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HYDROLYSIS OF CONDENSED PHOSPHATES IN NATURAL WATERS

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Abstract—An investigation was conducted on the rates of hydrolysis of pyrophosphate and tripolyphosphate to orthophosphate under laboratory conditions in various types of natural waters. The rates of hydrolysis of pyrophosphate varied from 0.08 to 0.21 mg P/l per 500 hr at 4° C and from 0.23 to 0.47 mg P/l per 500 hr at 20° C. The rates of hydrolysis of tripolyphosphate varied from 0.07 to 0.22 mg P/l per 500 hr at 4° C and from 0.34 to 0.5 mg P/l per 500 hr at 20° C.

Studies on Black Earth Creek located near Madison, Wisconsin, showed the presence of an apparent "natural" condensed phosphate that hydrolysed at approximately the same rate as tripolyphosphate.

INTRODUCTION

THE USE of condensed phosphate, especially tripolyphosphate, as builders in synthetic detergents has raised questions about the possible effect of these compounds on water quality. Two frequently mentioned possible effects are (1) fertilization of waters resulting in increased growth of aquatic plants, and (2) interference in water treatment processes such as coagulation and softening. SAWYER (1965) and SHANNON (1965) have recently discussed the problems of phosphorus in water supplies. In addition to the potential problems cited by SAWYER, *et al.* (1964) have shown that condensed phosphates can adversely affect lime-softening of water.

Numerous studies have shown that tripolyphosphate and a hydrolysis product, pyrophosphate, hydrolyse to orthophosphate in waste treatment facilities and natural waters. CLESCERI and LEE (1965*a*, *b*) have summarized these previous studies and also presented additional information on the hydrolysis of these compounds. These studies have shown that the rates of hydrolysis of these compounds under conditions similar to those encountered in natural waters are controlled by biochemical reactions in which the rates of hydrolysis are dependent on the numbers and types of microorganisms present in a water. The previous studies show a different rate dependent on the source of the water and temperature of the experiment. Since the previous studies were conducted under different conditions, it is desirable to compare rates of hydrolysis of tripolyphosphate and pyrophosphate in waters of different chemical composition under identical experimental conditions. This paper reports such an investigation and includes a study on the effect of temperature on the rates of hydrolysis of these compounds.

EXPERIMENTAL PROCEDURE

Analytical methods

Orthophosphate. The analysis of orthophosphate was accomplished by a method similar to the stannous chloride method for orthophosphate reported in STANDARD

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METHODS (1960) without extraction. This analytical method was modified for use on the Technicon AutoAnalyzer. The details of this modification were presented by SHANNON (1965).

All orthophosphate analyses were conducted on samples that had been filtered through a 0.45 μ Millipore HA Filter.

Condensed phosphates. Condensed phosphates were defined in this investigation as the amount of increase in orthophosphate that was found after mild acid hydrolysis of the sample. Studies by LEE *et al.* (1965) have shown that both tripolyphosphate and pyrophosphate are measured by this procedure. In addition to these compounds, there is evidence that naturally occurring organic phosphate compounds are also measured by this method. The mild acid hydrolysis was accomplished by adding a small amount of H_2SO_4 and HNO_3 to the sample and autoclaving for 30 min at 15 psi. The details of the procedure were reported by LEE *et al.* (1965). The orthophosphate concentration of the hydrolysed samples was determined by the procedure described above after neutralization of the acid with NaOH. The condensed phosphate concentrations were obtained by subtracting the concentrations of orthophosphate found in the sample without hydrolysis from those found for the sample that had been hydrolysed. All condensed phosphate analyses were made on samples that were filtered through a 0.45 μ Millipore Filter prior to hydrolysis.

Total phosphate. The total phosphate analyses were accomplished by boiling the sample in the presence of concentrated H_2SO_4 and HNO_3 for at least 3 hr. The details of this procedure have been reported by LEE *et al.* (1965). After the strong acid digestion, the sample was neutralized with NaOH, filtered through Whatman No. 1 filter paper to remove boiling chip debris, and the orthophosphate content of the sample was determined as described above. The total phosphate analyses were performed on unfiltered samples. Therefore, the particulate matter in the sample was subject to the strong acid hydrolysis.

The study has substantiated the results of LEE *et al.* 1965) in the need for separate calibration curves for condensed and also total phosphate due to the salt effect caused by the neutralization products of the hydrolysed solution. Calibration curves were prepared using known concentrations of orthophosphate that were carried through the hydrolysis reactions. Examples of the differences in absorbance for a 1 mg P/l orthophosphate, condensed phosphate procedure, and total phosphate procedure were 0.410, 0.430, and 0.460, respectively.

Calcium and magnesium. The calcium and magnesium concentrations were determined on an atomic absorption spectrophotometer, Perkin–Elmer Model 303.

pH Measurement. The pH was measured with a Beckman Model N or GS pH meter.

Dye tracer measurements. A Turner Fluorometer Model 111 with 546 and 590 mμ filters and high volume continuous flow cell was used to measure the concentration of DuPont's Pontacyl Brilliant Pink B dye used in tracer studies. The dye tracer field data were corrected for temperature using calibration curves run at various temperatures. Sampling for the dye tracer study was accomplished by pumping the water with a submersible pump, located at midstream, through the Turner Fluorometer.

Reagents. All reagents were A.C.S. reagent grade unless otherwise specified, except for sodium tripolyphosphate which was anhydrous High Purity from Victor Chemical Company.

Phosphate sample preservation. The phosphate samples were preserved by adding 3 ml of chloroform to 300 ml of sample. The samples were stored at 4° C until analysed. All glassware used was acid rinsed to remove sorbed phosphates from detergents used in cleaning.

Laboratory hydrolysis investigations

The laboratory hydrolysis studies were conducted in glass bottles of 2.5 l. capacity. The samples were incubated in the dark in constant temperature rooms at 4 ± 1° or 20 ± 1° C. After temperature equilibration, either pyrophosphate or tripolyphosphate was added to a 2 l. portion of the water sample. Periodically, samples were taken from these bottles and analysed for various forms of phosphates.

Water samples were collected from Lake Mendota and Black Earth Creek, both of which are located near Madison, Wisconsin. The Lake Mendota samples were taken from an untreated water supply intake on 11 February, 1965. This intake was located 8 ft below the surface at a place where the lake is 20 ft deep, and 600 ft from shore at the Water Chemistry Laboratory. The low-hardness water was prepared using 1 l. of Lake Mendota water and 9 l. of distilled water. The Black Earth Creek water samples were taken at stations BEC5 and BEC8 (see Fig. 1) in February 1965. The BEC5 water sample contained apparent "natural" condensed phosphate as defined by the condensed phosphate analytical procedure.

Field hydrolysis investigations

The field hydrolysis investigations were conducted on Black Earth Creek. This stream is located approximately 20 miles west of Madison, Wisconsin, near the villages of Cross Plains and Black Earth. Cline (1963) has discussed the hydrology of this stream, while Collier (1963) has discussed the sediment discharge characteristics of the stream.

The drainage basin has an area of 46 miles^2 and is located in hilly terrain with about 400 ft difference in elevation. In this basin the creek is approximately 11 miles in length and is classified by the Wisconsin Conservation Department as a trout stream. The creek winds through outwash and alluvium of Pleistocene and Recent Age which forms the valley floor.

The average annual rainfall for the basin is 30 in/yr, of which 7 in/yr infiltrates and recharges the ground water reservoir. In the basin the ground water moves in the general direction of Black Earth Creek and is discharged into the creek. Ground water is the main source of the flow in Black Earth Creek, the exception being during and immediately after precipitation. The United States Geological Survey has maintained a gaging station at BEC12 (see Fig. 1) since February 1954. This gage is 0.7 miles east of the village of Black Earth, which is on the western edge of the upper Black Earth Creek Drainage Basin. An average flow of 31 ft^3/sec has been recorded at this station during these years. The high flow occurs during the spring thaw, usually in late March or early April, which increases the flow up to about 400 ft^3/sec for a period of several days to a week. The rest of the year Black Earth Creek at the gaging station has a flow around 20 ft^3/sec, with a slow decrease in flow from June to August.

A map of upper Black Earth Creek is presented in Fig. 1. The creek originates in a marshy area in the eastern part of the drainage basin. It receives discharge from the ground water reservoir along its entire length with approximately 46 per cent of the flow at the gaging station originating upstream from station BEC5. The creek passes through and receives the waste waters from Cross Plains, which had a population of 1066 people in 1960. The major contributor of wastes to the creek is the Cross Plains primary sewage treatment plant. In addition to domestic wastes, this treatment plant also receives waste waters from a creamery. The treatment plant is presently operating above its designed capacity and is under order from the Wisconsin State Board of Health to improve its facilities. The treatment plant dicharges primary treated sewage effluent intermittently into the creek. This type of discharge is referred to as a slug of sewage effluent. The creamery is also a codefendant with the treatment plant as the possible source of problems related to the fish kills that instigated the Board of Health's inquiry and action. The fish kill problem is related to the low dissolved oxygen concentration in the creek below the treatment plant during the night.

Black Earth Creek sampling by the University of Wisconsin Water Chemistry group was started on a monthly basis in January 1965. The following is a location description of the sampling stations on Black Earth Creek by number.

Station number	Location and description
BEC0	½ mile upstream from village of Cross Plains.
BEC1	Upstream edge of the village of Cross Plains.
BEC2	In the village of Cross Plains.
BEC3	Downstream edge of the village of Cross Plains. The sewage effluent from the village is discharged just upstream of this station.
BEC5	Approximately 1 mile downstream from BEC3.
BEC8	Approximately 2 miles downstream from BEC3.
BEC10	Approximately 3 miles downstream from BEC3.
BEC12	Approximately 4½ miles downstream from BEC3. The USGS gage is located at this station.
BEC13	Approximately ½ mile downstream from BEC12.

The field hydrolysis studies included investigations on the amounts and forms of phosphorus compounds in Black Earth Creek. In addition, a slug of sewage effluent was tagged with Pontacyl Brilliant Pink B dye. The concentration of dye and phosphorus compounds were determined.

EXPERIMENTAL RESULTS

The results of the laboratory studies will be presented first, followed by field studies.

Laboratory studies

Each laboratory hydrolysis investigation was carried out using 2 l. of the sample water equilibrated at either 4° or 20° C. Pyrophosphate or tripolyphosphate was added to give a total phosphorus concentration of approximately 0.6 mg P/l. The pH was measured after the condensed phosphate addition. An analysis sample of approximately 100 ml. was withdrawn initially and at different intervals of time, and the three phosphate procedures were run in triplicate. The triplicate results gave ±0.003mg P/l

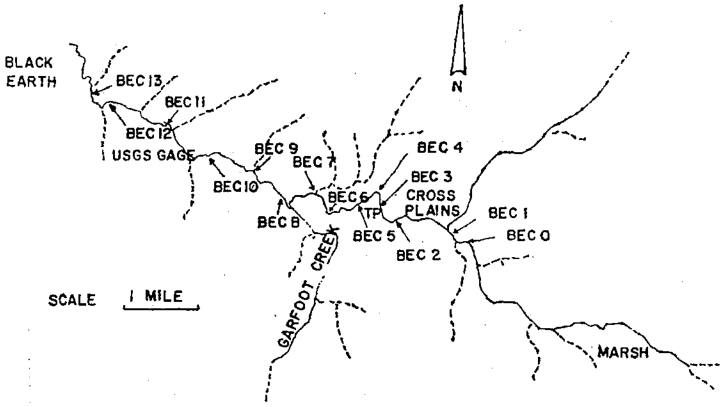

FIG. 1. Map of Upper Earth Creek.

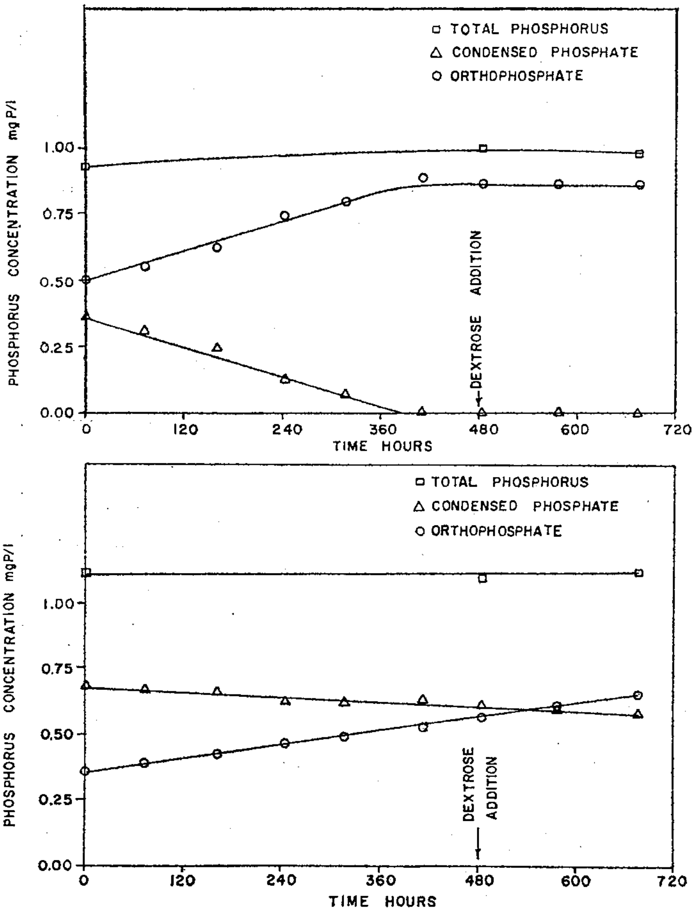

FIG. 2. Hydrolysis of pyrophosphate in Lake Mendota water. pH 8.4, Ca^{++} 25 mg/l, Mg^{++} 36.2 mg/l. Upper 20° C, lower 4° C.

for the orthophosphate and condensed phosphate procedures and were ±0.033 mg P/l for the total phosphorus procedure.The rate of decrease of the condensed phosphate and the rate of increase in orthophosphate were measured for approximately 500 hr. All hydrolysis water samples were aerated for 30 min each day of the study. At the end of the 500 hr period, dextrose was added to certain of the water samples to stimulate bacterial growth. The hydrolysis of the condensed phosphates in these water samples was examined for an additional 200 hr. These solutions were aerated continuously during this period.

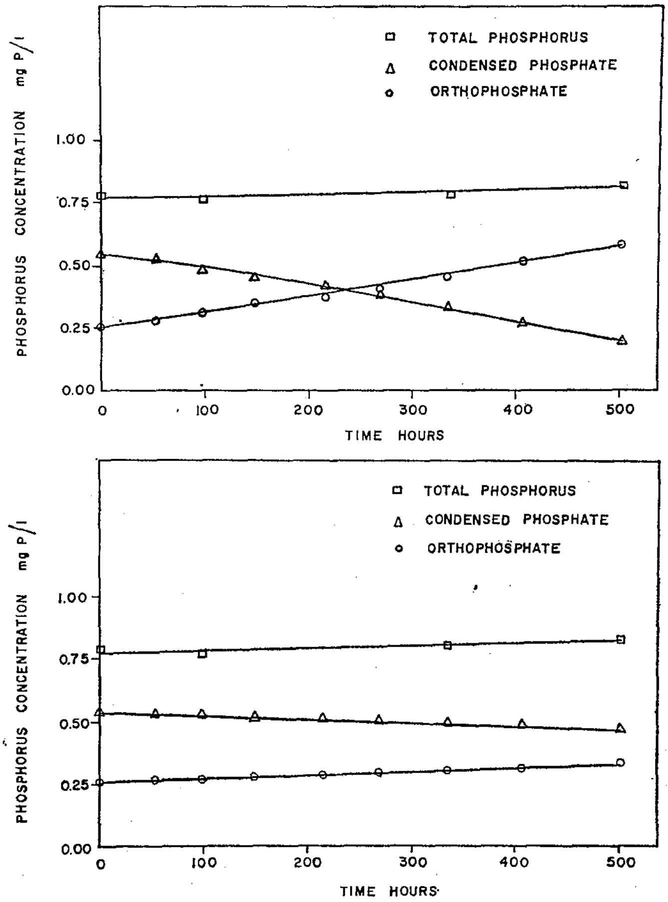

FIG. 3. Hydrolysis of tripolyphosphate in Lake Mendota water. pH 8.4, Ca^{++} 25 mg/l, Mg^{++} 36.2 mg/l. Upper 20° C, lower 4° C.

Typical data for the hydrolysis of pyrophosphate and tripolyphosphate is presented in FIGS. 2–6. The complete data for this study is presented by SHANNON (1965). In general, these studies show that the disappearance of pyrophosphate and tripolyphosphate and the appearance of orthophosphate proceeds at essentially a constant linear rate in each of the waters studied. With few exceptions, the decrease in the condensed phosphate equalled the increase in the orthophosphate. The difference between the sum of the orthophosphate plus condensed phosphates and the total phosphate is due to the presence of particulate phosphorus (organisms and detritus) in the sample. The orthophosphate and condensed phosphate analyses were performed on filtered samples. It is apparent from these figures that the addition of 50 ppm of dextrose did not alter the rates of hydrolysis of these compounds. This result is different from that found by CLESCERI and LEE (1965*a*) where the addition of dextrose increased the rate of hydrolysis. The difference in experimental conditions of the two studies may account for these results. In this study the sample was stored in the dark while Clesceri and Lee samples were exposed to continuous illumination. Based on the turbidity and appearance of the sample, Clesceri and Lee had large algal populations in the sample, while there was no visible evidence of algae in these samples.

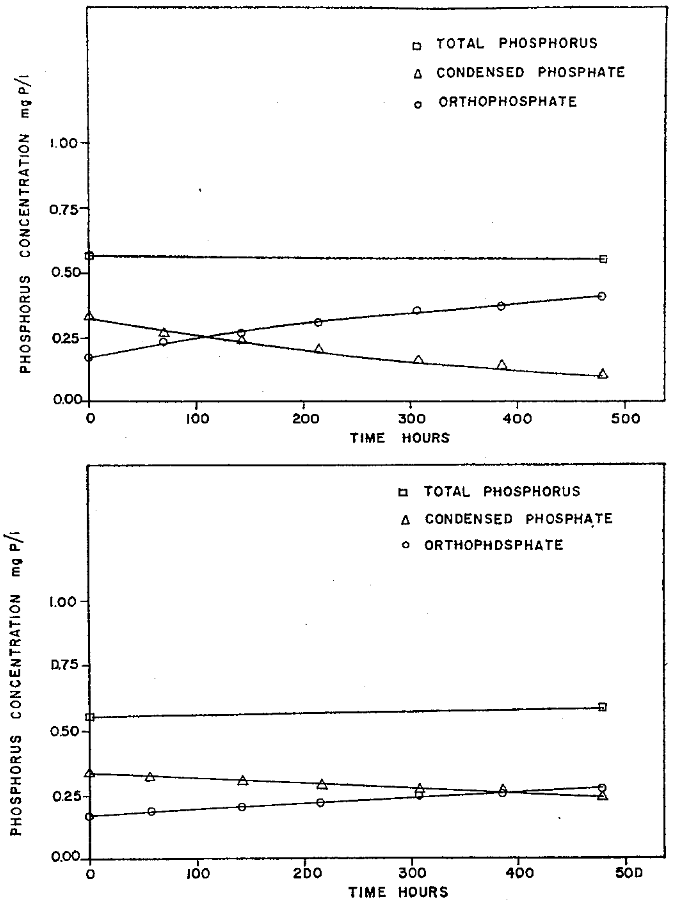

FIG. 4. Hydrolysis of pyrophosphate in Black Earth Creek water. pH 8.6, Ca^{++} 45.4 mg/l, Mg^{++} 36.8 mg/l. Upper 20° C, lower 4° C.

In order to compare the rates of hydrolysis of these compounds in the various waters and experimental conditions, the amount of hydrolysis that took place in a 500 hr period was computed for each run. In those runs which show a deviation from the linear relationship, only the initial part of the curve was used. The results of these computations are presented in TABLE 1.

TABLE 1. RATE OF HYDROLYSIS OF CONDENSED PHOSPHATES

Run No.	Temperature (°C)	Type	Concentration of condensed phosphates Initial (mg P/l)	Final (mg P/l)	Computed rate of hydrolysis (mg P/l/500 hr)
Distilled water, added condensed phosphates					
3	20	pp	0.454	0.297	0.163
4	4	pp	0.704	0.685	0.020
5	20	tp	0.528	0.157	0.370
6	4	tp	0.545	0.528	0.013
Lake Mendota water, added condensed phosphates					
7	20	pp	0.359	0.000	0.472
8	4	pp	0.678	0.606	0.075
9	20	tp	0.542	0.202	0.339
10	4	tp	0.535	0.463	0.072
Low hardness water, added condensed phosphates					
11	20	pp	0.326	0.150	0.407
12	4	pp	0.323	0.121	0.211
13	20	tp	0.518	0.302	0.500
14	4	tp	0.512	0.297	0.224
Black Earth Creek water, added condensed phosphates					
15	20	pp	0.326	0.104	0.232
16	4	pp	0.330	0.235	0.099
17	20	tp	0.525	0.153	0.388
18	4	tp	0.522	0.414	0.114
Black Earth Creek water, apparent "natural" condensed phosphates					
19	4	n	0.434	0.307	0.133
20	20	n	0.437	0.130	0.321

Pyrophosphate—pp; tripolyphosphate—tp; apparent "natural" condensed phosphate—n.

The apparent "natural" condensed phosphate reported in this table as Runs 19 and 20 and shown in FIG. 6 is a sample of Black Earth Creek water that was obtained just downstream from point of discharge of the Cross Plains sewage effluent. This sample did not contain any added condensed phosphates. At the time that this sample was taken there was no condensed phosphate in the stream above the point of discharge of sewage effluent; it is reasonable to propose that the condensed phosphate found in this sample was derived from the sewage effluent. It is interesting to note that this "natural" phosphate hydrolysed at approximately the same rate as that found for pyrophosphate and tripolyphosphate.

The rates of hydrolysis in distilled water were somewhat higher than CLESCERI and LEE (1965*b*) reported for the hydrolysis of these compounds in sterile lake water. No attempt was made in the current study to keep the sample sterile and, therefore, the hydrolysis found could be due to the presence of small numbers of microorganisms in the sample.

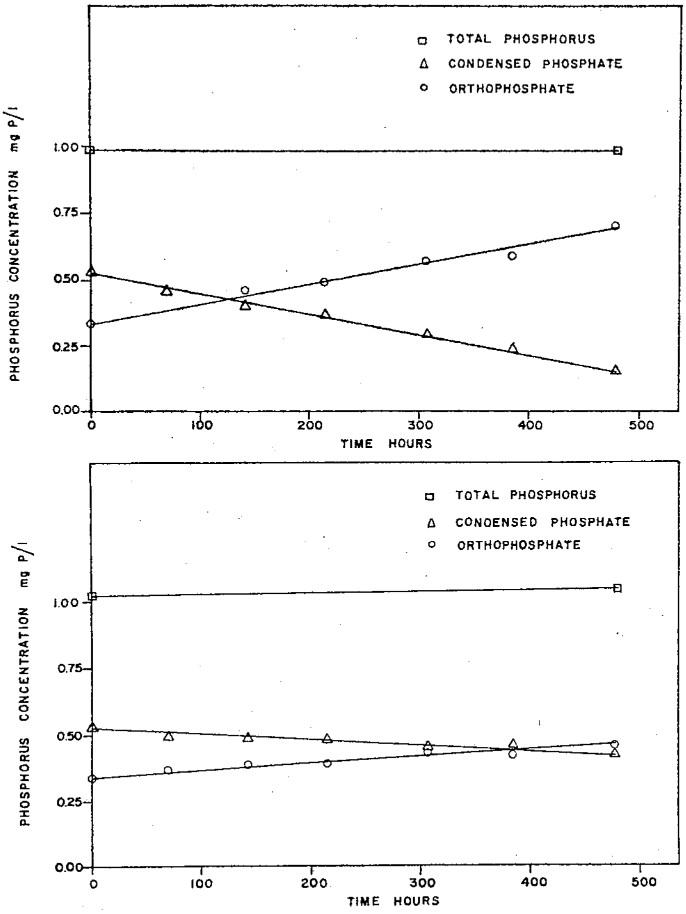

FIG. 5. Hydrolysis of tripolyphosphate in Black Earth Creek water. pH 8.6, Ca^{++} 45.4 mg/l, Mg^{++} 36.8 mg/l. Upper 20° C, lower 4° C.

The studies on the various types of natural waters showed approximately the same rate of hydrolysis irrespective of the source of the water. However, there was a factor of two-to-five fold increase in rate when the temperature was 20° C as compared to 4° C. This temperature dependence could be due to an increased rate of metabolic activity at the higher temperature. Also, it is possible that the numbers and types of organisms in the sample were different for the two temperatures.

Field studies

Hydrolysis in situ *in Black Earth Creek.* An attempt to determine the rate of hydrolysis in the stream of the apparent "natural" condensed phosphate as defined by the analytical condensed phosphate procedure was made. It was known that the Cross Plains sewage treatment plant was a large contributor of apparent "natural" condensed phosphate to Black Earth Creek from the previous collected data on the creek. This data will be presented later.

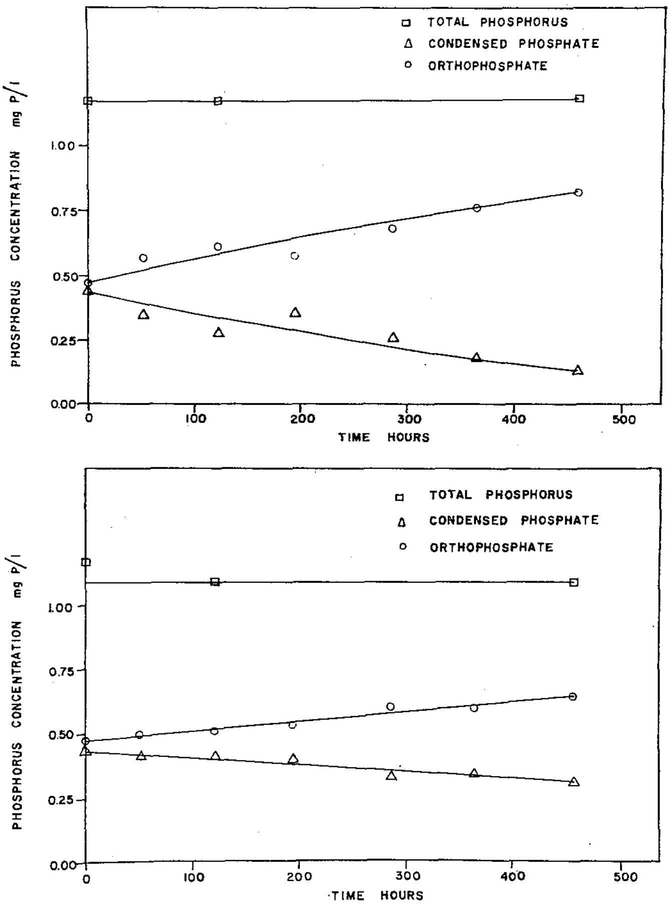

FIG. 6. Hydrolysis of apparent "natural" condensed phosphate in Black Earth Creek water. pH 7.9, Ca^{++} 31.8 mg/l, Mg^{++} 38.8 mg/l. Upper 20° C, lower 4° C.

On 14 May, 1965, a known amount of Pontacyl Brilliant Pink B dye was instantaneously injected into the first portion of a sewage slug being discharged from the Cross Plains sewage treatment plant at 11.06 a.m. This primary sewage treatment plant discharges its effluent intermittently. The duration of this discharge varies. The slug of sewage effluent was of approximately 30 min duration and discharge to the creek was continuous during this time. The concentration of dye, dissolved oxygen and temperature were determined at BEC5 approximately 1 mile downstream from the sewage treatment plant discharge. In addition, a sample of the creek water was obtained in the dye patch for initial phosphate concentrations and samples of water were taken every 15 min at BEC5 for phosphate analysis. The dye tracer curve, temperature and dissolved oxygen are presented in FIG. 7. The temperature increased with the heat of the day as would be expected. The dissolved oxygen decreased during the dye tracer curve of the slug of sewage effluent. Although the dissolved oxygen was supersaturated with respect to the atmosphere, the decrease was probably due to consumption by biochemical oxygen demand of the sewage effluent. The dye curve was used to determine the

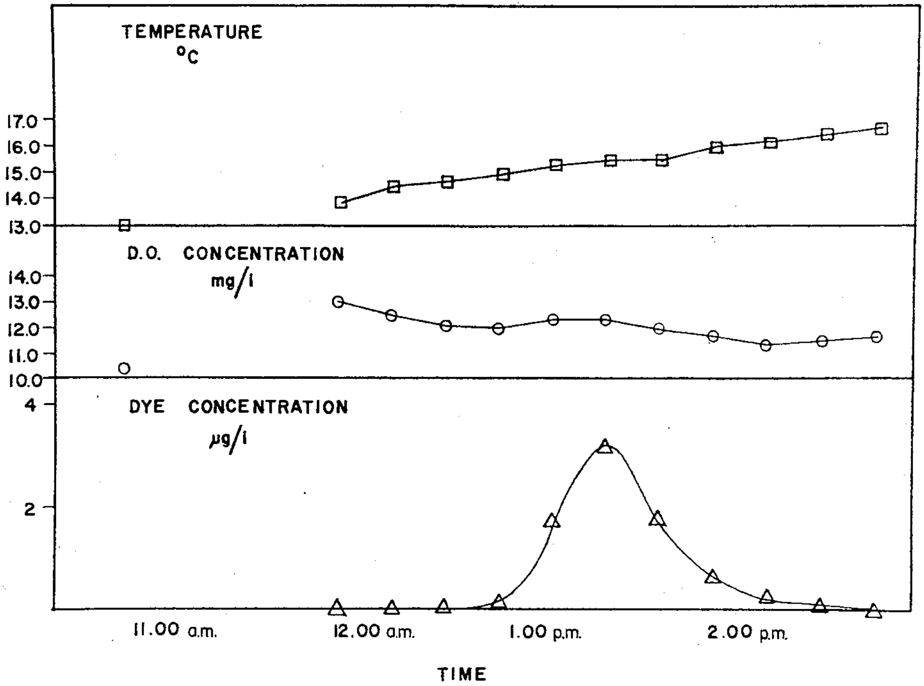

FIG. 7. Dye tracer study data for Black Earth Creek. 14 May, 1965 at BEC5.

travel time between the sewage treatment plant outlet above station BEC3 and the monitoring station BEC5. A mean travel time was calculated to be 2 hr and 22 min and the median travel time was calculated to be 2 hr and 11 min. The discharge, 75 ft upstream from BEC5, was estimated to be 6 ft^3/sec. The dye curve gives an indication of dilution of groundwater and longitudinal dispersion in this reach of the creek. Examinaton of the dye tracer curve shows that this reach of the creek has a rather large amount of longitudinal dispersion as shown by the fact that in a distance of one mile downstream, approximately 2 hr were required for the concentration of dye to decrease below detectable limits. The high longitudinal dispersion coefficient for this reach of the creek is due in part to the fact that the Wisconsin Conservation Department has placed logs in the stream at frequent intervals to provide additional fish habitats. These logs are positioned in the stream so that a large number of small pools are formed which tend to create short circuiting and mixing in the creek.

FIGURE 8 shows the total phosphorus, condensed phosphate and orthophosate values during the dye tracer experiment and the initial concentrations in the dye patch. Examination of this figure shows that the initial concentrations of orthophosphate, condensed phosphate and total phosphorus were 0.304, 0.124, and 0.515 mg P/l, respectively, at BEC3 in the dye patch, while some 2.5 hr later the mean concentration for orthophospate was 0.319 mg P/l with ranges for condensed phosphate and total phosphororus of 0.098 to 0.140 mg P/l and 0.450 to 0.612 mg P/l, respectively. It is also readily apparent from this study that the concentrations of orthophosphate and apparent "natural" condensed phosphate were reasonably constant during the sampling period. However, marked changes are noted in the total phosphorus concentration during this period. This variability could be due in part to the fact that the total phosphorus analysis included the particulate matter in the sample and, therefore, variations in the amount of suspended matter in the sample could account for the total phosphorus results. This is particularly true since the stream normally appears quite turbid at BEC5.

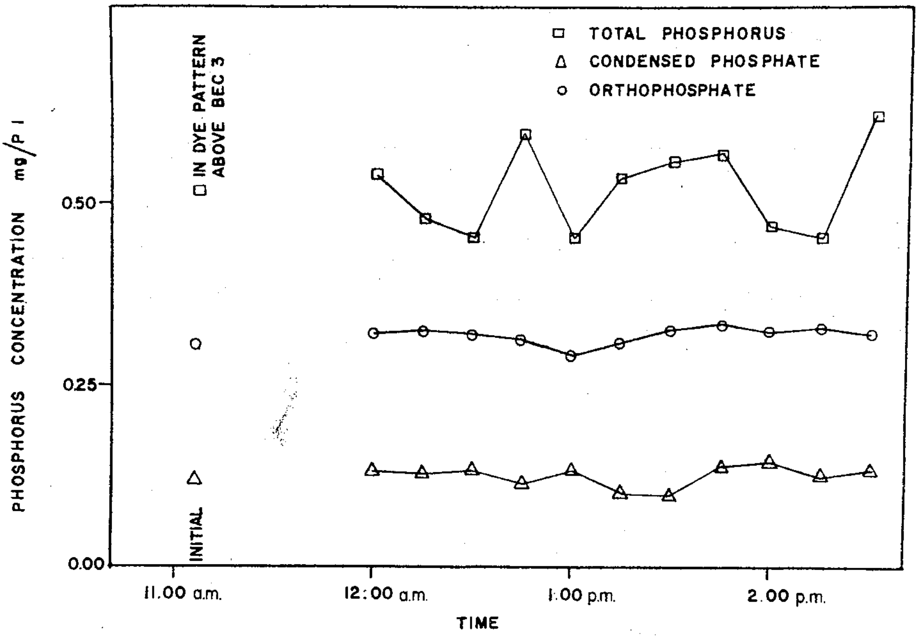

FIG. 8. Phosphate data for dye tracer study for Black Earth Creek. 14 May, 1965 at BEC5.

Based on the concentrations of the various forms of phosphate in the single initial grab sample of water, it is seen that no significant hydrolysis of the apparent "natural" condensed phosphate occurred in the slug of sewage effluent in 2.5 hr as it passed downstream to BEC5. Actually, if the rates of hydrolysis obtained in the laboratory studies are applied to field conditions, no detectable hydrolysis of condensed phosphates would be expected in a 2–3-hr-period. In order to use the dye tracer technique of studying the *in situ* rate of hydrolysis of the apparent "natural" condensed phosphate, a much longer reach of creek would have to be studied, and also frequent samples of the upstream water at BEC3 would have to be taken to determine variability of the initial concentrations of the various forms of phosphorus in the stream. This study has shown that there is not a marked increase in rate of hydrolysis of condensed phosphate in this stream as compared to laboratory studies.

Black Earth Creek phosphate studies

In order to obtain data on the amounts and various types of phosphorus compounds present in Black Earth Creek, a monitoring program was initiated. This study included monthly samples over a distance of approximately 15 miles, daily samples for 15 days during spring runoff, and hourly samples during one day.

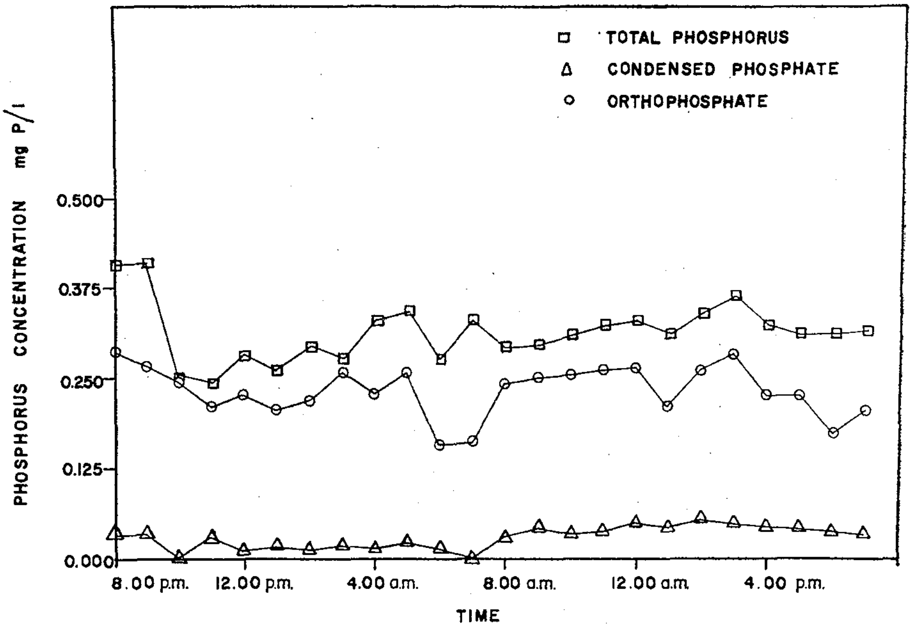

FIG. 9. 24 hr survey on Black Earth Creek. 12–13 March, 1965 at BEC1.

All of these samples were analysed for orthophosphate, condensed phosphate and total phosphorus. The results of these studies are summarized below. The complete data for these studies is presented by SHANNON (1965).

24-hr-survey. Since previous studies had shown that the phosphorus concentration was highly variable from station to station and at various times, a 24-hr-survey was conducted on 12 and 13 March, 1965. Seven stations, BEC1, BEC2, BEC3, BEC5, BEC8, BEC10 and BEC12+13, were sampled hourly. Station BEC12 was sampled ten times from 2.00 a.m. to 11.00 a.m. on 13 March, 1965, and station BEC13 was sampled the other fourteen times during the 24 hr survey. At each station the pH and temperature were measured and a water sample for the phosphate determinations was preserved. The hourly total phosphorus, condensed phosphate, and orthophosphate values are presented in FIGS. 9, 10, and 11.

It is helpful at this point to review the setting of the Black Earth Creek Stations with regard to potential sources of phosphorus. Black Earth Creek is located in a small highly fertile valley. This fact in itself suggests that an important source of phosphorus during periods of surface runoff would be material leached from the soil; extensive farming is practiced in the valley with corn being the principal crop. In addition to commercial fertilizers, large amounts of manure are spread on the soil from dairies (farms). Therefore, it is reasonable to expect that surface runoff would carry fertilizers

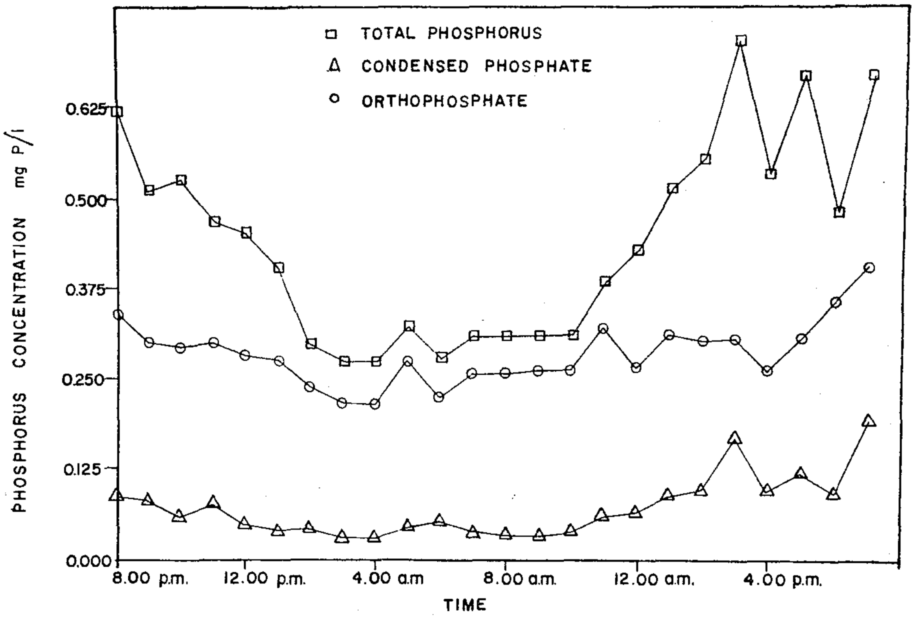

FIG. 10. 24 hr survey on Black Earth Creek. 12–13 March, 1965 at BEC5.

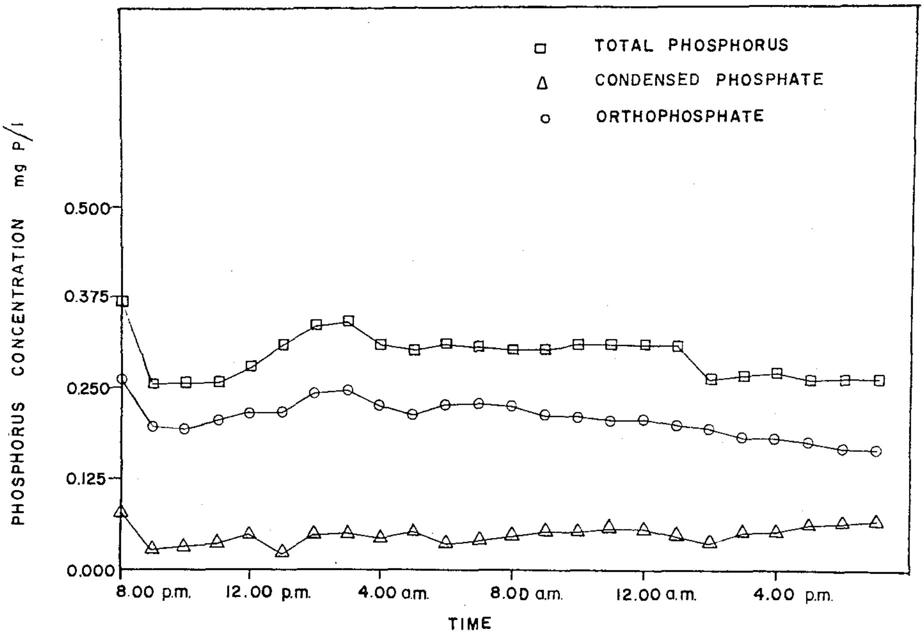

FIG. 11. 24 hr survey on Black Earth Creek. 12–13 March, 1965 at BEC12 and BEC13.

from the farmland. A third possible source of phosphorus is from several dairies that are located along the creek. Although dairy clean-up operations could bring phosphorus to the stream in the clean-up water, this source would probably be most significant when there is surface runoff. With the possible exception of the latter, the amounts of phosphorus contributed to the stream during the 24 hr survey were small since the ground was frozen and snow-covered. Therefore, surface runoff was minimal during the survey. The discharge into the stream at the time of study was due to ground water and waste water effluents. The mean discharge in the creek at BEC12 during the survey was 29 ft^3/sec. In addition to domestic sewage, another possible source of phosphorus to the creek is the septic tanks from the numerous farms that line the creek bank. As previously mentioned, the Cross Plains treatment plant effluent contains waste waters from a creamery which may be a major contributor of phosphorus.

Examination of the data obtained during this 24 hr survey, as presented in FIGS. 9 and 11, shows that the majority of the phosphorus present in the creek at all stations is measured as orthophosphate. However, all stations do show small amounts of compounds that are measured by the condensed phosphate procedure. The presence of condensed phosphates would be expected downstream from BEC3 since the sewage effluent should contain small amounts of these compounds. However, it is somewhat surprising to find these compounds at BEC1. Based on the data available, it is reasonable to propose that the apparent condensed phosphate at BEC1 is derived from natural sources in the marsh and is probably an organic phosphorus compound, which is hydrolysed to orthophosphate by the condensed phosphate analytical procedure. The difference in the concentrations of orthophosphate plus condensed phosphate and total phosphorus represents the particulate phosphorus and any difficult-to-hydrolyse organic phosphorus compounds.

Although there was considerable variation of all types of phosphorus at each station, the largest variation and highest concentrations were observed at BEC3, which is immediately downstream from the sewage treatment plant. These variations are due to (1) intermittent discharge of sewage effluent and (2) variation in the concentrations of phosphates in the effluent with time of day. The temperature range for all stations during the survey was 2.7 to 7.5° C. FIGURE 12 presents the high, low and mean apparent "natural" condensed phosphate values for each station during the 24 hr survey. All stations show a mean concentration of apparent "natural" condensed phosphate which is equal to or above the sodium tripolyphosphate level that causes interference with water treatment (COHEN *et al.* 1959). Although station BEC3 shows the highest apparent "natural" condensed phosphate values, the leveling effect due to mixing and dilution by ground water was observed at station BEC5, which had the highest mean concentration. The increase in apparent "natural" condensed phosphate downstream from BEC5 was probably due to drainage from farms along the stream bank.

It should be pointed out that no attempt was made in this study to verify the presence of pyrophosphate and tripolyphosphate in the stream. Therefore, it is not known whether or not the compounds measured as condensed phosphate would, in fact, interfere in water treatment processes.

"*Spring thaw*"*studies.* During the period of 29 March, through 13 April, 1965, daily samples were collected at BEC1, BEC5, BEC8, and BEC13. The mean daily discharge as measured at BEC12 and conductance of the water during this period is presented

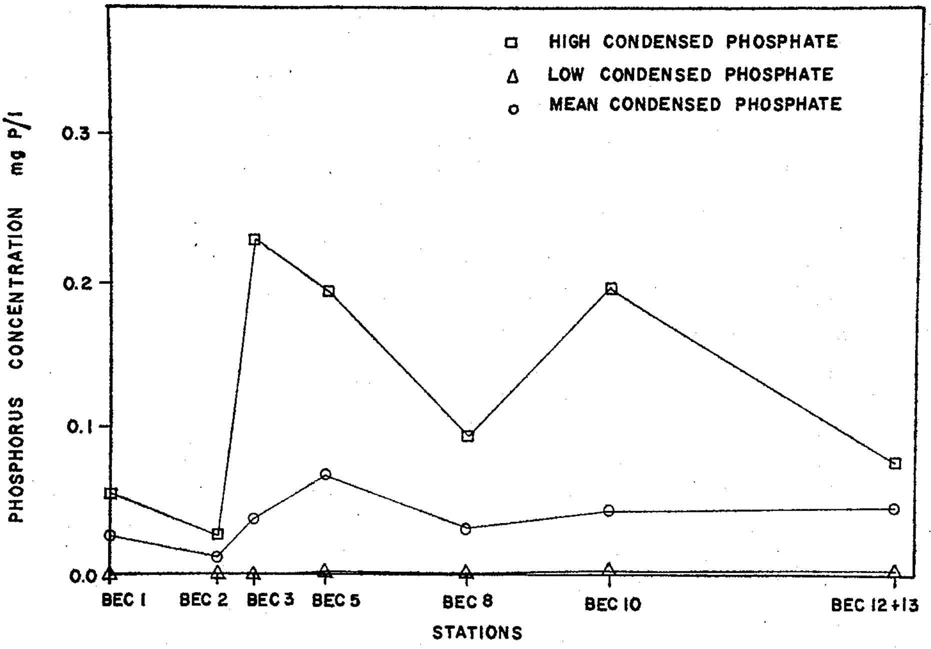

FIG. 12. 24 hr survey of apparent "natural" condensed phosphate in Black Earth Creek. 12–13 March, 1965.

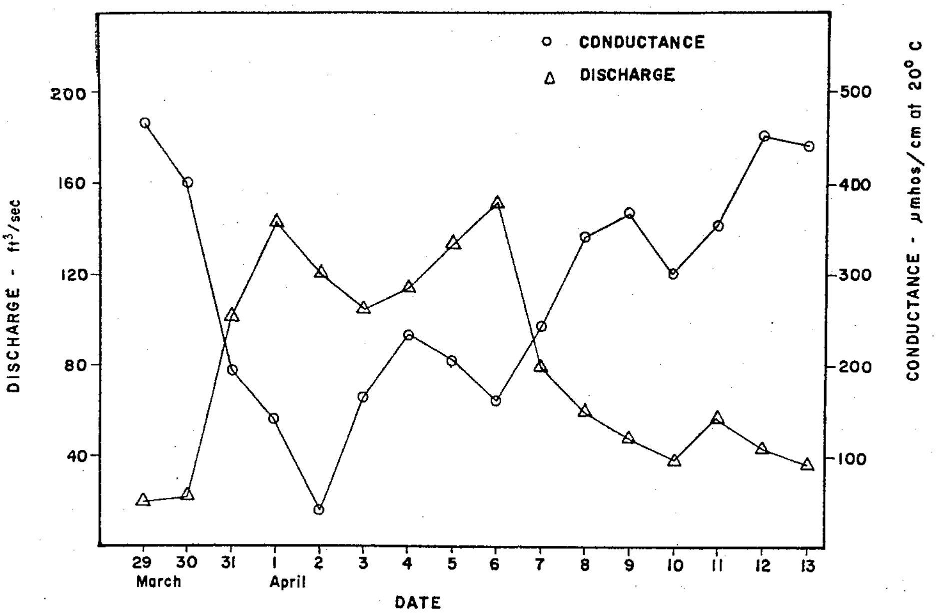

FIG. 13. Conductance and discharge of Black Earth Creek at BEC12 during spring "thaw" 1965.

in FIG. 13. Examination of this figure shows a maximum discharge of 143 ft^3/sec on 1 April. The discharge in the stream up to 13 April was due to melting of snow. Rain, on 4 April, increased the discharge to a maximum of 153 ft^3/sec on 6 April. After this date the flow gradually returned to normal. As expected, the specific conductance of the stream showed an inverse relationship to discharge. This can be accounted for by dilution of the base flow with snow melt waters and runoff of rainwater. The phosphorus data for BEC1, BEC5, and BEC13 are presented in FIGS. 14, 15, and 16, respectively.

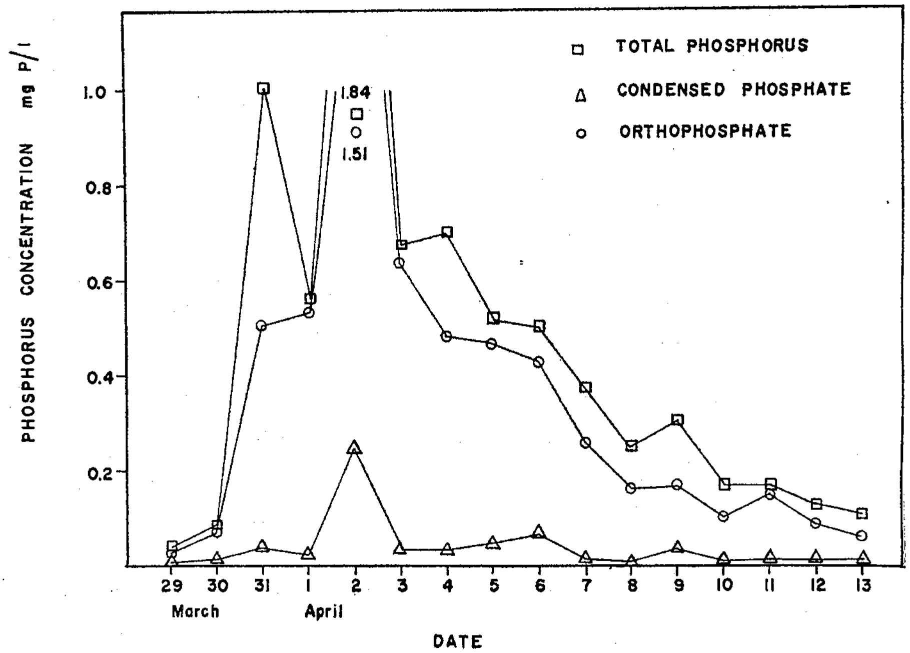

FIG. 14. Phosphorus concentrations in Black Earth Creek during spring "thaw" 1965 at BEC1.

Examination of FIG. 14 shows the flushing action of the spring thaw in the marsh and watershed above BEC1, thereby releasing unusually large concentrations of apparent "natural" condensed phosphate which decreased to the usual low levels after the spring thaw. As can be seen from this data, all forms of phosphorus increased markedly during the peak flow period, and the majority of the phosphorus detected was in the orthophosphate form. The high concentrations of phosphorus gradually declined to normal levels by the end of the spring thaw period.

Monthly sampling program. The results of the monthly program (data not presented) show that during periods of base flow, approximately 20 ft^3/sec at BEC12, the orthophosphate concentration above BEC3 and below BEC8 were a few tenths or less of a mg P/l, while the total phosphorus was approximately a tenth of a mg P/l higher than the orthophosphate. The condensed phosphates for these stations ranged from non-detectable to 0.02 mg P/l. However, at BEC3, BEC4, and BEC5 concentrations of all forms of phosphorus were considerably higher, with condensed phosphate concentrations in the order of 0.05 mg P/l at BEC4. The higher concentrations of phosphorus

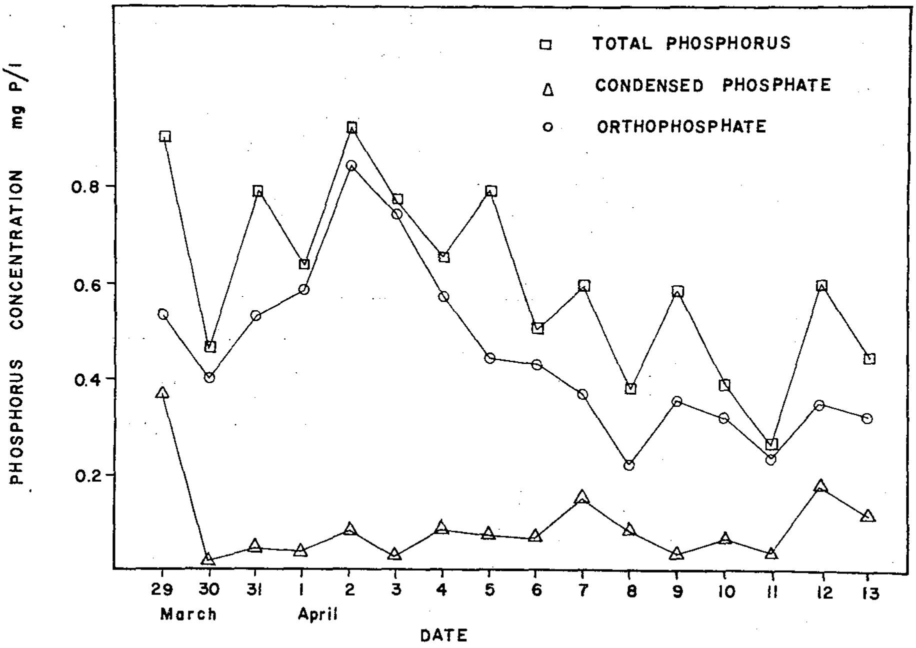

FIG. 15. Phosphorus concentrations in Black Earth Creek during spring "thaw" 1965 at BEC5.

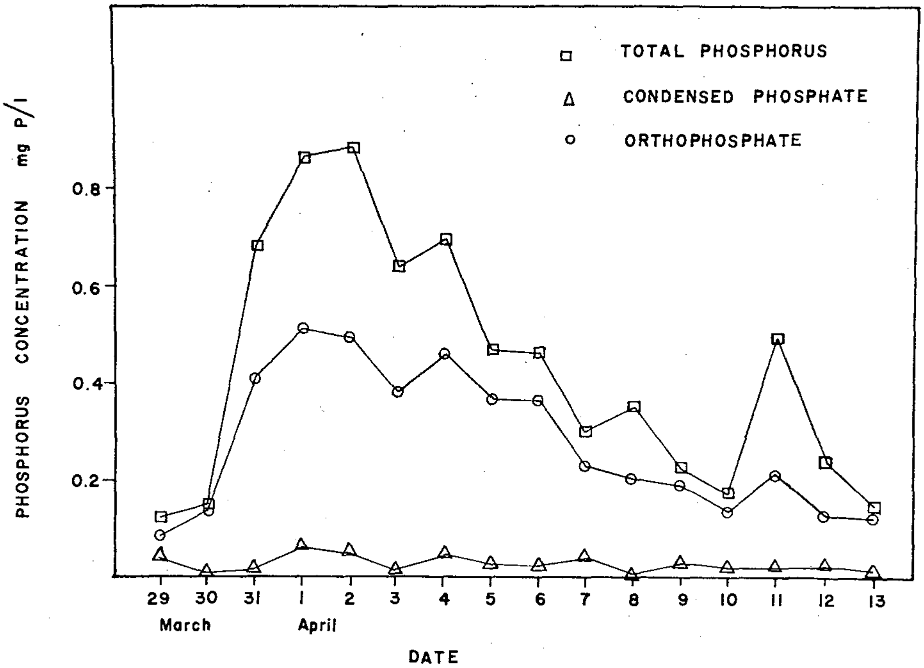

FIG. 16. Phosphorus concentration in Black Earth Creek during spring "thaw" 1965 at BEC13.

at these stations were expected since the Cross Plains sewage effluent is discharged to the stream just above BEC3. The decrease in phosphorus downstream from BEC4 would be expected because of dilution by ground water and uptake by aquatic plants in the stream. Bortleson and Wang (1966) have shown that during periods of high discharge in the summer and fall, the phosphorus concentrations at all stations on Black Earth Creek show a marked increase. It is apparent from these studies that while the conductance of the samples decreased with increased discharge, all forms of phosphorus, as measured in this study, increased with increased discharge. The majority of the phosphorus found in this study was orthophosphate. This result is of particular importance in eutrophication studies, since it appears that a significant part of total phosphate contributed by a stream to a lake could be transported during a few days of high flow each year. Studies on the sources of nutrients to a lake should pay particular attention to sampling during periods of high flow, since large amounts of apparently readily available phosphorus can be contributed by certain streams.

DISCUSSION

Previous studies on the hydrolysis of condensed phosphates in aqueous solution have shown that pyrophosphate and tripolyphosphate hydrolyse ultimately to orthophosphate. Engelbrecht and Morgan (1959), Morgan and Engelbrecht (1960), Sawyer (1952), and Karl-Kroupa *et al.* (1957) reported that the rate of hydrolysis of condensed phosphates was greatly increased by biological acitivity. Clesceri and Lee (1965*a*, *b*) showed that the hydrolysis of pyrophosphate and tripolyphosphate in Lake Mendota water was mainly the result of microbial activity.

Biological activity

In this investigation the effect of biological activity on the rate of hydrolysis of pyrophosphate and tripolyphosphate was most noticeable at 4° C. For example, the increase in the rate of hydrolysis of pyrophosphate at 4° C, in the different water samples studied, varied from four to ten times the rate in distilled water. In the different water samples at 20° C the pyrophosphate hydrolysis rate was roughly two to three times the rate of hydrolysis in distilled water, while the rate of hydrolysis of tripolyphosphate at 20° C in distilled water was the same order of magns thitude ae range reported for the control tripolyphosphate solution by Karl-Kroupa *et al.* (1957). In the different water samples at 4° C the rate of hydrolysis of tripolyphosphate varied from five to twenty times the rate of hydrolysis in distilled water. The water samples containing the apparent "natural" condensed phosphate showed similar hydrolysis rates to the hydrolysis of tripolyphosphate in the Black Earth Creek water sample.

No apparent increase in the rate of hydrolysis at 4° C or 20° C of pyrophosphate in distilled water or Lake Mendota water was observed due to continuous aeration and the addition of dextrose. No change was apparent in the hydrolysis rate in the low hardness water containing pyrophosphate or tripolyphosphate with continuous aeration and the addition of dextrose. Clesceri and Lee (1965*a*) reported that glucose (dextrose) increased the rate of hydrolysis of condensed phosphates in Lake Mendota water. They found that the rate of hydrolysis of tripolyphosphate was increased more than the rate of hydrolysis of pyrophosphate by the addition of glucose (dextrose) to the water studied. The explanation for the difference in results for the dextrose addition could be due to the different conditions used in the experiment, as explained previously.

Temperature effect

The effect of temperature on the rate of hydrolysis was observed in all water samples investigated and was different for each water sample. The rate of hydrolysis of pyrophosphate in the different waters at 20° C varied from two to eight times the rate of hydrolysis at 4° C for the same water sample. The tripolyphosphate hydrolysis rate in the different water samples varied from two to twenty-eight times the rate of hydrolysis at 4° C for the same water sample at 20° C. The rate of hydrolysis for the water containing apparent "natural" condensed phosphate at 20° C was more than twice the rate of hydrolysis at 4° C. SAWYER (1952) showed the temperature effect on the rate of hydrolysis of pyrophosphate and tripolyphosphate at 20° C to be two and three times, respectively, the rate at 5° C in sewage. SMITH *et al.* (1956) reported the temperture effect on the rate of hydrolysis of pyrophosphate and tripolyphosphate at 20° C was two and approximately five times, respectively, the rate of hydrolysis at 5° C in Ohio River water samples.

Condensed phosphate stability

This investigation indicated that the stability towards hydrolysis of the two condensed phosphates (pyrophosphate and tripolyphosphate) varied with the chemical, physical and biological environment of the water studied. In distilled water pyrophosphate was more stable than tripolyphosphate at 20° C while the stability was equal, if not reversed, at 4° C. In Lake Mendota water tripolyphosphate was more stable at 20° C, and both condensed phosphates had about the same stability at 4° C. This agreed with CLESCERI and LEE's (1965*a*) study, in which they reported tripolyphosphate was more stable than pyrophosphate in Lake Mendota water at room temperature. In the low hardness water pyrophosphate was more stable than tripolyphosphate at 20° C, and both condensed phosphates had about the same stability at 4° C. In Black Earth Creek water pyrophosphate was more stable than tripolyphosphate at 20° and 4° C. The apparent "natural" condensed phosphates in a Black Earth Creek water sample had a stability similar to that found for tripolyphosphate in the Black Earth Creek water sample.

Calcium and magnesium effect

GREEN (1950) and CLESCERI and LEE (1965*b*) reported a calcium effect on the rate of hydrolysis of condensed phosphates in their water samples. They found that the rate of hydrolysis increased with an increase in calcium concentration. In this investigation the high and low hardness waters at 20° C showed no apparent calcium or hardness effect. The lack of evidence in this study for the calcium effect at 20° C could be due to the inhibitory effect on the rate of hydrolysis of condensed phosphates by magnesium reported by GREEN (1950) or due to the complex character of the natural waters being studied. However, there was an increase in the rate of hydrolysis of the condensed phosphates in the low hardness water when compared with the high hardness Black Earth Creek and Lake Mendota water samples at 4° C. This increase in the rate of hydrolysis of the condensed phosphates correlates with the increase in the Ca/Mg concentration ratio in the waters studied. The increase in rate of hydrolysis of condensed phosphates in Black Earth Creek over the rate in Lake Mendota water at 4° C best illustrates the so-called calcium effect, since both water samples have similar pH and magnesium concentrations. The effect of calcium and magnesium on the rate of hydrolysis of condensed phosphates in natural waters needs more study to be understood.

Rate of hydrolysis of condensed phosphates in natural water samples

The important fact found in this investigation which agrees with most of the previous data was the extremely slow hydrolysis of condensed phosphates in aquatic environments similar to the natural surface waters. Using the apparent "natural" condensed phosphate found in the Black Earth Creek water sample from BEC5 as an example, it would require approximately 1800 hr or 78 days for the apparent "natural" condensed phosphate in this water sample to become completely hydrolysed at 4° C. It would take 765 hr or 32 days at 20° C for the complete hydrolysis of the apparent "natural" condensed phosphate initially found in this water sample. At the initial concentration of 0.49 mg P/l apparent "natural" condensed phosphate, the condensed phosphate could be a potential problem many miles downstream. This problem is alleviated in varying degrees by diffusion, dilution by ground water and surface water, and sorption of the condensed phosphates during their movement downstream.

SUMMARY

This study on the rate of hydrolysis of pyrophosphate and tripolyphosphate showed the slowness of the reaction in natural surface waters and the dependency of the rate of hydrolysis on the temperature, Ca/Mg concentration ratio, and biological activity. These hydrolysis rates for the condensed phosphates are at least an order of magnitude slower than the half-lives of hydrolysis reported by SMITH *et al.* (1956). This may be due to the order of magnitude difference in condensed phosphate concentrations studied. The 24 hr survey showed that apparent "natural" condensed phosphates do exist at levels that would interfere in water treatment in Black Earth Creek. However, studies would have to be initiated to ascertain whether or not the apparent "natural" condensed phosphates would actually interfere in water treatment processes. Studies are planned on the nature of the apparent "natural" condensed phosphate found in this study in the drainage of marsh water during periods of high discharge.

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