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NUTRIENT TRANSPORT BY SEDIMENT-WATER INTERACTION

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F I N A L R E P O R T

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ABSTRACT

NUTRIENT TRANSPORT BY SEDIMENT WATER INTERACTION

This report presents the results of a series of laboratory tests to investigate phosphate transport in sediments subjected to one dimensional consolidation type loading. P-32 techniques are employed. The results indicate that measurable transport occurs for phosphate concentrations on the order of 2 mg p/gm dry soil or more and for loads in excess of the preconsolidation load for the samples.

In addition, the report discusses models for the exchange of phosphates between sediment or soil in lakes and lake waters. These models are expressed in a form that allows them to be used to predict the environmental impact of construction operations in aquatic environments. Three modes of interaction are discussed: 1) exchange due to new soil surfaces being exposed, 2) exchange due to the dispersion of soil particles in the water, and 3) release due to forced drainage of water from sediments. The conditions under which each mechanism might be influential are discussed and mathematical models are developed for quantitative predictions.

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*sediment-water interfaces

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INTRODUCTION

In a previous report, Moore and Silver (1972) reviewed the literature concerning the role of sediments in eutrophication. The first part of the report summarized data available on the nutrient contents in aquatic systems. Data for phosphate concentrations in sediments and waters were presented for a variety of geographic locations.

The second part summarized mechanisms that had been presented in the literature for describing the mobility of phosphates in aquatic systems. The mechanisms reported were organized on the basis of the type of chemical transformation involved.

The third part described a newly developed laboratory technique for measuring the transport of phosphates due to hydrodynamic gradients set up in the pore water during one dimensional consolidation tests. Preliminary test results were presented.

The present report describes the results of an extensive series of tests performed on Kaolinite clay using the one dimensional consolidation ion transport apparatus. Conclusions concerning quantities and modes of transport are given. In addition, this report discusses techniques for modelling nutrient transport in aquatic systems. Mathematical models are presented for predicting the rate of recharge of lake phosphate due

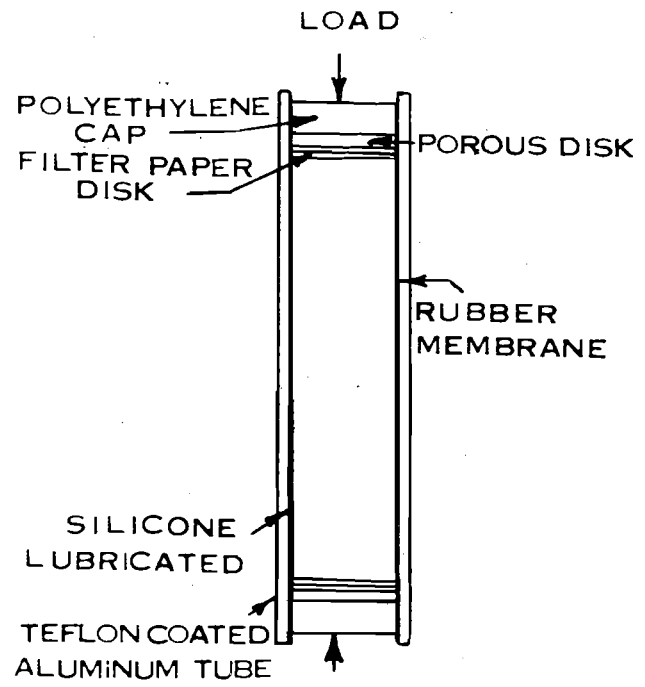
to diffusion out of sediments for the case where the phosphate content of the lake is initially zero. This hypothetical case would represent the situation in which undefined action would clean up the lake water but not affect the phosphate content in the sediment. Extensions to a variety of other situations are also presented.

LABORATORY STUDIES OF MOBILITY OF PHOSPHATES UNDER ONE DIMENSIONAL CONSOLIDATION

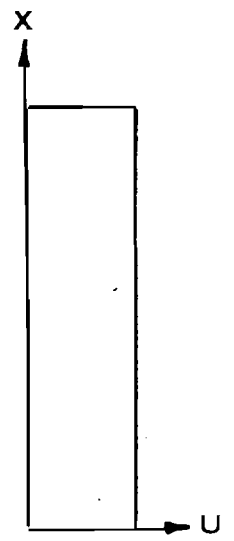
Experimental Procedure

If the load on a layer of highly compressible porous saturated soil such as clay is increased, the layer will compress as the excess water drains out of the soil. This process is termed consolidation. The added load or pressure per unit of area that produces consolidation is known as the consolidation pressure or consolidation stress. In the process of consolidating, the excess water pressure decreases and the effective stress (stress carried by soil skeleton) increases. After a long (theoretically infinite) time the excess hydrostatic pressure becomes equal to zero and the total consolidation pressure becomes the effective stress. It is assumed that flow of water is vertical only and drainage is from upper and lower surfaces of the sample. It is also assumed that the consolidation stress is uniform throughout the sample.

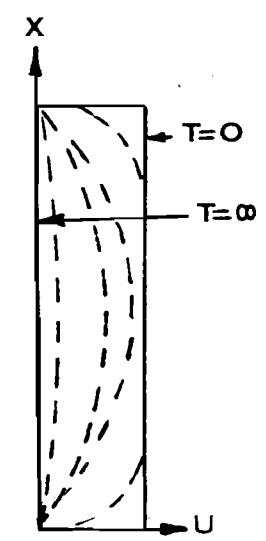
The time dependency of distribution of effective stress in the soil is shown in Fig. 1C. It may be seen that for soil the reduction in pore water pressure is not only time dependent but is also a function of position along the cylinder. This is because resistance to flow of water in soils arises throughout the mass due to the low permeability.



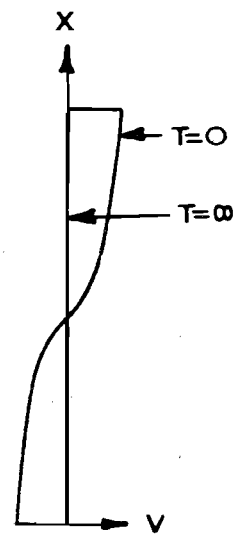
A



B



C



D

Fig. 1 Consolidation test conditions, (A) apparatus, (B) initial excess pore pressure distribution, (C) time dependent pore pressure dissipation, and (D) time dependent water flow velocity.

Because the ends of the sample are at atmospheric pressure, the water will begin to flow out to both ends of the sample in a time dependent manner. Water moving through the pores in the soil mass will drag ions with it. Therefore, the hydraulic gradient causes the gradual movement of the ions out of the soil. The velocity of the pore water depends on position and time, this relationship being shown in Fig. 1D. Minimum effective pressure occurs at the two ends of sample, therefore the maximum velocity will be at these points. Similarly, the minimum velocity will be in the center of the sample has zero velocity. Because electrostatic and electrodynamic forces tend to hold the ions to the soil particles, ions will flow with the water at a velocity equal to or less than the velocity of the water.

The experimental program was designed to study the phenomenon of phosphate ion transport as a function of hydraulic pressure gradient and of overall ion concentration in the pore fluid. Because we wish to measure transport of phosphorus under hydrodynamic pressure gradients, transport due to the other process must be minimized. In particular, diffusion due to chemical concentration gradients must be eliminated. To accomplish this, the phosphorus concentration throughout the sample was held constant. Nevertheless, it should be noted that self diffusion, defined as interdiffusion of identical ions under no chemical gradient, introduced an artifact into the data for which a correction was applied.

The soil used in this investigation was Grundite Bond Clay from A. P. Green Refractory Products in Joliet, Illinois. Illite is a clay mineral having a generalized formula $(OH)_4 (K, Ca_{0.5}, Na)_{1.68} (Si_{7.30}, Al_{0.70}) (Al_{0.949} Fe_{1.94}, Fe_{0.38}, Mg_{0.80})_{20}$. The material is uniform with an average

grain diameter of approximately 2 microns. Solid particles are plate shape and the ratio of diameter to thickness is about 10 to 1.

Potassium dihydrogen phosphate crystals (KH_2PO_4) dissolved in water were used as the phosphate solution because most investigators have concluded that the ionic form of phosphate in the soil would be H_2PO_4^- . P^{32} carried in hydrochloric acid as KH_2PO_4 was dispersed in the solution for tagged samples. A quantity of P^{32} having an initial activity of 1 m ci/ml and 51 ci/mg P was obtained from Amersham/Searle for use in this investigation.

The variables examined in the present experimental program were:

- 1) effects of magnitude of pore pressure gradient on phosphorus transport, and
- 2) effect of overall phosphorus concentration on the phosphorus transport.

Two types of tests were performed. The principal test type consisted of consolidating a series of samples having the same overall phosphorus concentration, but using consolidation stresses of 0, 0.1, 0.5, 1, 2, 4 and 8 kg/cm^2 . An auxiliary type of test was performed to provide data for correcting for self diffusion. In these tests, effectively zero loading was maintained for different lengths of time and for the various phosphorus concentrations used. These tests allowed for determining the variation in self diffusion coefficient as a function of phosphorus concentration.

Three master samples, one tagged with P^{32} and the other two untagged, were prepared for each phosphate concentration. These samples were consolidated to 1 kg/cm^2 . Sections from these master samples were used for investigation of the mobility of phosphate at the different loadings.

The amount of water used for preparing the slurry was determined by experimenting to obtain a consistency that was sufficiently fluid to allow the air bubbles to be expelled by gentle vibration. The actual amount of added solution was 406 ml of water for 400 gr of dry soil. The phosphorus concentration of the slurry in the different tests was calculated to obtain 0.005, 0.2, 1 and 2 mg phosphorus for one gr of dry soil. The different concentrations of KH_2PO_4 solution were obtained by diluting a stock solution of 17.30 gr KH_2PO_4 in 2 liters of water.

In each set of tests two kinds of bulk samples were made. One contained KH_2PO_4 solution and the other contained KH_2PO_4 solution containing a trace amount of P^{32} . In order not to have any concentration differences in the samples, the amount of total added phosphorus for the untagged and tagged samples was exactly equal. The slurry was placed in a teflon coated tube with 10 3/4" length, 2" outside diameter and 1 3/4" inside diameter. The consolidation tube was lightly lubricated inside with Dow Corning Silicon Oil. A rubber membrane was vacuum expanded within the tube (see Fig. 1A). In each set of master samples, three tubes were used, one for tagged slurry and two for untagged slurry. A polyethylene loading cap, a porous plastic disk and a filter paper disk were introduced before filling the tube with slurry. When sufficient paste was introduced into the tube, a filter paper, a porous plastic disk and a polyethylene cap were placed at the top. The polyethylene caps were drilled through for expulsion of water. The porous disks were deaired by boiling.

The samples were then one dimensionally consolidated with drainage from both sides by applying weights through a loading yoke. The loading increments used were: 1 kg, 2 kg, 4 kg, 8 kg and 16 kg that gave consoli-

dation stresses equal to 1/16, 1/8, 1/4, 1/2 and 1 kg/cm² respectively. Each load was allowed to stand until compression had effectively ceased. For each increment a curve of compression versus time was obtained. Homogeneity and uniformity of the samples were critical in determining the increment of loading. Small load increments give uniform samples since the soil particles shift their position gradually and the skeleton of soil compacts uniformly. Using this procedure it is possible to obtain almost identical particle orientation distributions throughout the sample. According to Rowell, et al (1967) one month is required for equilibrium of P³² -P³¹ to be obtained in soils. Consolidation of 1 kg/cm² required one month and therefore it is assumed that the P³² was uniformly distributed in tagged sample.

After the master samples had been consolidated to 1 kg/cm², they were extruded from the tubes and sectioned into 0.750 inch high pieces as shown in Fig. 2. Five pieces were available from each tube, therefore each set of three master samples yielded material for five individual investigations.

For the final test series, teflon coated tubes with 2 7/8" height, 2" outside diameter and 1 3/4" inside diameter were used to contain a tagged section sandwiched between two untagged sections. The tubes were assembled by introducing a polyethylene loading cap, a porous plastic disk and a filter paper followed by a 3/4" untagged section, a 3/4" tagged section and 3/4" untagged section obtained from the master samples. Finally, a filter paper, porous plastic disk and polyethylene loading cap were placed at the top.

The five samples so prepared were one dimensionally consolidated with drainage from both ends. During consolidation the samples were kept wet

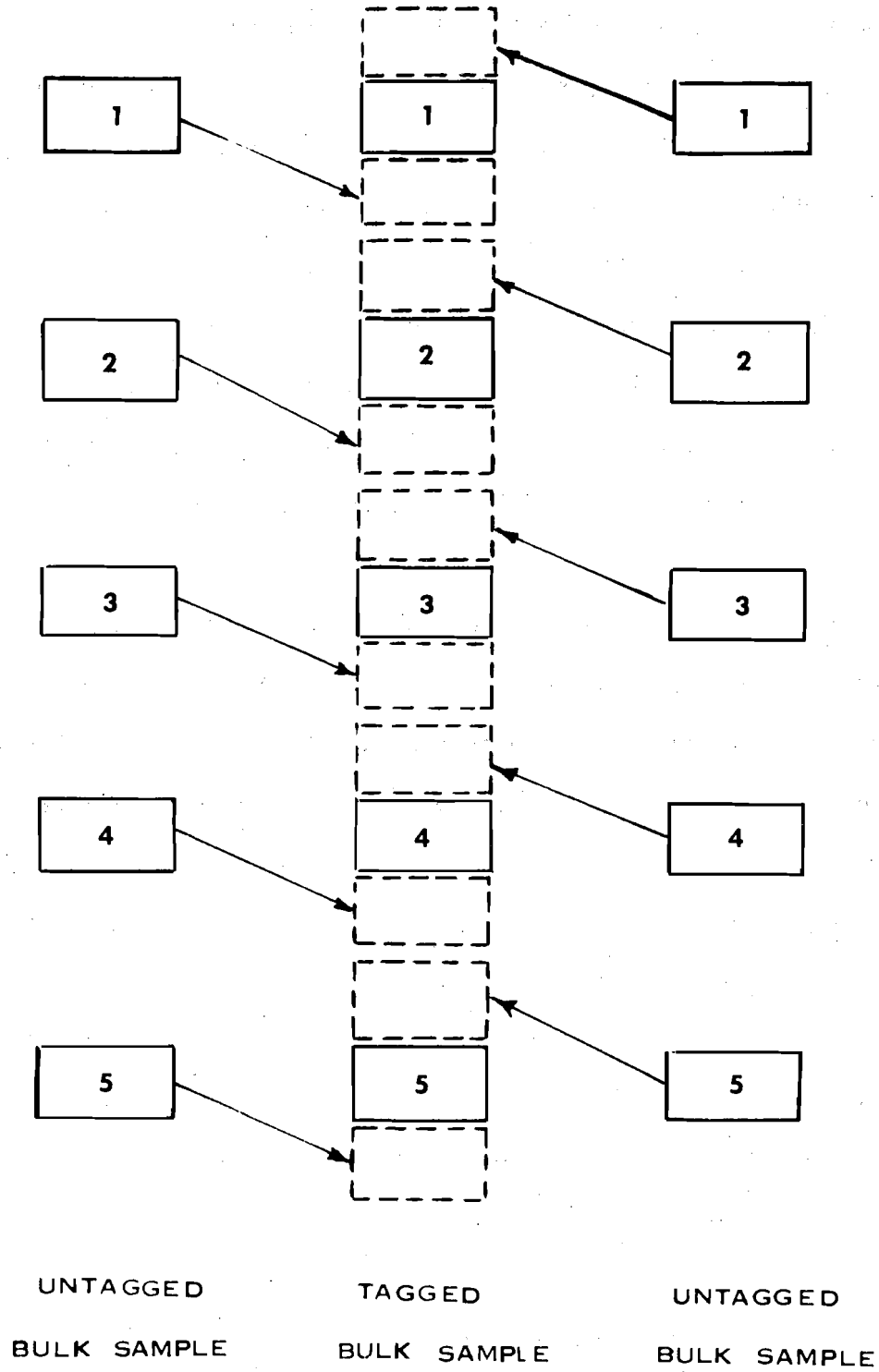


Fig. 2 Assembly of individual test samples from master samples

to prevent water loss due to evaporation. The final stresses employed were 0, 0.1, 0.5, 1, 2, 3 and 8 kg/cm², and the desired stress was applied in a single increment. Deflection versus time was monitored during loading. A total of 25 individual samples were tested.

After consolidation ceased, the samples were extruded from the tube gradually and sectioned into pieces of 0.01" thickness. Sectioning started from one end and slices of 0.01" were taken in sequence. From each sample 180-200 sections were obtained. Sections were placed in aluminum foil and over dried for 24 hours. Each section was individually ground as finely as possible and was placed in a preweighted planchet. Approximately 0.500 grams of powder was smoothed and compacted in the planchets with the aid of a fitted plunger. The planchets and powder were then weighted to 0.1 mg accuracy.

Radioactivity assay was done by Nuclear-Chicago model 8703 gas flow counting system. The number of counts is proportional to the counting time and is also a function of the weight of the sample. It was determined that the relationship between weight and counts is linear. In this investigation ten minutes counting for approximately 500 mg of dry sample was used. The weight of the 0.01" sections of samples were approximately 500 mg and thus the entire section was counted. The average of the two countings was taken for the individual sections. In order to normalize the values for the sections, the counts were expressed in counts per minute per gram of dry soil. Each sample had been divided into about 200 sections. Because only the center one third of the sample was tagged, the average counts from the first and the last ten sections were taken as background in each sample.

Data available from the tests are the weights of the sections and the time and counts given as a printed output by the Nuclear-Chicago equipment. These numbers were punched on computer cards individually for computer analysis. Some 8000 data points were accumulated for these tests.

Analysis of Test Results

The effect of self diffusion must be considered in quantitatively evaluating the results of these tests. By eliminating both chemical and hydrodynamic diffusion, the distribution of the radioactive species can be used to determine the self diffusivity of phosphate. The phosphate system is complicated, and phosphate not only exists in readily exchangeable dissolved forms, but also in forms which exchange only slowly with the solution. Therefore the diffusion coefficient will vary with time if the diffusing ions are removed from the system by sorption or exchange.

There are several factors playing distinct roles in phosphate fixation in soils such as type of soil, particle size, pH, temperature, organic content and the time of reaction. Comparing the distribution curves for different concentrations indicates that more P^{32} diffused at higher concentrations. This suggests that at very high concentrations of added P, the mobility of P increases because the exchange capacity of the soil is more than satisfied.

The time and concentration dependent self diffusion coefficient of phosphate in the test soil was examined experimentally. In these tests, soils at each of the P concentrations were prepared by equilibrating with P^{32} over a period of four weeks. This period gives uniform labelling of the moist soil. During this time P^{32} will equilibrate rapidly with a

certain fraction of the soil P and then more slowly with further fractions. Radioactive and nonradioactive soil plugs were placed in contact and the resulting diffusion was determined as a function of distance by the sectioning technique previously described.

The objective of the experiments for self diffusion was to allow for correcting the experimental data for the contribution due to self diffusion. In order to obtain an accurate correction for self diffusion, the tests were performed for the times and phosphate concentration actually used in the second phase tests.

The P^{32} distribution curves for tests performed at various consolidation pressures are shown in Fig. 3. These curves are drawn in two parts. The dots represent data points for total transport after consolidation. The solid lines represent the contribution due to self diffusion determined from the experimental tests in which effectively zero loading was maintained. In sandwiching the tagged section between the untagged sections, water and soil particles are initially at a single interface and the P^{32} is distributed uniformly. In the process of consolidation, water and soil particles will not stay in their initial position. When a load is applied to the sample, the soil particles will compress inward and the liquid will drain outward. The amounts of movement will depend on the applied load. Drainage of water causes a change in the void ratio of the sample. The void ratio is defined as the ratio of volume of voids to the volume of solids. This change can be evaluated from the water content of the samples at the initial and final states. For a given sample under consolidation pressure, the distance moved by the fluid and the distance moved by the soil particles from the initial interface can be evaluated from the initial and final void ratios.

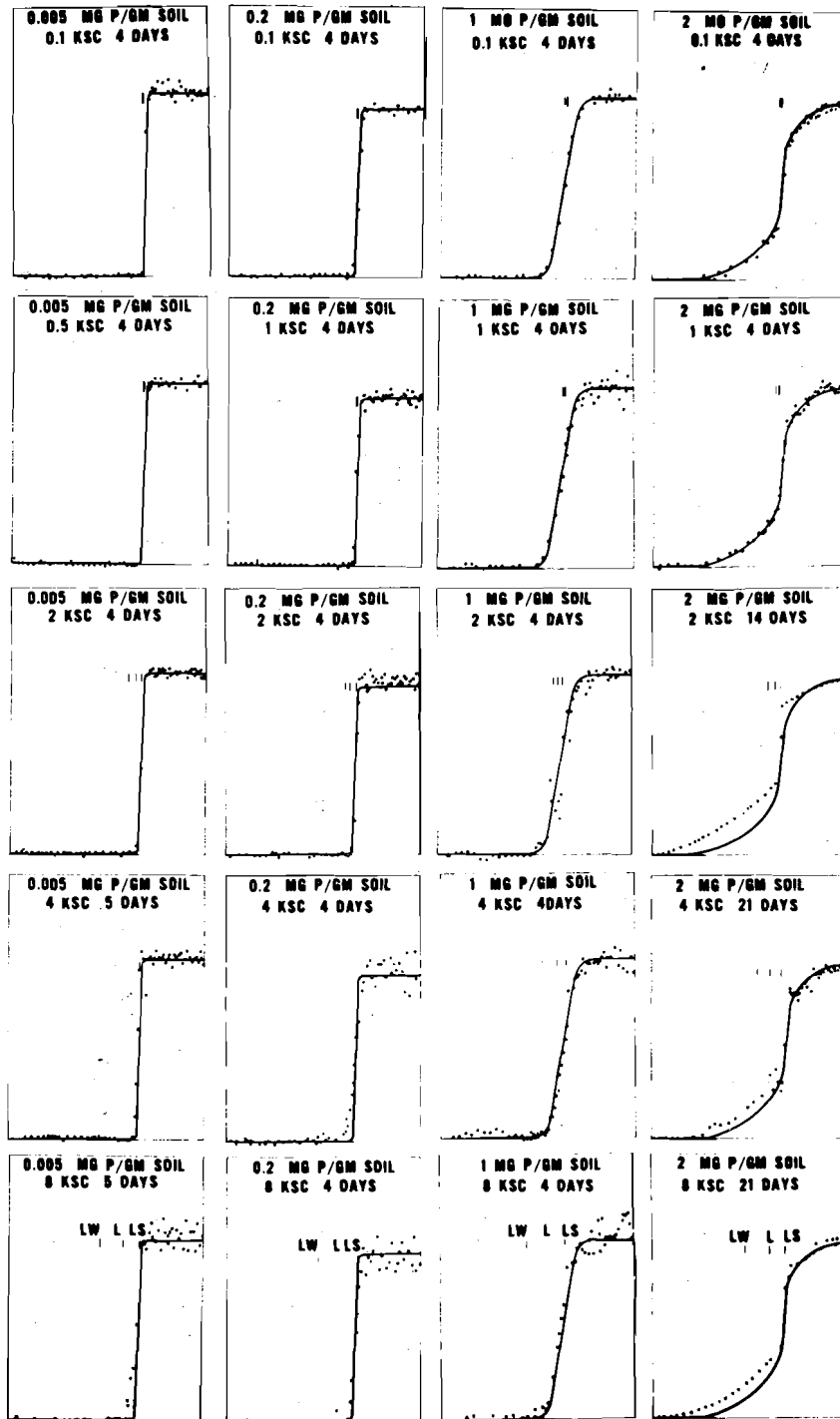


Fig. 3 Total transport data with self diffusion superimposed plotted as normalized counts/min/gr versus normalized distance.

In Fig. 4, L, LW and LS denote the initial length of tagged sample, the final length over which initially tagged water is distributed, and the final length over which the initially tagged soil is distributed respectively. LS and LW are obtained:

$$LW = L \frac{1 + \frac{1}{e_f}}{1 + \frac{1}{e_i}} \qquad LS = L \frac{1 + e_f}{1 + e_i}$$

where e_i = void ratio before loading

e_f = void ratio after loading.

The values of L, LW and LS are shown on Fig. 3.

Discussion of Test Results

The effect of non-self diffusion dependent transport of P can be evaluated by reference to Fig. 3. The solid curves represent the predicted distribution of P^{32} due only to self-diffusivity and the dots represent the actual distribution of P^{32} in the samples after consolidation. Thus, whenever the data points lie outside of the self-diffusion curve, it may be presumed that some additional transporting mechanism is operating. The assumption in designing this experimental series was that such additional transport would be due to hydrodynamic transport due to water flowing out of the sample.

Reference to Fig. 3 shows that transport in excess of that attributable to self diffusivity clearly occurred in the 2 mg P/gr of dry soil for consolidation stresses of 2, 4 and 8 kg/cm². In addition, there is evidence of additional transport for 0.2 mg P/gr of dry soil for 4 kg/cm² loading.

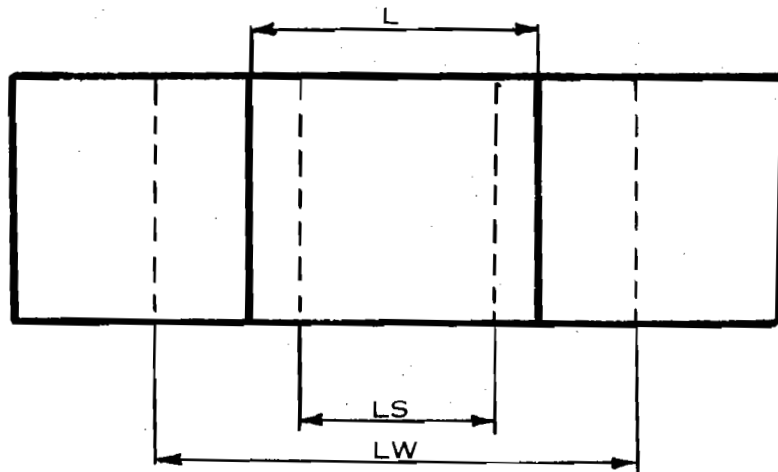


Fig 4. Initial tagged-untagged interface (L), and limits of tagged water (LW) and tagged soil (LS) after consolidation

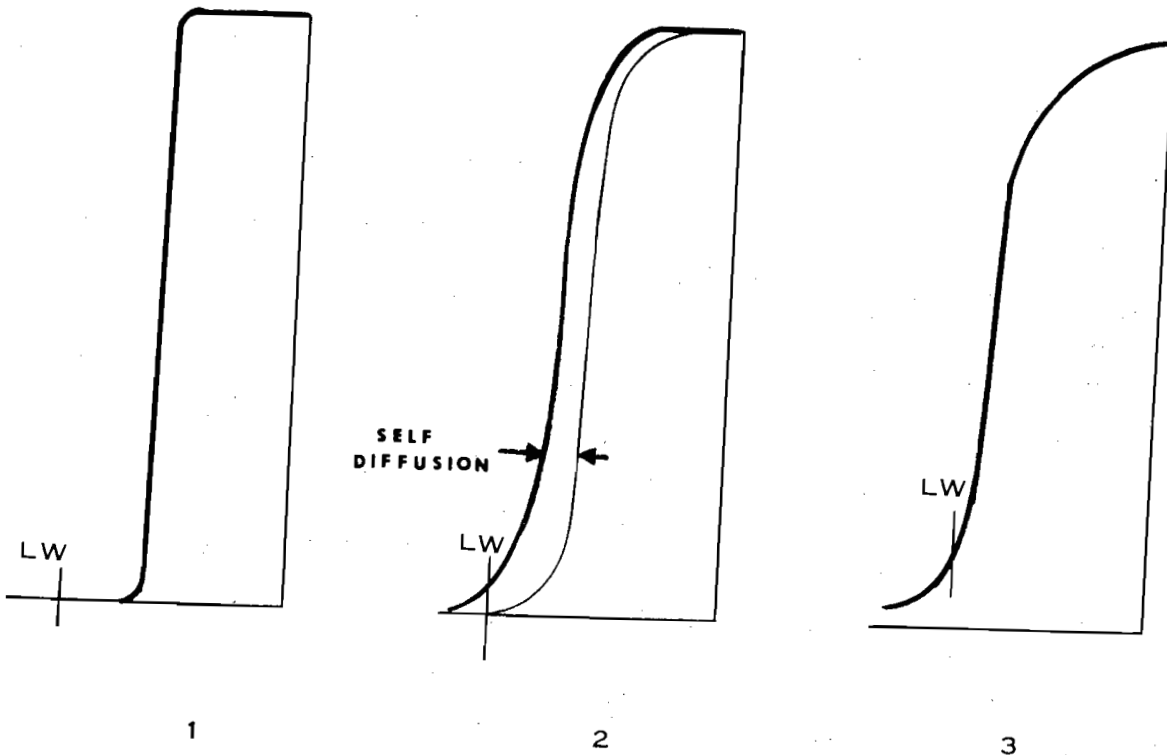


Fig. 5 Idealized modes of ion transport test results

However, this result is viewed with some doubt since that sample performed poorly during consolidation. In particular, the sample was loaded eccentrically and tipped excessively during consolidation. Some soil was lost from the tube in the process. In all other cases, while some non-self diffusion dependent transport may have occurred, the resolution obtainable from the experimental technique employed was not sufficient for its detection.

In assigning a mechanism to explain the non-self diffusion dependent part of the ion transport, it is useful to compare the actual data points with the final length over which the initially tagged water was distributed after consolidation. This length is denoted by LW on Fig. 3. The simplest possible hydrodynamic flow related model is that the radioactive P would extend outward only as far as LW (or the outer limit of self diffusion if that exceeds LW). Depending on the location of the distribution curve with respect to LW, three mechanistic modes as shown in Fig. 5 may be postulated:

1. The amount of transported water is larger than the amount of transport of ions shown by the distribution curve. This implies that ions are not being transported with the water. This mode was observed at low added P concentrations (0.005, 0.2, 1 mg P/gr dry soil). It is likely that because of the low concentration of phosphate, essentially all of the added ions are sorbed onto the clay particles and the flow of water did not cause them to be released. For these cases transport could conceivably be initiated at higher applied consolidation pressures, though this was not observed in these tests.

2. The distribution curve terminates exactly at LW + the self diffusion distance. This can be interpreted as strong evidence for the transporting of ions by the water alone. Ions move as much as the water flows, therefore

the ion-transport depends simply on the flow. This case was observed at higher phosphate concentrations and for high consolidation stresses (2 mg P/gr dry soil and 2, 4 and 8 kg/cm²). This phenomenon could be explained by a combined mechanism. A part of the transport would be due to flow carrying ions to LW. The transport beyond LW would be accounted for by self diffusion of phosphate ions in the water. This self diffusion would result in tagged phosphate diffusing out into initially untagged water. On a semi-quantitative basis, this mechanism appears promising for explaining the experimental observations. The validity of this mechanism is further supported by the observation that for consolidation of stresses below the preconsolidation stress (1 kg/cm²) where there was little or no additional compression upon reconsolidating the samples (2 mg P/gr dry soil, 0.1 and 1 kg/cm²), self diffusion alone was capable of explaining all of the observed transport.

3. Transport of ions extends beyond LW plus self diffusion. This case was not observed in these studies.

In summary, for low added phosphate concentrations and for low consolidation stresses, all phosphate transport could be accounted for by self diffusion alone. At high added phosphate concentrations and for high consolidation stresses, phosphate transport could not be explained by either self diffusion or transport with a uniformly advancing water interface alone, but could be semi-quantitatively accounted for by a mechanism involving a combination of these two factors.

Conclusions

1. Self diffusion alone appears to explain the total transport for low P concentrations (0.005, 0.2 mg P/g dry soil) (see Fig. 3).
2. Self diffusion alone appears to explain the total transport for all concentrations at stresses less than or equal to the preconsolidation stress of 1 kg/cm² (2 mg P/g dry soil, 0.1 and 1 kg/cm²).
3. For low concentrations and low consolidation stresses the experimental techniques were not sensitive enough to allow for drawing definite conclusions, however self diffusion alone appeared to explain the results. The apparent lack of transport due to flowing water may have resulted from the ions being sorbed onto the clay particles.
4. Self diffusion alone cannot explain the total transport for high concentrations (2 mg P/gr dry soil) and high stresses (2, 4, 8 kg/cm²).
 - a) A simple mechanism based on uniform flow of water in all pores is not satisfactory for explaining the excess transport for these concentrations and stresses. Radioactive phosphate extends beyond the tagged-untagged water interface for these cases.
 - b) A conceptual model based on combination of flow transport and self diffusion appears to be able to explain these data.

MODELS FOR PHOSPHATE TRANSPORT IN AQUATIC SYSTEMS

In developing a mathematical model for phosphate transport in aquatic system, a number of factors must be considered. In previous, work Moore and Silver (1972) presented some 250 mechanisms reported in the literature whereby phosphate could be transported in aquatic systems. Of these, some involved, directly or indirectly, transport into or out of sediments.

Clearly not all mechanisms are of equal importance. The effectiveness of any given mechanism depends upon three factors:

1. The frequency with which the mechanism occurs. Take for example a randomly chosen mechanism - the utilization of adsorbed phosphorous by bacteria. A critical factor is the number of bacteria engaged in this process.
2. The rate of turnover of the mechanism. Returning to the example of bacteria, this factor is incorporated in the rate at which the adsorption process occurs.
3. The quantity of phosphate transferred each time the mechanism operates.

The quantitative importance of a given mechanism is reflected in the product of these three factors. Before these products can be formed, data on the three factors must be available.

In evaluating the impact of a given mechanism on eutrophication processes, two other factors must be considered.

1. The distance of transfer. Some mechanisms, such as adsorption by plant roots, involve transport over microscopic distances. Other mechanisms, such as surface fish dying and falling to the lake bottom, involve long distances of transfer.
2. The chemical state of the phosphate after transfer. Some mechanisms release phosphate in a highly useable form, other mechanisms tie up phosphate or release it in a less useable form.

Any attempt to model the fate of phosphates in the total aquatic environment must consider these factors also.

Role of Sediments in Eutrophication

The phosphate contents of many sediments are quite high. Therefore, they must not be ignored as a potential source of nutrients for eutrophication processes. In an attempt to assess this role, the literature review of Moore and Silver (1972) has been summarized in quantitative terms. From this, certain general conclusions have been drawn concerning the role of sediments in eutrophication.

Figure 6 is a diagram which depicts reported phosphate concentrations in water in mg/ℓ. The data are plotted in order of increasing P concentration. The ordinate is dimensionless - each point represents one value reported in the literature and each observation is arbitrarily plotted one graph division above the previous observation. If one wished to assign mathematical significance to the diagram, it is that the slope of the diagram is proportional to the frequency of reporting of any given mechanism in the literature. The purpose here, however, is to provide a visual means of describing phosphate content limits. Shown on Figure 6 are lines representing:

1. the minimum phosphate contented threshold, or level below which eutrophication does not appear to be a problem (.01 mg/ℓ),
2. the threshold for accelerated growth, or level above which eutrophication has been observed to be a significant problem (0.1 mg/ℓ), and
3. the maximum concentration recommended by the Calumet conferees (.033 mg/ℓ).

The source of a fourth line labeled threshold for release by sediments will be explained subsequently.

Figure 7 presents a similar representation for data reported in the literature for phosphate contents of sediments. In this figure the heavy points (or lines, when a range of values was indicated) represent cases

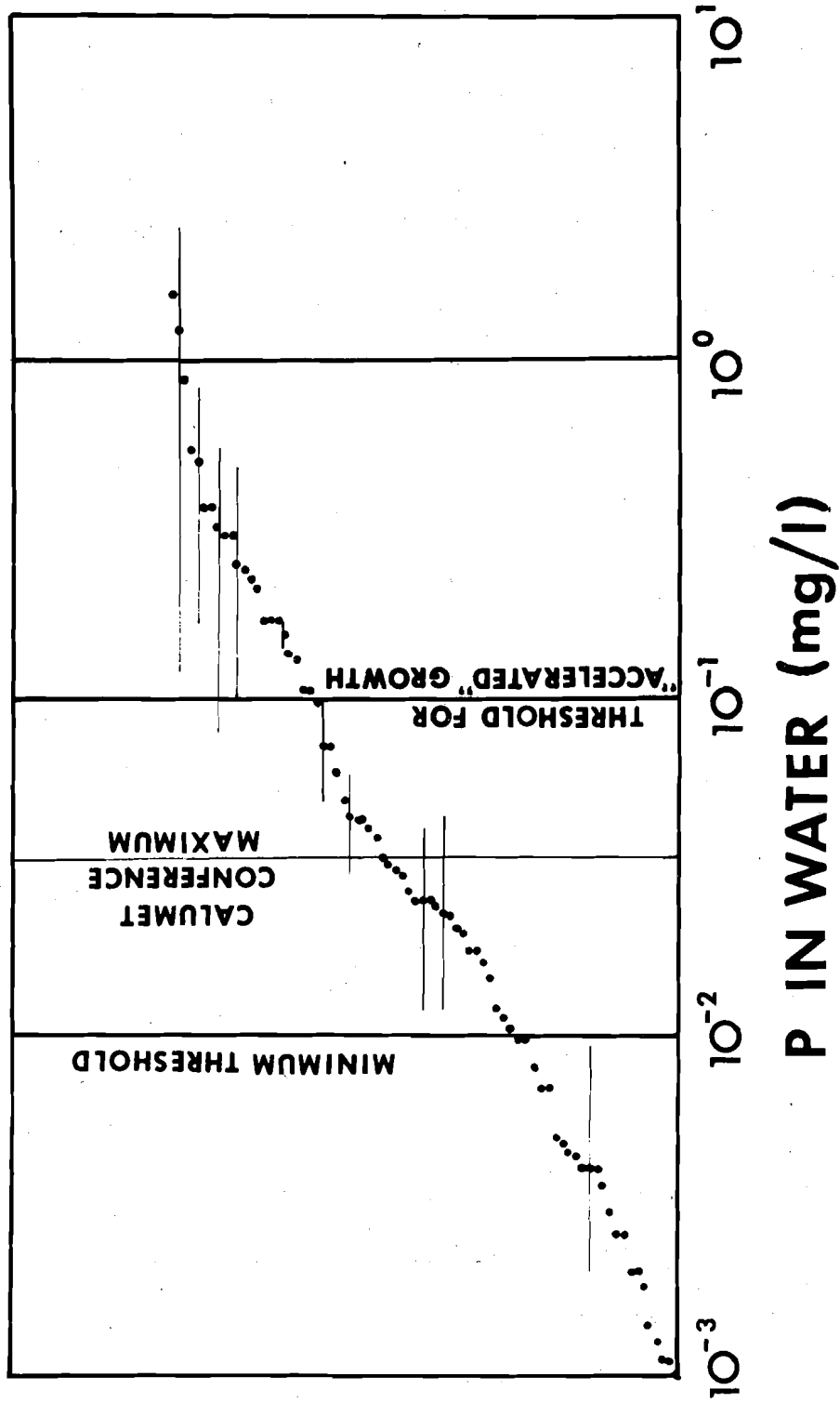


Fig. 6 Reported Phosphate Concentrations in Water

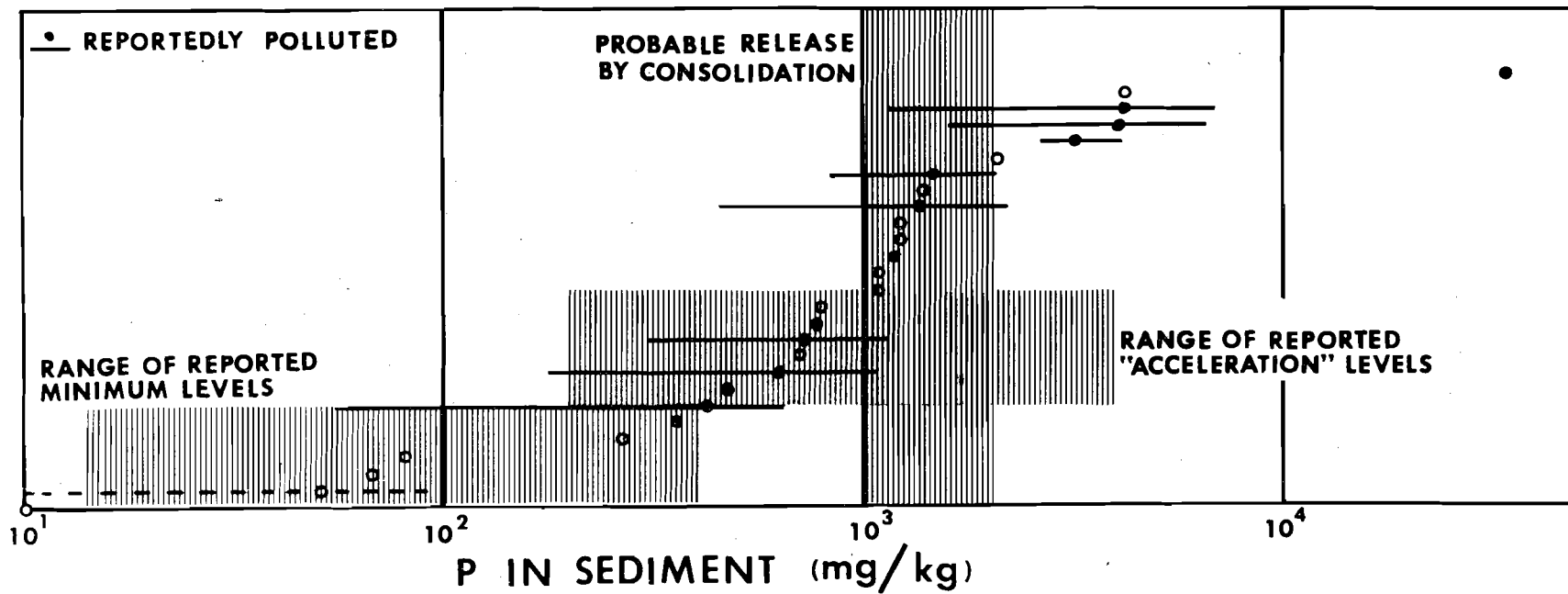


Fig. 7 Reported Phosphate Concentrations in Sediment

where it was specifically pointed out in the literature that eutrophication was a problem. Figure 8 presents a plot of phosphate contents in water (mg/l) versus phosphate contents in sediments (mg/kg) for those cases where both values were reported in the literature. The two dotted slope lines show what are considered to be reasonable bounds on the data. The solid slope line is rule of thumb best fit line which puts the sediment phosphate concentration (mg/kg) at 10,000 times the phosphate concentration in the water (mg/l). While this is a rule of thumb correlation, it appears to be relatively strongly established by the data presented.

The data in Figures 6, 7 and 8 can be effectively inter-related. Consider the two dotted lines on Figure 8 to be reasonable bounds of sediment phosphate concentration as a function of water phosphate concentration. Thus for any value of water phosphate concentration one can obtain a pair of probable bounding values for sediment phosphate concentration. Table I lists the range values for the special limits shown on Figure 6. These limits are shown as banded regions on Figure 7. Again the ordinate has no significance. These values agree quite well with the heavy dots representing cases where eutrophication was reported as being a problem. Thus it may be concluded that 300 mg/kg phosphate in sediment correlates with the threshold value for phosphate in the water. This, by back correlation, reinforces the Calumette conference decision of an upper limit of .033 mg/l ($.033 \times 10000 \approx 300$).

Table I. Sediment Phosphate Content Probable Ranges

Condition	Value in Water	Range in Sediment
Minimum threshold	.01 mg/l	14-400 mg/kg
Threshold for accelerated growth	.1	200-4000

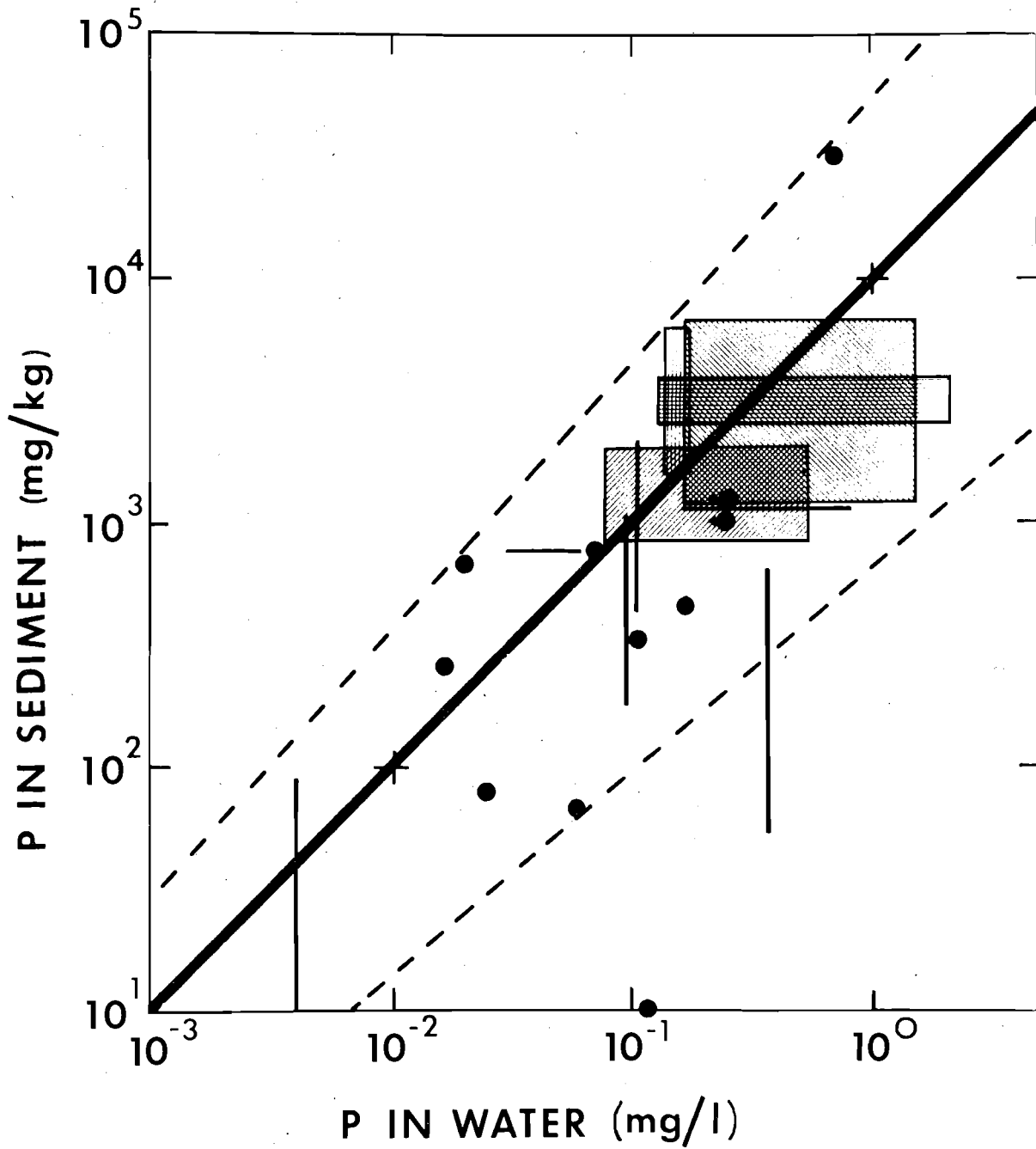


Fig. 8 Water Phosphate Concentrations Versus Sediment Phosphate Concentrations

Eutrophication Potential of One Dimensional Consolidation

Also shown in Figure 7 is the range of values within which measureable movement of phosphate due to one dimensional consolidation was first observed in the laboratory results presented previously in this report. Using the principles employed in Table 1 and using an average consolidation movement threshold value of 1500 mg/kg (1.5 mg/gm), a range of corresponding values for phosphate contents in waters is found to be .035 to 2.5 mg/l. This probable threshold range is shown on Figure 6. It may be seen that the probable threshold range for phosphate movement due to one dimensional consolidation falls within the range of both the Calumette conference maximum and the threshold for accelerated growth. It may be concluded that release of phosphates from sediments due to consolidation type loadings will most probably not occur except in aquatic systems where eutrophication is already a problem. Thus engineering operations resulting in the initiation of one dimensional consolidation processes may aggravate eutrophication where it is currently a problem, but such operations are not likely to initiate problems in areas where eutrophication is not currently a problem. In order to test the applicability of this generalization to a particular situation, it is first necessary to determine if the system is at the steady state equilibrium ratio of the order of 10,000 to 1. If this relationship holds then in all probability the generalization can be applied.

Eutrophication Potential of Dispersion

Engineering operations such as dredging which cause complete dispersal of sediments in water are a potential source of nutrients. A series of tests was performed using Lake Michigan sediments to evaluate the quantity

of phosphate released by complete dispersal. The sample locations are shown in Figure 9. The sediments were agitated for twenty four hours with distilled water. The water was then decanted from the sediment and was passed through a $.45\mu$ microporous filter. The phosphate contents of the water and of the sediment were then determined. The test results are presented in Figure 10. Linear regression analysis indicates that the ratio of total phosphate to phosphate dislodged upon shaking with distilled water is of the order of 1500 to 1. Thus the equilibrium ratio for completely dispersed soil particles releases seven times as much phosphate into the water as the overall equilibrium ratio based on Figure 8. The total quantity of phosphate released will depend upon the ratio of the volume of sediment disturbed to the volume of water through which the phosphate is distributed.

Eutrophication Potential of Diffusion

Diffusion processes can become important wherever an interface exists between soil and water. Such interfaces always exist at lake bottoms and may be created whenever large chunks of soil are released into the water.

By the reasoning previously developed based on Figure 8, it would appear that diffusion processes would not result in any net transfer of phosphate into or out of lakes where the 10,000:1 ratio exists between phosphate concentrations in sediments and waters.

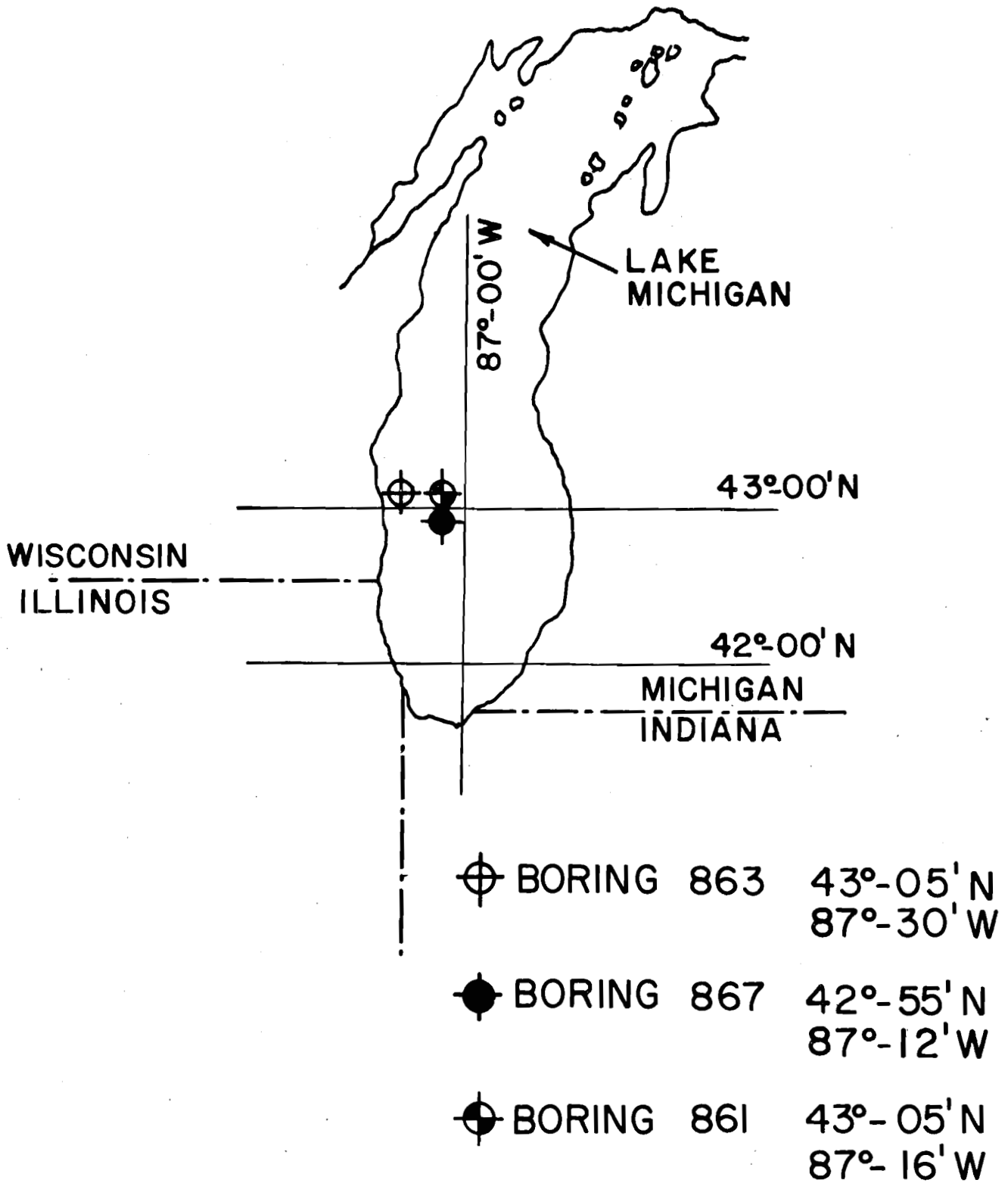


Fig. 9 Location of Lake Michigan Samples

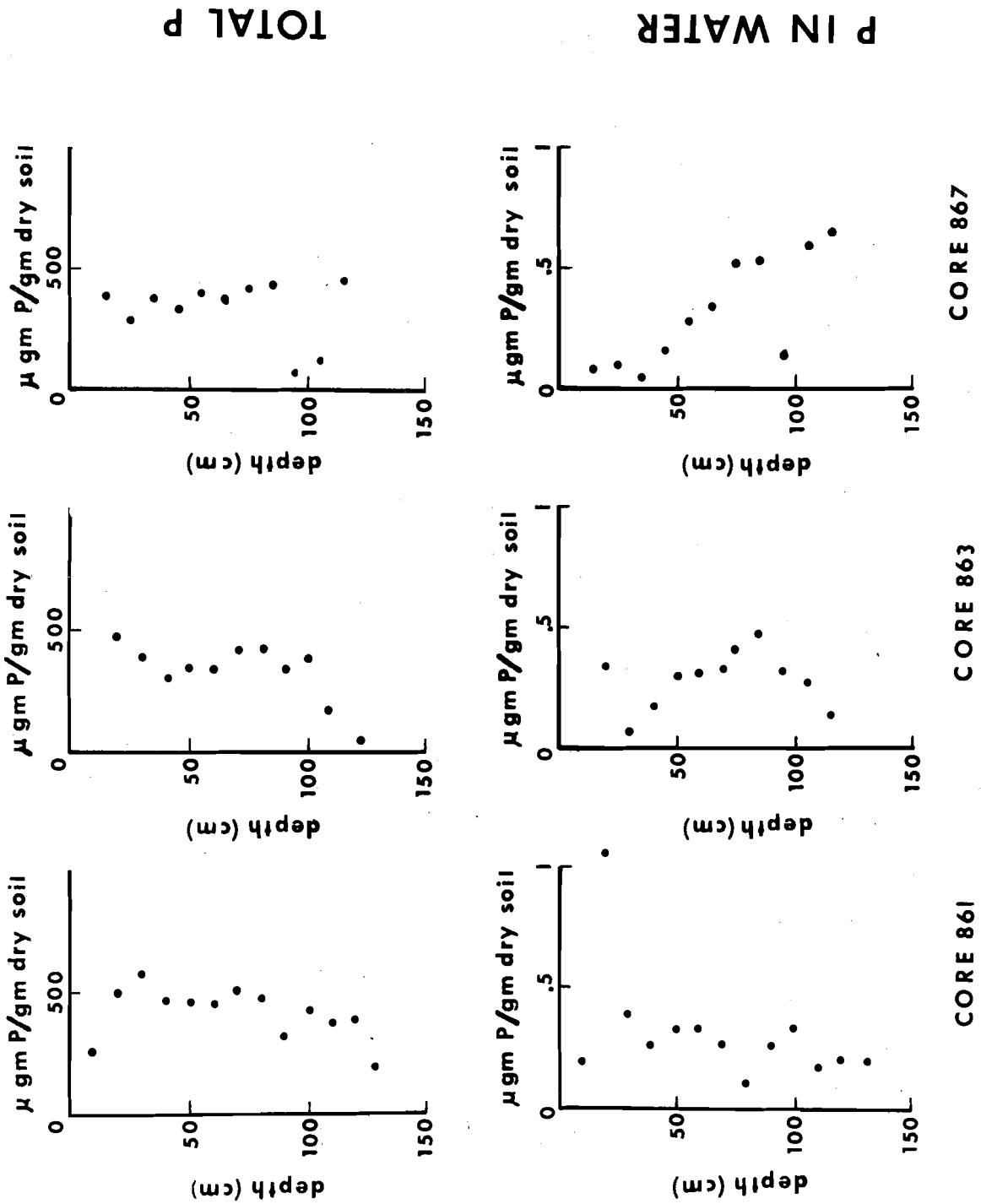


Fig. 10. Phosphate Concentrations In Lake Michigan Sediments and In Water After Thorough Mixing With Sediments

Conclusions Concerning the Role of Sediments in Eutrophication in Lakes at Equilibrium

Arguments presented in the last sections lead to the following conclusions for lakes where there exists a 10,000:1 equilibrium ratio between phosphate concentrations in sediments and in lake waters:

1. In lakes where eutrophication is currently a problem, consolidation processes may lead to aggravation of the problem.
2. In lakes where eutrophication is not a current problem, consolidation processes will not likely create problems with eutrophication.
3. In such systems at equilibrium, a) diffusion processes will not result in a net infusion of phosphates into the lake, and b) processes involving thorough mixing of sediment particles with water will result in a net transfer of phosphate to the water.

Eutrophication Potential in Systems Not at Equilibrium

In the previous sections, a basis has been developed for concluding that there is an equilibrium ratio between phosphate concentrations in sediments (mg/kg) and phosphate concentrations in lake waters (mg/l). This ratio is of the order of 10,000 parts in sediment to 1 part in water. No exchange of phosphates between sediments and water would be anticipated due to diffusion in aquatic systems where this equilibrium ratio currently exists.

However, it is possible that man-imposed action may result in an unbalance of this equilibrium situation. It is highly likely that legislation and social pressures may result in the quality of water influent to lakes becoming significantly better. Thus it is reasonable

to ask what the role of sediments would be in contaminating relatively pure water introduced into aquatic systems.

Mathematical models have been developed to represent the hypothetical situation of a body of water which, by some means, has had the phosphate removed from the water but which has not had the phosphate removed from the sediment. The sediment could then be expected to provide phosphate for recharge to the lake. The models seek to provide a relationship between time and percentage recharge. Such a relationship is important because if the recharge rate is high, then attempts to reduce the phosphate contents of lakes would be futile unless simultaneous efforts were made to reduce the phosphate contents of the sediments or to retard the recharge rate.

Three models have been developed and are presented in the Appendix. All of the models are predicated on the following assumptions:

1. The sediment has a phosphate concentration which is constant with depth. Results reported by Moore and Silver (1972) as well as the data in Figure 10 substantiate this approximation.
2. The sediment is infinitely deep. This, of course, is not true. However, the total phosphate stored in sediments is great relative to that required to recharge the lake fully. A single recharge of the lake would not significantly reduce the phosphate contained in the sediment. Thus, with respect to the behavior of the mathematical model, the sediment may be taken to be infinitely deep without loss of accuracy.
3. The sediment water interface is taken to be sharply defined with following conditions assumed.
 - a) distinct diffusion coefficients on either side of the interface
 - b) no net storage of phosphate at the interface

- c) a partition factor of 10,000:1 between concentrations on either side of the interface at all time greater than zero.
- d) equilibrium concentrations at time equal to infinity which have the same 10,000:1 partition factor.

The three models developed differ only with respect to their treatment of the lake conditions. Model 1 assumes the lake to be infinitely deep, Model 2 assumes the lake to have a finite depth, and Model 3 assumes the lake to have finite depth and to be perfectly stirred at all times.

The following parameters were used to model Lake Michigan:

k = partition factor = 1×10^4 (10,000:1)

D_1 = diffusion coefficient in sediment = 1×10^{-5} cm²/sec.

D_2 = diffusion coefficient in water = 1×10^{-3} cm²/sec.

L = lake depth = 650 cm

C_{10} = initial phosphate concentration in sediment = 3000 mg P/kg soil

The results of these computations are shown in Figure 11 as plots of average phosphate concentration as a function of time. Time zero is taken as the time when the lake is perfectly phosphate free. The plot shows average phosphate concentration computed as total phosphate crossing the sediment-water interface divided by the assumed depth of the lake.

It may be seen that the solution for an infinitely deep lake (Model 1) predicts average concentrations in excess of the equilibrium concentration of .03 mg P/l water. This, of course, results from forcing the concentration to be distributed over a depth, L . Model 2 which is based on a finite depth, L , shows the expected asymptotic approach to an average concentration of .03 mg P/l water. However, the time at which Model 1 reaches 90% of

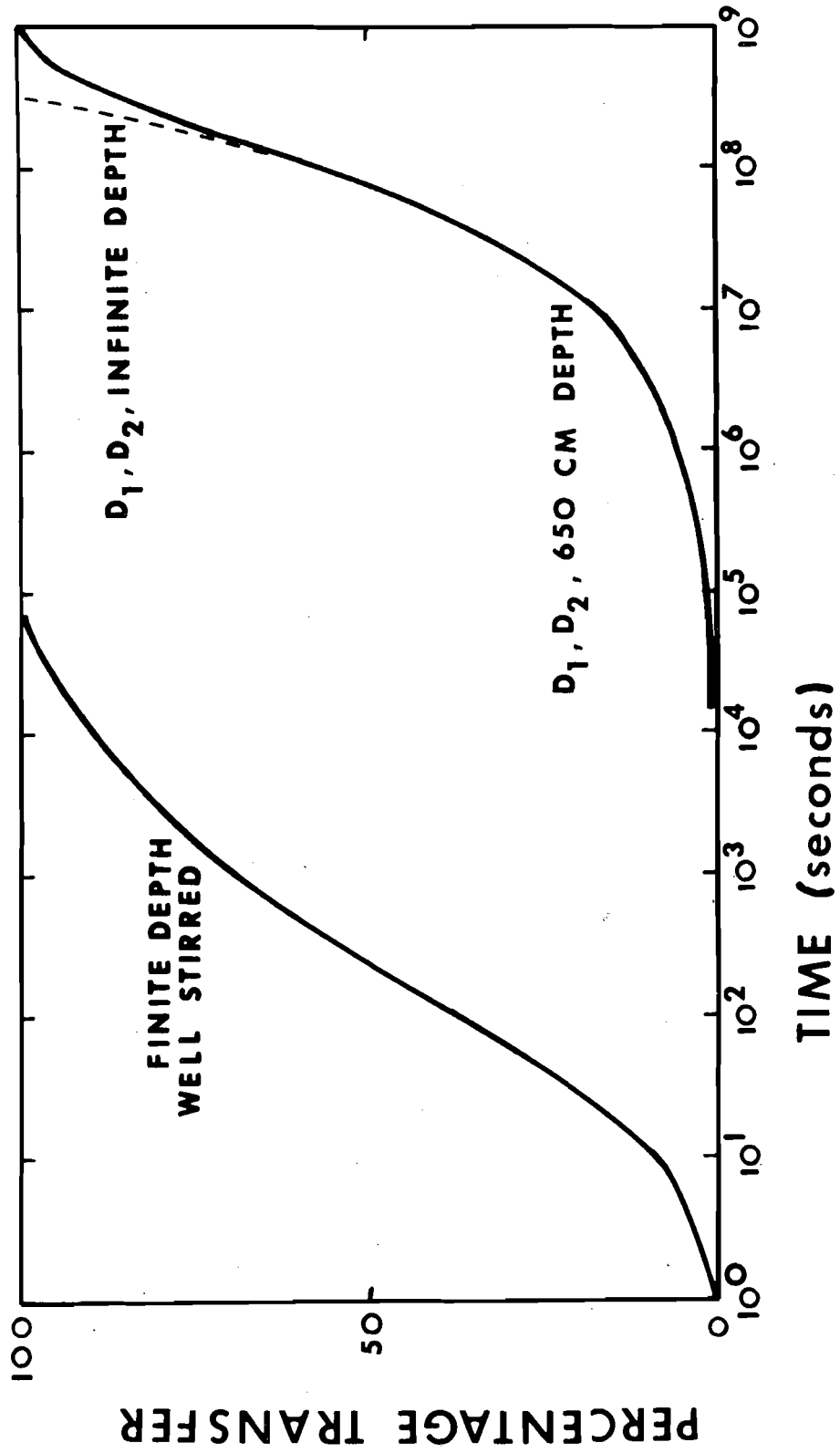


Fig. 11 Predicted Phosphate Recharge as a Function of Time
For Lake Michigan

.03 mg/l is 2.6×10^8 seconds as compared with 3.6×10^8 seconds for the finite depth model (Model 2). For times less than 1×10^8 seconds the two models give essentially the same concentrations. Thus the simpler Model 1 gives accurate predictions for early times and is relatively close when the equilibrium concentration is approached. Reference to Appendix A shows that the form of the Model 1 solution is much simpler than the Model 2 solution.

The major discrepancy occurs between the Model 3 solution and the Model 1 and Model 2 solutions. Model 3 predicts that if the lake is perfectly stirred recharge will occur at a much faster rate. The time for 90% recharge is 1.6×10^4 seconds as compared with approximately 3×10^8 seconds for Models 1 and 2. This represents the difference between 4.5 days and 10 years. In physical terms well stirred implies that the phosphate concentration is at all times kept constant throughout the lake. Well stirred conditions may, but need not, result from actual physical mixing of the water. Any of the mechanisms reported by Moore and Silver (1972) that result in transport and release of phosphate within the water can have the same effect as stirring. Had the well stirred model predicted recharge times of the order of months, the lake might be considered well stirred within this time frame. However, the lake could not be considered to be well stirred within the context of a time frame of days.

Model 3 does, however, indicate that mixing effects can be extremely important in the solution of this problem. While a more precise model within the hydrologic regime is beyond the scope of this work, it is felt that such analyses should be performed. It may be concluded, however, that recharge of initially cleaned lakes by diffusion of phosphates from sediments can be expected to be 90% complete within at most 10 years and

possibly considerably less than 10 years. Design lives for projects involving cleanup of lakes will clearly exceed this 10 year period. Thus it is essential that diffusion recharge be considered in the design of such projects.

The above models can be applied to situations other than the recharge to perfectly clean lakes by polluted sediments. Because the model is linear, the percentage recharge of partially cleaned lakes may be directly treated. Moreover, phosphate transfer from water to sediment may be predicted for cases where excessively polluted water is introduced into lakes. Figure 12 plots percentage transfer versus time for the three models. The concentration of phosphate at any time, t , is obtained by multiplying the factor obtained from Figure 12 by

$$\frac{C_{20} - C_2 \text{ equil}}{k} - (C_{10} - C_1 \text{ equil})$$

where:

C_{20} = initial concentration in the water

$C_2 \text{ equil}$ = concentration in the water at equilibrium

C_{10} = initial concentration in the sediment

$C_1 \text{ equil}$ = concentration in the sediment at equilibrium

It should be noted that the concentration values for the sediment should be in values of mg P/cm³ of sediment. Conversion may be made from concentrations in mg P/kg sediment by the following relationship for saturated soils:

$$C_o = \frac{\bar{c}_o}{\frac{1}{GS} + w}$$

AVERAGE P CONTENT IN LAKE (mg/l)

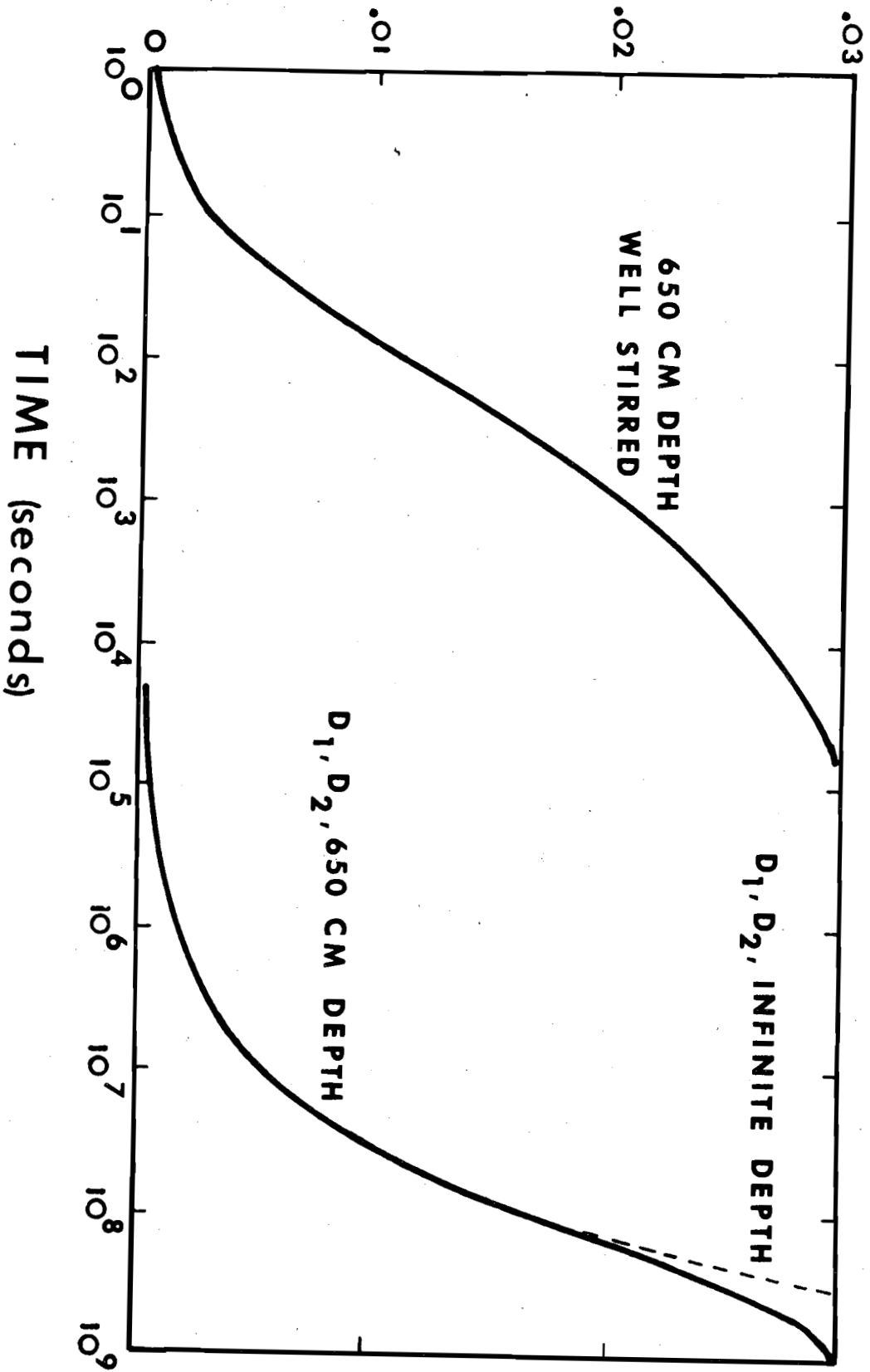


Fig. 12 Percentage Transfer Versus Time For Unbalanced Lakes

where: C_o = concentration as mg P/cm³ sediment
 \bar{C}_o = concentration as mg P/kg dry soil
 G_s = specific gravity of the soil solids
 w = water content of sediment

The solutions obtained above are not only applicable to transfer between water and underlying sediments. They may also be used to treat exchange between water and earthwork structures (dikes, dredging disposals, etc.) and between water and relatively large chunks of soil placed in the water. This last case must be approached with caution because a chunk of soil may not satisfy the mathematical requirements of an "infinitely deep" soil deposit.

Prediction of the Effects of Engineering Operations on Eutrophication

Whenever an engineering operation is undertaken in aquatic environments, a danger exists of initiating or aggravating eutrophication problems by releasing additional nutrients from soils into the aquatic environment. Conversely, the possibility also exists of removing nutrients from waters through diffusion into relatively unpolluted soils used in construction projects. The models developed above may be used to obtain quantitative estimates to a variety of problems of these types. The various types of operations may be divided into four categories.

1. Exposure of new soil surfaces. Operations that result in the exposure of new soil surfaces in the aquatic environment will result in transfer of phosphate nutrients either into or out of the water if the water and soil are not initially at equilibrium conditions. Problems of this type arise from such operations as exposure of new surfaces by

dredging, underwater excavation, underwater landslides, construction of dikes and underwater embankments. These problems may be treated by using any of Models 1, 2 or 3. The total quantity of phosphate transferred as well as the percentage of equilibrium may be computed as a function of time.

2. Dispersion dynamics. Operations that thoroughly disperse soil into discrete particles or groups of particles may result in the release of phosphate into the aquatic environment. Typical engineering operations involving dispersion are dredging, sediment redistribution by changing current patterns, and operations involving the resedimentation of soils (hydraulic filling). Only limited data are available, however the equilibrium ratio for Lake Michigan soils of 1500:1 provides a basis for estimating the approximate quantities to be released. It is suggested, however, that individual cases be treated separately. The total quantity of sediment involved must be known because the total phosphate content may be used up before the equilibrium ratio is reached.

3. Compression hydrodynamics. Loadings which result in dynamic outflow of water from soils may result in transport of ions into the aquatic environment. Such situations may arise in any operation that results in one dimensional consolidation processes. Typical examples would include any case where the soil stress is increased due to additional loading being applied. Such increased loadings would result from construction of embankments or from placing foundations for structures on the lake bottom. At present these problems can be treated semiquantitatively based on the results presented in this report.

More complicated construction problems can be treated as a combination of the three situations cited above. However, in such situations each case would need to be treated individually.

RELATIONSHIP TO WATER RESOURCES PROBLEMS

The preceding phase of this research as reported in UILO-WRC-72--0050 Research Report No. 50, the Role of Sediments in Eutrophication -- A Preliminary study by the authors provided information on the distribution of phosphates in aquatic systems and the possible mechanisms for exchange of phosphates between sediments and waters. This report has correlated the information previously reported, has presented conclusions concerning the physical aspects of exchange, and has developed mathematical models to be used in predicting both total exchange and time rate of exchange for a variety of situations.

These solutions have been developed so that they may be applied to the prediction of the environmental impact of various earthwork construction that might be undertaken in aquatic environments. While it is not possible to treat specific cases in this report, the principles developed have been presented in a manner which allows them to be relatively easily applied to any given case. The authors believe that such studies are essential if the quality of our aquatic environments are to be improved. Clearly, the role of sediments in eutrophication processes is important. Any action which

1. disturbs in place sediments,
2. results in an unbalance in concentration of phosphate between sediments and waters, or
3. results in water being forced out of sediments

may result in further pollution of lake waters. This report has outlined the potential seriousness of the contribution of phosphates from sediments and has presented analytical tools to be used in their evaluation. It is hoped that these tools may likewise be used to control problems of eutrophication.

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APPENDIX: Mathematical Models

Model 1: Diffusion into infinitely deep lake from an infinitely deep sediment.

Consider diffusion in a two phase system where in region 1 (the sediment) $x > 0$, the diffusion coefficient is D_1 , the initial concentration is C_0 and the ultimate concentration is C_1 . In region 2 (the water) $x < 0$, the diffusion coefficient is D_2 , the initial concentration is zero (i.e. a "clear" lake), and the ultimate concentration is C_2 .

The diffusion equations are:

$$\frac{\partial C_1(x,t)}{\partial t} = D_1 \frac{\partial^2 C_1(x,t)}{\partial x^2} \quad x > 0 \quad (\text{Region 1}) \quad (1)$$

$$\frac{\partial C_2(x,t)}{\partial t} = D_2 \frac{\partial^2 C_2(x,t)}{\partial x^2} \quad x < 0 \quad (\text{Region 2}) \quad (2)$$

The initial conditions are:

$$C_1(x,0) = C_0 \quad (3)$$

$$C_2(x,0) = 0 \quad (4)$$

The boundary conditions are:

$$C_1(\infty, t) = C_0 \quad (\text{finite}) \quad t < \infty \quad (5)$$

$$C_2(-\infty, t) = 0 \quad (\text{finite}) \quad t < \infty \quad (6)$$

$$C_2(0, t) = k C_1(0, t) \quad t > 0 \quad (7)$$

$$D_1 \frac{\partial C_1}{\partial x} = D_2 \frac{\partial C_2}{\partial x} \quad (\text{no storage at interface}) \quad t > 0 \quad (8)$$

The solution of this problem has been presented by Crank (1964) to be

$$C_1(x_1 t) = \frac{C_0}{1 + \frac{1}{k} (D_2/D_1)^{\frac{1}{2}}} \left[1 + \frac{1}{k} (D_2/D_1)^{\frac{1}{2}} \operatorname{erf} \frac{x}{2\sqrt{D_1 t}} \right] \quad (9)$$

The total quantity of phosphate diffusing across the $x = 0$ boundary in time t is given by:

$$M_t = \int_0^t D_1 \frac{\partial C_1}{\partial x} \Big|_{x=0} dt \quad (10)$$

$$\frac{\partial C_1}{\partial x} = \frac{C_0 \frac{1}{k} (D_2/D_1)^{\frac{1}{2}}}{\left[1 + \frac{1}{k} (D_2/D_1)^{\frac{1}{2}} \right] \sqrt{\pi D_1 t}} e^{-x^2/4D_1 t} \quad (11)$$

$$D_1 \frac{\partial C_1}{\partial x} \Big|_{x=0} = \frac{C_0 \frac{1}{k} \sqrt{D_2}}{\left[1 + \frac{1}{k} (D_2/D_1)^{\frac{1}{2}} \right] \sqrt{\pi}} \cdot \frac{1}{\sqrt{t}} \quad (12)$$

so that

$$M_t = \int_0^t \frac{C_0 \frac{1}{k} \sqrt{D_2}}{\left[1 + \frac{1}{k} (D_2/D_1)^{\frac{1}{2}} \right] \sqrt{\pi}} \cdot \frac{1}{\sqrt{t}} dt \quad (13)$$

$$M_t = \frac{2C_0 \sqrt{D_2}}{k\sqrt{\pi} \left[1 + \frac{1}{k} (D_2/D_1)^{\frac{1}{2}} \right]^{\frac{1}{2}}} \sqrt{t} \quad (14)$$

Model 2: Diffusion into a lake of finite depth, L , from an infinitely deep sediment.

Consider diffusion in a two phase system where in region 1 (the sediment) $x < 0$, the diffusion coefficient is D_1 , the initial concentration is C_0 , and the ultimate concentration is C_1 . In region 2 (the water of depth, L) $0 \leq x < L$, the diffusion coefficient is D_2 , the initial concentration is zero (i.e. a "clean" lake), and the ultimate concentration is C_2 .

The diffusion equations are:

$$\frac{\partial C_1(x,t)}{\partial t} = D_1 \frac{\partial^2 C_1(x,t)}{\partial x^2} \quad x < 0 \quad (\text{Region 1}) \quad (1)$$

$$\frac{\partial C_2(x,t)}{\partial t} = D_2 \frac{\partial^2 C_2(x,t)}{\partial x^2} \quad 0 < x \leq L \quad (\text{Region 2}) \quad (2)$$

The initial conditions are:

$$C_1(x,0) = C_0 \quad (\text{finite}) \quad (3)$$

$$C_2(x,0) = 0 \quad (4)$$

The boundary conditions are:

$$C_1(-\infty, t) = C_0 \quad (\text{finite}) \quad t < \infty \quad (5)$$

$$\frac{\partial C_2(L, t)}{\partial x} = 0 \quad (6)$$

$$C_2(0, t) = k C_1(0, t) \quad t > 0 \quad (7)$$

$$D_1 \frac{\partial C_1}{\partial x} = D_2 \frac{\partial C_2}{\partial x} \quad (\text{no storage at interface}) \quad t > 0 \quad (8)$$

Laplace transforms may be conveniently employed to solve this problem.

A transformed solution for region 2 is

$$C_2(x,p) = B \cosh \left(\sqrt{\frac{p}{D_2}} x \right) + A \sinh \left(\sqrt{\frac{p}{D_2}} x \right) \quad (9)$$

$$\frac{\partial C_2(x,p)}{\partial x} = B \sqrt{\frac{p}{D_2}} \sinh \left(\sqrt{\frac{p}{D_2}} x \right) + A \sqrt{\frac{p}{D_2}} \cosh \left(\sqrt{\frac{p}{D_2}} x \right) \quad (10)$$

Putting Eq. (10) into Eq. (6) gives

$$A = - B \tanh \left(\sqrt{\frac{p}{D_2}} L \right). \quad (11)$$

Putting Eq. (11) into (6) gives

$$C_2(x,p) = B \cosh \left(\sqrt{\frac{p}{D_2}} x \right) - B \tanh \left(\sqrt{\frac{p}{D_2}} L \right) \sinh \left(\sqrt{\frac{p}{D_2}} x \right). \quad (12)$$

Expressing the hyperbolic terms as exponentials and simplifying gives

$$C_2(x,p) = B \frac{\cosh \left[\sqrt{\frac{p}{D_2}} (L-x) \right]}{\cosh \left[\sqrt{\frac{p}{D_2}} (L) \right]} \quad (13)$$

A transformed solution in region 1 is

$$C_1(x_1,p) = E e^{\sqrt{\frac{p}{D_1}} x} + F e^{-\sqrt{\frac{p}{D_1}} x} + C_0/p \quad (14)$$

$$\frac{\partial C_1(x_1,p)}{\partial x} = \sqrt{\frac{p}{D_1}} E e^{\sqrt{\frac{p}{D_1}} x} - \sqrt{\frac{p}{D_1}} F e^{-\sqrt{\frac{p}{D_1}} x} \quad (15)$$

Boundary condition (5) implies $F = 0$ therefore

$$C_1(x,p) = Ee^{\sqrt{\frac{p}{D_1}} x} + C_0/p \quad (16)$$

Putting (16) and (13) into (8) gives

$$E = -B \sqrt{\frac{D_2}{D_1}} \tanh \left(\sqrt{\frac{p}{D_2}} L \right) \quad (17)$$

Putting (16) and (13) into (7) gives

$$E + \frac{C_0}{p} = kB \quad (18)$$

Solving (17) and (18) simultaneously gives

$$B = \frac{C_0/p}{k + \sqrt{\frac{D_2}{D_1}} \tanh \left(\sqrt{\frac{p}{D_2}} L \right)} \quad (19)$$

$$E = -\frac{C_0}{p} \left[\frac{\frac{D_2}{D_1} \tanh \left(\sqrt{\frac{p}{D_2}} L \right)}{k + \sqrt{\frac{D_2}{D_1}} \tanh \left(\sqrt{\frac{p}{D_2}} L \right)} \right] \quad (20)$$

Putting (19) and (11) into (9) gives

$$C_2(x,p) = \frac{C_0}{p} \left[\frac{1}{k + \sqrt{\frac{D_2}{D_1}} \tanh \left(\sqrt{\frac{p}{D_2}} L \right)} \right] \frac{\cosh \left[\sqrt{\frac{p}{D_2}} (L-x) \right]}{\cosh \left[\sqrt{\frac{p}{D_2}} L \right]} \quad (21)$$

The inverse transform of (21) may be obtained as follows:

Expanding (21) as exponentials and expressing as an infinite series gives

$$C_2(x,p) = \frac{C_0}{k} \sum \frac{(-[1 - \sqrt{\frac{D_2}{D_1}} \frac{1}{k}])^n}{(1 + \sqrt{\frac{D_2}{D_1}} \frac{1}{k})^{n+1}} \left[\frac{e^{-(2nL+x)\sqrt{\frac{p}{D_2}}} + e^{-[2(n+1)L-x]\sqrt{\frac{p}{D_2}}}}{p} \right] \quad (22)$$

Eq. (22) can be inverted from tables as

$$C_2(x,t) = \frac{C_0}{k} \sum \frac{(-[1 - \sqrt{\frac{D_2}{D_1}} \frac{1}{k}])^n}{(1 + \sqrt{\frac{D_2}{D_1}} \frac{1}{k})^{n+1}} \left[\operatorname{erfc} \left(\frac{2nL+x}{2\sqrt{D_2 t}} \right) + \operatorname{erfc} \left(\frac{2(n+1)L-x}{2\sqrt{D_2 t}} \right) \right] \quad (23)$$

The total quantity of phosphate diffusing across the boundary $x = 0$ is most easily obtained as

$$M_t = \int_0^L C_2(x,t) dx \quad (24)$$

and is given by

$$M_t = \frac{C_0}{k} \sum \frac{[-(1 - \sqrt{\frac{D_2}{D_1}} \frac{1}{k})]^n}{(1 + \sqrt{\frac{D_2}{D_1}} \frac{1}{k})^{n+1}} \left[\frac{2\sqrt{D_2 t}}{\sqrt{\pi}} \exp - \left[\frac{(n+1)L}{\sqrt{D_2 t}} \right]^2 \right. \\ \left. - 2(n+1)L \operatorname{erfc} \left[\frac{(n+1)L}{\sqrt{D_2 t}} \right] - \frac{2\sqrt{D_2 t}}{\sqrt{\pi}} \exp \left[- \left[\frac{nL}{\sqrt{D_2 t}} \right]^2 \right] + 2nL \operatorname{erfc} \left[\frac{nL}{\sqrt{D_2 t}} \right] \right] \quad (25)$$

Model 3: Diffusion into a well stirred lake of finite depth, L , from an infinitely deep sediment.

Consider diffusion in a two phase system where in region 1 (the sediment) $x < 0$, the diffusion coefficient is D_1 , the initial concentration is C_0 , and the ultimate concentration is C_1 . In region 2 (the water of depth, L) $0 \leq x \leq L$, the water is always well stirred, the initial concentration is zero (i.e. a "clean" lake), and the ultimate concentration is C_2 .

The diffusion equation in region 1 is:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (1)$$

The initial condition is:

$$C(x,0) = C_0 \quad (2)$$

The boundary conditions are:

$$C(\infty,t) = C_0 \quad (\text{finite}) \quad (3)$$

The total ions content of the system is constant and the concentration in region 2 is uniform. This may be expressed mathematically by defining

$$y(x,t) = \int_x^{\infty} [C_0 - C(x',t)] dx' \quad (4)$$

as being the amount of ions leaving the system that were contained between planes at distances x and ∞ from $x = 0$. This is necessary (Wilson, 1948) to avoid non-Sturm-Liouville boundary conditions at $x = 0$. Now

$$\frac{\partial y(x,t)}{\partial t} = - \int_x^{\infty} \frac{\partial C(x',t)}{\partial t} dx' \quad (5)$$

Putting Eq. (1) into Eq. (5) gives

$$\frac{\partial y(x,t)}{\partial t} = - \int_x^{\infty} D \frac{\partial^2 C(x',t)}{\partial (x')^2} dx' \quad (6)$$

Integrating once and introducing Eq. (3) gives

$$\frac{\partial y(x,t)}{\partial t} = - D \left[0 - \frac{\partial C(x,t)}{\partial x} \right] = D \frac{\partial C(x,t)}{\partial x} \quad (7)$$

Taking derivatives of (4) with respect to x gives

$$\frac{\partial y(x,t)}{\partial x} = - C_0 + C(x,t) \quad (8)$$

$$\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{\partial C(x,t)}{\partial x} \quad (9)$$

Putting (9) into (7) gives

$$\frac{\partial y(x,t)}{\partial t} = D \frac{\partial^2 y(x,t)}{\partial x^2} \quad (10)$$

The boundary condition at $x = 0$ is introduced by considering the total ions in the system. The total ions in region 1 is given by $y(0,t)$; while the ions in the water is given by

$$C_2(x,t) = \frac{1}{k} C_1(0,t) = \frac{1}{k} \frac{\partial y}{\partial x} \Big|_{x=0} + \frac{C_0}{k} \quad (11)$$

Thus for a constant quantity of ions in the system

$$y(x,t) - \frac{L}{k} \frac{\partial y}{\partial x} = \frac{LC_0}{k} \quad (x = 0) \quad (12)$$

This boundary condition is of the Sturm-Liouville type except for the presence of the constant, $-\frac{LC_0}{k}$. Let

$$y(x,t) = -C_0 x + f(x,t) \quad (13)$$

Putting (13) into (12) gives

$$-C_0 x + f(x,t) + \frac{LC_0}{k} - \frac{L}{k} \frac{\partial f(x,t)}{\partial x} = \frac{LC_0}{k} \quad (14)$$

Thus Eq. (12) becomes

$$f(x,t) - \frac{L}{k} \frac{\partial f(x,t)}{\partial x} = 0 \quad (x = 0) \quad (15)$$

Applying initial condition (2) to Eq. (4) gives

$$y(x,0) = 0 \quad (16)$$

Putting (16) into (13) gives

$$f(x,0) = C_0 x \quad (17)$$

Equation (10) is transformed from y to f by taking derivatives of (13)

$$\frac{\partial f(x,t)}{\partial t} = \frac{\partial y(x,t)}{\partial t} \quad (18)$$

$$\frac{\partial f(x,t)}{\partial x} = \frac{\partial y(x,t)}{\partial x} + C_0 \quad (19)$$

$$\frac{\partial^2 f(x,t)}{\partial x^2} = \frac{\partial^2 y(x,t)}{\partial x^2} \quad (20)$$

Thus (10) becomes

$$\frac{\partial f(x,t)}{\partial t} = D \frac{\partial^2 f(x,t)}{\partial x^2} \quad (21)$$

Equation (3) becomes

$$f(x,t) = C_0 x \quad \text{at} \quad x = \infty \quad (22)$$

Thus the equations to be solved are (15), (17), (22), and (21):

$$\frac{\partial f(x,t)}{\partial t} = D \frac{\partial^2 f(x,t)}{\partial x^2} \quad (21)$$

$$f(0,t) - \frac{1}{k} \frac{\partial f(0,t)}{\partial x} = 0 \quad (15)$$

$$f(x,0) = C_0 x \quad (17)$$

$$f(\infty,t) = C_0 x \quad (22)$$

Laplace transform techniques may be applied. The transform of (21) is

$$pF(x,p) = D \frac{d^2 F(x,p)}{dx^2} - F'(x,0+) \quad (23)$$

From (17)

$$F'(x,0+) = C_0 x \quad (24)$$

Putting (24) into (23) gives

$$pF(x,p) = D \frac{d^2 F(x,p)}{dx^2} - C_0 x \quad (25)$$

The transform of (15) is

$$F(x,p) - \frac{L}{k} \frac{dF(x,p)}{dx} = 0 \quad (x = 0) \quad (26)$$

A solution to (25) obeying condition (22) is

$$F = Be^{-\sqrt{\frac{p}{D}}x} + \frac{C_0 x}{p} \quad (27)$$

Differentiating (27) with respect to x gives

$$\frac{dF}{dx} = -\sqrt{\frac{p}{D}} B e^{-\sqrt{\frac{p}{D}}x} + \frac{C_0}{p} \quad (28)$$

Evaluating at $x = 0$ gives

$$\left. \frac{dF}{dx} \right|_{x=0} = -\sqrt{\frac{p}{D}} B + \frac{C_0}{p} \quad (29)$$

Putting (27) and (29) into (26) gives

$$B = \frac{\sqrt{D} C_0}{p \left(\frac{\sqrt{D}}{L} k + \sqrt{p} \right)} \quad (30)$$

Putting (30) into (27) gives

$$F(x,p) = \frac{C_0}{k} L \frac{\frac{\sqrt{D} k}{L} e^{-\frac{x}{\sqrt{D}} \sqrt{p}}}{p \left(\frac{k\sqrt{D}}{L} + \sqrt{p} \right)} + \frac{C_0 x}{p} \quad (31)$$

Inverse transforms from tables give

$$F(x,t) = \frac{C_0 L}{k} \left[-e^{\frac{k}{L} x} e^{\frac{Dk^2}{L^2} t} \operatorname{erfc} \left[\frac{k\sqrt{Dt}}{L} + \frac{x}{2\sqrt{Dt}} \right] + \operatorname{erfc} \left[\frac{x}{2\sqrt{Dt}} \right] \right] + C_0 x \quad (32)$$

From (13)

$$y(x,t) = \frac{C_0 L}{k} \left[- e^{-\frac{kx}{L}} e^{-\frac{Dk^2}{L^2} t} \operatorname{erfc} \left[\frac{k\sqrt{Dt}}{L} + \frac{x}{2\sqrt{Dt}} \right] + \operatorname{erfc} \left[\frac{x}{2\sqrt{Dt}} \right] \right] \quad (33)$$

The total quantity transferred across the boundary is then

$$M_t = y(0,t) = \frac{C_0 L}{k} \left[1 - e^{-\frac{Dk^2}{L^2} t} \operatorname{erfc} \left[\frac{k\sqrt{Dt}}{L} \right] \right] \quad (34)$$