diluted by the river water until it reaches the bay. As the river flows out into the shipping channel, there is further dilution. The prevailing wind and currents causes the river to swing south along the shoreline as shown by phosphate levels. Selected soluble phosphate measurements showed that orthophosphate constitutes from fifty to ninety per cent of the total phosphate measured. This may reflect the degree and rate of hydrolysis occurring in Thunder Bay waters. The chloride and ammonia levels followod the same movement into the bay and the same dilution patterns.

The calcium levels reflect the contribution of groundwater from limestone sources in the river basin (Table 61). The river plume can be clearly distinquished visually or through colorimetric measurement at the sampling sites in the bay. The natural color would be composed of yellow organic acids which could interact with the soluble calcium. The measurement of oxidizable calcium at sampling sites revealed that a significant amount of calcium was being bound up by the organic material, together with acid-extractable phosphate. This interaction is lower at bay sites (Ba and Bu) because of the dilution and lower levels of calcium and organic material. In the main river, this involvement is highest where organic color was at a high level.

The suspended solids also play a role in the movement of nutrients in Thunder Bay waters. The river had a high level of suspended solids.

Table 58

Distribution of Selected Parameters at Specific Sites
Thunder Bay River and Thunder Bay

Year	Range	River	Br1	Br2	Br3	Mo1	Mo2	Mo3	Ba1	Ba2	Ba3	Ba4	Ba5	Ba6	Sewage
Soluble Phosphate (mg/l)															
	Max	0.22													
1971	Min	0.06	-	-	0.75	-	0.20	-	-	-	0.20	-	-	-	11.0
	Mean	0.14													
Total Phosphate (mg/l)															
	Max	0.165	0.62	0.62	3.70	0.50	1.00	0.82	0.35	0.56	0.37	0.47	0.35	0.47	43.0
1970	Min	0.100		0.10	0.43	0.20	0.21	0.13	0.18	0.09	0.12	0.14	0.18	0.18	11.0
	Mean	0.142		0.31	1.19	0.33	0.44	0.43	0.26	0.32	0.27	0.28	0.29	0.29	27.0
	Max	1.04	4.84	1.10	1.55	0.54	1.62	1.10	0.82	1.25	1.66	0.97	1.10	1.12	
1971	Min	0.15	0.26	0.15	0.29	0.10	0.08	0.09	0.25	0.18	0.18	0.29	0.31	0.18	-
	Mean	0.43	1.93	0.48	0.87	0.33	0.58	0.48	0.59	0.54	0.46	0.56	0.70	0.53	
Ammonia Nitrogen (mg/l)															
	Max				0.095						0.035				
1970	Min		-		0.010	-	-	-	-	-	0.018	-	-	-	
	Mean	0.022		0.017	0.052						0.026				8.1
	Max	0.30			1.15				1.48						
1971	Min	0.10	-		0.018	-		-	neg		-		-		-
	Mean	0.16		0.012	0.660		neg		0.74	0.015		0.022		neg	
Nitrate Nitrogen (mg/l)															
1970		-	-	-	0.025	-	0.006	-	-	-	0.010	-	-	-	-
Chloride (mg/l)															
1970		8.9	-	-	16.6	-	10.3	12.5	-	9.8	9.4	11.2	-	9.8	96
	Max	5.0		12.5	8.0		6.0	6.0		6.0	6.5	6.5			
1971	Min	3.5	-	4.0	4.0		4.0	4.5		4.5	5.0	4.0			-
	Mean	4.5		6.8	6.2	5.0	4.8	5.2	4.0	5.2	7.5	5.2	4.0	4.5	

Table 58 (Cont'd.)

Year	Range	River	Br1	Br2	Br3	Mo1	Mo2	Mo3	Ba1	Ba2	Ba3	Ba4	Ba5	Ba6
Soluble Calcium (mg/l)														
1971	Max	71.0	38.2	84.0	84.0	24.0	100.0	64.0	-	71.0	75.0	75.0	54.0	-
	Min	20.0	31.8	30.4	24.0		19.6	22.0		22.0	18.7	22.0		
	Mean	41.8	35.0	52.0	43.6		44.4	24.2		48.5	37.2	41.4		
Oxidizable Calcium (mg/l)														
1971	Max	40.0	-	49.0	17.0	-	48.0	65.0	-	27.5	16.0	29.6	50.0	-
	Min	8.0		8.0	5.0		2.0	4.2		12.0	4.0	3.0		
	Mean	21.8		20.4	10.9		22.1	24.2		18.5	11.8	15.6		
Suspended Solids (mg/l)														
1970	Max	-	-	-	14.0	-	8.0	-	-	4.0	12.0	7.0	-	-
	Min										4.0	4.4		
	Mean										7.2	5.7		
1971	Max	17.0	-	18.0	15.0	-	18.0	14.0	-	22.0	15.0	16.0	6.0	-
	Min	3.6		3.2	6.0		4.8	4.4		5.2	4.0	3.2		
	Mean	8.0		8.3	8.7		9.6	8.7		10.7	7.4	7.9		
Acid-Extractable Phosphate (mg/l)														
1970		-	-	-	-	-	0.08	-	-	-	0.10	-	-	-
1971	Max	1.10	-	0.28	1.35	-	1.35	1.16	-	0.93	0.32	0.40	0.17	-
	Min	0.05		0.04	neg		0.05	neg		0.11	neg	0.22		
	Mean	0.46		0.14	0.40		0.40	0.27		0.43	0.16	0.27		
pH														
1971	Max	8.17	8.12	8.30	8.25	7.80	8.20	8.20	-	7.90	8.23	7.78	-	-
	Min	7.85	8.00	7.94	7.38		7.90	7.84		7.88	7.92	7.73		
	Mean	8.03	8.06	8.11	7.92		8.04	8.00		7.89	8.09	7.75		
Color (mg-Carbon/l)														
1971	Max	56.4	38.8	56.5	55.8	0.0	50.0	42.6	-	23.2	35.1	5.0	-	-
	Min	5.0	20.0	4.4	3.8		10.0	8.2		21.9	2.5	0.0		
	Mean	40.4	29.4	38.9	25.3		30.0	27.2		22.5	21.7	2.5		

Table 58 (Cont'd.)

Year	Range	River	Bu1	Bu2	Bu3	Bu4	Bu5	Bu6	Bu7	Bu8	Bu9	Bu10	Sewage
Soluble Phosphate (mg/l)													
1971		0.14	-	-	0.13	-	-	-	-	-	-	-	11.0
Total Phosphate (mg/l)													
	Max	0.165		1.70	0.39	0.39	0.47	0.58		0.26	0.28		43.0
1970	Min	0.100	0.28	0.30	0.07	0.37	0.10	0.25	-	0.18	0.22	0.16	11.0
	Mean	0.140		0.84	0.25	0.38	0.26	0.44		0.22	0.25		27.0
	Max	1.04		0.78	2.26	1.16	1.72			0.42	0.38	0.23	
1971	Min	0.15	0.07	0.16	0.23	0.28	0.37	0.37	-	0.25	0.18	0.20	-
	Mean	0.43		0.44	0.84	0.62	0.76	0.37		0.32	0.28	0.22	
Ammonia Nitrogen (mg/l)													
1970		0.022	-	-	-	-	-	-	-	-	0.008	-	8.1
Chloride (mg/l)													
1970		8.9	-	-	9.0	-	-	-	-	-	9.4	-	96.0
	Max	5.0			6.0					6.0			
1971	Min	3.5	4.5	3.5	3.5	4.0	4.5	4.0	4.0	5.0	-	4.5	-
	Mean	4.5			4.8					5.5			
Soluble Calcium (mg/l)													
	Max	71.0		26.4	50.0	26.4	26.0					42.0	
1971	Min	20.0	-	22.0	17.9	19.0	24.4	50.0	-	24.0	15.2	25.0	-
	Mean	41.8		24.4	26.9	22.7	25.1					33.5	
Oxidizable Calcium (mg/l)													
	Max	40.0		18.0	17.0		21.0						
1971	Min	8.0	-	4.3	1.1	23.0	10.0	12.0	-	6.0	-	17.0	-
	Mean	21.8		11.8	9.3		15.3						
Color (mg-Carbon/l)													
	Max	56.4		107.0	54.5	56.3	10.0						
1971	Min	5.0	23.2	23.2	0.0	0.0	5.0	36.9	-	25.0	-	neg	-
	Mean	40.4		51.5	26.2	28.2	7.5						

Table 58 (Cont'd.)

Suspended Solids (mg/l)

Year	Range	River	Bu1	Bu2	Bu3	Bu4	Bu5	Bu6	Bu7	Bu8	Bu9	Bu10
	Max			9.0	9.0	8.0	11.0	15.0			8.0	
1970	Min	-	5.6	5.0	3.0	2.0	4.0	3.0	-	4.0	4.0	-
	Mean			6.3	5.8	4.3	8.0	7.3			6.0	
	Max	17.0		11.6	9.2	5.6	7.0				6.0	5.2
1971	Min	3.6	4.0	5.0	2.8	5.0	4.0	7.6	-	-	2.8	4.0
	Mean	8.0		5.1	6.7	5.3	5.0				4.4	4.6

Acid-Extractable Phosphate (mg/l)

Year	Range	River	Bu1	Bu2	Bu3	Bu4	Bu5	Bu6	Bu7	Bu8	Bu9	Bu10
1970		-		-	-	0.025	-	0.[illegible]5	-	-	0.425	-
	Max	1.10		0.27	0.84	0.19	0.12				0.25	
1971	Min	0.05	0.27	0.01	0.07	0.16	0.01	0.03	-	-	0.11	0.08
	Mean	0.46		0.15	0.21	0.18	0.08				0.18	

pH

Year	Range	River	Bu1	Bu2	Bu3	Bu4	Bu5	Bu6	Bu7	Bu8	Bu9	Bu10
	Max	8.17		7.98	8.36							
1971	Min	7.85	-	7.55	7.75	7.70	7.72	-	-	-	8.38	-
	Mean	8.03		7.72	8.11							

Total Phosphate at Selected Depths (mg/l)

Depth (ft)	Mo1	Mo2	Mo3	Ba1	Ba2	Ba3	Ba4
Surface	0.30	-		-	0.25	0.25	0.28
3	0.30	0.43	0.43	0.20	0.25	0.28	0.37
6	0.38	0.42	0.28	0.18	0.39	0.28	0.32
9	0.25	0.33	0.23	-	-	-	-

Table 59

1970 Mean Monthly Phosphate (mg/1) for Thunder Bay and River Survey

Date		Breakwall			Mouth		
	River	Br1	Br2	Br3	Mo1	Mo2	Mo3
8/70	0.215	-	0.42	0.55	0.23	0.42	0.82
9/70	0.165	0.19	0.19	1.36	0.22	0.34	0.53
10/70	0.200	0.25	0.50	1.10	0.40	0.57	0.45
11/70	0.150	-	0.16	0.25	0.28	0.31	0.30
Mean	0.180	0.22	0.32	0.81	0.28	0.41	0.52

Date	Ba1	Ba2	Ba3	Ba4	Ba5	Ba6
8/70	0.24	0.23	0.22	0.21	-	-
9/70	-	0.23	0.16	0.23	0.18	0.18
10/70	0.35	0.33	0.30	0.30	0.29	0.29
11/70	0.14	0.43	0.32	0.39	0.26	-
Mean	0.25	0.31	0.25	0.28	0.24	0.24

Date	Outer Bay - Buoy							
	Bu1	Bu2	Bu3	Bu4	Bu5	Bu7	Bu8	Bu9
9/70	-	-	0.16	-	0.10	0.18	0.22	0.16
10/70	-	0.80	0.36	0.35	0.34	0.44	-	-
11/70	0.28	-	0.42	-	-	-	-	-
Mean	0.28	0.80	0.31	0.35	0.22	0.31	0.22	0.16

Table 60

1971 Mean Monthly Phosphate (mg/1) for Thunder Bay and River Survey

Month		Breakwall			Mouth		
	River	Br1	Br2	Br3	Mo1	Mo2	Mo3
Jun	-	-	0.90	1.09	-	0.38	0.55
Jul	0.35	0.26	0.34	0.52	0.27	0.31	0.38
Aug	0.49	4.84	0.33	0.60	0.28	0.57	0.22
Sep	0.42	1.31	0.28	1.18	0.54	0.57	0.73
Oct	0.45	-	-	1.12	-	0.91	0.50
Mean	0.43	2.14	0.46	0.90	0.33	0.55	0.48

Bay

Month	Ba1	Ba2	Ba3	Ba4	Ba5	Ba6
Jun	-	0.42	0.35	0.54	-	-
Jul	0.25	0.78	0.28	0.33	0.30	0.30
Aug	0.82	0.58	0.43	0.68	1.10	1.12
Sep	-	-	0.81	-	-	-
Oct	-	-	0.30	-	-	-
Mean	0.53	0.59	0.43	0.52	0.70	0.71

Outer Bay - Buoy

Month	Bu1	Bu2	Bu3	Bu4	Bu5	Bu6	Bu8	Bu9	Bu10
Jun	-	0.38	0.57	0.52	0.43	-	0.39	0.38	-
Jul	-	0.30	0.23	0.30	0.28	-	0.25	-	0.23
Aug	0.07	0.41	1.05	0.72	1.27	0.37	0.26	-	0.20
Sep	-	-	1.44	-	-	-	-	0.18	-
Oct	-	-	0.37	-	-	-	-	-	-
Mean	0.07	0.36	0.73	0.51	0.66	0.37	0.30	0.28	0.22

Table 61

Calcium in Thunder Bay Watershed

Thunder Bay

Date	Site	Natural Ca (mg)	Oxidized Ca (mg)	pH
Summer 1971	River	76.0	34.0	-
	Br2	84.5	16.0	-
	Br3	83.0	18.0	8.10
	Mo2	85.5	21.4	8.20
	Mo3	60.2	18.7	-
	Ba2	74.0	5.3	-
	Ba3	67.0	8.8	8.16
	Ba4	64.5	8.1	-
	Bu3	32.3	7.2	8.36
	Bu5	25.5	15.5	-
	Bu8	24.0	9.2	-
	Bu10	33.5	8.5	-
	Mean	59.2	14.2	8.20
Fall 1971	River	30.6	15.6	8.01
	Br2	37.3	8.3	8.11
	Br3	36.5	4.3	8.07
	Mo2	31.5	12.5	8.05
	Mo3	36.3	7.3	8.02
	Ba3	29.7	8.7	8.10
	Ba4	24.0	16.0	7.73
	Bu2	25.6	8.7	7.52
	Bu3	23.0	4.3	7.98
	Bu5	24.4	15.0	7.72
	Mean	29.9	10.1	7.93

Watershed

Location	Range	Natural Ca (mg)	Oxidized Ca (mg)	pH	Ext. PO_4
Main River	Max	80.0	61.8	8.36	1.39
	Min	38.0	9.7	7.60	0.09
	Mean	48.1	25.4	8.19	0.41
Main Trib.	Max	54.0	37.5	8.22	0.85
	Min	26.8	4.4	7.96	neg
	Mean	38.0	18.1	8.09	0.43
Streams	Max	43.0	16.2	8.40	0.82
	Min	36.4	3.0	7.97	neg
	Mean	40.5	9.3	8.19	0.27

Comparable levels were found in Thunder Bay (Bu3, Bu5, Ba3, Ba4, Mo2, and Mo3), possibly from the cement dust fallout. These solids did contain acid-extractable phosphate, especially in the areas (Bu3 and Mo2) where dissolved phosphate levels were high (Table 62). The amount of phosphate extracted with acid was constant over a two-year period (0.24 mg). The milligrams of phosphate extracted for each milligram of suspended solids recovered was also constant at 0.033 mg.

Most of the oxygen-temperature profile results (Table 63), indicated the lack of a thermocline in the inner bay and river where the river current has an influence. There was sufficient dissolved oxygen (mean of 7.3 ppm) for intolerant cold-water fish species and intolerant organisms according to Michigan Water Resources Commission (1967), Water Quality Standards (Appendix IV). The measurement at various depths reflected the slight depletion of oxygen as depth increases and the cooling of water with depth. The phosphate measurements at similar depths (Table 64) showed that the selection of the three to six feet depths as sampling area would represent the uniform composition of the water at the sampling site.

The sewage plant data (Tables 47, 48, 65, and 66), indicated that the amount of plant effluent and its composition varies with season, day and amount of rainfall. The highest flows were recorded during the spring and early summer of the year and did not appreciably affect the levels of the chemical parameters. The beginning and middle of the week had the highest level of components measured in the composite sewage samples. The removal of BOD and suspended solids reflect that of a primary treatment facility. The nutrient levels indicate that the treatment is not affecting nitrogen levels and is enhancing the amount of phosphate that is present in the discharge of the effluent.

Table 62

Acid-Extractable Phosphate of Thunder Bay Suspended Solids

Date	Site	Susp.Solids (mg/l)	Tot. PO4 (mg/l)	Extrac.PO_4 (mg)	PO_4/Solid (mg/mg)
9/70	Ba3	7.5	.28	.30	.040
	Bu3	7.0	.23	.14	.020
	Bu5	10.0	.18	.24	.024
	Bu8	6.0	.26	.36	.060
	Bu9	4.0	.28	.10	.025
10/70	Mo2-3	8.0	.32	.28	.035
	Ba3	7.3	.32	.24	.034
	Bu1	5.0	.70	.10	.020
	Bu3	4.0	.26	.21	.050
	Bu5	8.3	.34	.20	.024
	Bu7	9.5	.54	.36	.038
11/70	Ba3	7.5	.35	.33	.044
	Bu1	6.0	.28	.21	.035
	Bu3	7.0	.38	.10	.014
	Bu5	4.0	.28	.12	.030
Mean		7.0	0.34	0.24	0.033
6/71	Mo2	6.8	.44	.05	.007
	Ba2	8.1	.42	.16	.020
	Ba4	6.4	.54	.26	.040
	Bu2	5.1	.38	.05	.010
	Bu3	4.9	.57	.04	.008
	Bu4	5.3	.52	.12	.023
	Bu8	6.0	.39	.18	.030
7/71	Mo3	12.5	.38	.19	.017
	Ba4	12.5	.33	.27	.021
	Bu3	8.0	.23	.08	.010
	Bu5	7.0	.37	.10	.014
	Bu10	4.0	.23	.08	.020
8/71	Mo2	5.9	.58	.35	.058
	Ba3	5.1	.43	.19	.038
	Ba4	4.8	.68	.22	.056
	Ba5	6.0	1.10	.17	.028
	Bu3	6.0	1.05	.15	.025
	Bu6	5.8	1.05	.07	.010
9/71	Mo2	8.2	.57	.20	.024
	Ba3	6.6	.92	.20	.030
	Bu3	9.2	2.26	.84	.090
10/71	Mo2	10.0	.91	1.05	.105
	Ba3	5.9	.30	.25	.042
	Bu3	8.4	.37	.57	.068
Mean		6.8	0.62	0.24	0.033

Table 63

Dissolved Oxygen(mg/l) and Temperature(C) Profile in Thunder Bay

Site		Surface	3 ft.	6 ft.	9 ft.	12 ft.	18 ft.	Bottom
8/11/71								
9th St.	DO	7.5	7.5	7.5	-	-	-	-
	Temp	21.5	22.0	22.0	-	-	-	-
River	DO	7.4	-	7.2	-	7.4	7.5	7.3
	Temp	21.0	-	22.0	-	21.0	18.0	17.5
Br3	DO	7.5	7.6	7.6	-	7.5	7.4	7.2
	Temp	21.0	21.5	22.0	-	20.5	19.5	18.0
Mo3	DO	7.4	7.5	7.5	-	7.5	7.6	7.4
	Temp	20.0	19.5	20.0	-	19.5	19.5	18.0
Ba3	DO	7.5	-	7.4	-	7.5	7.3	7.2
	Temp	19.5	-	18.5	-	18.5	17.0	16.0
Ba6	DO	6.9	7.2	7.3	7.2	7.2	7.2	6.9
	Temp	16.0	16.5	16.5	16.5	16.0	16.0	15.5
8/28/71								
River	DO	7.1	7.0	7.0	7.0	7.0	6.9	6.8
	Temp	18.4	18.2	18.0	18.2	18.0	17.8	17.6
Br2	DO	7.1	7.0	7.0	7.0	7.0	7.0	-
	Temp	18.8	18.5	18.0	18.2	18.2	18.2	-
Mo2	DO	7.3	7.3	7.3	-	7.2	7.1	6.7
	Temp	18.4	18.2	18.2	-	18.0	17.8	17.6
Ba3	DO	7.3	-	7.3	-	7.3	7.2	7.1
	Temp	18.2	-	18.0	-	18.0	18.0	17.5
Bu3	DO	7.9	-	7.9	-	8.0	7.9	7.8
	Temp	17.7	-	17.5	-	17.5	17.3	17.3
Bu8	DO	7.5	-	7.3	-	7.1	-	6.6
	Temp	19.2	-	18.5	-	17.8	17.2	17.0
Bu10	DO	7.3	-	7.3	-	7.3	7.0	6.7
	Temp	18.5	-	18.2	-	17.8	17.2	17.0
9/15/70								
Ba2	Temp	20.0	-	19.0	18.0	17.5	17.0	17.0
10/15/70								
Bu5	Temp	17.0	-	17.0	16.0	16.0	16.0	15.0

Table 64

Phosphate Measurement(mg/l) at Various Depths in Thunder Bay

Date	Site	Surface	3 ft.	6 ft.	9 ft.	Mean
8/28/70	River	-	0.10	0.05	-	0.075
	Br3	-	0.60	0.70	-	0.650
9/8/70	River	-	0.15	0.16	-	0.150
	Br2	-	0.20	0.23	-	0.215
	Br3	-	0.85	1.05	-	0.950
10/12/70	Ba1	-	-	0.18	-	0.18
	Ba2	-	0.25	0.35	-	0.30
	Ba3	-	0.27	0.33	-	0.30
	Ba4	-	0.37	0.31	-	0.34
10	Mo2	-	0.50	0.54	-	0.52
	Mo3	-	0.51	0.47	-	0.49
11/1	Ba2	0.25	0.25	0.23	-	0.243
	Ba3	0.25	0.28	0.23	-	0.253
	Ba4	0.28	0.37	0.30	-	0.317
11/5/70	Mo1	-	0.30	0.28	0.25	0.276
	Mo2	-	0.37	0.30	0.33	0.333
	Mo3	-	0.25	0.18	0.23	0.220
Mean	River	-	0.12	0.11	-	0.116
	Br2	-	0.20	0.23	-	0.215
	Br3	-	0.72	0.88	-	0.800
	Mo1	-	0.30	0.28	0.25	0.276
	Mo2	-	0.44	0.42	0.33	0.400
	Mo3	-	0.43	0.28	0.23	0.360
	Ba1	-	-	0.18	-	0.180
	Ba2	0.25	0.25	0.29	-	0.263
	Ba3	0.28	0.28	0.28	-	0.280
	Ba4	0.28	0.37	0.32	-	0.323

Table 65

Monthly Means (mg/l) by Day for Alpena Sewage Effluent

Month	M.G.D.	Cl$^-$	Sol.PO$_4$	Tot.PO$_4$	NH$_3$	NO$_3$	Hard	Alk
				Sunday				
9/70	-	96	8.0	14.8	6.7	0.46	-	-
10/70	1.70	97	-	26.1	-	-	-	-
12/70	2.36	-	3.6	10.3	14.0	-	-	-
1/71	1.67	198	12.8	22.0	10.8	0.37	185	-
2/71	1.95	140	14.5	20.5	15.8	0.92	280	-
3/71	4.29	240	10.8	18.0	5.4	0.90	318	-
4/71	4.30	212	6.2	11.6	1.7	1.26	322	-
5/71	2.88	161	9.8	16.2	5.2	0.77	320	-
6/71	3.40	235	9.8	12.8	8.5	0.90	-	-
7/71	4.10	120	5.8	26.4	6.2	0.25	278	238
8/71	2.39	85	10.0	13.2	6.2	0.07	232	216
9/71	2.92	80	8.4	24.5	8.0	0.25	201	-
10/71	1.55	90	12.7	20.1	15.8	0.20	244	-
12/71	2.49	265	8.9	11.8	9.2	0.40	-	224
Mean	2.55	156	9.3	17.7	8.7	0.52	264	226
				Tuesday				
9/69	-	-	-	18.0	-	-	-	-
9/70	2.47	89	8.0	20.6	9.6	0.30	-	-
12/70	2.62	-	12.8	25.2	7.1	0.56	-	-
1/71	1.88	125	11.7	25.0	5.2	0.36	146	-
2/71	1.99	102	18.5	26.0	15.5	0.39	271	-
3/71	3.51	215	16.0	25.0	8.4	0.76	318	-
4/71	5.20	180	5.2	12.0	1.8	0.96	324	-
5/71	4.48	160	9.2	18.6	5.0	0.78	270	-
7/71	2.97	90	9.8	21.5	6.7	0.31	202	192
8/71	3.56	175	15.5	18.7	15.7	0.28	226	203
10/71	2.20	80	12.8	16.7	13.7	0.23	249	-
11/71	1.85	160	16.5	28.3	10.7	0.86	276	220
12/71	2.22	140	16.1	17.9	7.5	0.21	348	232
Mean	2.84	138	12.7	21.0	8.9	0.50	263	212

Table 65 (Cont'd.)

Month	M.G.D.	Cl^-	Sol. PO_4	Tot. PO_4	NH_3	NO_3	Hard	Alk
				Wednesday				
9/70	2.31	103	-	25.0	-	-	-	-
10/70	1.86	-	16.0	30.5	-	-	-	-
12/70	2.62	-	11.3	24.4	9.1	0.68	-	-
1/71	1.94	228	12.3	19.5	6.5	-	-	-
2/71	2.02	246	17.0	26.2	17.2	0.78	254	-
3/71	3.92	175	8.0	15.5	5.0	0.62	313	-
4/71	5.10	185	5.3	11.6	0.8	1.03	328	-
5/71	4.01	193	8.6	16.2	5.4	1.42	326	-
6/71	4.72	167	8.6	15.1	6.3	1.85	-	-
7/71	2.84	90	12.8	20.4	10.0	0.22	242	-
8/71	2.83	170	15.7	21.8	8.5	0.21	223	194
9/71	2.52	75	8.4	24.6	7.7	0.26	195	-
11/71	1.79	245	15.0	28.0	10.3	1.12	283	212
12/71	5.68	90	4.4	5.5	1.5	0.58	233	136
Mean	3.15	163	11.0	20.3	7.5	0.80	266	181
				Thursday				
9/69	-	-	-	18.1	-	-	-	-
9/70	2.33	102	11.4	32.0	5.7	-	-	-
10/70	2.00	-	19.0	30.0	-		-	-
11/70	2.17	-	13.5	27.0	-	-	-	-
12/70	2.70	-	11.2	21.0	5.5	0.59	-	-
1/71	1.95	312	12.7	31.5	10.5	0.34	204	-
2/71	2.00	106	18.0	27.0	17.0	0.94	229	-
3/71	2.86	248	10.5	18.0	6.1	0.78	290	-
4/71	4.42	230	6.1	12.0	1.8	1.06	296	-
5/71	3.43	170	8.6	20.5	4.0	0.62	270	-
7/71	3.92	100	13.7	18.0	6.7	1.07	277	-
8/71	3.28	120	8.0	22.6	4.0	0.08	254	210
9/71	2.92	100	6.7	18.2	6.5	0.13	222	-
10/71	1.69	100	16.5	25.0	15.8	0.25	249	-
11/71	1.56	110	20.6	32.8	11.4	0.50	246	218
12/71	2.98	150	12.2	15.9	4.0	0.48	365	232
Mean	2.68	154	12.7	23.1	7.8	0.57	263	220

Table 66

Alpena Sewage Effluent Means (mg/l) for Specific Days

1970

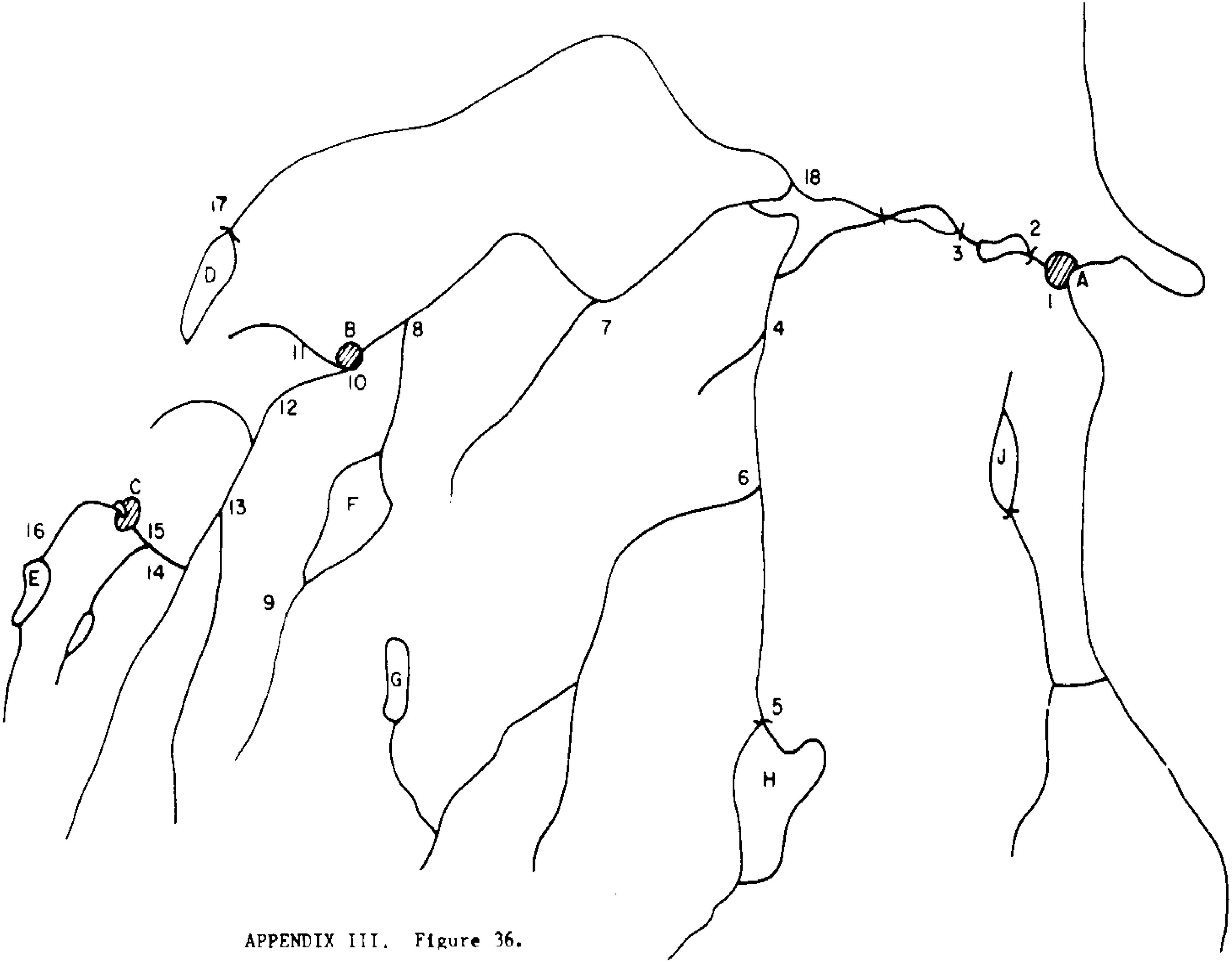
Day	Sol.PO_4	Tot. PO_4	Cl^-	Cl_2	NH_3	NO_3	Deter.
Sun	8.0	20.5	97	0.86	6.6	0.46	-
Mon	15.5	26.8	118.5	-	14.0	0.27	-
Tues	13.5	24.2	89	1.80	7.8	0.34	1.10
Wed	12.2	25.6	100	0.75	8.5	0.36	-
Thur	9.6	24.6	39	1.50	8.2	0.60	2.00
Fri	-	23.6	-	-	-	-	-
Sat	17.0	31.7	116	1.40	-	-	
Mean	12.6	25.3	93.3	1.26	9.0	0.41	1.55

1971

Day	Sol.PO_4	Tot.PO_4	Cl^-	NH_3	NO_3	pH	Alk	Hard	Det.	Fe
Sun	10.7	18.4	188	7.6	0.91	7.42	224	292	0.73	-
Tues	9.3	21.1	137	7.2	0.60	7.30	201	256	-	0.77
Wed	11.6	25.8	190	8.0	1.12	7.50	223	301	-	0.91
Thur	10.8	19.8	200	6.8	0.85	7.37	201	266	1.20	0.80
Mean	10.6	21.3	179	7.4	0.87	7.40	212	279	0.97	0.83
IN	8.4	13.2	134	6.8	0.87	7.40	215	280	-	-
OUT	8.7	16.7	160	7.1	1.22	7.45	215	280	-	-

Appendix III. Resources of Thunder Bay Watershed Geographic Sites and Sampling Locations.

THUNDER BAY WATERSHED SAMPLING LOCATIONS



APPENDIX III. Figure 36.

Table 67

Description of Thunder Bay Basin Geographic Sites

Site	Geographic Location	Description
A	City of Alpena	Located on Thunder Bay, main river and Besser Lake are within city limits.
B	Village of Hillman	Located near the county line with a population of 450.
C	Village of Atlanta	Located at the junction of M32 and M33 with a population of 1000
D	Rush Lake	The floodwaters of the Rush Lake flow into North Branch which is controlled by a dam in Montmorency County.
E	McCormick Lake	The main branch flows through the lake where the original dam is in dis-repair.
F	Fletcher Pond	The backwaters of the dam on the Upper South Branch has formed an expansive floodwaters in Alpena and Montmorency Co.
G	Beaver Lake	A deep, spring-fed lake that has a natural flow into Beaver Creek.
H	Hubbard Lake	A large natural lake, 3 by 7 miles in size, whose level is controlled by a dam where flow is into Lower South Branch.
J	Devils Lake	A bog, marsh lake with much sedimentation and a dam controlling level, with overflow entering North Branch Devils River.
	Main Branch Thunder Bay River	In Montmorency County, the river is 13.0 miles in length, flowing through brushwood and cleared areas, passing from McCormick Lake through Lake Fifteen into backwaters at Atlanta. Elevation 875-1100. In Alpena, County, the river is 25.5 miles long before it reaches the 7-mile dam pond. The remainder of the river passing through the three reservoirs of the 7-mile, 4-mile, and 9th St. dams

Table 67 (Cont'd.)

Site	Geographic Location	Description
		is 11.0 miles long. All types of terrain is along the shores - forest, brush, marsh, cleared areas. Elevation is 650 to 775 feet.
K	Devils River	Swiftly moving stream, clear water (2-3 ft.) over gravel-rock bottom, sand banks, 10 to 12 feet wide with holes near mouth.

Appendix III: Table 68

Description of Limnological Sampling Stations in Thunder Bay Basin

Site	Water Resource	Location	Station Description
1	Main Branch	Alpena	Depth: 15 to 20 feet. Width: 150 to 175 feet. At the mouth of the main branch of the river the water drops off quickly at the breakwall where sample was taken five feet off shore. The shipping channel is dredged periodically so that the bottom and sides are silted and sparse of vegetation.
2	Main Branch	Ninth Street Bridge	Depth: 4 to 10 feet. Width: 100 to 150 feet. Current is dependent on dam operation, rocky bottom, and extensive growth on stones and large boulders.
3	Main Branch	Four Mile Dam	Depth: 2 to 4 feet. Width: 50 to 100 feet. Bottom type: Rocky with gravel and rock slabs. Vegetation: Some aquatic growth and algae. Current flow depends on operation of dam.
4	Lower South Branch	M-32 Bridge	Depth: 6 to 8 feet. Width: 20 to 25 feet. Bottom type: Silt-sand bottoms in holes and gravel and sandy in fast water. Vegetation: Heavy in clear, swift water and on sandbanks. Current is moderate-to-fast in ripples and shallow-rocky areas. Most deep holes have a large accumulation of wood and some vegetation on muddy-sandy bottoms.
5	Lower South	Hubbard Lake	Depth: 2 to 4 feet. Width: 30 to 50 feet. Bottom type: Sand and gravel marl. Vegetation: Some submerged growth and algae on rocks Swift current below dam as clear water. (Above Hubbard Lake, river has a moderate flow and is somewhat turbid from swamp areas - 3 to 4 feet deep.)

Table 68 (Cont'd.)

Site	Water Resource	Location	Station Description
6	Wolf Creek	Hubbard Lake Road Bridge	Depth: 4 to 8 feet. Width: 40 to 60 feet. Bottom type: Soft mud-silt and sand, little aquatic life and vegetation. Slight turbidity, with brown color and slow current.
7	Bean Creek	M-32 Bridge	Depth: 2 to 4 feet. Width: 10 to 15 feet. Silt bottom, very slow current, abundant vegetation as a drainage stream from swamp areas with brown color.
		Bean Creek Road Bridge	Depth: 1 to 3 feet. Width: 12 to 18 feet. Moderate current over rocks into intermittent holes, with silt-sand bottoms, clear and colored, few aquatic animals and little vegetation.
8	Upper South Branch	M-32 Bridge	Depth: 3 to 5 feet. Width: 40 to 60 feet. The level of this branch is controlled by a dam on Fletcher Pond. Flows swiftly over gravel-rocky bottom. Somewhat turbid with aquatic growth on rocks. (Mud-sand bottom at mouth, 4 to 6 feet deep.)
9	Upper South Branch	Turtle Lake Bridge	Depth: 4 to 6 feet. Width: 20 to 30 feet. Above Fletcher Pond, the stream has a swift current with a sand, gravel-rocky bottom and vegetation in siltation at bottom and sides of pools.
10	Main Branch	Hillman Dam	Depth: 3 to 6 feet. Width: 40 to 60 feet. Clear water and swift current below dam, with clay-silt bottom and gravel with algae. Crayfish are abundant.
11	Brush Lake and Creek	Dam at Hillman	Depth: Flows directly from lake over dam into main branch. Fast over rocks with algae growth, clear and colored
12	Main Branch	M-32 Bridge	Depth: 3 to 6 feet. Width: 30 to 50 feet. Turbid water with large amounts of sedimentation. Rock-clay bottom. River becomes turbid below the mouths of Gilchrist and Hunt Creeks as it flows into Hillman Pond.

Table (Cont'd.)

Site	Water Resource	Location	Station Description
13	Gilchrist Creek	M-33 Bridge	Depth: 2 to 4 feet. Width: 20 to 30 feet. Swift current in rapids over gravel-rocky bottoms. Holes at stream curves with sand-fine gravel bottom. Aquatic growth and siltation along banks.
14	Hunt Creek	At Mouth	Depth: 1 to 3 feet. Width: 15 to 20 feet. Rapid stream flow over rocks and gravel. Clear non-turbid water with siltation and vegetation along shore.
15	Main Branch	Atlanta Dam	Depth: 2 to 4 feet. Width: 30 to 40 feet. River flows from the Atlanta Pond over a dam used to control lake level. Current is swift over a rock-gravel bottom. Some aquatic growth on the stones.
16	Main Branch	McCormick Lake	Depth: 2 to 3 feet. Width: 15 to 20 feet. The headwaters of the Thunder Bay River is at the lake. Lake level-controlling dam is in disrepair. River flows swiftly over a clay-marl bottom with gravel and sand. Water is clear and has chalky color. Vegetation along lowlands and floodplains is extensive.
17	North Branch	Rush Lake	Depth: 1 to 2 feet. Width: 10 to 15 feet. A dam controls the Rush Lake Flood Area, so stream flows moderately fast through a swampy area over a sand bottom with siltation and vegetation along the shore. (Above Sunken Lake, river has a rocky, gravel bottom. Below the lake, the bottom is sand-muck with clay banks and hard outcrop bottom.)
18	North Branch	Male Corners Bridge	Depth: 6 to 8 feet. Width: 50 to 60 feet. Slowly moving, clear and colored, over sand bottom with some vegetation. Highly variable flow derived almost entirely from direct surface run-off draining fine, imperivous soils.

Appendix IV. Michigan Water Quality Standards

Appendix IV

Michigan Water Quality Standards
(Michigan Water Resources Commission, 1967)

DISSOLVED OXYGEN (mg/l)

Domestic Water Supply - Present at all times in sufficient quantities to prevent nuisance.

Recreation (Body Contact) - Present at all times in sufficient quantities to prevent nuisance.

Agricultural-Commercial - Average daily not less than 2.5, nor any single value less than 2.0.

Fish and Aquatic Life - At the average low river flow of 7-day duration expected to occur in 10 years the following D.O. values shall be:

Intolerant fish-cold water species - Not less than 6 at any time.

Intolerant fish-warm water species - Average daily D.O. not less than 5, nor shall any single value be less than 4.

Tolerant fish-warm water species - Average daily D.O. not less than 4, nor any single value less than 3.

TOXIC AND DELETERIOUS SUBSTANCES

Domestic Water Supply and Agricultural - Conform to current USPHS Drinking Water Standards as related to toxicants.

Recreation (Body Contact) - Limited to concentrations less than those which are or may become injurious to the designated use.

Fish and Aquatic Life - Not to exceed 1/10 of the 96-hour median tolerance limit obtained from continuous flow bio-assays where the dilution water and toxicant are continuously renewed except that other application factors may be used in specific cases when justified on the basis of available evidence and approved by the appropriate agency.

TOTAL DISSOLVED SOLIDS (mg/l)

Domestic Water Supply - Shall not exceed 500 as a monthly mean nor exceed 750 at any time. Chloride monthly mean shall not exceed 75, nor shall any single value exceed 125.

Recreation (Body Contact) - Limited to concentrations less than those which are or may become injurious to the designated use.

Fish and Aquatic Life - Standards to be established when information becomes available on deleterious effects.

APPENDIX IV (Cont'd.)

NUTRIENTS

(Same for all Uses)

Nutrients originating from industrial, municipal, or domestic animal sources shall be limited to the extent necessary to prevent the stimulation of growths of algae, weeds and slimes which are or may become injurious to the designated use.

TEMPERATURE (F)

Domestic Water Supply - The maximum natural water temperature shall not be increased by more than 10F.

Recreation (Body Contact) - Maximum - 90F.

Fish and Aquatic Life - In water capable of supporting:

	Ambient	Allowable Increase	Maximum Limit
Intolerant Fish-cold water species	32° to natural maximum	10°	70°
Intolerant Fish-warm water species	32° to 35°	15°	
	36° to natural maximum	10°	85°
Intolerant Fish-warm water species	32° to 59°	15°	
	60° to natural maximum	10°	87°

HYDROGEN ION (pH)

Domestic Water Supply - pH shall not have an induced variation of more than 0.5 unit as a result of unnatural sources.

Recreation (Body Contact) - Maintained within the range 6.5 to 8.8 with a maximum induced variation of 0.5 unit within this range.

Fish and Aquatic Life - Maintained between 6.5 and 8.8 with a maximum artificially induced variation of 1.0 unit within this range. Changes in the pH of natural waters outside these values must be toward neutrality (7.0).