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NUTRIENT RELEASE FROM ANAEROBIC SEDIMENTS

By Paul L. Freedman,¹ A. M. ASCE and Raymond P. Canale,² M. ASCE

INTRODUCTION

White Lake is annually plagued with excessive growths of aquatic weeds and algae (9,10,29). These problems have been attributed to high nutrient loadings from various municipal and industrial discharges (29). A sewage-diversion spray-irrigation project was implemented in the basin to divert nutrient loadings, improve water quality, and solve the regional wastewater disposal problems (7). Pomeroy, Smith, and Grant (24) have demonstrated that sediment releases can maintain nutrient concentrations in overlying waters at concentrations high enough to support significant algal growth. The existence of nutrient rich sediments and anaerobic bottom waters in White Lake suggests that sediment nutrient regeneration might prevent or delay expected improvement in the lake following nutrient diversion. This study was initiated to investigate this hypothesis. Specifically, the objectives of this study were to: (1) Quantify the magnitude of the anaerobic sediment nutrient release; (2) evaluate this release with respect to its effects on lake chemistry; and (3) examine alternative techniques for calculating sediment nutrient flux rates.

The importance of lake sediments in controlling nutrient concentrations in overlying waters has long been a subject of concern. Mortimer (20,21) concluded from his studies on English lakes that various mechanisms exist (e.g., absorption and complexation) in superficial oxidized sediment layers which may prevent the transport of materials from the sediments to overlying anaerobic waters. More recently, it has been demonstrated that the disappearance of this oxidized microzone (as might occur during hypolimnetic anoxia) results in a substantial release of nutrients from the sediments (22). Harter (11) found that eutrophic lake sediments have a large capacity to temporarily absorb phosphorus and later release it. In laboratory experiments, Porcella, Kumazi, and Middlebrooks (25) also demonstrated that sediments possess a large potential for sediment

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nutrient release. Despite these studies and numerous others, there does not now exist sufficient information to quantitatively predict the magnitude of nutrient release or uptake by sediments (4,12).

It is difficult to predict nutrient regeneration because the mechanisms that govern the exchange are complex. These mechanisms involve physical, chemical, and biological processes that are not easily separated. In this study, it was decided to describe the sediment system operationally to avoid problems. Given a specific sediment environment, regardless of the mechanisms, a methodology was established to calculate sediment-water nutrient exchange. This information can be later incorporated into more mechanistically complex models that may be used to predict nutrient conditions in the sediment and overlying water.

Description of Study Area.—White Lake is located 0.4 km (0.25 miles) inland from the eastern shore of Lake Michigan connected via a narrow channel (Fig. 1). Intensive limnological monitoring and modeling efforts have been conducted to assess the response of the lake to sewage diversion and spray irrigation (10). These investigations have shown White Lake to be a highly productive

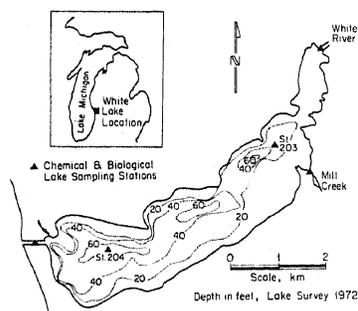


FIG. 1.—White Lake, Muskegon County, Michigan

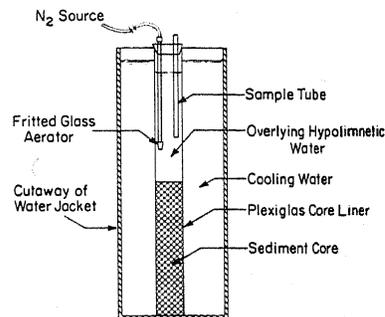


FIG. 2.—Laboratory Apparatus Designed for Column Nutrient Release Studies

system. Chlorophyll *a* concentrations often exceed 40 $\mu\text{g}/\text{l}$ and peak summer carbon uptake rates may be 100 $\mu\text{g C}/\text{m}^3/\text{hr}$. Macrophyte growth covers approximately one-fifth of the lake, with densities as high as 150 gms/m^2 . Nutrient concentrations are excessive. Average total phosphorus concentrations are between 50 $\mu\text{g P}/\text{l}$ and 75 $\mu\text{g P}/\text{l}$, winter nitrate and ammonia concentrations can exceed 300 $\mu\text{g N}/\text{l}$ –400 $\mu\text{g N}/\text{l}$, and dissolved silicon concentrations often approach 5 $\text{mg Si}/\text{l}$. The lake is dimictic with 60 days–75 days of summer hypolimnetic anoxia.

Methods.—A three-phase study was devised to achieve the objectives of this investigation. The first task was to measure nutrient concentrations in the sediments and assess their potential for release and exchange with overlying waters. The second phase involved a laboratory study to simulate the lake bottom and measure the sediment-water nutrient flux. The third phase was an in-situ study of actual conditions of nutrient release. The results from each of these studies were evaluated collectively to develop a quantitative description of the sediment nutrient flux.

The methodology employed for sediment sampling is documented elsewhere (5,10). Briefly, sediment cores were taken with a gravity Benthos corer from four lake stations at various times during the ice-free season. This report only considers in detail the cores taken on August 8 and specifically at station 203. This location and time most closely approximates the conditions (oxygen concentrations, temperature, etc.) that existed in the laboratory and in-situ studies. Sediment cores were transported in their plexiglass core liners to an on-shore laboratory. While cooled with lake water, the sediments were extruded into a nitrogen-filled glove box. The nitrogen chamber was designed to prevent oxidation of the anaerobic sediments and insure the chemical stability of the system. The extruded sediment core was sectioned into 1-cm and 2-cm slices while in the chamber for detailed concentration profile analysis. Each slice was packed into a Mini-Ram (Creative Scientific Corp.), a small commercial piston-cylinder filtration system. The filter unit was removed from the chamber and the interstitial waters were separated from the sediment by applying mechanical pressure to the piston and forcing the waters through a 0.2- μ polycarbonate (Nucleopore) filter. The filtrate was acidified to a pH of approx 4.0 to prevent precipitation and adsorption and then frozen with dry ice. Samples were later thawed and analyzed for nutrients. All chemical analyses were performed on a Technicon Auto Analyzer II using colorimetric techniques. Phosphorus concentrations were determined using the ascorbic acid reduction technique catalyzed by antimony (23) with a persulfate digestion for total phosphorus (18). Ammonia was determined with the Berthelot reaction (28). The standard reduction of a silico-molybdc complex was used to determine the concentration of silicon. These techniques are documented in detail elsewhere (10).

The laboratory simulation phase of this study was designed to transfer the sediment-water environment from the lake to the laboratory where it could be closely monitored. A sediment core was placed in a water-cooled darkened chamber designed to maintain ambient lake temperature $\pm 2^\circ$ C. The sediment core did not extend the entire length of the liner but was covered by approx 1.5 l (43.2 cm of depth) of hypolimnetic water. The liner was sealed at the top and a fritted glass tube inserted to mid-depth in the water. A slow stream of nitrogen gas was forced into the water through this tube to facilitate mixing of the over-lying waters and insure anaerobic conditions. The flow rate was adjusted to insure complete mixing of the overlying waters yet minimize disturbance of the sediment-water interface. The apparatus is shown in Fig. 2. The overlying water was periodically sampled through a glass tube (submerged to mid-depth), and then filtered through a 0.2- μ polycarbonate filter. The samples were preserved and later analyzed for nutrients according to the methods previously outlined. An electrode was occasionally submersed in the water to monitor dissolved oxygen.

The third phase of the study involved the in-situ monitoring of the sediment-water nutrient exchange process. A plexiglass chamber as shown in Fig. 3 was placed on the lake bottom by scuba-equipped divers. The chamber isolated a portion of the sediment bottom and its overlying water. A miniature 12-volt DC bilge pump was used to circulate waters within the chamber. Circulation from the pump was adjusted with a rheostat to provide mixing but maintain an undisturbed sediment layer. A Martec II submersible oxygen electrode was

inserted into the chamber with electrode leads running to the surface. Oxygen was continually monitored. A capillary tube was inserted into the chamber through a stoppered port. This tube extended from the lake bottom to the surface. Water samples from the chamber were periodically withdrawn through this tube into a receiving syringe. Water was first drawn through the capillary tube to

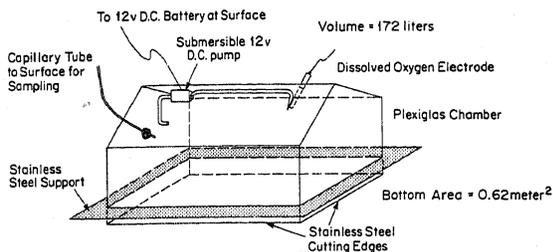


FIG. 3.—In-Situ Chamber Designed to Study Nutrient Release

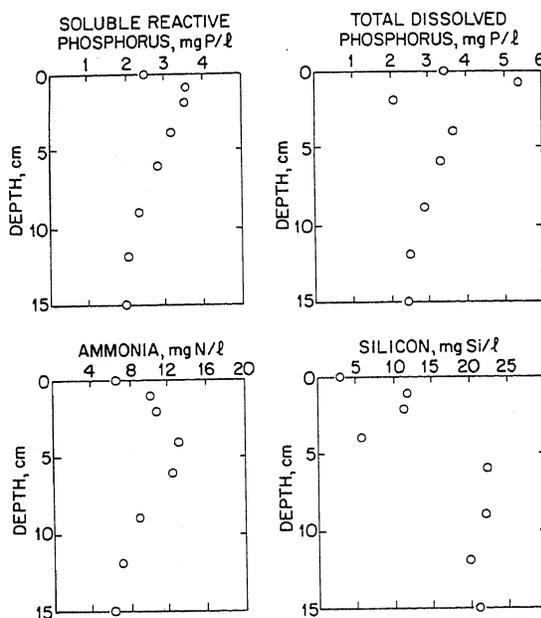


FIG. 4.—Sediment Interstitial Nutrient Concentrations Station 203, White Lake, August 8, 1974

flush its contents. Water samples were immediately filtered and stored for later nutrient analysis. No sampling was conducted during the first day to insure the establishment of anaerobic conditions in the sediments and overlying waters. Sampling then continued for 3 days until the system was disrupted by rough weather.

RESULTS

High nutrient concentrations were measured in the sediment interstitial waters (see Fig. 4). Examination of the data from the top 5 cm of sediment reveals significant concentration gradients between the sediments and the overlying waters. Estimated concentration gradients were, respectively, 6.1 mg Si/l/cm, 3.4 mg N/l/cm, 2.36 mg P/l/cm soluble reactive phosphorus, and 3.4 mg/l/cm total dissolved phosphorus. High nutrient concentrations and associated gradients were also measured in cores from other stations and dates and are documented elsewhere (5, unpublished study by the first writer).

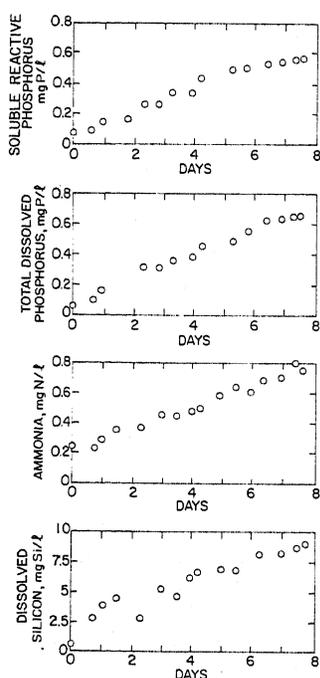


FIG. 5.—Laboratory Sediment Column Nutrient Release Study July 12–20, 1974, White Lake

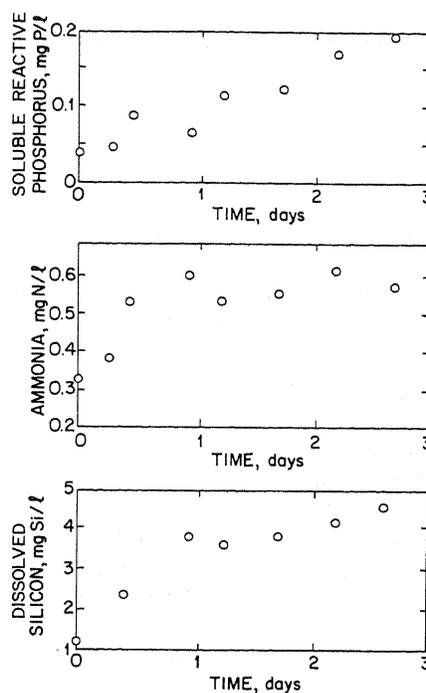


FIG. 6.—In-Situ Sediment Chamber, Nutrient Release, July 14–17, 1974, White Lake

The laboratory column experiment revealed significant nutrient flux rates from the sediments to the overlying waters. Results from this experiment are depicted graphically in Fig. 5. Throughout the 8-day period of study, the system remained anaerobic. Observed concentrations in the overlying waters increased drastically. Dissolved reactive phosphorus concentrations increased from 0.05 mg P/l–0.56 mg P/l, while total dissolved phosphorus increased from 0.05 mg P/l–0.67 mg P/l. Ammonia increased from 0.23 mg N/l–0.78 mg N/l and silicon increased from 2.2 mg Si/l–8.7 mg Si/l. Nutrient flux rates were calculated from nutrient release data and the area and volume of the experimental apparatus. The

calculations result in the following average anaerobic sediment nutrient flux rates: 27.2 mg P/m²/day of soluble reactive phosphorus; 34.3 mg P/m²/day of total dissolved phosphorus; 29.3 mg N/m²/day of ammonia; and 347 mg Si/m²/day of silicon.

The results from the in-situ chamber study revealed similarly high sediment-water nutrient flux rates. A plot of the measured water nutrient concentrations from the experiment is shown in Fig. 6. Concentrations for soluble reactive phosphorus increased from 0.013 mg P/l-0.199 mg P/l, ammonia increased from 0.33 mg N/l-0.61 mg N/l, and silicon increased from 1.1 mg Si/l-4.5 mg Si/l. Results from the total phosphorus measurements were not reliable because of sample digestion problems. Nutrient flux rates were calculated to be 19.0 mg P/m²/day for soluble reaction phosphorus, 35.1 mg N/m²/day for ammonia, and 247 mg Si/m²/day for silicon.

ANALYSIS

The results from the sediment analysis indicate a high potential for sediment nutrient release. Concentrations in the sediments were orders of magnitude larger than those of the overlying waters (Fig. 4). Examination of the factors and mechanisms creating the observed concentration profiles is presented elsewhere (5, unpublished study by the first writer). Berner (3) has suggested that transport of dissolved species from the sediment can be described by

$$J_i = -D\theta \frac{dC_i}{dz} \dots \dots \dots (1)$$

in which J_i = diffusive flux of specie i ($M/L^2/T$); D = effective diffusion coefficient (L^2/T); C_i = concentration of specie i (M/L^3); z = depth in sediment (L); and θ = porosity (dimensionless). This Fickian description of the transport, in which the flux is directly proportional to a concentration gradient, has been generally utilized by researchers attempting to model this phenomenon (13,17,19,26). However, the transport across the sediment-water interface is a result of a combination of factors including molecular diffusion, biodisturbance, physical mixing, tortuosity, etc. The diffusion coefficient used in Eq. 1 is then a effective diffusion or transport coefficient. This does not include advective transport, however, which is typically insignificant (3). Diffusion coefficients found in other studies do not necessarily have wide applicability. Often, Eq. 1 is used to describe only diffusional transport within the sediment environment, but not across the water interface.

A theoretical nutrient flux can be calculated from Eq. 1 given the nutrient concentration gradients measured in this study. Porosity values of 0.95 were measured in the upper few centimeters of White Lake sediment. The unknown required for the calculation is the diffusion coefficient. Numerous researchers have attempted to evaluate this coefficient in sediments. Estimates range widely between 3×10^{-5} cm²/s to 1×10^{-7} cm²/s (2,8,13,14,17). Many of these estimates apply to consolidated sediments (which have porosities well below 0.95) or to deep sea sediments that exist in high pressure low temperature environments. These estimates are inappropriate for White Lake because the sediments are loose and flocculent and exist at relatively low pressures and warm temperature.

Although appropriate correction factors could be made for temperature, porosity, and tortuosity, etc., these calculations would no doubt be inaccurate. Manheim (17) has measured diffusion coefficients in systems of unconsolidated sediments with varying porosities. His results are shown in Fig. 7. For unconsolidated sediments (porosity 0.80 or larger) the diffusion coefficient ranged from $1 \times 10^{-5} \text{ cm}^2/\text{s}$ to $2 \times 10^{-5} \text{ cm}^2/\text{s}$. These estimates do not include factors such as biodisturbance or physical mixing. Using a value of $1.5 \times 10^{-5} \text{ cm}^2/\text{s}$, theoretical

TABLE 1.—Summary of Nutrient Flux and Diffusion Calculations

| Nutrient (1) | Measured Flux Rates, in milligrams per square meter-day | | | Calculated flux rate, in milligrams per square meter-day (5) | Calculated Diffusion Coefficient ($\times 10^{-5} \text{ cm}^2/\text{s}$) | | |
|-----------------------------|---|------------------|-------------|--|---|------------------|-------------|
| | Column (2) | Respirometer (3) | Average (4) | | Column (6) | Respirometer (7) | Average (8) |
| Soluble reactive phosphorus | 27.2 | 19.0 | 23.1 | 29.1 | 1.41 | 0.99 | 1.20 |
| Total dissolved phosphorus | 34.3 | — | 34.3 | 41.8 | 1.23 | — | 1.23 |
| Ammonia | 29.3 | 35.1 | 32.2 | 44.3 | 1.05 | 1.26 | 1.15 |
| Silicon | 347 | 247 | 297 | 72.3 | 6.94 | 5.14 | 6.04 |

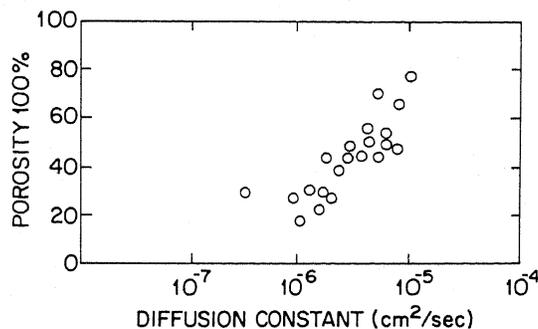


FIG. 7.—Correlation of Diffusion Coefficients with Porosity (16)

flux rates were calculated for the various nutrients based on observed concentration gradients. These calculated rates are $29.1 \text{ mg P/m}^2/\text{day}$ soluble reactive phosphorus, $41.8 \text{ mg P/m}^2/\text{day}$ total dissolved phosphorus, $44.3 \text{ mg N/m}^2/\text{day}$ ammonia and $72.3 \text{ mg Si/m}^2/\text{day}$ silicon.

The basis for the previous estimates is derived from laboratory and field measurements. These flux rates, however, are still only theoretical predictions. The laboratory and in-situ studies provide an opportunity to verify these

predictions. A comparison of the calculated nutrient release rates and the actual measured flux rates is shown in Table 1. Good agreement exists between calculated and measured diffusion rates for all nutrients except silicon. The small differences in the calculated and measured results can be explained by a lack of horizontal and temporal homogeneity in the sediment system (5, unpublished study by the first writer). Although the experiments were performed within a 2-week period and all work was performed within a 150-m radius of station 203, there may be sufficient variability in this time and spatial span to account for the discrepancies. Explanations for the disagreement in the silicon flux rates are speculative. Auer and the second writer (1) have described significant spring diatom blooms in White Lake with an associated rapid die-off. Particulate silicon will eventually settle to the sediments and decay. It is possible that the measured flux was a result of biodegradation of this material as well as sediment release from the lower sediments. It is questionable that this will occur with the other major nutrients (nitrogen and phosphorus) because of differences of concentrations, biomass, and lability. More data are required to clarify this discrepancy.

In the same manner that nutrient flux rates can be calculated from a measured concentration profile, the diffusion coefficient can be calculated given a measured flux rate and a concentration gradient. The results from these calculations are also shown in Table 1. Except for silicon, it is apparent that $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$ – $1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ is a reasonable range for the diffusion coefficient. These values are higher than most reported in the literature. The difference probably results from differences in the characteristics of the study area, such as degree of consolidation, porosity, and tortuosity, temperature, and viscosity.

Lung (15) developed short and long-term sediment models for White Lake using a diffusion coefficient considerably less than that reported herein ($2 \times 10^{-6} \text{ cm}^2/\text{s}$). This model, however, is intended to describe an average for the entire sediment profile. It describes transport in the deeper sediments as well as across the sediment-water interface.

The methodology used in this study to quantify sediment nutrient flux rates has been demonstrated to be convenient and could well be applied to other systems. There is satisfactory agreement among the three techniques employed during this study. Thus, in-situ measurements may not always be necessary if sediment coring or laboratory column experiments, or both, can be performed. In other systems in-situ measurements may be required, for example if the depth to the sediments is more than 2 atm of pressure depth. In this case, problems in laboratory experiments could arise from gas (CH_4 , H_2S , etc.) expansion and evolution or other problems associated with large changes in pressure.

Although nutrient flux rates have been calculated for White Lake, it is not a simple task to quantify the impact of the sediment release on the nutrient chemistry of the overlying waters or relate this to the response of White Lake to the wastewater diversion. Complex physical, chemical, and biologic processes govern the fate of nutrients released into the lake waters. These include circulation, biologic uptake, physical adsorption and settling, and chemical and biological conversion of the various dissolved forms of nitrogen and phosphorus. As a result, a detailed quantitative analysis of the data and calculations obtained in this study must be performed with a sophisticated multicomponent limnological model. However, approximate calculations can reveal the general significance

of this source of nutrients, ignoring complicating factors. One such calculation assumes that the lake receives a steady homogeneous release of nutrient from the sediments with no other contributing loads or kinetics. A material balance for the lake can be expressed as

$$0 = \frac{VdC_i}{dt} = J_i A - QC_i \quad \dots \dots \dots (2)$$

or more simply

$$\bar{C}_i = \frac{J_i A}{Q} \quad \dots \dots \dots (3)$$

in which V = total lake volume (L^3); \bar{C}_i = steady-state concentration of specie i in lake (M/L^3); t = time (T); J_i = flux (release) rate ($M/L^2/T$); A = area of anaerobic sediments available for release (L^2); and Q = outlet flow (L^3/T). Using average nutrient flux estimates (Table 1), an available area of 5 km² (one-half the total lake area), and an outlet flow of 15.3 m³/s, the resulting steady-state water concentrations would be 95 µg P/l soluble reactive phosphorus, 143 µg P/l total dissolved phosphorus, and 137 mg N/l ammonia. If the wastewater diversion project were to significantly reduce nutrient loads to the lake, the effects of the sediment nutrient release would be highly significant. The preceding calculated steady-state concentrations are sufficient to support excessive plant growth. Based on a phosphorus to chlorophyll a ratio of 1.5 (6), the sediment released nutrients could alone support an algal populations of 95 µg chlorophyll a /l.

An alternative approach for calculating the sediment impact on the lake chemistry would assume the hypolimnion to be an isolated system with no source or effluent flows and no nutrient loadings except for the sediments. A material balance equation for this case can be simply expressed as

$$V_H \frac{dC_i}{dt} = J_i A \quad \dots \dots \dots (4)$$

in which V_H = volume of hypolimnetic waters (L^3). Solving this equation, assuming zero initial concentrations, $C_i = J_i At / V_H$. Using this approach, sediment contributions to the hypolimnion could cause increases of 250 µg P/l soluble reactive phosphorus, 382 µg P/l total dissolved phosphorus, and 362 µg N/l ammonia in a period of 2 months.

Measurements of peak hypolimnetic summer nutrient concentrations show 120 µg P/l total dissolved phosphorus and 550 µg N/l ammonia (10). Corresponding measured epilimnetic concentrations were less for both species resulting from factors such as phytoplankton depletion. These data indicate that the previously mentioned rough calculations might be reasonable for ammonia release but would be questionable for phosphorus. However dissolved phosphorus concentrations as measured in the hypolimnetic waters were possibly low due to precipitation of iron and phosphorus in the sampling and analysis steps (10).

A comparison can be further made between the sediment nutrient flux and the tributary loads to White Lake. The average 1974 tributary nutrient loads to White Lake have been calculated to be 49.3 kg/day of total dissolved phosphorus, 80.1 kg/day of total phosphorus, 424 kg/day of nitrate plus ammonia,

and 4,564 kg/day of dissolved reactive silicon. Multiplying the average measured sediment flux rates by the available area of the lake, the sediment derived nutrient loads to White Lake are 115 kg/day for soluble reactive phosphorus, 171 kg/day for total dissolved phosphorus, 161 kg/day for ammonia, and 1,485 kg/day for silicon. Although both loading rates are of the same order of magnitude, note that anaerobic sediment release does not occur throughout the year. The anticipated phosphorus load reduction resulting from the sewage diversion project is 23% (10). Sediment nutrient release could overshadow this effect.

A noteworthy observation can be made regarding the ratios of the measured sediment nutrient releases. The calculated flux ratio of Si:N:P are approx 10:1:1. This compares with estimated ratios expected in algal biomass of 44:12:1.5 (6). The differences in the two sets of ratios can be explained in terms of two factors. First the loadings to the sediments may not be biomass dominated. More likely, there exist differences in reactivity of the nutrients within the biomass, and thus all compounds are not released simultaneously. For example, although ammonia may be released steadily from the breakdown of aminated organics, associated phosphorus would only be released during anaerobic periods. During aerobic periods phosphorus would be scavenged and stored by oxidized iron compounds.

It is recognized that the calculations herein of sediment influence on White Lake waters do not represent a distinct quantification of the process but merely a qualitative assessment, intended to place their influence in some perspective. Questions arise concerning the steady nature of the nutrient flux and its response to temporal variations in loading. The complexity of associated sediment processes prevent accurate quantification without a complete systems model. Research in this area is presented elsewhere (15,16). However, it appears that the sediments at present are contributing significant amounts of nutrients to the overlying waters. Consequently, anticipated improvements in lake water quality resulting from the land treatment project may be delayed.

SUMMARY AND CONCLUSIONS

A multiphase research program was designed to assess the significance of anaerobic sediment nutrient release in White Lake. This involved field monitoring, laboratory experiments, and in-situ measurements. Results from these studies were in general agreement for both phosphorus and nitrogen. Average sediment nutrient release rates were 25.1 mg P/m²/day soluble reactive phosphorus, 38.0 mg P/m²/day total dissolved phosphorus, and 36.2 mg N/m²/day ammonia. The associated net diffusion coefficient across the sediment-water interface was calculated to be 1.0×10^{-5} cm²/s- 1.5×10^{-5} cm²/s. Theoretical and experimental results for silicon release were not in good agreement. Speculative explanations for the discrepancy were given.

Assessment of the influence of the sediments on lake water quality improvements suggest that the sediments have the potential to contribute nutrients to the overlying waters at levels sufficient to support troublesome plant growths. As a result, any improvement in water quality resulting from the sewage diversion could be delayed.

ACKNOWLEDGMENTS

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APPENDIX II.—NOTATION

The following symbols are used in this paper:

- A = area of sediment available for release (L^2);
- C_i = concentration of species i (M/L^3);
- D = diffusion coefficient (L^2/T);
- J_i = diffusive flux of specie i ($M/L^2/T$);
- Q = river flow (L^3/T);
- t = time (T);
- V = volume of water overlying the sediment (L^3);
- V_H = volume of hypolimnion (L^3);
- z = depth (L); and
- θ = porosity (dimensionless).