

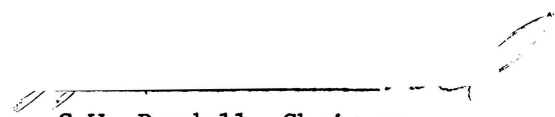
EFFECTS OF SEDIMENT ON WATER QUALITY IN
THE OCCOQUAN RESERVOIR,

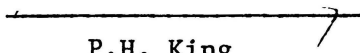
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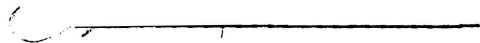
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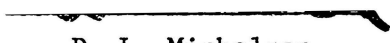
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in
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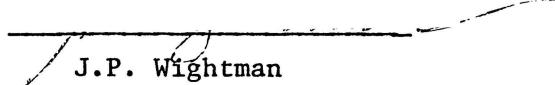
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I INTRODUCTION

The Occoquan Reservoir, which is formed by the combined flows of Bull Run and Occoquan Creek, is located in Northern Virginia, between Fairfax County and Prince William County. The watershed has a drainage area of about 570 square miles.

Studies have shown that the quality of water in the Occoquan Reservoir has deteriorated much during recent years. The most thorough of these studies was made by Dr. Clair N. Sawyer of Metcalf & Eddy in April 1970(1). He concluded that the existing serious water quality problem in the reservoir was largely the result of sewage treatment plant discharges to Bull Run and its tributaries. The treated effluents contain large quantities of nitrogen and phosphorus which add to the reservoir nutrient load and accelerate eutrophication. In order to remedy the poor water quality in the reservoir, plans were made to build an advanced wastewater treatment plant which is to be completed in 1976. How soon the reservoir water quality begins to improve or whether it will improve at all, after the treatment plant is completed has become a matter of conjecture(2). The principal questions that have not been answered are: 1. What quantities of nutrient chemicals are transported into the reservoir from non-sewage sources such as silt and, 2. What is the fate of nutrients that are deposited in the reservoir sediments?

During periods of rainfall, large quantities of silt are washed down from the watershed with the surface drainage as a result of land erosion. This silt ultimately becomes part of the bottom sediment in the streams and the reservoir through sedimentation. Since silt usually transports significant amounts of nutrients which have been accumulated by ion-exchange and sorption mechanisms to the sediment, silt may become a significant non-sewage cause of eutrophication. The major nutrients of interest are nitrogen and phosphorus.

Another major contributor to sediment build-up is microorganisms, which concentrate dissolved nutrients during their life-cycle. After death, many of these organisms are not consumed and they settle, carrying with them nutrients which are then deposited on the sediment.

Of the two nutrients of greatest concern, the availability of phosphorus is of primary interest for study because phosphorus does not enter the aquatic system by atmospheric fixation as does nitrogen, and is most likely to be deficient and therefore limit primary productivity of the aquatic ecosystem.

Reservoir sediments are usually subjected to many changing conditions such as variations in dissolved oxygen concentration, pH, temperature, dissolved nutrient concentration, etc. These changing conditions affect the transfer of nutrients between sediment and the overlying water.

The purpose of this investigation was to define the relationship between silt and sediment and water quality in the reservoir as affected by phosphorus concentration. After the building of the advanced

wastewater treatment plant, high quality water will be maintained in the tributary streams of the watershed. This study was designed to find out whether unabated siltation will continue the eutrophication process and to evaluate how the sediment layers, a result of many years of accumulation, will affect the water quality of the reservoir. A primary concern was to study how phosphates are released from sediment to the overlying water under different conditions, and whether sediment acts as a source or sink for phosphates.

II LITERATURE REVIEW

The following is a review of literature relevant to this investigation. The areas reviewed are analytical methods for phosphates, properties of sediments, phosphate exchange with sediments, and efforts to restore reservoirs by controlling eutrophication.

Analysis of Phosphates

Analyses of different forms of phosphates in natural waters are made for various reasons. Some are undertaken for purposes of water pollution control, others for a range of biological and chemical studies, particularly studies related to productivity and eutrophication.

Most determination procedures are based on the formation of 12-molybdo-phosphoric acid and its reduction to a blue heteropoly compound. However, procedures which measure vanadomolybdophosphoric acid may be usefully applied for waters containing high concentrations of phosphates, as illustrated by Wentz and Lee(3). At least seven reductants have been employed for the formation of phosphomolybdenum blue. Stannous chloride has been most widely used as shown by the literature and general practice. However, the use of ascorbic acid has been reported by quite a few investigators (4, 5, 6) to be simple, reliable and superior to all other methods. It also has the advantage of producing a stable color. In marine work, ascorbic acid is now being used in probably more than 90% of all analyses. Its use is

recommended for analysis of freshwaters in a few manuals and as a tentative method in the most recent edition of Standard Methods(7).

In the measurement of lake water phosphorus, Rigler(8) suggests that the concentration of inorganic phosphate is much lower than indicated by the molybdenum blue test. Hydrolysis of organic phosphate compounds during the test is suspected to be the major source of error.

Properties of Sediments

Sediments closely resemble soil in their properties. For this reason, sediments may be regarded as soils of a special type. For example, Mortimer referred to them as 'underwater soils' (9). For this reason, agricultural research finding can be validly applied to sediment. The research of soil or sediment has a dual function. For investigators in agronomy or fishery, research information can be used to maximize the nitrogen and phosphorus availability for plant or fish nutrient. While, on the other hand, investigators interested in pollution control are concerned about how to maximize the unavailability of the various forms of nitrogen and phosphorus and to prevent their re-entry into water courses.

Since sediments come primarily from erosion of the land by water and, to an appreciable extent, by wind, the chemical properties of the sediment are closely related to the source from which the sediment was derived. However, as a result of the selective nature of the erosion process, there are significant differences between them. Sediments are generally higher in silt, clay, and organic matter.

Massey and Jackson (10) found that under conditions of average erosiveness, the water-eroded soil material contained 2.1 times as much organic matter, 2.7 times as much nitrogen, 3.4 times as much available phosphorus, and 19.3 times as much exchangeable potassium as the soil from which it was derived.

Since one important feature of the sedimentation process is the sorting of the particles by size according to the degree of movement of water, it is not surprising to find that many sediment characteristics are related to the depth of the overlying water. Fink(11, 12) found that most of the characteristics which are usually associated with high productivity, increased considerably with increasing depth of water. Thus, when compared with the sediments deposited near the edge or with the soils in the watershed, the sediments in the center of a lake are enriched in clay, organic matter, nitrogen and phosphorus.

McKee et al.(13) have pointed out that the bed of a lake which man has not polluted seriously, and which has not received large amounts of land runoff, will resemble the soils of the surrounding land. As man has 'civilized' an area by plowing fertilized fields and discharging sewage and industrial wastes into the water, the sediment assumes different characteristics due to the materials that became a part of them. Materials present in the sediment become more numerous, the soil chemistry more complex, and biological populations more numerous and complex. Therefore, sediments reflect man's influence on the entire water system.

Phosphate Exchange with Sediments

The sediment in a body of water must be considered an integral part of the aquatic system. Investigators are concerned about the effects of the sediment on the quality of the overlying water. However, many investigators consider sediments more important as a sink rather than as a source of phosphates.

Harter(14) studied the phosphorus adsorption capabilities of the sediment from a eutrophic lake in Connecticut. He found that lake sediment could adsorb large amounts of loosely bonded phosphorus and suggested this as evidence that large additions of phosphorus into the lake may be held temporarily and subsequently released to growing plants and algae.

Hepher(15) studied the fate of phosphorus added to fishponds in Israel for the purpose of fertilization. He found that the phosphates rapidly disappeared from the water, mainly by being precipitated as calcium phosphate, while a certain amount was adsorbed by the bottom mud and soil. He noticed that phosphate fixation was higher when the mud was mixed with the water of the pond. He also noted that the lakes in Israel had high calcium content.

Kimme and Owen (16), using mud from Lake Wasser, Texas, found that the mud adsorbed most of the phosphate and that plankton or chemical precipitation had a lesser effect on taking the phosphate out of the water column. Latterell et al.(17) found that the bottom sediments of three lakes in Minnesota had a high degree of absorptive

capacity for phosphates. In laboratory experiments, sediments were mixed with water enriched with 0.05 to 42 mg/l of phosphate as phosphorus. The sediments absorbed from 0.0005 to 0.526 mg of phosphorus per gram of sediment. Desorption occurred only in water with a very low phosphate content. Similar results were reported by Gessner (18) from studies of the turbid Amazon River. He noted that when soluble phosphorus concentrations exceed 0.01 ppm, phosphorus was sorbed by suspended soil.

Shukla(19) et al., in a study of 25 sediments from nine soft water and five hard water Wisconsin lakes, found that these sediments varied considerably in their ability to sorb added inorganic phosphorus, but, in general, non-calcareous sediments sorbed more added phosphorus than calcareous sediments. The authors postulated that a gel complex of hydrated iron oxide is the major phosphorus-sorbing component of sediments.

While agreeing that some portion of sediment phosphorus recycles and may be available for algal growth, Shapiro(20) argued strongly that sediments act primarily as a sink rather than as a source for phosphorus. He took issue with those who advocated that phosphorus, accumulated in the bottom deposits of lakes, constitutes a vast reservoir capable of supporting plant growth in the event that all input of phosphorus is shut off. The inefficiency of the recycling process was noted.

Considerable research has tended to show that sediments may be more important as a sink rather than as a source for nutrients.

Data presented by Holt(21) showed that the sediments studied do not release significant amounts of phosphorus even after adsorbing a large amount from the surface water. An AWWA report in 1970 (22) indicated that only part of the nutrients incorporated into bottom deposits become available for subsequent biological growth in the overlying water. The report also indicated that a significant proportion of the nitrogen and phosphorus in streams and lakes is in the form of refractory biological materials which are very resistant to degradation.

Fitzerald (23) also supported the contention that sediment phosphorus is not always available to support the growth of algae. He found that under aerobic conditions, lake muds utilized in the experiments supported little or no growth. On the other hand, it was observed that lake mud could efficiently sorb phosphates. This suggested that the sorption of phosphorus by lake muds under aerobic conditions could be used to remove phosphorus from lake water.

An investigation of algae decomposition provided additional support for the view that sediment nutrients are not always available to the overlying water. Jewell & McCarty(24), and Foree & McCarty(25) found that a large fraction of algae was resistant to decomposition under aerobic and anaerobic conditions. This refractory portion, averaging 40 % by weight, exhibited degradation rates of only a few percent per year.

Mechanism Governing Availability

Quite a few investigators have found that sediments frequently act as a source of nutrients. Accumulation and release of nutrients must be understood to determine how nutrients in water affect the productivity of aquatic ecosystems. Possible mechanism regulating sediment-water exchange have been studied and discussed by many investigators(26). Availability of nutrients to the overlying water seemed to depend upon complex chemical, biological and physical relations.

Mortimer(27) found that as long as oxygen concentration is greater than 1 mg/l, bottom sediments will not give up their nutrients to the water column. However, as the mud-water interface of the lake becomes anaerobic, ammonium, ferrous, manganese and phosphate ions will be transferred to the water column.

Serruya(28) postulated from his investigation of Lake Kinneret that sediments may actively contribute to the nutrient supply, and cause a winter algal bloom. He stressed the need to study the release mechanism.

Frink(11) indicated that the depth at which the sediment is still capable of supplying nutrient remains unknown. He concluded that this reservoir of nutrient in sediments should be capable of supporting plant growth for sometime even if all nutrients are excluded from the overlying water.

As for the question of whether sediments act as a nutrient source for algae, Porcella et al. (29) found that different types of sediments varied in their ability to support algal growth and that this was related to the amount of available phosphorus measured in the sediments. The authors believed that although the amount of phosphorus released from the sediments varied with the type of sediment, it seemed apparent that all the available phosphorus eventually would be extracted from the 15 centimeter layer of sediment they used. They also suggested that organic material increased phosphorus release from sediments by serving as a substrate for anaerobic bacteria, which in turn would cause a lowering of sediment pH and increase solubilization of phosphate. It was expected that anaerobic conditions would lower the redox potential and the pH and that both of these reactions could lead to release of phosphorus. However, the aerobic solubilization of phosphorus could not be evaluated because even in the aerobic microcosms the sediments were anaerobic.

Fillos & Molof (30), using a multipoint electrode, found that aerobic conditions exist only at the mud surface, which may be only a few millimeters thick, and that anaerobic conditions exist immediately beneath. They showed that the release of nutrients increased appreciably when the dissolved oxygen concentration fell below a value of about 1.5 mg/l. In the case of phosphates, the increase seemed to be a result of the response of bacteria to low oxygen levels. The anaerobic release seemed to be the result of the adsorptive capacity of the mud surface when conditions become reductive.

McKee et al.(13) discussed broadly various physical, chemical and biological mechanisms through which sediments exert their impact on surface waters. The role of sediments varies with their composition, the amount of mixing with the water, and the occurrence of biological transformations between the sediments and the water. The authors also pointed out how the composition of sediments in turn reflect activities in other phases of the aquatic system.

Duursma (31) stated that interaction processes between natural waters and underlying sediments could ^{be} modeled as diffusion processes. The coefficient of diffusion could be estimated and the phenomena could be described quantitatively. From model studies, Shih & Gloyna(32) reported that the sorption-desorption mechanisms exerted on the molecular solute by bottom sediments was significant in mathematical modeling of solute transport. The mass transfer of sorbate across the sediment interface was dependent on turbulence of water phase, characteristics of the solute and sediments, and ecological factors.

Brinkhurst(33) pointed out the relative importance of nutrient input and recycling within the lake for a series of lake types. The mechanism of nutrient exchange was as yet unknown, even though this knowledge is central in the development of any theory for the control of eutrophication.

Jitts(34) made some studies on the influence of pH, particle size, amounts of organic matter, iron content and phosphate concentration on the adsorption of phosphate by bottom deposits taken from sites in rivers in Australia. He found that the ability of silts to adsorb

phosphate was directly related to the iron-organic matter content ratio. Organic matter depressed phosphate adsorption.

It has been suggested and observed by Pomeroy(35) that sediments act as a buffer on the phosphate content of the water. Exchange experiments were set up by shaking weighed amounts of suspended sediments with known volumes of water for one hour. The suspensions were filtered and the phosphate content of the water was measured. It was found that the exchange with and adjustment to overlying water was continuous and rapid. Poisoning with formalin resulted in even more rapid saturation. He also found that the total exchange capacity of the sediments depended upon the depth at which phosphate effectively exchanges with the water. He stated that ten centimeters of sediment contains enough exchangeable phosphate to replace that in the water at least 25 times.

Stumm and Leckie(36) estimated a maximum phosphorus transfer for an undisturbed sediment-water interface of 0.000009 mole per square meter per day ($0.27 \text{ mg/m}^2/\text{day}$). They also noted that in the Bering Sea and the Pacific Ocean, interstitial sedimentary water contains phosphate concentrations of up to 30 to 90 times higher than those in the overlying water.

In a study of phosphorus release from bog lake muds, Zicher et al.(37), using a radioactive superphosphate placed at various depths below the mud surface, found that the percentage as well as the amount of phosphorus released to the water was very small with

virtually no phosphorus released from depths greater than one-fourth of an inch below the mud surface. They also found that agitated systems have about twice the concentration of soluble phosphorus in the water phase as do undisturbed systems. This was considered as further evidence for the ability of sediments to hold chemicals against the leaching effect of dilute natural waters.

The role of biological activities on phosphate availability has been of interest to many investigators. Hooper & Elliot(38) suggested that certain benthic ciliates are capable of splitting inorganic phosphate from rather dilute solutions of organic phosphates that occur in lake and pond sediments. They also reported that lowering the pH reduced the enzyme activity of the strain tested. Their experiments suggested that anaerobic conditions not only produced an unfavorable environment for the ciliates, but also inhibited the release of phosphate by the cells.

Bacteria living both within and at the surface of the mud affect nutrient exchange. McKee et al.(13) reported studies made by many investigators on exchange mechanisms that affected both directly and indirectly the availability of phosphates.

Restoring of Reservoirs by Controlling Eutrophication

Hasler(39) suggested that eutrophication can be controlled through guided eutrophication. The author cited three case histories in which water qualities in lakes were improved through corrective measures. A detailed case history was available for Lake Washington. In 1956, Edmondson et al.(40) showed that there was an increase in productivity in the lake during 1955 corresponding to the great increase in treated sewage added to the lake because of the growth of adjoining communities. In 1963, a program of diversion of the sewage effluents to Puget Sound was started and many investigators (39, 40, 41) found that the lake had shown significant improvement in the quality and the clarity of water. Cores taken in the same localities for the period 1958-1970 also showed a clear maximum phosphorus content of the sediment which was laid down in the years of maximum enrichment. However, nitrogen did not show a corresponding maximum (41),

Peterson et al.(42) reviewed briefly lake rehabilitation techniques with emphasis on several techniques used on lakes impaired by eutrophication and sedimentation. Experiences with each of the renovation techniques were included. The techniques reviewed were nutrient inactivation with Al(III), dilution/flushing, aeration, management of aquatic plants by physical, chemical and biological controls.

Sheffield(43) studied the effect of nutrients on the restoration of a highly degraded lake, Lake Eola in Florida. Six methods considered

were: dredging, algacides, drawdown, aeration, chemical coagulation, and pollution source elimination. After reviewing the results, the method selected consisted of a partial lake drawdown, elimination of pollution sources, and treatment with an algacide. Although the program did not return the lake to its natural state, several problems associated with the pollution sources were solved. The drawdown process enhanced oxidation of bottom sediment and eliminated problems associated with the production of hydrogen sulfide. Renovation of the lake bottom utilizing sand enhanced benthic production and provided ideal substrate for the transplanting of macrophytes. Also it was determined that the sources of nutrients entering any degraded lake must be controlled prior to any restoration project. Among the many techniques, aeration, a widely used technique, was shown to be valuable and relatively inexpensive(42, 44). Stumm and Leckie(36) postulated that the removal of sediments by dredging not only would release large amounts of nutrients, but would also reduce the buffering capacity of the lake and consequently its resistance to external changes. Gahler(45) found that the technique for elimination of sediment nutrient release by addition of chemicals which form hydrous oxides and insoluble phosphates, may only provide temporary relief from undesirable algal growth.

From studies of sediments from Paradise Lake in Canada, Hynes and Greib(46) concluded that early reports of little movement of phosphate through muds are erroneous, and that there is a great potential store of nutrient salts in enriched muds. This would greatly delay recovery of lakes that have been rendered eutrophic by pollution. They also

suggested that a polyethylene sheet laid on the sediments of valued lakes may serve to rehabilitate them more rapidly.

III EXPERIMENTAL METHODS

The following is a description of the experimental methods utilized. The analytical methods for phosphates were obtained from the literature whereas the availability assay was developed for this study.

Analytical Methods for Phosphorus

To properly study the release of phosphorus, a reliable analytical method for the determination of phosphates must be used. From studies made during this investigation, the ascorbic acid method was selected as the method of choice because of its stability, simplicity and reliability. However, the conventional stannous chloride method was used during the early part of the study because proper detection equipment was not available. The results obtained during this time were considered to be preliminary and no phosphate data obtained before July 1973 has been incorporated into this dissertation.

To perform the ascorbic acid method a standard curve was prepared. Since all of the points fell on the same straight line, a multiplication factor was used for convenience to extend the curve. Fresh reagents were prepared and mixed each week. Readings were made at 880 m μ with a Bausch and Lomb Spectronic 20 spectrophotometer. A standard solution was also included in each batch of determinations to check the accuracy. The reproducibility was found to be $\pm 3\%$ for orthophosphate determinations.

Evaluation tests, such as the effect of the amount of reagent, time, temperature, and sample size on color development, were made on the ascorbic acid method and it was found to be reliable and superior to the conventional stannous chloride method for all situations (Table XXIV).

For total phosphate determinations, the potassium persulfate method was used and was found to be satisfactory.

Determination of Phosphate Content in the Sediment

The sediment samples were dried and ground by a hand grinder and a mortar and pestle. The ground samples were passed through a 100 mesh screen.

The extract solution for the available phosphate method was made with care since the result was sensitive to slight variations in the concentration of the extract. A slight modification was made on the available phosphate method presented by Jackson(47). A Burrell wrist-action shaker was used for the soluble phosphate and the available phosphate determinations.

For reasons of safety and because of the limited laboratory facilities, the potassium persulfate method was chosen for total phosphate determinations. After digestion of the samples, digested solutions were not neutralized as is done with water samples. The neutralization step was omitted because it was found that it caused a precipitate which also removed some phosphates. This should not affect the phosphate determination because the digested solutions

were diluted 25 times for the final determinations. pH measurements made on these diluted samples after adding reagents were found to be same as regular water samples.

Sample Collections

Water samples were collected weekly in conjunction with the Occoquan Watershed Monitoring Program. The samples were not preserved with mercurous chloride since it was found to interfere with phosphate color development. Water samples were filtered through membrane filters that had been soaked in demineralized water.

Surface sediment samples were collected with an Eckman dredge. Usually only the top two inches were collected for analysis. A Wildco sampler was used for core sampling, but was found to perform very poorly.

During warm weather sediment samples were put into a cooler as soon as possible. In the laboratory core samples were stored in the freezer. However, surface sediment samples were not frozen because freezing would alter the properties of the sediment.

Availability Assay

To study how the sediment in the Occoquan Reservoir would affect water quality, some kind of assay had to be developed which would permit the isolation of the effect of different parameters. The following equipment and procedures were developed and utilized for this purpose:

Reactor

Pyrex glass culture tubes, 25 mm OD, 200 mm long were chosen as reactors for this investigation. Besides having the advantages of being safe to handle, easy to wash, easy to stock and available in large quantities, they also had a uniform internal diameter which was very crucial. It was interesting to note that 50 ml of water in the tubes was exactly five inches. Also, unlike big cylinders, they could be put into different constant temperature baths easily.

Procedure

Sediment samples homogenized with a blender were used. The sediment had to be introduced into the reactor carefully, not allowing the sediment to come in contact with the side of the tube. This was to guard against any increase in the surface area available for nutrient transfer which would give erroneous results. A piece of glass tubing connected to a propipet was used to suck up the sediment samples and introduce them into the tubes. One serving of sediment of about 1.75 inches deep was put into each tube (Figure 1).

50 ml of deionized water was introduced slowly and carefully into each tube so that the sediment surface area would be uniform. This was done by connecting a small tygon tube to the jet of the wash bottle. This reduced the strength and turbulence of the water coming out of the wash bottle. The water was introduced about 20 minutes after the sediment was introduced. This time period was adhered to as close as possible to avoid any inconsistency which might affect the rate of release.

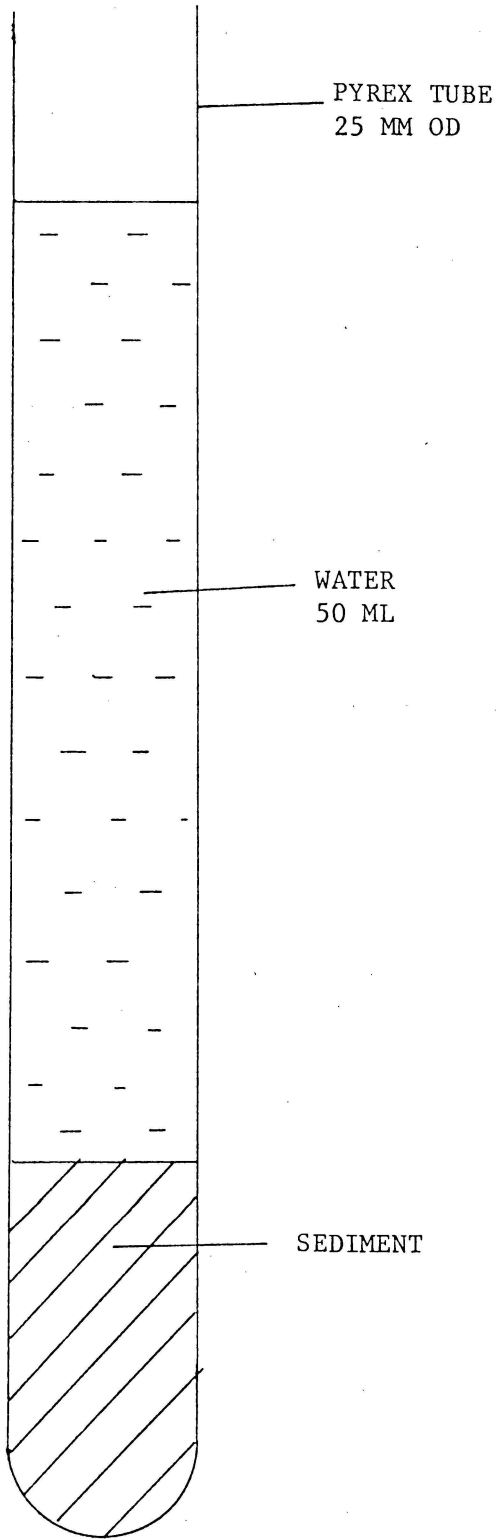


FIGURE 1. AVAILABILITY ASSAY REACTOR

Sediment and water levels in the tube reactor were marked with a magic marker. This marking was used to show whether the sediment shrank or expanded. To avoid confusion, the tubes were all marked to show the conditions the system was to undergo. The tubes were put into a paper box partitioned to hold the tubes in an upright position. Then the tubes were put into a 20°C incubator.

After a week, the tubes were taken out. The overlying water in each tube was poured out carefully and analyzed for orthophosphate concentration. Calculations were made to give the rate of phosphate release in $\text{ug/cm}^2/\text{week}$.

Studies of different parameters

Each parameter under study was varied, keeping other parameters constant if possible, thereby permitting the study of the singular effect of each parameter on the availability of nutrients. Several control reactors were always run simultaneously under the same conditions with every batch of experiments. This not only made relevant comparison possible but it also made it possible to study the reproducibility of this assay and the variation of sediment properties from the same station. Bull Run(I) sediments were used unless otherwise stated. Station I sediment was of primary concern because Bull Run has a high phosphate concentration in both the water and sediment, and has more frequent occurrences of algal blooms. For tests on some parameters such as temperature, dissolved oxygen concentration, and phosphate concentration, station V sediments were also used.

Different stations - Sediment samples collected from seven locations in the Occoquan Reservoir as listed in Table I and shown in Figure 2 were studied using the availability assay. This made possible comparison of the nutrient availability of sediments at different locations of the reservoir.

Temperature - Five different temperature conditions were used other than 20°C. Water baths equipped with thermal regulators were used for 25°C and 30°C, constant temperature incubators were used for 35°C and 45°C, and a refrigerator was used for an approximate temperature of about 4°C.

Depth of water - Different amounts of water were used to study the height of overlying water. Longer culture tubes of 300 mm were used to provide a longer column.

Depth of sediment - This study was performed by putting varying amounts of sediment into the reactors. This set of tests was also used to indicate if the amount of sediment introduced to assay was crucial.

Sample treatment - Tubes with sediment in place were subjected to different conditions such as freezing, drying and autoclaving before water was introduced into the tubes.

Drying of the surface - Sediment tubes were left out for different lengths of time to evaluate the effect of this length of time on the assay.

pH - Water of different pH's were prepared by adding sufficient amounts of acid or alkali while monitoring the solution with a Corning pH meter using a combination pH electrode. The final pH was also measured to study the buffering capacity of the sediment.

TABLE I

Location of Sampling Stations on the Occoquan Reservoir

Station	Location
I	on the Bull Run arm of the reservoir right at the Old Yates Road bridge
II	on the Occoquan Creek, about one mile above the confluence with Bull Run
III	Ryan's Dam
IV	Jacob's Rock
V	Sandy Run
VI	at the Fairfax County Water Authority Dam
VII	Hooes Run, about half mile above the confluence with the reservoir proper

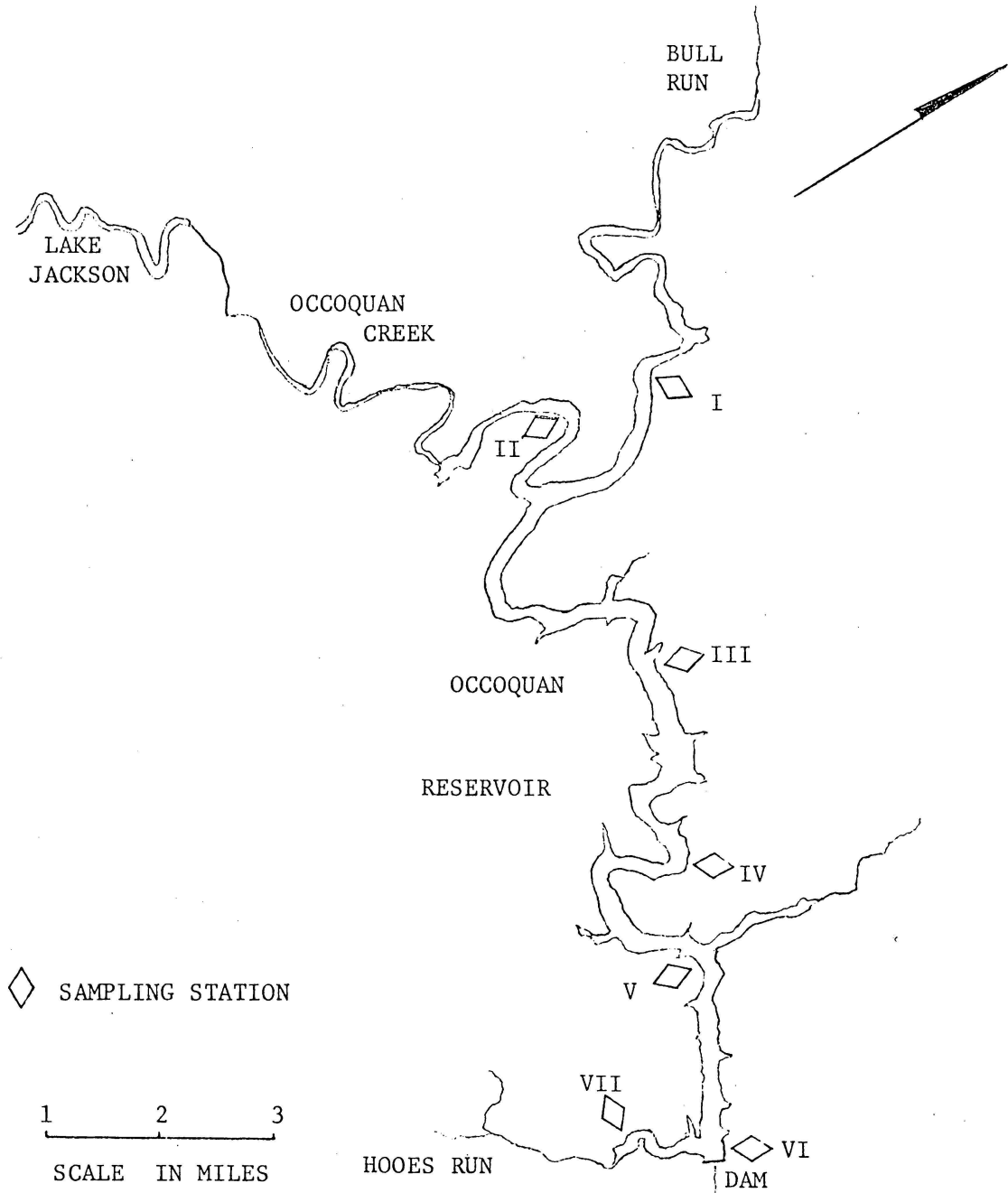


FIGURE 2. OCCOQUAN RESERVOIR MAP SHOWING LOCATION OF SAMPLING STATION

Mixing - A glass rod was used to mix the water in the tubes without disturbing the sediment surface.

Physical barrier - Experiments were conducted after covering the sediment surface with varying thicknesses of white, water-testing sand. (99.8% pure silica, approx. 60-120 mesh)

Metallic ions - Assays were run by adding varying amounts of aluminum chloride, ferric chloride and calcium chloride solutions.

Biological activities - Attempts were made to study the effect of biological activity on phosphate release by adding glucose, formalin, and antibiotics such as penicillin and chloromycetin. The pH was measured for the formalin solution, since it changed the pH of the system.

Dissolved oxygen (DO) concentration - Many attempts were made to set up a DO free system. DO free water was prepared by bubbling nitrogen gas into boiled deionized water. Then sufficient amounts of sodium sulfite were added to insure DO free conditions for a seven day period. After introducing the treated water into the tubes, the system was closed with rubber stoppers sealed with parafilm to control gas transfer and to prevent the stopper from popping out.

Simultaneous assays with sodium chloride solutions that gave an identical sodium ion concentration were performed to find out how such a concentration of sodium ion would affect the availability of nutrients. Flushing tests were also made to see how the reversal back to aerobic conditions would affect the availability of nutrients.

Phosphate concentration - Reactors with overlying water containing different phosphate concentrations were set up. Simultaneous assays were also run with sediments from station V to provide a contrast with variation in sediments. Flushing tests were made for station I to see how that would subsequently affect the water after the water was changed.

Flushing - Five reactors were run simultaneously for six weeks. The overlying water in each reactor was exchanged weekly with new deionized water and examined for phosphates. The average rate of release was calculated and plotted with respect to time.

Release of other nutrients - A set of assays was conducted to determine the magnitude of the rate of release of nutrients besides phosphates. The overlying water in each reactor was tested for orthophosphates, total phosphates, nitrite, nitrate, ammonia, total kjeldahl nitrogen, total organic carbon and total iron.

Reliability - A few reactors were set up under identical conditions to study the variance of results. The experiment was repeated a few times and the averages and standard deviations were calculated. In studying the parameters, duplicates were usually run. More identical tests were used if better reliability was desired. Consistency is very important in an assay like this. Also, consistency was significantly improved as finesse was developed for handling the sediment through much practice.

Sediment studies

Sediments from the seven stations previously mentioned were examined for their physical properties such as phosphate, organic and water contents. Sediment samples taken at different times and different grabs taken at the same time from station I were also studied. This gave some insight into the local and seasonal variations in the properties of the sediments within the same region.

Cores

A few core sediment samples taken from different locations in the reservoir were studied for the variation of phosphate content with depth of sediment.

IV RESULTS

The results of this research investigation are grouped according to the purpose of the specific experiment. During the initial phase it was necessary to establish the accuracy and reliability of the assay procedure. The results of these experiments are presented first. After assay evaluation, the developed procedure was used to isolate and evaluate the effect of various environmental variables on sediment phosphate release and to observe differences in sediments from various parts of the reservoir. These results are presented in the latter part of the chapter. All dates mentioned here refer to 1973.

Evaluation of the Assay Procedure

The following sets of tests were made to evaluate the reliability of the availability assay. The primary concern was to see whether consistent results could be obtained and whether they could be applied to the actual reservoir situation.

Effect of depth of water

The initial reason for running this test was to find out how the depth of overlying water in the tube reactor would affect the rate of release of phosphates. Table II shows that the rate of release was not affected by up to 90 ml of water which was about nine inches deep in the reactor. This was a static system and the phosphates released probably remained at the lower region of the water column. Thus, nothing could be said about the effect of the concentration of

TABLE II

AVAILABILITY ASSAY EVALUATIONEffect of depth of water on rate of Release of Phosphates at 20°C

Depth of Water	Final Phosphate Concentration	Rate of Release
inches	ug/ml	ug/cm ² /week
3	0.625	4.69
4	0.463	4.63
5	0.339	4.26
6	0.345	5.18
7	0.290	5.08
8	0.245	4.90
9	0.220	4.95
	Average	4.81
	Standard Deviation	0.31

Distilled water and station I sediment used
 Depth of sediment -- 1.75 inches

phosphate in the overlying water. In the assays, a band of concentrated solution could be observed to be suspended about an inch above the sediment. It was observed that the bottom three inches of water had a phosphate concentration twenty times higher than that of the top portion. In other words, the water above three inches had a very low concentration of phosphates. This test also indicated that the depth of water routinely used for this assay was satisfactory because 50 ml of water produced a column about five inches deep in the reactor.

Effect of depth of sediment

A test was run to see how the depth or amount of sediment in the assay reactor affected the rate of release. Table III shows that it was not crucial. The reason is that the standard deviation is still within normal fluctuation as compared to those in Table V .

This result meant that within the normal range, the rate of release under the same condition depended mainly on the surface area and not the amount of sediment or water on either side of the interface.

Therefore, we can say that in this reservoir, the depth of sediment will not significantly affect the rate of release. In other words, the sediment which is some distance beneath the surface will not contribute significant amount of nutrients to the overlying water.

Table III seems to show that the rate of release reaches a peak for sediment three inches deep. Since the original purpose of this experiment was to find out the effect of slight variations in the amount of sediment on the rate of release, no duplicates were run at the same time. This peak may be due to unusual fluctuations in this

TABLE III

AVAILABILITY ASSAY EVALUATIONEffect of Depth of Sediment on Rate of Release of Phosphates at 20°C

Depth of Sediment inches	Rate of Release $\text{ug/cm}^2/\text{week}$
1	5.13
2	5.50
3	5.75
4	5.00
5	4.75
Average	5.23
Standard Deviation	0.40

Station I sediment and 50 ml deionized water used

assay and may be even due to different tube lengths used to accommodate the extra amount of sediment. Therefore, not much can be said at this point until more tests are run. This uncertainty should in no way affect the results since the depth of sediment of 1.75 inches was adhered closely to throughout the experiments that followed.

Effect of sample treatment

Sample treatment significantly affected the rate of release. Table IV shows that drying reduced the rate of release, whereas autoclaving of sediment increased the rate of release about four times. The ramification of this was that the sediment could not be sterilized by autoclaving without changing the properties of the sediment drastically.

Effect of exposing sediment surface to air

This test was run to see how the length of the time between putting sediment into the tube and putting water above the sediment affected the rate of release. Figure 3 shows that the rate was almost the same within the first hour. However, the rate decreased significantly after the first hour. This was probably due to the formation of an oxidized crust which lowered the rate of release. Flushing test was also made to see whether this crust decreased future release. It was found that the oxidized crust affected the rate of release only for the first week (Table IV).

Effect of gas formation

It was observed that except for very low temperatures, gas pockets formed in the sediment. Higher rates of release could be expected when air pockets were present because they would give higher

TABLE IV

AVAILABILITY ASSAY EVALUATIONEffect of Sample Treatment on Rate of Phosphate Release at 20°C

Sample Treatment	Rate of Release	
	ug/cm ² /week	
	First Week	Second Week*
normal	6.00	5.50
Dried 104°C	0.31	4.69
Autoclaved	23.44	
Air dried 41 hours	0.44	8.40

Station I sediment and 50 ml deionized water used

* Flushing test

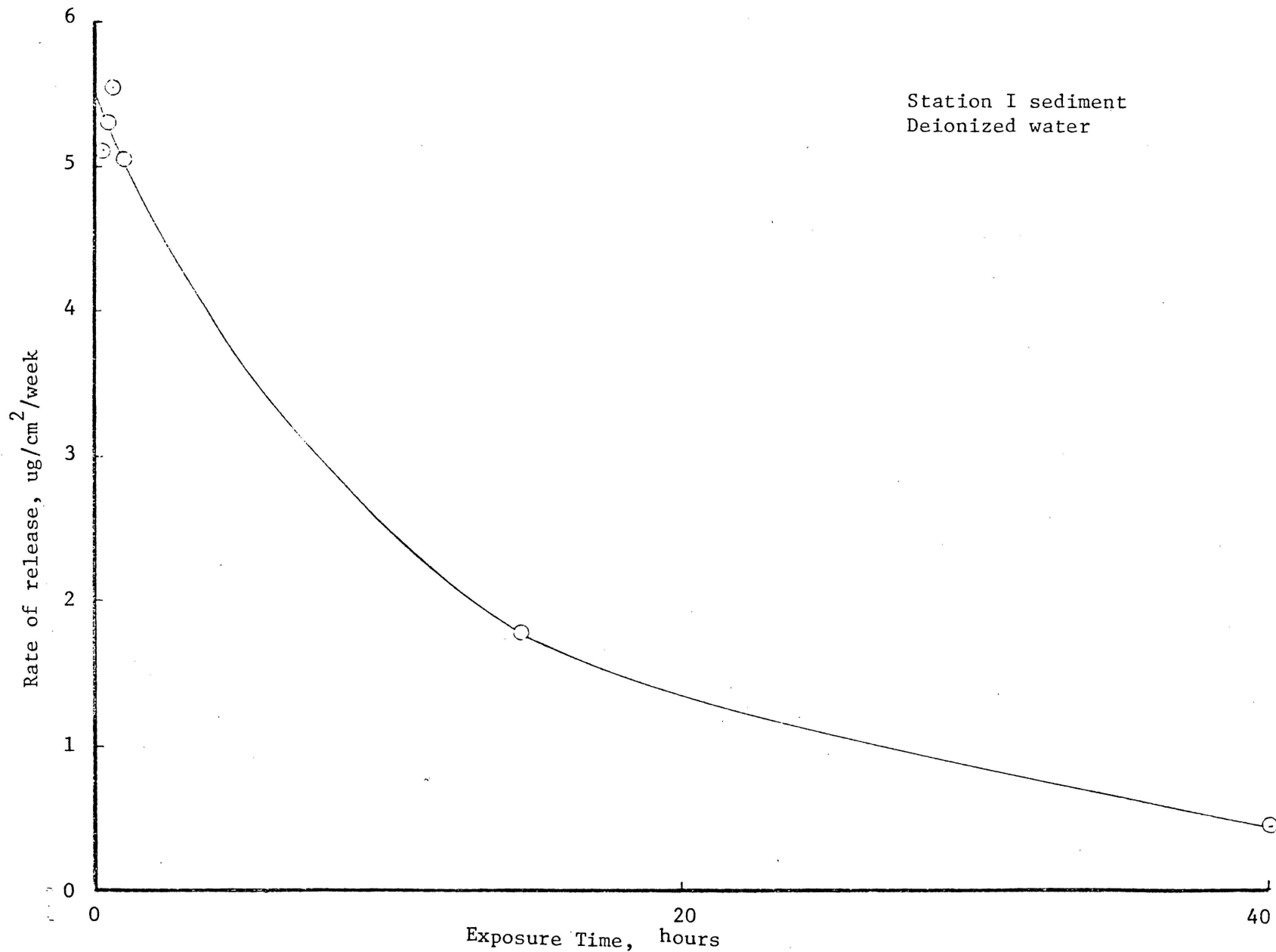


FIGURE 3: EFFECT OF EXPOSING SEDIMENT SURFACE TO AIR ON RATE OF RELEASE DURING AVAILABILITY ASSAY

porosity to the sediment and also would mix the sediment. Thus nutrients trapped below the surface which would otherwise not be available would be released to the water by air breaking through the sediment surface. Nothing could be done about this. However, the results should not be affected much because at 20°C the sediment surface was usually not broken up within a week.

Effect of Biota

During spring and summer, larvae could be seen on the surface of the sediment. Worms of the family Chironomidae was also observed on sediments from deeper stations. The presence of larvae could cause problems in the availability assay. It was not desirable because they would give unexpected and unpredictable amounts of phosphate release. However, this problem was solved after the blending technique was used.

Blending Technique

In an effort to improve homogeneity of samples, a blender was acquired June 28, 1973. The samples were usually blended for about one minute and it was found to be a very helpful technique. The analytical reproducibility was much enhanced as expected, e.g. organic content from $\pm 0.5\%$ to $\pm 0.05\%$, water content from $\pm 1\%$ to $\pm 0.01\%$. Furthermore, transferring sediment samples into reactor tubes was much easier. The blending process possibly killed all the larvae in samples because worm tracks were seen in reactors before the blending process was used, but were not found after using the blending process.

Effect of sample variation

An intensive study of the physical and chemical properties of sediment samples from station I showed that there were differences in properties even among different grab samples from the same station taken at the same time (Table XV to XIX). This kind of variation complicated the investigation since similar behavior of samples from the same station could not be assumed.

The variation of assay results obtained from samples taken from the same station at different times is shown in Table V along with the average value and standard deviation. Standard deviations were also calculated for data obtained from identical tests. It could be seen that even though the deviation was quite high for the tests on samples collected at different times, the standard deviation for tests on samples taken at the same time under the same conditions was quite low. The assay results for station I sediment under normal conditions obtained up to this point were also found to be significantly different from each other. These difficulties were overcome by blending the samples well and comparing only those results obtained at the same time using the same grab sample.

Correlation of assay with reservoir conditions

The development of an assay procedure in this investigation was an attempt to imitate the actual reservoir system to permit study of factors under laboratory conditions. Unquestionably, the assay performed in the laboratory was not exactly the same as the actual situation. However, if it approximates "in situ" conditions the results can still be expected to apply to the actual system.

TABLE V

AVAILABILITY ASSAY EVALUATION

Variation of Rate of Release of Phosphates from Samples
of Station I Sediment at 20°C

Date	Rate of Release ug/cm ² /week	No. of Test	Standard Deviation
9-17	5.75	4	.5279
10-2	4.26	5	.288
10-3	6.00	3	.626
10-4	6.49	3	.356
10-15	5.25	5	.230
10-23	8.04	3	.320
11-13	5.67	5	.310
Average	5.92		
Standard Deviation	1.16		

The static condition used was a realistic choice because the water in the reservoir flows quite slowly. Of course, it can be argued that the silt-laden water, after a heavy rain, resembles a stirred suspension system. However, the silt suspension came from silt and scoured stream sediment washed down from the watershed. Therefore, the suspension system would be suitable for the study of silt but not for the study of sediment. It is true that a slow flowing continuous system may be more realistic, but this is not easy to set up in a small laboratory as compared to the availability assay and the difference in results would almost surely be very small. The dark condition used was also a realistic choice because the bottom of the reservoir is always very dark.

Sediment was a better choice than silt in an investigation like this because silt has different properties from sediment. For example, sediment is more jelly like, having larger amounts of organic and biological matter, and therefore it affects water quality differently. Further, silt does not have a long term direct effect on water quality like that of sediment.

From the results of the evaluation tests, it was concluded that the assay procedure was satisfactory. However, the comparison of results to evaluate the effect of a single parameter must be made on results obtained at the same time using the same grab sample. With this limitation it is believed that the result obtained with the use of this assay can be applied to the actual system.

Further validity of this assay is confirmed by the fact that many of the observations in the laboratory were found in the actual reservoir situation. It was found that whenever anaerobic conditions existed during the summer, the phosphate concentration in the bottom of the reservoir increased. However, during the fall season, when bottom condition was aerobic and temperature was considerably lower, the bottom nutrient concentration was much lower. It was also observed from the assay that there was gas production especially for warmer temperatures. The same was observed in the reservoir. During warm weather, gas bubbles could be seen especially when the bottom was disturbed by a dredge or an anchor. However, this was not observed during the winter.

Evaluation of the Effect of Environmental Factors on Sediment Phosphate Release

After establishing the limitations and proper techniques of the assay, the procedure was used to provide information concerning factors that affect the release of phosphorus in the reservoir. The following are the results and observations in the study of the different environmental factors as measured by the availability assay.

Location differences

Sediments from all the seven stations were evaluated for phosphate release rate and the results are listed in Table VI. Station I sediment gave the highest release. Station II sediment had a significantly

TABLE VI

AVAILABILITY ASSAY

Release of Phosphates from Sediments taken from
Different Stations at 20°C

Station	Rate of Release ug/cm ² /week
I	5.75
II	2.56
III	3.88
IV	3.25
V	3.00
VI	3.12
VII	0.025

50 ml deionized water used
Depth of sediment--1.75 inches

lower rate of release than Station I sediment. Station VII had a much lower rate of release, about two orders of magnitude below the others. It is also interesting to note that the rate of release decreases with distance downstream toward the dam. Based on the differences observed, sediment from Stations I & V were selected for environmental factors evaluation studies.

From a study made on interstitial water, Station V sediment was found to have a much higher interstitial phosphate content than Station I sediment. The results are given in Table VII. This could probably be related to small particle sizes and more colloidal characteristics of sediment downstream in the reservoir.

Effect of temperature

Sets of assays were run at six different temperatures: 4, 20, 25, 30, 35, & 45°C. As seen in Table VIII, the rates of release were all very much lower at 4°C for both Station I and V. For Station I, the rate increased with rising temperature until about 30°C. The value for 35°C was lower but a sharp increase occurred at 45°C. Much microbial growth was observed for reactors at 35°C which probably accounted for the lower value. This together with the fact that only orthophosphate concentration was measured removes any implication that the rate of phosphate release was caused by temperature change. The reason is that organic phosphates do not respond to orthophosphate tests.

The sediment shrank considerably at 4°C. This was accompanied by a release of water from the sediment. For higher temperatures gas

TABLE VII

Analysis of Interstitial Water

Station	Total Dissolved Solids mg/l	Orthophosphate Concentration mg/l
I	370	.030
V	400	.150

TABLE VIII

AVAILABILITY ASSAYEffect of Temperature on Phosphate Release for Station I and V

Temperature °C	Rate of Release ug/cm ² /week	
	I	V
4	0.23	0.02
20	4.1	2.7
25	4.4	2.1
30	5.5	1.6
35	3.6	1.1
45	7.3	1.9

Deionized water used

productions were observed. This undoubtedly is related to the degree of bacterial activity.

Applying the result to the reservoir conditions, we can say that the rate of phosphate release is quite low during winter when the temperature of the hypolimnion is usually quite low--sometimes as low as 4°C. On the other hand, the rate of release is higher during the summer when the bottom water temperature is much higher--sometimes over 20°C.

Effect of metallic ions

The effect of three metallic ions, iron, calcium and aluminum, on the release of phosphate from Station I sediment was studied. The results were not conclusive and the tests done were not very reproducible. This probably caused by the forming of loose precipitate on the surface of the sediment by the metallic ions. Also, the overlying water was very clear even at a low concentration of 2 mg/l of metallic ion.

Effect of dissolved oxygen (DO) concentration

Considerable difficulties were encountered with this experiment. Besides making DO free water, it was necessary to maintain an anaerobic system for the entire seven day period. Quite a few attempts were unsuccessful because the system failed to maintain an anaerobic condition for the required period of time.

DO free water was prepared by boiling demineralized water to drive out all the dissolved gases. The boiled water was bubbled with

nitrogen gas until it had cooled. Finally, known amounts of sodium sulfite was added to ensure DO free conditions. Comparatively high concentrations of sodium sulfite were used because it was found that low concentrations did not succeed in maintaining anaerobic conditions. After chemical addition the tube reactor was plugged with a rubber stopper, and then parafilm was used to seal the stopper and prevent it from popping out.

At the end of the week, the DO concentration of the system was checked immediately after the seal was removed. The pH of the overlying water was also checked to see whether there was any change in pH, which might influenced the rate of release. It was found that the pH remained about the same.

The numerical data for Stations I & V sediment are shown in Tables XXV & XXVI in the Appendix and illustrated by Figure 4. From an examination of the results, it can be seen that anaerobic conditions drastically increased the rate of phosphate release. It was also noticed that higher doses of sodium sulfite enhanced the rate of release. The reason was due to a more reduced condition.

In order to find out how sodium ions affect the release, simultaneous assays were run using sodium chloride, making the concentration of sodium ion corresponding to that used for sodium sulfite. It was found that the rate of phosphate release was much lower with increasing concentration of sodium chloride. This further showed that the increased rate of release with sodium sulfite addition was due to the reduced conditions rather than to effects of the sodium ions.

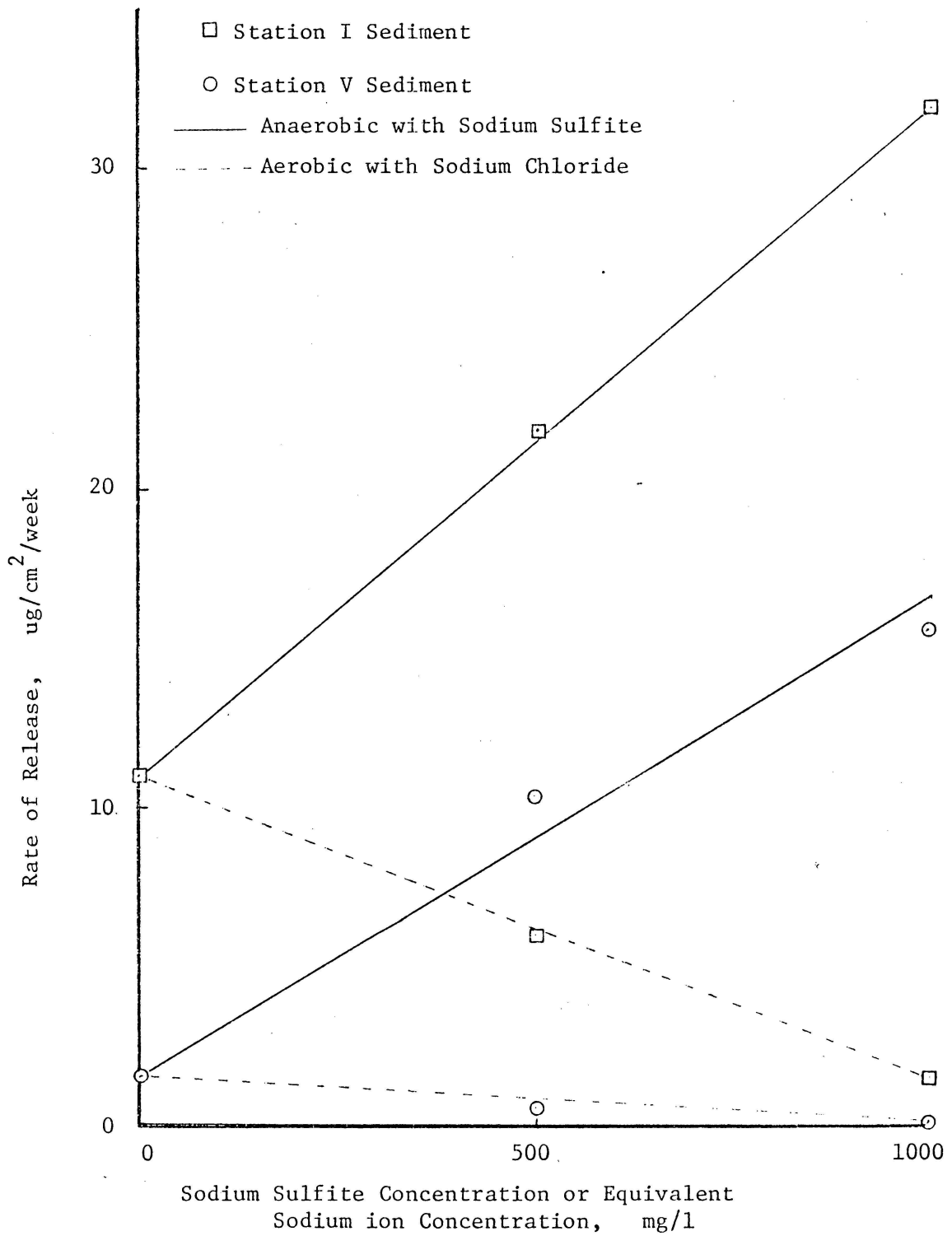


FIGURE 4. EFFECT OF ANAEROBIC CONDITION AND SODIUM ION CONCENTRATION ON THE RATE OF PHOSPHATE RELEASE AT 20°C

Several other observations were made during the study. Sediments in the anaerobic condition shrank about 3 to 4 mm each and no gas pockets was observed. The overlying water was very clear, which indicated that there was rather low bacterial activity in the water. Also, the sediment turned much darker with black streaks or spots, which indicated that reduction reactions took place inside the sediment. None of the above conditions were observed in the aerobic control reactors. For the reactors with corresponding concentration of sodium chloride, overlying water was also clear which indicated low bacterial activity.

Effect of sand layer on the sediment surface

White, water-testing sand was put on top of the sediment in different depths to evaluate the effect on phosphate release. (Figure 5 and Table XXVII in the Appendix) It was difficult to make an exact measurement of the thickness of sand in discrete centimeters. Nevertheless, using the approximate depths the results show that the rate of release was significantly reduced. The curve shows that the rate of release decreased gradually for the first centimeter of sand, but additional depth produced a drastic reduction. This indicates that the sediment a few millimeters below the surface does not contribute much nutrient to the overlying water of a static system.

Since 60 to 120 mesh sand was used in this experiment, we can expect that the thickness of the sediment layer that would cause an equal reduction in phosphate release would be smaller. Since the

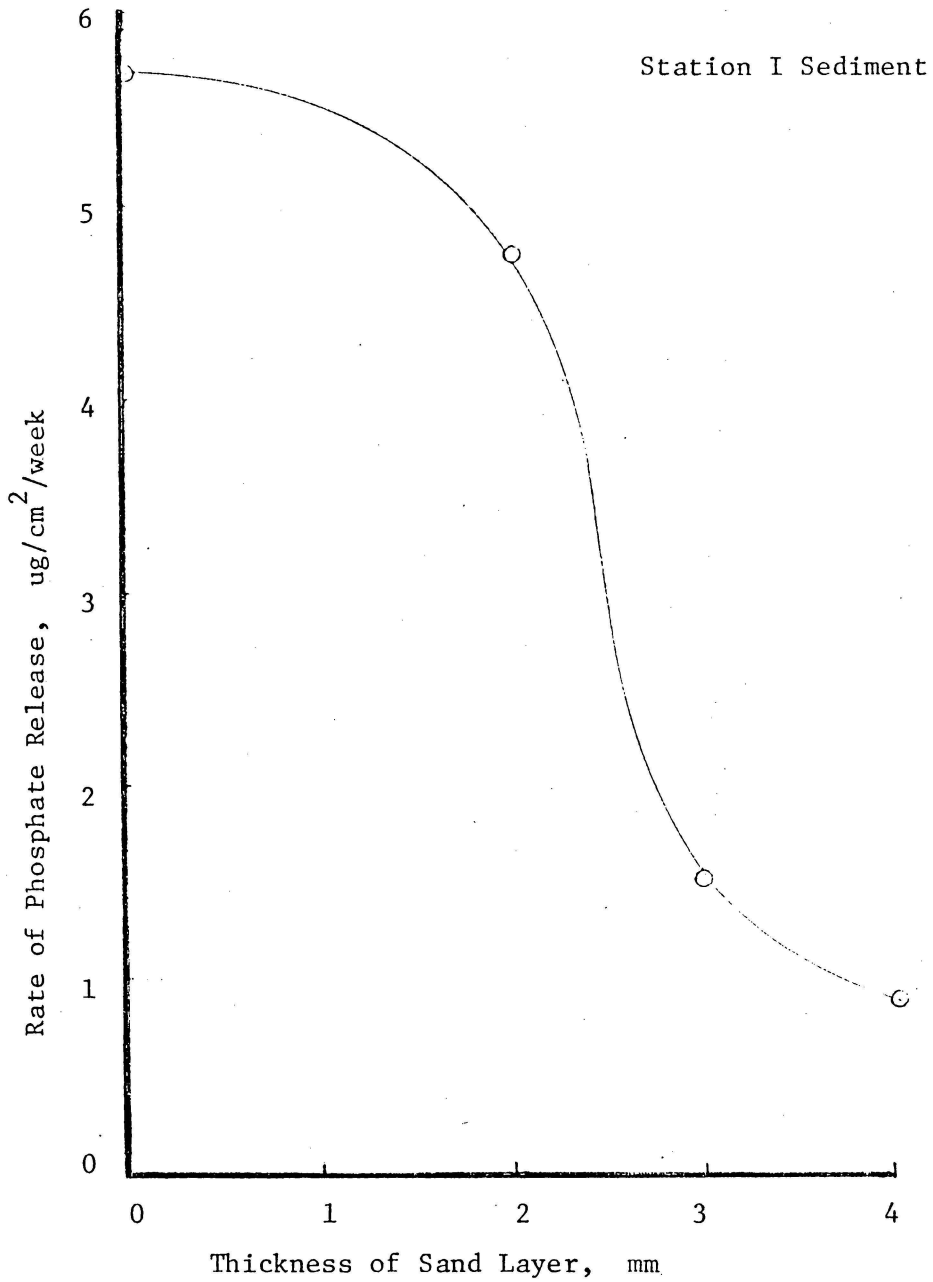


FIGURE 5. EFFECT OF PHYSICAL BARRIER ON THE RATE OF PHOSPHATE RELEASE AT 20°C

size of sediment particles is usually much smaller the porosity would be smaller and greater inhibition with depth should occur. Table IX shows the particle size distribution of Station I sediment. We can see that more than ninety percent is finer than 120 mesh. It should be noted that the particle size distribution of sediments at the other stations were lower than at Station I.

Effect of pH

The pH in natural waters fluctuates quite a bit. This is especially true during an algae bloom when the pH may go above 10. For this reason, assays were run with water of different pH's. Table X shows that there were no significant differences in the rate of phosphate release for pH's between 3 to 11. However, outside this range, the rate of release increased drastically. These results show that pH changes in natural waters generally will affect the rate of release since the pH in natural waters is seldom beyond the range of 3 to 11. The final pH of the system for each reactor was also measured at the end of the assay period. It was found that the sediment acted as a rather good pH buffer for the overlying water between a pH range of 4 to 11.

Effect of phosphate concentration in the overlying water

Assays were run with different concentrations of phosphates in the overlying water using Station I sediment. The same was repeated for sediment from station V sediment by simultaneous testing. The results were calculated and tabulated in Tables XXVIII and XXIX in the Appendix, and the isotherm was plotted in Figure 6. The amount of

TABLE IX

Particle Size Distribution for Station I Sediment

U.S. Standard Sieve Number	Particle Diameter micrometers	Percent finer than
60	250	98.631
100	150	95.760
140	106	91.203
200	75	85.211
230	63	82.464
325	45	71.976

TABLE X

AVAILABILITY ASSAYEffect of pH on the Release of Phosphates at 20°

Initial pH	Final pH	Rate of Release ug/cm ² /week
2.00*	2.2*	27.5*
2.00	2.2	21.3
3.00	3.9	7.04
4.00	6.4	7.04
5.00	6.5	7.38
7.00	6.8	7.98
9.00	6.7	7.69
11.00	6.95	7.04
12.00	9.5	47.5

* adjusted with sulfuric acid rather than hydrochloric acid

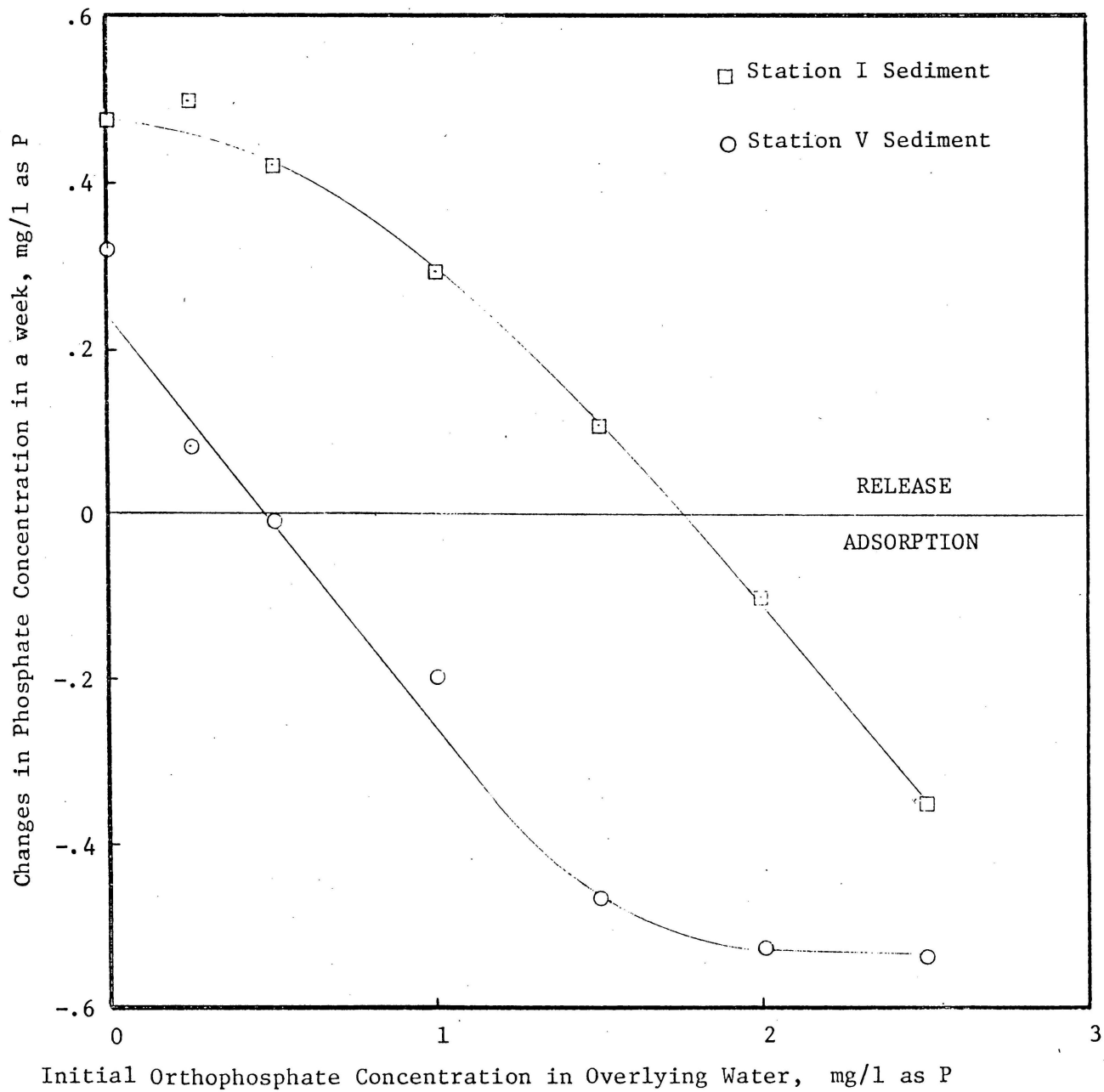


FIGURE 6. RELEASE-ADSORPTION ISOTHERM AT 20°C

phosphate released from the sediment decreased with an increase in the overlying water phosphate concentration until a point was reached where the sediment started to adsorb it. The transition point for Station I was 1.75 mg/l and for Station V was about 0.49 mg/l.

The ramification of the results from this set of assays is significant. Many early investigators had shown that sediment was a sink for phosphate. Then, there were a few who successfully showed that sediment served as a source of phosphates. From this investigation, we can postulate that sediments serve as a sort of buffer having a critical concentration. Above the critical concentration, sediment serves as a sink, and as a source below that. This property is termed here as "availability critical concentration" (ACC).

Another thing that could be seen was that not only may different sediments have different critical concentrations, but the shape of the adsorption isotherms may be different. This means that investigators may be working on different sides of the critical concentration and so have apparently contradicting results. Also, this would mean that the test done with sediment from one area may give results quite different from that of another area as could be seen from the variation of properties within the same reservoir (Tables VI, XIV to XVIII). This showed clearly that the availability characteristics depend on the properties of the sediment which vary considerably. Clearly investigators should not make generalized conclusions about sediments without having complete knowledge of the sediment properties.

Additional assays were run for a temperature of about 4°C with an initial phosphate concentration of 2.5 mg/l in the overlying water. (Tables XXVIII & XXIX) It was found that lowering the temperature increased the rate of adsorption. It is reasonable to expect the isotherm to shift to the left and the availability critical concentration to be lower as the temperature drops. In the Occoquan Reservoir the normal temperature was between 4 to 15°C and, therefore, critical concentration would be much lower than that found for 20°C.

It should be pointed out that adsorption is not the only means by which phosphates are being added to the sediments. Other ways observed are from dead algae and fallen leaves. This means that phosphates can still be added to the sediments even though the concentration of phosphates in the overlying water may be below the available critical concentration.

Effect of flushing

A set of five reactors was set up to study the effect of flushing with clean water. The overlying water was taken out weekly and analyzed for phosphates, then demineralized water was put back into each reactor. This process was repeated for five weeks. The results, plotted in Figure 7, show a gradual decrease of the rate of release with flushing. It was found that the rate of release decreased about 12.5% with flushing at the end of each seven day period.

Flushing assays were also made with the reactors used for anaerobic tests (Table XI) and phosphate concentration tests (Table XII).

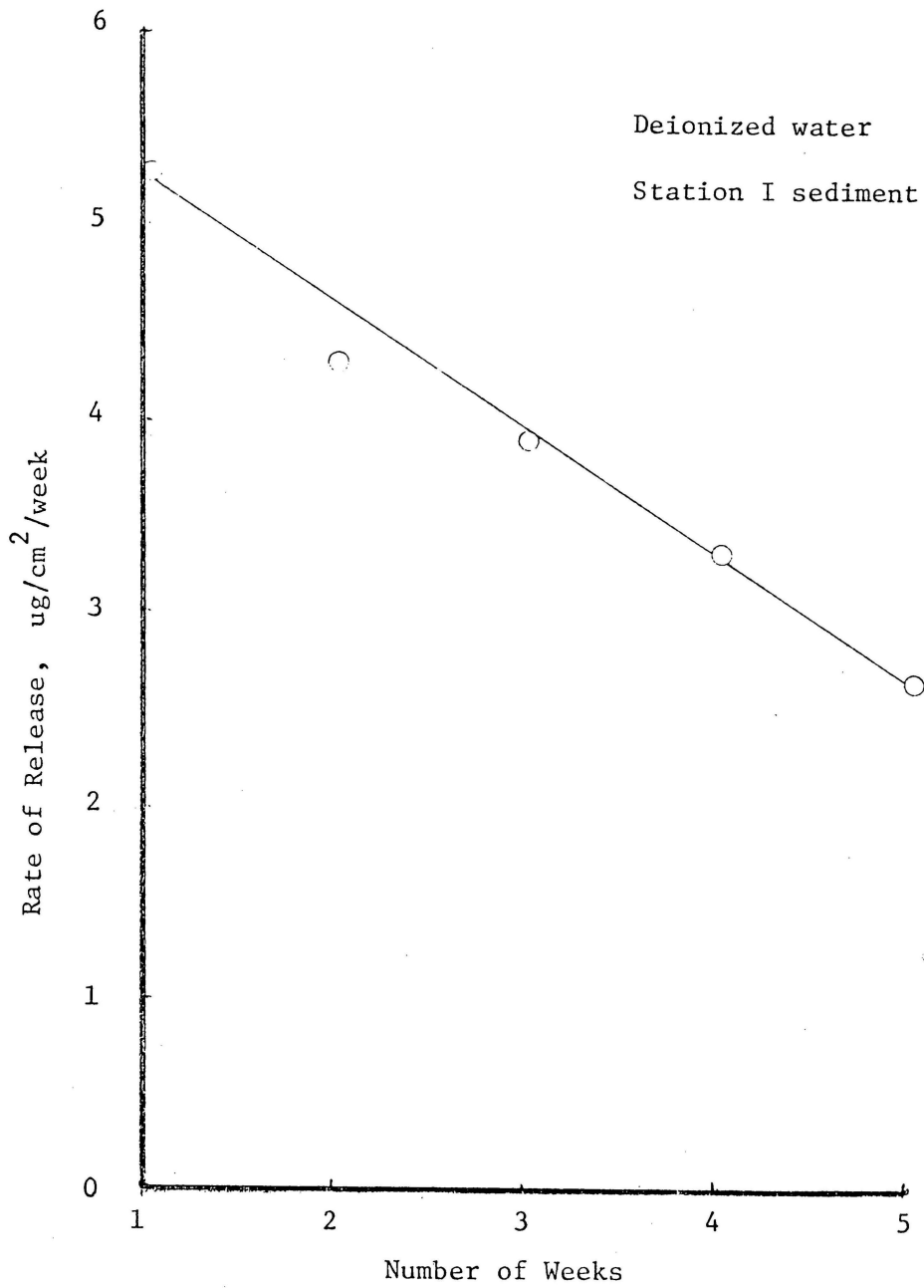


FIGURE 7. EFFECT OF FLUSHING ON THE RATE OF PHOSPHATE RELEASE AT 20°C

TABLE XI

AVAILABILITY ASSAYEffect of Flushing on the Rate of Release at 20°CDissolved Oxygen Concentration

First Week Conditions	Rate of Release		% Decrease
	ug/cm ² /week		
	First Week	Second Week*	
Aerobic	11.09	1.54	86
Aerobic NaCl(1)	5.94	2.09	65
" NaCl(2)	1.33	3.98	-200
Anaerobic Na ₂ SO ₃ (1)	21.88	7.51	66
" Na ₂ SO ₃ (2)	31.88	9.15	71

* conditions reverted back to normal, i.e. aerobic, and no chemicals added
adjusted from 11 days to 7 days

(1) and (2) are equivalent sodium ion concentration as sodium sulfite concentration of 500 and 1000 mg/l respectively

TABLE XII

AVAILABILITY ASSAYEffect of Flushing on Rate of Release at 20°CPhosphate Concentration Tests

Initial Phosphate Concentration	Rate of Release		% Decrease
	First Week	Second Week	
0.00	5.90	2.53	57
0.25	9.38	2.93	69
0.50	11.56	2.66	77
1.00	16.09	3.45	79
1.50	20.16	4.52	78
2.00	23.75	4.12	83
2.50	26.95	3.21	88

* adjusted from 11 days to 7 days
 second week conditions reverted back to normal,
 i.e. aerobic, no initial phosphate concentration.

The results of these assays indicate how adverse conditions which enhanced the rate of release would affect the system even after flushing and conditions have returned back to normal, i.e., aerobic conditions, etc. The reading for the second week was adjusted from eleven to seven days. The delay in reading was caused by bad weather. It was found that after an adverse condition, the rate of release was still higher than normal even after conditions had reverted back to normal. This set of assays showed that adverse conditions such as an anaerobic condition should be avoided if release of nutrients is undesirable, since they may cause unfavorable residual effects. It is also interesting to note that sediment does not immediately release the large amount of phosphate it has previously adsorbed.

Effect of microbial activity

Many attempts were made to study the effect of microbial activity on sediment phosphate release. On the whole, biological activities in sediments are hard to monitor. However, even though the results here were not as consistent as other assays, some trends could be detected from average values.

Antibiotics such as penicillin and chloromycetin were used. From five identical assays for each of the antibiotics, it was found that 50mg/l of penicillin decreased the rate of release about 15%, and chloromycetin decreased it about 40%.

Formalin was used at different concentrations as shown in Table XIII. Since formalin changed the pH of the system, the pH of the formalin solution at different concentrations were measured. It was observed

TABLE XIII

AVAILABILITY ASSAYEffect of Microbial Activity on the Rate of PhosphateRelease at 20°C

Formaldehyde added ml	pH	Rate of Release ug/cm ² /week
0	7.2	5.13
.05	6.7	.323
.1	6.5	.075
.2	6.0	.323
.4	5.0	.150
.5	4.8	.150
1.0	4.5	.238
2.0	4.3	.388
3.0	4.2	.075

50 ml deionized water water
Station I sediment used

that the overlying water was clear for all concentrations of formalin and no gas pockets were found for high concentrations. This indicated that biological activities in both the overlying water and the sediment was much reduced with the addition of formalin. Table XIII shows that the addition of formalin drastically reduced the rate of release, much more than the two antibiotics.

Penicillin is a gram positive antibiotic while chloromycetin is a broad spectrum antibiotic. However, formalin inhibits more of the microorganisms. Comparing the action of these three agents, we can say that bacteria play an important part in the release of phosphates from the sediment under normal conditions. This could be confirmed and correlated with the assays on the effect of temperature, salt concentration, etc.

Glucose was added to study the effect of an energy source added to the overlying water. It was found that there was much gas production, causing the sediment to be very loose. Also, there was a lot of brown growth in the water as a result of the biological activities. The phosphate readings were very erratic and were not meaningful because of the organic matter present.

Release of Other Nutrients

A set of five reactors were run simultaneously to evaluate the release of nutrients other than phosphate. Station I sediment was used. Analyses run besides orthophosphate were: total phosphate, total organic carbon, iron, nitrite, nitrate, ammonia and total kjeldahl nitrogen. The results are tabulated in Table XIV with averages and standard deviations. These data give the magnitude of release of other nutrients. The orthophosphate was found to be about $83\% \pm 3\%$ of the total phosphate. It is believed that this percentage can be used to extrapolate the total phosphate release in the other experiments. We can also see that most of the nitrogen released was in the form of ammonia. The total organic carbon data were not reported, because the analytical results were not reliable.

An examination of the standard deviations calculated shows that the standard deviation was quite high for nitrate and nitrite, but not for other nutrients. Low standard deviations reveal that the results were rather consistent. Therefore, we can say that this availability assay was quite satisfactory for showing release trends except for nitrite and nitrate.

TABLE XIV

AVAILABILITY ASSAYRelease of Various Nutrients at 20°C

Reactor No.	Rate or Release ug/cm ² /week					Average	Standard Deviation
	1	2	3	4	5		
Ortho- phosphate	5.6	5.5	6.1	5.9	5.3	5.67	.311
Total Phosphate	6.8	6.6	6.9	7.1	6.6	6.81	.195
Nitrite	.100	.688	1.062	.500	.125	.495	.404
Nitrate	5.46	10.75	2.94	8.94	2.69	6.15	3.596
Ammonia	76.25	80.94	78.44	78.44	74.06	77.63	2.594
TKN	101.08	94.49	98.39	102.79	95.95	98.54	3.451
Iron	8.12	8.62	8.62	9.62	8.75	8.75	.545

50 ml deionized water used

Station I sediment--1.75 inches deep

Constituents of the Reservoir Sediment

Studies made on the constituents of the sediments enabled correlation of the results of the assays. Sediments from each of the seven different areas in the reservoir were examined for organic, water and phosphate content. The results are tabulated in Tables XV through XXIII.

Regional variations

Tables XV and XVI show that water and organic contents seemed to be related. Both were higher for Stations III to V. This was probably related to the smaller particle size of the sediment at these stations. Sediments from these stations were usually more jelly like. Stations I and VII were higher in sand content and lower in both water and organic contents.

Soluble phosphate, available phosphate and total phosphate tests were made for all seven stations. Sediment samples were dried and stored. When used, they were ground and sieved through 100 mesh screen. The soluble phosphate results tabulated in Table XVII do not show much differences except for station I which was much higher than the other stations. The low value in this test showed that much of the phosphates in the sediment were not in the soluble form.

Available phosphate and total phosphate tests gave more information about the phosphate content of the sediments. Table XVIII and Table XIX shows that Bull Run(I) sediments were higher in phosphates than any of the other stations. The total phosphate content of the sediments

TABLE XV

Water Content of Sediments from the Seven Stations

Date	5-10	5-30	6-28	7-17	9-10	
Station No.	Water Content, Percent by Weight					Average
I	52.98	56.71	53.07	52.61	61.81	55.44
II	61.20				66.40	63.80
III	62.20				68.65	65.42
IV	63.53				68.35	65.94
V	67.79	65.88	64.15	65.97	68.51	66.46
VI					64.98	64.98
VII	50.19				51.06	50.62

TABLE XVI

Organic Content of Sediments from the Seven Stations

Date	5-10	5-30	6-28	7-17	9-10	
Station No	Organic Content, Percent by Weight					Average
I	5.70	6.56	6.40	6.54	7.49	6.54
II	7.35				8.46	7.90
III	6.78				8.69	7.74
IV	7.73				9.56	8.64
V	8.50	9.91	9.70	10.15	10.29	9.71
VI					9.52	9.52
VII	4.96				6.59	5.78

TABLE XVI I

Soluble Phosphate Content of Sediments from
the Seven Stations

Station No	Soluble Phosphate as ug Phosphorus/g sediment
I	.531
II	.063
III	.100
IV	.200
V	.100
VI	.150
VII	.063

TABLE XVIII

Available Phosphate Content of Sediments from
the Seven Stations

Station No.	Available Phosphate as ug P/ g sediment
I	140
II	34.5
III	60
IV	53.8
V	40.5
VI	42.5
VII	17

TABLE X IX

Total Phosphate Content of Sediments from
the Seven Stations

Station No.	Total Phosphate as ug P/ g sediment
I	977
II	548
III	879
IV	781
V	695
VI	735
VII	172

decreased with distance downstream in the main body of the reservoir except in the aerated section near the Dam. Occoquan Creek(II) had a much lower phosphate content than Bull Run. It is interesting to note that Occoquan Creek has a larger watershed which is mostly agricultural land.

Hooes Run sediment (VII) had a much lower phosphate content than all other stations. The sediment there was produced by large amounts of silt washed from housing development sites and the layers are relatively new. There is an absence of sewage treatment plants and agricultural activities in the Hooes Run Watershed.

The different properties of the sediments from different areas provided a good basis for evaluating the validity of the availability assay. From a comparison it was found that the phosphate release rate correlated closely with the total phosphate content of the sediment.

Variations with time

Sediment samples taken at Station I at different times of the year were examined for organic and phosphate contents (Tables XX & XXI). These results together with those in Tables XIV and XV show that the properties of the sediments vary with time. It is interesting to note that the organic content values are higher during September and October which is about the end of the algae growing season.

Local variations

An extensive study was made of Station I sediment samples taken not only at different times of the year, but different grabs taken

TABLE XX

Variation of Organic Content of Sediments from Station I with Time

Date	Organic Content Percent by Weight
5-9	5.70
5-30	6.56
6-28	6.34 6.45
7-17	6.54
9-10	7.49
10-3	7.51 7.17 7.27
11-7	6.07 6.55 6.06
11-20	6.52

TABLE XXI

Variation of Total Phosphate Content of
Sediments from Station I with Time

Date	Total Phosphate ug P/g sediment
Summer	950
Summer	938
9-10	860
10-3 (1)	1000
10-3 (2)	1063
11-7	906
11-20	1125

(1) and (2) are different grab samples taken the same day

in the same hour. It was found that there were variations in properties with time and variations in the phosphate content of sediment in one local area. These results confirmed the earlier finding that availability assay can only be compared with the same sample.

Variations with sediment depth

Generally, the sediments in the reservoir were not deep enough to allow good core sampling. Also, the core sampler available was not a good one. Core samples were taken at all stations and Station III yielded the best sample. It was interesting to note that leaves were found throughout the different depths of the sediment. As shown in Table XXII, the sediment surface usually had a rather high phosphorus content and decreased with depth gradually. This was not true with Station V, however. Table XXIII shows that for Station V sediment, the highest value for water content, organic content and total phosphate content occurred at a depth of 3 to 6 inches.

TABLE XXII

Total Phosphate of Core Sediment Samples

Station (Date)	Depth inch	Total Phosphate ug / g sediment
II (9-19)	0 - 2	594
	2 - 4	525
	4-- 6	494
III (12-12)	0 - 2	797
	2--4	516
	4 - 6	478
	6 - 8	456
	8 -10	441
	10-12	438
V (7-17)	0 - 3	812.5
	3 - 6	937.5
	6 - 9	672
	9 -12	650
V (9-19)	0 - 2	766
	2 - 4	791
	4 - 6	875
	6 - 8	641

TABLE XXIII

Chemical Properties of Core Sediment Sample
from Station V

Depth	Water Content	Organic Content	Total Phosphate
inch	% by wt.	% by wt.	ug P/ g sediment
0 -- 3	60.91	9.27	812.5
3 -- 6	62.34	9.70	937.5
6 -- 9	59.46	9.03	672
9 --12	54.60	9.04	650

Core taken on 7-17-73

V DISCUSSION

A study of the relationship of sediment to reservoir water quality should also be concerned about where the nutrient in the sediment came from and how much is carried down from the watershed by the silt. Knowing the source and quantity of nutrient input provides information about the nature and type of nutrient entering and some basis for controlling the source.

Phosphate content in the streams in the Occoquan Watershed had been examined for over a year at the time of this report. The results can be found in the file of the Occoquan Watershed Monitoring Laboratory and also published in the quarterly reports of the Occoquan Watershed Monitoring Program(48). It has been found that the phosphate content in Bull Run at Yates Ford is always higher than that in Occoquan Creek. The difference is especially great during periods of low rainfall. It should be pointed out that Upper Bull Run at Catharpin has a very low phosphate content. However, by the time it has reached Yates Ford the concentration has increased twenty times or more. There is not much farmland in the Bull Run subwatershed, but there are eleven large waste treatment plants. Data has shown that the major sources of nutrient to Bull Run are the waste treatment effluents.

It is interesting to note how this high phosphate concentration in Bull Run affects subsequent water quality both directly and indirectly. The availability assay showed that the release from

Station I sediment was higher than that from Station II sediment, regardless of dissolved oxygen or temperature conditions. This result is apparently confirmed by actual situation from the reservoir. The water at Station I has consistently had a higher phosphate content than Station II and all of the other stations. The higher concentrations are undoubtedly directly affected by the higher phosphate concentrations flowing down Bull Run but it is also likely that the higher release rate of nutrients in that arm has a significant effect on the observed concentration. The release from sediment mainly affects the bottom water and is most significant during adverse conditions. The sediment in the Bull Run arm of the Reservoir(I) had a significantly higher phosphate content than sediment from the Occoquan Creek arm (II). The effects can also be seen downstream, for Stations III to VI sediments had higher phosphate content than Station II sediment. A further point is that the Occoquan Creek subwatershed is almost two times the size of the Bull Run subwatershed.

In order to study more carefully how much nutrient is carried down the watershed, a detailed nutrient budget study should be made. This could be done if the samples from the automatic samplers installed at the different stream stations in the watershed were all analyzed for phosphates as well as for suspended solids.

Sample variations

Seasonal variation was a significant cause for the difference in the property of the sediment and was well recognized by the investigator. However, the study of the organic content and phosphorus content of

sediments from Station I showed that there were differences in properties between different grab samples taken from the same station around the same time. This variation is probably intensified by the narrow topology of the reservoir. It was also suspected that the sediment flows slowly. The reason is that the gradient of the bottom is rather steep, about a drop of forty feet in about five miles, and the sediment is quite soft.

Correlation of assay results with the properties of sediment

By relating the phosphate release (Table VI) to the properties of sediments in the different stations (Tables XV to XXIII), we can draw quite a few valuable correlations. Table XI and Table XIX showed that for Station I, total phosphate is not very much higher than Stations II to VI, but available phosphate is much higher. The rate of release was clearly affected by the phosphate content, but it was not a direct relationship.

Table XVII showed that the soluble phosphate concentrations of the sediments are very low percentages of the total phosphate and no correlations could be drawn. This revealed that the release of phosphates from sediments into the overlying water must be a more complicated process than just solubilizing. The phosphates released must come from the breaking down of the insoluble total phosphates in the sediment by some biological or physical-chemical means. Bacterial activity is probably a very important means in breaking down organic phosphates. Benthic organisms such as protozoa and oligochaetes also help to alter the sediment by their movement and life process.

As noted earlier in Table VI, Station VII sediment had an extremely low phosphate release, about a hundredth of that of sediments from the other six stations. However, the total phosphate content was only about one-fifth of that of the other sediments. This shows that the phosphate in Hooes Run sediment was not readily available for release to the overlying water. The reason might be caused by the fact that Hooes Run sediment is not a typical lake sediment, but rather soil washed down from housing developments upstreams.

Effect of salt concentrations

The assays for the study of anaerobic conditions gave us some insight into the effect of salt concentration on the rate of phosphate release. Figure 3 showed that sodium chloride reduced the rate of release. The reduction was inversely proportional to the concentration of sodium chloride. The slope of this inverse proportion is different for different sediment. It should be noted that this reduction may be due to the lowering of bacterial activity rather than just a physical-chemical effect.

This result can be applied to sea water, Since the salt concentration in sea water is so much higher--about 33,000 mg/l, we can expect the rate of release of phosphorus to be much lower. Extrapolating the curve showed that the release of phosphate is almost negligible at about 1100 mg/l. Therefore, sediment in sea or ocean may well act as an effective sink for phosphates. Recommendation is made here for more investigations of seawater-sediment systems.

Restoration of the reservoir

One of the primary interests of this investigation was to see whether and how the Occoquan Reservoir water quality could be restored. After the building of the advanced waste treatment plant, water flowing down Bull Run should be of rather high quality. Availability assays showed that flushing with demineralized water decreased the amount of phosphate release gradually and linearly. Since clean stream water flowing into the reservoir will still contain a small amount of phosphate, we can expect water quality in the Occoquan Reservoir to recover, though at a rather slow rate.

The question whether sediment in the Occoquan Reservoir will serve as a sink or source of phosphates is often raised. Assays done on the effect of phosphate concentration in the overlying water showed that it depends on the availability critical concentration(ACC). Figure 6 showed that at 20°C, the ACC for Station I was 1.75 mg/l and was 0.49 mg/l for Station V. Answering the previous question, it can be said that phosphate will be continuously released as long as the phosphate concentration of the improved quality water is below the ACC, which is different for different areas of the reservoir. Above the ACC, the sediment will adsorb phosphates. Also, the amount released or adsorbed will depend on the ACC of the area.

It should be noted that the ACC obtained in this investigation was for normal conditions(i.e., 20°C, aerobic). The nutrient equilibria is upset by changes in temperature and dissolved oxygen conditions. It is interesting to note that anaerobic conditions

occur quite often during summer time when the temperature is high. These two conditions occurring together intensify the unfavorable release of phosphates.

A factor that would help to reduce the release of phosphate from the sediment is the deposition of nutrient-poor silt. Figure 5 already showed that the release of phosphate was drastically reduced by a thin layer of sand. Therefore, if the silt coming into the reservoir is low in phosphate, we can expect the release of phosphate to become insignificant after the accumulation of a few millimeters of silt on the surface of the sediment. Of course, we should note that the above was based on the assumption that the sediment surface was not disturbed. In the actual situation, the sediment surface will be disturbed by the movement of benthic fauna and the production of gas in the sediment during hot weather. All these promote the upward transport of phosphate in the sediment. Therefore, we can expect the sediment to contribute more nutrient to the overlying water for a longer period of time than undisturbed sediment.

From the above, we can see that there are a few factors, both favorable and unfavorable, involved in the effects of sediment on water quality. Therefore, we cannot give an exact answer to how the phosphorus accumulated in the bottom deposits will affect eutrophication if all nutrient discharges into the Occoquan Reservoir are eliminated. However, we can still say that the level of phosphate in the reservoir will continue to drop, even though it may take quite a few years to drop to a low enough level. Of course, many will argue that the

phosphate level in the overlying water for a few years will still be high enough to support algal bloom. However, we can take comfort in the fact that lower concentrations of phosphate will cut down the frequency and severity of excessive algal blooms, resulting in overall improvement in water quality.

Comparison of results with previous investigators

The total phosphate content of sediments in the Occoquan Reservoir are listed in Table XI. With the exception of Station VII, the total phosphate values are between 0.5 to 1.0 mg/g of dry sediment. These compare pretty well with results by other investigators. From 25 samples from a small eutrophic lake, Frink(11) reported a range of 0.4 to 2.8 mg/g of sediment. Latterell(17) reported a range of 0.3 to 1.5 mg/g of sediment for three lakes in Minnesota. Fillos & Swanson (49) reported 1.1 and 1.3 mg/g for Lake Warner and Muddy River sediments respectively.

A lot of investigations on phosphate release were done with suspended sediment-water system and so cannot be compared with the rate of release results obtained in this study. Furthermore, not many investigators actually quantified the rate of release in terms of mass of phosphorus released per unit area per unit time. Pomeroy(35) estimated a daily exchange across a submerged and undisturbed surface of sediment to be on the order of $1 \text{ umole PO}_4^{-3}/\text{m}^2/\text{day}$ ($0.0217 \text{ ug}/\text{cm}^2/\text{week}$). From the concentration gradient of interstitial water, Leckie(36) estimated a maximum diffusional transfer rate of $9 \times 10^{-6} \text{ mole}/\text{m}^2/\text{day}$ ($.27 \text{ mg-P}/\text{m}^2/\text{day}$ or $0.19 \text{ ug-P}/\text{cm}^2/\text{week}$). Studying simulated sludge, Fillos and

Molof(30) found an average release rate of $3 \text{ mg-P/m}^2/\text{day}$ ($2.1 \text{ ug/cm}^2/\text{day}$). Using a continuous flow model, Fillos & Swanson(49) studied sediments from Muddy River and Lake Warner and obtained average phosphorus release rate of $9.6 \text{ mg/m}^2/\text{day}$ ($6.72 \text{ ug/cm}^2/\text{week}$) and $1.2 \text{ mg/m}^2/\text{day}$ ($0.84 \text{ ug/cm}^2/\text{week}$) respectively at 24°C . In this study, the average phosphate release rate for Station I sediment was $8.46 \text{ mg/m}^2/\text{day}$ ($5.92 \text{ ug/cm}^2/\text{week}$) at 20°C (Table V). Therefore, the experimental values compare favorably with each other and are all in the same order of magnitude. However, they are much higher than the estimated values. The low values were probably caused by the fact that those investigators did not include in their estimates bacterial activities which accelerate transfer of nutrients.

VI CONCLUSIONS

The investigation of the effect of the Occoquan Reservoir sediments on water quality led to the following conclusions:

1. The rate of release of phosphates was found to be unaffected by
 - a. pH changes in the normal range of natural water
 - b. depth of sediment
 - c. depth of overlying water
2. The rate of release of phosphates was enhanced by
 - a. anaerobic conditions
 - b. pH beyond the range found in natural water, i.e. below 3 or above 11
 - c. amount of phosphates in the sediment
 - d. rise in temperature
3. The rate of release was affected inversely by
 - a. high salt concentration
 - b. drying of sediment surface
 - c. physical barrier on the sediment surface
 - d. reduction of bacterial activities
4. Flushing with demineralized water lowered the rate of release. The lowering of the rate of release by flushing seemed to decrease gradually by a constant ratio.
5. Under normal conditions, other nutrients such as carbon and nitrogen are also released with phosphates. Nitrogen was mainly released as ammonia.

6. The sediment may act as a sink or source for phosphates, depending on the phosphate concentration in the overlying water. A critical availability concentration governs whether it serves as a sink or as a source. Also, this critical availability concentration is different for sediments from different areas.

7. Besides the finding from the assay, a study of the physical and chemical properties showed that the properties of the sediments in the Occoquan Reservoir have variations with respect to regions, depth, and time as well as variations within the same vicinity at the same time.

VII SUMMARY

The purpose of this investigation was to determine the effect of sediments in the Occoquan Reservoir on the water quality. Phosphate determination by the ascorbic acid method was first evaluated for its precision and accuracy. Assay was developed to measure the rate of nutrient phosphate release to the overlying water in a quiescent dark condition. The assay was evaluated to test for its reliability in giving valid conclusions. The assay was an attempt to provide a system similar to the actual system which could be used in the laboratory. Also, the effect of different parameters could be studied by varying conditions one at a time.

In this assay, it was found that the rate of release was not affected by normal pH changes, depth of sediment, or depth of overlying water. The rate release was found to increase with increase in temperature, phosphate content in sediments, and reduced anaerobic condition. The rate was adversely affected by high concentration of salt, drying on sediment surface, thickness of physical barrier, and reduction of bacterial activities. Flushing seemed to decrease the rate of release by a constant ratio.

Under normal conditions, sediments release other nutrients besides phosphates. However, it was found that whether the sediment served as a sink or source of phosphate was governed by the critical availability concentration which was different for different sediments.

A study of the properties of the reservoir sediment showed that there were variations with respect to time, station, and depth, as well as vicinity within the same station, in this reservoir.

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IX APPENDIX

TABLE XXIV

Comparison of Phosphate Determination MethodsEffect of Time on Color Development

Time Minutes	Stannous Chloride Method Absorbance	Ascorbic Acid Method Absorbance
0	0	0
0.5	.185	.010
1	.215	.030
1.5	.225	.165
2	.230	.195
2.5	.235	.200
3	.240	.200
3.5	.240	.200
4	.245	.200
5.	.248	.200
6	.250	.200
8	.253	.200
10	.258	.200
12	.260	.200
14	.267	.200
16	.270	.200
20	.272	.200
25	.280	.200
55	.260	.200
90	.250	.200
120	.245	.200

Phosphate Concentration of solution--0.25 ug/ml as P

TABLE XXV

AVAILABILITY ASSAY

Effect of DO Concentration on the Rate of Phosphate
Release at 20°C: Station I Sediment

Condition	Final pH	Rate of Release ug/cm ² /week
Aerobic	6.7	11.09
Aerobic NaCl(1)	6.8	5.94
Aerobic NaCl(2)	6.8	1.33
Anaerobic Na ₂ SO ₃ (1)	6.9	21.88
Anaerobic Na ₂ SO ₃ (2)	7.1	31.88

(1) and (2) are equivalent sodium ion concentration as sodium sulfite concentration of 500 and 1000 mg/l respectively

TABLE XXVI

AVAILABILITY ASSAY

Effect of DO Concentration on the Rate of Phosphate
Release at 20°C: Station V Sediment

Condition	Final pH	Rate of Release ug/cm ² /week
Aerobic	6.6	1.416
Aerobic NaCl(1)	6.4	.391
Aerobic NaCl(2)	6.3	.054
Anaerobic Na ₂ SO ₃ (1)	7.2	10.47
Anaerobic Na ₂ SO ₃ (2)	7.4	15.63

(1) and (2) are equivalent sodium ion concentration as sodium sulfite concentration of 500 and 1000 mg/l respectively

TABLE XXVII

AVAILABILITY ASSAY

Effect of Physical Barrier on the Rate
of Phosphate Release from Station I Sediment at 20°C

Thickness of Sand* mm	Rate of Release ug/cm ² /week
0	5.7
2	4.8
3	1.6
4	0.94

* White water testing sand, 99.8% pure silica
approx. 60-120 mesh

TABLE XXVIII

AVAILABILITY ASSAY

Effect of Phosphate Concentration on
Nutrient Exchange with Station I Sediment

Temperature °C	Phosphate Concentration mg/l as P		Difference
	Initial	Final	
20	0	.472	.472
	.25	.750	.500
	.50	.925	.425
	1.00	1.288	.288
	1.50	1.613	.113
	2.00	1.900	-.100
	2.50	2.156	-.344
4	2.50	1.988	-.512

TABLE XXIX

AVAILABILITY ASSAY

Effect of Phosphate Concentration on
Nutrient Exchange with Station V Sediment

Temperature °C	Phosphate Concentration mg/l as P		Difference
	Initial	Final	
20	0	.321	.321
	.25	.331	.081
	.50	.491	-.009
	1.00	.806	-.194
	1.50	1.031	-.469
	2.00	1.470	-.530
	2.50	1.980	-.530
4	2.50	1.940	-.575

TABLE XXX

AVAILABILITY ASSAYEffect of Flushing on the Rate ofPhosphate Release at 20°C

Date *	Rate of Release					Average	Standard Deviation
	ug/cm ² /week						
10-22	5.38	5.19	5.44	5.38	4.88	5.25	.230
10-29	4.45	4.84	3.98	3.98	4.14	4.28	.368
11-5	3.67	4.69	3.52	4.38	3.20	3.89	.618
11-12	2.58	3.67	3.25	4.53	2.50	3.31	.839
11-18	3.04	2.03	2.35	2.97	2.89	2.66	.445

* Test initially set up on 10-15-1973

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EFFECTS OF SEDIMENT ON WATER QUALITY IN

THE OCCOQUAN RESERVOIR

by

Yan Pui Samuel To

(ABSTRACT)

The purpose of this investigation was to determine the effect of sediments in the Occoquan Reservoir on the water quality. Phosphate determination by the ascorbic acid method was first evaluated for its precision and accuracy. An assay was developed to measure the rate of nutrient phosphate release to the overlying water in a quiescent dark condition. The assay was evaluated to test for its reliability in giving valid conclusions. The assay was an attempt to provide a system similar to the actual system which could be used in the laboratory. Also, the effect of different parameters could be studied by varying conditions one at a time.

In this assay, it was found that the rate of release was not affected by normal pH changes, depth of sediment, or depth of overlying water. The rate of release was found to increase with increase in temperature, phosphate content in sediments, and reduced anaerobic condition. The rate was adversely affected by high concentration of salt, drying on sediment surface, thickness of physical barrier, and

reduction of bacterial activities. Flushing seemed to decrease the rate of release by a constant ratio.

Under normal conditions, sediments release other nutrients besides phosphates. However, it was found that whether the sediment served as a sink or source of phosphate was governed by the critical availability concentration which was different for different sediment.

A study of the properties of the reservoir sediment showed that there were variations with respect to time, station, and depth, as well as vicinity within the same station, in this reservoir.