

considered efficient dissolved nutrient regenerators since they produce particulate organic phosphorus, and recycle very little of either filterable form. This has been observed by Pomeroy (1973) and Johannes (1964, 1974) who have stressed that bacteria are not the only nor even the major agents of nutrient regeneration especially in nutrient deficient systems.

The production of PO_4^{3-} by the phytoplankton occurs very rapidly (< 3 min) and can be expected to occur in nutrient deficient waters. In this environment internally stored phosphate (as polyphosphate) is low, so that the PO_4^{3-} can be quickly absorbed, transferred to the metabolic organic P pools, and a small fraction then excreted or leaked as PO_4^{3-} . Such rapid leakage of recently labelled ^{14}C organic material has been observed by Saunders (1972) and Dunstall and Nalewajko (1975), and consists of both low and high molecular weight substances. Fogg (1966) found that glycolic acid was a significant fraction of the DOC excreted by 23 species of phytoplankton. Since glycolic acid is an immediate product of photosynthesis (Basam et al. 1968) (produced by the splitting of a diphosphate sugar), leakage of a small portion of the considerable pool of organic phosphorus esters within the photosynthetic cycle should not be unexpected. Indeed, Basam et al. (1968) found that accompanying leakage of ^{14}C labelled glycolic acid out of isolated chloroplasts was 3-phosphoglyceric acid, dihydroxyacetone phosphate, fructose-1,6-diphosphate (sugar phosphate), pentose monophosphates (nucleotides), and several other phosphate esters. The ratio of these (but not all) phosphate compounds in the supernatant to that in the chloroplast was greater in

some cases to that of glycolic acid. Later studies using pre-labelled intact *Chlorella pyrenoidosa* found a considerable portion of $^{32}\text{P}_i$ and bound polyphosphates in the medium after 30 minutes.

The low molecular weight compounds leaked from the chloroplasts are from the same classes of compounds occurring in algal culture filtrates. Kruse and Stegman (1968) and Phillips (1964) found orthophosphate, nucleotides or poly nucleotides, and perhaps phosphorylated carbohydrates (sugar phosphates) in sea water containing algae equilibrated with $^{32}\text{P}_i$. These are the same compounds that are hydrolyzed by extracellular phosphatases and are effectively used as sources of DIP by algae.

Since PO_4^{3-} appears within 3 min after taking up DI^{32}P_i in North Gate Lake, it is apparent that metabolic PIP is derived from the pool of particulate phosphorus not far from the photosynthetic pathway. Phase hydrolyzable material (Table 5) was in greatest concentration in the surface strata of North Gate Lake as was the low molecular weight, low C:P ratio PO_4^{3-} (Figure 10) suggesting that a portion of PIP is derived from the particulate metabolic pool (1.4%, overlapping C:P ratios) (Figure 11). In addition, a portion of the PO_4^{3-} pool was recirculable as would be predicted by the presence of an acid phase whose substrates include sugar phosphates and nucleotides (Figure 20). The activity of this enzyme was found to be greatest above the chlorocline (Figure 12), which argues for a sestonic origin and a functional role in obtaining phosphate from excreted PIP.

However, a major portion of the total P pool (Figures 7 and 10), in North Gate Lake is filterable but not nondialyzable and represents

a colloidal or a high molecular weight fraction of PUP. This form of PUP (i.e., C/P) has a high C/P ratio and increases with depth (surface 5.83 of total P; 2 m 32.22; 5 m 34.62) while metabolic D/P (lower molecular weight) decreases (surface 42.9%; 2 m 11.5% 3; 5 m 13.8%). The production of P^{32} by the plankton results in a turnover time for metabolic P^{32} of 6.5 months on the average. This in no way represents the turnover of P^{31} in North Gate Lake since tracer equilibrium was far from achieved. The data indicate that most of the P^{31} pool is refractory and does not serve as a ready source of phosphorus for the plankton in North Gate Lake. Thus, PUP in acid bog lakes cannot be included in productivity forecasts from total phosphorus. When PUP is subtracted from total phosphorus, the prediction of productivity from total phosphorus begins to match the recognized trophic status of bog lakes (Buchanan 1957, Volleweider 1968).

Phosphorus Equilibria: Comparison of ^{32}P and ^{31}P Fractions

During the summers of this study (1973-75), PUP remained undetectable in the lake. However, at tracer equilibrium 6-10% of the $DI^{32}P$ tracer [turnover time (TT) = 5-29 min] remained filterable for time periods exceeding by several fold that of the turnover times for both particulate and dissolved phosphate. This can be considered the steady-state pool of phosphate-phosphorus that is maintained by the plankton through a balancing of secretion and uptake rates. These same low levels of equilibrium ^{32}P were noticed by Hägler (1956) with 97% particulate P with 2.9-5.2% of the ^{32}P remaining filterable (TT=10 min). Lean (1973) found that usually less than 4% of the total ^{32}P added remained as filterable ^{32}P . These values agree very well and may be

representative of Canadian shield temperate soft water lakes. Ballmann and Schiller (1974) found that less than 10% of the ^{32}P added to Jordan River or Lake Kinnear water remained in a filterable form, but turnover times were much longer (TT 13 hrs and 1.80 hrs, respectively). Peters (1975) looking at central European lakes, found from 0-7% of the tracer in solution at tracer equilibrium (average TT equalled 27 min). In Lago Maggiore during 1973-74, equilibrium filterable ^{32}P averaged 44%. This was much higher than expected and Peters (1975) proposed that unlike North American lakes, a higher level of filterable phosphorus available to the algae exists in European lakes. However, stable phosphorus analyses were not performed to confirm this hypothesis.

Where direct comparison of steady-state tracer levels with stable phosphorus distributions are available (Table 8), it can be seen that in the time periods of these experiments (which in all cases were followed for time periods several fold greater than that of the dissolved phosphate turnover time) tracer equilibrium levels were not established at levels equal to that of the equivalent stable counterpart. Thus, the ratios of the representative radiophosphate fractions (e.g., PUP, P/P) are not equivalent to the same stable fractions (Table 8). The fraction which was out of phase to the greatest extent (which caused the remaining calculated disequilibrium) is the same in all cases, the filterable fraction.

An average of 30% of the total stable phosphorus in Canadian shield lakes is filterable (Hägler 1966), but less than 10% of the ^{32}P at equilibrium is filterable. Thus, it appears that like North Gate Lake and seawater, a considerable portion of filterable phosphorus is not being cycled as rapidly as $DI^{32}P$ and the equilibrium level of

Table 9. The fractional distribution and the ratios of stable (^{31}P) and radioactive (^{32}P) phosphorus at tracer equilibrium in marine and freshwater systems.

Table 8.

Form	Part-P	FRP	FUP	FUP:FRP	FUP:Part-P	System	Source
$\bar{x}^{31}\text{P}$	75.8	8.9	15.3	1.71:1	0.20:1	Marine	Watt and Hayes (1963)
$\bar{x}^{32}\text{P}$	84.0	12.0	4.0	0.33:1	0.048:1		
$\bar{x}^{31}\text{P}$	64.5	5.9	28.7	4.68:1	0.44:1	Freshwater	Rigler (1964); Lean and Rigler (1974)
$\bar{x}^{32}\text{P}$	93.0	3.5	3.5	1.00:1	0.038:1		
$\bar{x}^{31}\text{P}$	45.0	6.0*	49.0	8.17:1*	1.09:1	Freshwater	Present work
$\bar{x}^{32}\text{P}$	82.5	12.0	5.0	0.44:1	0.061:1		

*Assumes a minimal detectable concentration of $3 \mu\text{g PO}_4\text{-P l}^{-1}$ since $^{31}\text{PO}_4\text{-P}$ was undetectable this ratio

the tracer is below that of the soluble total phosphorus; i.e., FIP is not turning over as quickly as orthophosphate. Thus, the pool of utilizable phosphorus is a small fraction of the filterable phosphorus pool.

If as found in central European lakes a higher level of filterable phosphorus (^{31}P) were cycling as rapidly as DI^{32}P , then the ^{32}P asymptote could be higher (Peterson 1975), which may in turn (if proven correct) indicate a lower level of FIP and a higher level of FIP in these systems. The greater the difference in the percentage of filterable ^{32}P from that compared to filterable ^{31}P , the greater the amount of non-cycling phosphorus; and the more important it becomes to determine the asymptotic values of filterable ^{32}P and ^{31}P .

In North Gate Lake (as in the other studies) FIP^{32}P levels vastly exceed the amount of FIP^{31}P (Figure 9). However, when looking at the metabolic (^{32}P) pools of phosphorus (Figure 28 and Table 8), it becomes apparent that FIP^{32}P levels are much greater than FIP^{31}P . Evidence such as this argues that stable ^{31}P distributions do not represent the metabolic cycling of phosphorus because ^{31}P fractions are dominated by refractory compounds which mask the actual cycling. Thus, the size of the chemically determined pools of phosphorus may have little relationship to their actual importance in the phosphorus cycle.

The Abiotic Formation of Colloidal Organic Phosphate

Olsen (1967) emphasized the importance of colloidal phosphorus to the understanding of phosphorus cycling. In short he felt that "significant progress in limnological phosphate research will depend

on a perfect differentiation of the liquid as distinguished from the colloidal state." Olsen (1958, 1964) emphasizes the importance of colloidal phosphorus and emphasizes the contribution of sediment clays to this fraction. Olsen (1967) suggested that adsorption to colloidal clay might account for the observations of Riegler (1966) concerning chemical (i.e., FIP analysis) over estimates of DIP. He reasoned that upon addition of small amounts of orthophosphate (e.g., DIP) adsorption would take place especially if the colloids were in an oxidized state.

Evidence exists that FIP does not equal free DIP in natural waters. In addition, it is apparent that the acid hydrolysis of FIP is not the reason for this discrepancy. However, the adsorption of phosphate to organic colloids may well account for this anomaly.

The evidence for this hypothesis is as follows. Riegler (1968), working with anion exchange resins observed that while DI^{32}P was removed efficiently (96%) by the resin, FIP (42%) was not. He noted that FIP was initially taken up by the resin like DI^{32}P , but with time it increased in the effluent along with FIP. However, DI^{32}P was still removed from solution. The explanation was that large organic molecules would react with the resin exhausting the exchange capacity at which time the organics plus attached FIP would appear in the effluent. However, DI^{32}P , it was thought, could still penetrate the pores of the resin and be removed from solution.

Koenigs and Hooper (1976) demonstrated that the organic colloids of North Gate Lake were too large to penetrate the apparent "pores" of the resin and would likely coat the outside of the resin bead. This is supported by the observations of Eliassen et al. (1965) who found that the organic colloids in the water coated the resin particles and

reduced the number of exchange sites. This presents another explanation of continued removal of DIP^{32}P by the resin. The active sites of the organic colloid may be still active which would in addition to the resin remove DIP^{32}P from the lake water as was shown with the MAD-2 resin experiments in this study.

Jones and Spencer (1963) demonstrated that ion exchange resins could not remove all the phosphate from natural sea water (31% removal) while phosphate removed from artificial sea water equaled 98%. In addition, they concluded (as did Chamberlain and Shapiro 1973; Kuenzler et al. 1963; Murphy and Riley 1962; Edwards et al. 1965 and Strickland and Solorzano 1966) that it was difficult to be confident that any increase in FRP was the result of the acid hydrolysis of organic phosphorus, so that the dissociation of inorganic complexes of phosphate should be considered as the possible cause of the effects observed (Koenings and Hooper 1976).

Westland and Bolocziar (1976) found that river water salted with DIP and extracted by ion exchange did not result in 100% recovery of the salted DIP upon elution. They attributed the losses to the brown adsorbed material that was irreversibly bound to the resin. Substances such as lignins have many polar sites capable of binding to the resin. Again Bharath and Riego (1975) suggest that colloidal phosphates that pass through a 0.45 μ membrane react with acid molybdate and are reported as DIP. However, DIP salted and non-salted river water analyzed by ion exchange resulted in only 74% recovery of FRP while distilled water standards resulted in a recovery of 97%.

Similar results were obtained by Koenings and Hooper (1976) who showed that ion exchange extraction of phosphate standards resulted in

in 99% removal, while samples containing FRP complexed to COM was removed at 82% and 67% depending on contact time of the FRP with the oxidized complex. If the potential complexing COM-iron colloid was removed by in situ dialysis, 99% of FRP was recovered as DIP. Thus, it was reasoned that COM is directly responsible for the nonrecovery of FRP as DIP, and that the FRP chemical method measures both bound and free orthophosphate. Koenings and Hooper (1976) demonstrated the actual formation of this colloidal complex through the use of both radioisotopes and stable chemistry in natural lake water.

Abiotic complexing may be responsible for the underestimation of free DIP compared to FRP measurements (Rigler 1968), but Lean and Rigler (1974) also reported that the biota may be responsible for a filterable ^{32}P component that does not react as orthophosphate. This indicates that both colloid formation through interaction of phosphate with COM and iron (DIP + FRP), and the formation of FR^{32}P may interfere with DIP^{32}P uptake kinetics. However, abiotic fixation does not occur rapidly enough to affect short-term tracer studies [the time dependent phenomenon found by Koenings and Hooper (1976) and Fried and Dean (1955)]. However, after enough time for equilibration with the lake solids (particulate and colloidal), the newly formed FR^{32}P is utilized much less rapidly than DIP^{32}P (Figure 26).

Evidence of the time dependent formation of colloidal FR^{32}P in situ is available from my tracer studies. FR^{32}P levels equalled 5-10% of total ^{32}P at tracer equilibrium after 1-2 hrs, but increase to 15-20% of total ^{32}P after 5-7 days. Colloidal FR^{32}P formation will be greater when phosphate levels are low. In such systems complexed phosphate may be a significant fraction of FRP, but in phosphate-rich systems the

Influence of colloidal-bound phosphate may be insignificant.

The significance of colloidal bound phosphate

While experimental evidence could account for the discrepancy between FRP and DIP, the more important question remains to be answered: can the biota use this complexed phosphate? In a standardized bioassay procedure Walton and Lee (1972) suggest no difference in the usage of FRP and orthophosphate by algae. However, a high level of DIP was used and this led the authors to conclude that these results might not apply to low nutrient systems. This is supported by Fried and Dean (1955) who found that the more phosphate added to an ion exchange system the less of the total present was adsorbed. Thus, at a level of FRP sufficient to saturate colloidal exchange sites, an insignificant fraction of the FRP may exist complexed to the colloid. At undersaturating levels of FRP a higher level of the phosphate may exist in a colloidal form.

When $DI^{32}P$ is added to a saturated system, it remains as $DI^{32}P$, but when $DI^{32}P$ is added to an unsaturated system, a significant fraction over time forms colloidal FRP. In a saturated system simulated by Koenigs and Hooper (1976), COM reduced the formation of bound phosphate, however, in an unsaturated system (such as in this study) colloidal reactive phosphate dominates the inorganic phosphorus fraction. This causes $FR^{32}P$ cycling to deviate from that obtained with $DI^{32}P$.

In North Gate Lake the formation of COM-iron bound phosphate increased the turnover time of the orthophosphate from 5-10 min to ~3.5 hrs, and also reduced the amount of phosphorus available to the plankton. $DI^{32}P$ at tracer equilibrium averaged close to 15% of total

^{32}P at the surface, and 2.5% at 2 m, while $FR^{32}P$ at tracer equilibrium averaged close to 65-70% of ^{32}P at both depths. Thus, while 85-97.5% of the $DI^{32}P$ was absorbed by the seston, only 30-35% of the $FR^{32}P$ was absorbed (Figure 26, Table 7). Jackson and Schindler (1975) found that less than 5% of the total ^{32}P was associated with sediment humic acid-iron associations, but they believed even at this level that this binding had considerable ecological significance. It was believed to lower the availability of phosphate to aquatic algae.

Finally, FUP formation may provide a second phosphorus component that can react with the COM-iron complex. Hesse (1973) found that phytic acid reacts with the same minerals as phosphate which reduces the action of the hydrolytic enzyme phytase. Sinks (1966) reports that organic phosphorus esters such as adenosine triphosphate and glycerophosphate (in addition to pyrophosphate) can react with calcium in the same manner as orthophosphate. Chondroitinsulphate did not produce this action, so it was concluded that polysaccharides are not responsible for this reaction. This phenomenon is reminiscent of Shapiro's (1957) results of yellow organic matter adsorbing to iron colloids, reducing iron precipitation. The importance of complex formation of metals with phosphate esters and pyrophosphate is that these potential components of the FUP pool may, like phytic acid, become less susceptible to the action of hydrolytic enzymes such as Phase. This would reduce the availability of the phosphorus in the FUP to the seston.

Abiotic complex formation in natural waters involving either

oxidized clay of COK-iron colloids, decreases the cycling rates of both inorganic and organic phosphorus. Since complex formation is a time dependent process, the results from both short term $DI^{32}P$ kinetic and $Pu^{32}P$ utilization experiments may not reflect the actual cycling of available phosphorus.

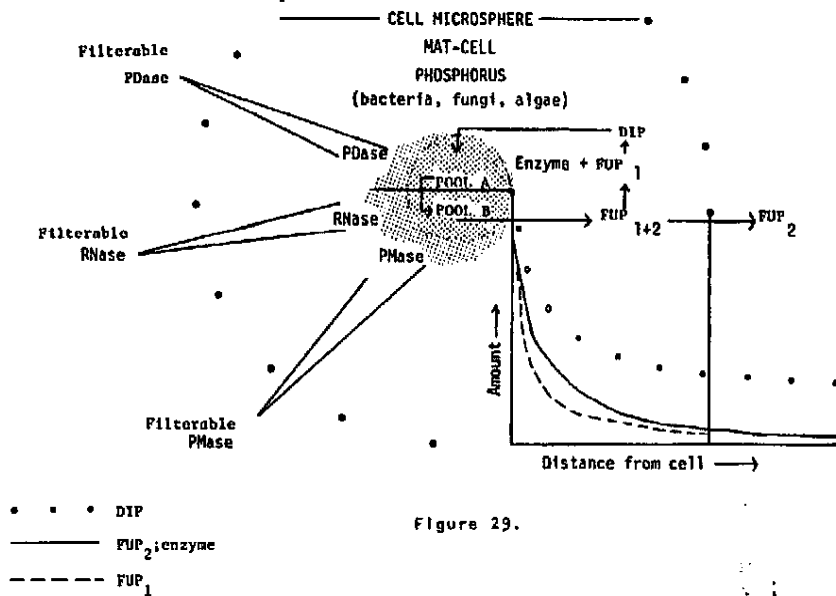
The diffusion layer gradient and its importance to phosphorus metabolism

The movement of inorganic phosphorus out of and into the seston occurs very rapidly in North Gate Lake. Two forms of phosphorus are involved in the transfer. The first is DIP which is removed from the soluble phase at rates approaching 15 min^{-1} . At the same time phosphorus is being returned to the soluble phase from the particulate pool. Thus, excretion is a very important process in maintaining adequate inorganic phosphorus in the dissolved phase. During darkness the phytoplankton absorbed phosphate to a greater extent than during the day when PFP was released (Figure 25). Apparently, the photosynthetic reactions are accompanied by a much more rapid leakage of phosphate due to a more rapid turnover of cellular phosphorus. In pelagic nutrient poor systems such a reaction may actually induce changes in detectable PFP concentrations on a diel basis (Figure 25).

The second form of phosphorus transferred from the particulate phase to the aqueous phase is PVP. The PVP pool consists of low molecular weight compounds of recent metabolic origin leaked by the plankton, and larger molecular weight compounds of colloidal size. A portion of the $Pu^{32}P$ pool can be utilized by the seston as a source of phosphorus but >75% is refractory (Figure 20). In addition, a net production of PVP was observed in the phytoplankton strata in the light but a net

Figure 29. Phosphorus metabolism within the microenvironment of a phytoplankton or bacterial cell. PVP = fallible unreactive phosphorus, Phase = Phosphomonoesterase, Phase = Phosphodiesterase, RNase = Ribonuclease, DIP = dissolved inorganic phosphate.

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reutilization occurred in the dark. Thus, the FUP pool is partially controlled by the competing metabolic reactions of production and selective utilization.

The question now becomes why do cells when faced with an already nutrient deficient intra- and extracellular status excrete or form refractory FUP? The model (Figure 29) of the microphosphorus cycle of a nutrient deficient cell is an attempt to explain the presence of two differentially utilizable pools of FUP, and the presence of particulate and soluble enzyme activity.

A cell has a micro-diffusion layer surrounding it which can determine its ability to compete for nutrients with other cells (Gulbert 1970). Schwamcher and Whitford (1963) showed that the uptake of ³²P was three times faster in the presence of a current which reduced the size of the diffusion layer. Whitford (1960) determined the thickness of this layer to be approximately 0.25 mm. The diffusion of nutrients into and out of this layer was dependent on the current speed, water temperature, and the size of the molecule. Larger organic molecules diffuse much slower than small inorganic nutrients. It is within this layer that the cell exerts its maximum effect by both extracting and excreting inorganic and organic molecules. The reactions and the concentrations of reactants and products within this microenvironment is under the control of the cell. For example, the excretion of dissolved organic carbon will increase the viscosity of this micro zone which may reduce the sinking rate of the organism. This increased viscosity will also decrease the rate of diffusion affecting the rate of exchange of nutrients, metabolites and other compounds between the cell and the water. This is especially valid for large organic molecules (e.g.,

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enzymes) which diffuse much slower than smaller inorganic molecules (e.g., DIP).

Halamy and Horvack (1964) found that several hydrolytic enzymes important to cellular metabolism are located in a compartment between the cell wall and the cell membrane of *E. coli* including Phase. This enzyme functioned to make available the phosphate of phosphomonoesters when the inorganic phosphate of the medium was exhausted. During such a reaction the liberated phosphate did not equilibrate with the external phosphate pool, but was selectively removed from solution. The factor limiting the uptake was the diffusion of inorganic phosphate through the compartment (i.e., diffusion layer) containing Phase.

Periplasmic enzymes and binding proteins (e.g., phosphate binding protein) used in substrate transport include over 26 macromolecules including the enzymes Diase, Release, and alkaline Phase (Heppel 1971). Hydrolytic periplasmic and truly extracellular enzymes in bacteria are considered to be analogous to the lysosomal enzymes of mammalian cells, but instead of an internal location are compartmentalized on the cell's outer membrane and in the micro-diffusion layer.

These same enzymes are known to be extracellular in algal cells as well (e.g., Kuenzler 1970, Aronson 1971, Kuenzler and Perras 1965, Berman 1970), and have been found in solution in the open water and interstitial water of the *Sphagnum* mat in North Gate Lake. Acid Phase (a matter enzyme for the location of mammalian lysosomes) was found by Leo and Knutson (1973) in *Chlamydomonas reinhardtii* to be attached to both sides of the cell's outer membrane. It is this enzyme along with alkaline Phase that increases in activity in algae during nutrient deficient conditions. One would expect the lake water to dilute the

extracellular enzyme concentration, and the enzyme products to the point where they would be useless, e.g., far below the K_m of the enzyme. Such is the case for the acid Phase in North Gate Lake where the K_m is from 23 to 140 μM PTPP or a maximum of 2.2 mg l^{-1} of organic $\text{PO}_4\text{-P}$. The substrate concentration in the lake is $\sim 7 \text{ ug l}^{-1}$ $\text{PO}_4\text{-P}$. However, the diffusion layer provides a mechanism for preventing enzymes, and enzyme product and/or substrate dilution by maintaining these molecules at the cell surface. Thus, the role of extracellular enzymes becomes one of digestion of intracellular organic phosphorus compounds, and the resorption (recapture) of the products (Heppel 1971), and the supply of phosphate from external sources as well as internal sources when phosphate becomes deficient in lake water.

Increased production of PTPP has generally been observed in visible cells of algae and bacteria when phosphate becomes limiting (e.g., Kuenzler 1970, Johannes 1964). This is also the time when Phase activity increases suggesting a possible correlation of purpose. That is that the hydrolytic enzyme may be acting on excreted PTPP. A functional relationship has been established between external and internal phosphorus pools and the activity of Phase in algae and bacteria (Rhee 1973, Fitzgerald and Nelson 1966, Harold 1963). The internal polyphosphate pool decreases following nutrient depletion from the medium. Once the internal as well as the external pool is reduced to a minimum value, the cell produces Phase. It stands to reason that the function of the newly produced enzyme would be to provide inorganic phosphate for the cell.

When faced with nutrient deficient conditions (carbon, nitrogen or phosphorus), *Euglena gracilis*, *Pseudomonas aeruginosa*, and *Escherichia*

could degrade a portion of the cellular protoplasm. This progressive degradation represents a mechanism for providing the cell with breakdown products for utilization in continued maintenance of basic metabolic processes (Bertini et al. 1965; Karyama and Hattizo 1965, 1966; Neter et al. 1966; and Mackelvie et al. 1968). The external diffusion barrier creates a compartment adjacent to the external surface of the plasma membrane in which the concentration of a metabolite may be different from either the intra- or extracellular pool and from which partial recapture or reutilization may occur (Rabbin and Wilson 1969).

In a similar manner algae and bacterial cells in a phosphorus deficient environment (as in North Gate Lake) may use external Phases to degrade excreted organic phosphorus esters (PUP_{1+2}) (Figure 29) and absorb the liberated inorganic phosphates. Over time a portion of the organic phosphate may be lost from the diffusion layer and appear as PUP_2 (Figure 29). PUP_2 would have to pass through the enzyme layer to become free in the water column accounting for the refractory nature of a considerable portion of the free PUP pool (Figure 20). Thus, the appearance of PUP during phosphorus deficient conditions represents a net loss from the microdiffusion layer due to either the instability of the enzymes to degrade it, or simple inefficiency. This loss over time is also a source of the considerable pool of free enzymes found in North Gate Lake.

In phosphorus poor waters, the plankton have very little phosphorus stored as polyphosphate. It is this pool of internal cell phosphorus that receives absorbed phosphate (Shee 1973). If this pool is small then the phosphorus absorbed will be rapidly transferred from it (pool A) to the organic phosphorus fraction (pool B), e.g., RNA (Figure 29). It is

from this pool that short term PUP first arises (Figure 16). Such a rapid production of PUP would not be expected to take place in nutrient sufficient waters since the absorbed phosphate (DP^{32}P) would have to equilibrate with a very large pool of stored polyphosphate before being excreted as an organic compound. Extracellular leakage of PUP may follow carbon excretion since comparative studies of extracellular production by plankton samples indicate that such release is higher in oligotrophic (phosphate poor) than in eutrophic (phosphate rich) systems (Saunders 1972).

Several other important predictions can be made from this model. For example, if you have sufficient polyphosphate phosphorus, the Phase would be expected to be considerably reduced, the uptake kinetics would be linear, and the uptake rate of DP^{32}P would follow photosynthesis. There would be a diel difference in uptake rate with a high rate in the day time falling to a minimum at night. In addition, since this would be a phosphorus sufficient system, a diel difference in PUP concentration would not be expected. In contrast, a phosphorus deficient system would have a considerable pool of active Phase, exponential uptake kinetics, and very little diel difference in uptake rates. However, the PUP might well be expected to change on a diel basis with a minimum at night.

Finally, the relative importance of the process of algal autolysis (i.e., death and decay) compared to excretion by viable cells in the production of PUP may in part be determined by the nutrient status of the system studied. In a nutrient deficient system the zooplankton graze heavily on the phytoplankton so that actual algal autolysis is

unimportant (Lean 1975). However, in a nutrient sufficient system the algae may not be as digestible by the zooplankton or may simply bloom and die. In this case the contribution of death and decay to the production of PUP may be very significant (Hilner 1975). Thus, in nutrient sufficient systems zooplankton grazing, plankton excretion are less important, whereas bacterial action and algal autolysis are more important in nutrient regeneration compared to nutrient deficient systems where the opposite holds true.

Phosphorus Flow in North Gate Lake

A preliminary model of phosphorus flow in the surface of North Gate Lake has been developed (figure 30). Of particular importance are the pool size differences representing the disequilibrium that was found to occur between ^{32}P and ^{31}P fractions. For this reason only approximate values for rates of transfer of phosphorus between compartments can be assigned. The value of the line represents the importance of the inter-compartment transfer whereas the size of the compartment is in relation to the fraction of each pool at apparent equilibrium.

The most important transfer between compartments takes place between the DI^{32}P pool and the Part- ^{32}P compartment. This rate is measured in minutes (e.g. $10\% \text{ min}^{-1}$) with a calculated turnover time of 4-9 min depending on the depth sampled. Since the internal pool of stored polyphosphate is low in these phosphate deficient waters, absorbed DI^{32}P is immediately transferred to organic linkages, and a very small portion (2-3% of total ^{32}P) is very quickly leaked back into solution as PU^{32}P (Fraction 1). A portion of this product is immediately

Figure 30. The cycling of phosphorus by the season in North Gate Lake. Circled areas are proportional to the amount of phosphorus in each fraction at tracer equilibrium. Arrows indicate the magnitude of phosphorus flow.

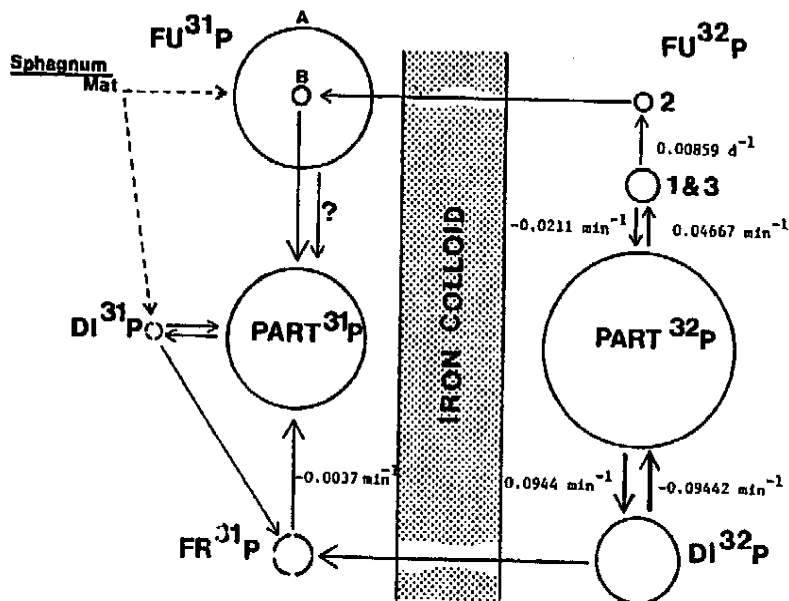


Figure 30.

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reabsorbed at a rate almost equivalent to its production. This can also be measured in minutes. However, the major source of Pu^{32}P (which is still a minor fraction of Pu^{31}P) comes from long term excretion measured in weeks with a turnover time as long as 6.5 months (fraction 2). Again a portion (10-25% depending on the depth) can be reused (fraction 3) within minutes. It is obvious that given an available organic substrate the plankton can use it as a source of phosphate just as effectively as DIP.

However, Pu^{31}P never approaches equilibrium with the larger Pu^{31}P pool (up to a 10-fold difference). Thus, cycling Pu^{31}P represents a small portion (B) of the Pu^{31}P pool. It is this minor fraction that interacts with the Part- ^{31}P compartment. The major fraction of the Pu^{31}P (A) is of colloidal size and is very refractory. Its turnover time can be measured in months, perhaps as long as one year.

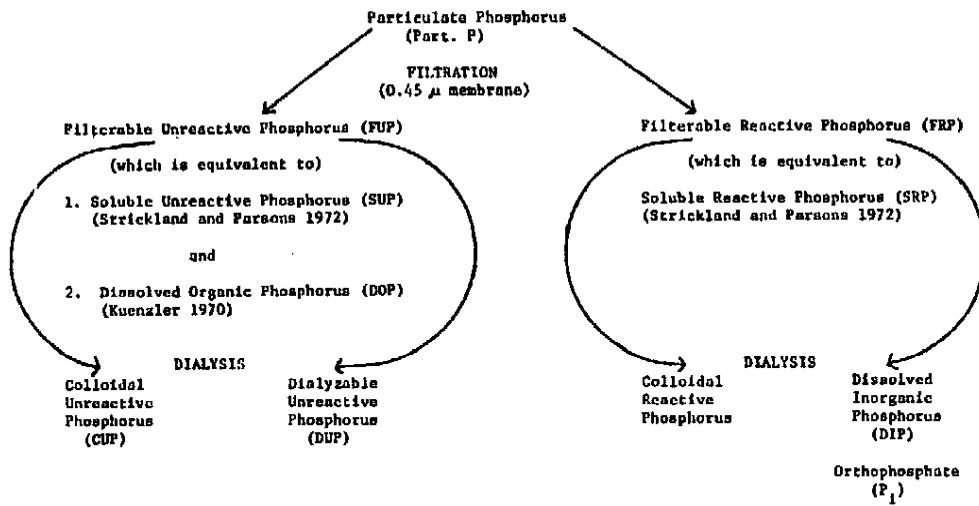
An undetectable pool of FR^{31}P was found in the euphotic zone, and any added DI^{32}P is slowly bound by a CoK-iron colloid to form FR^{32}P . There appears to be competition between the season and the colloidal fraction for orthophosphate. Through mass action, free DI^{32}P is converted to bound FR^{32}P . This bound FR^{32}P can still be used by the plankton (algae and bacteria) as a source of inorganic phosphate, but instead of a turnover time of minutes as with DI^{32}P , the turnover time increases to nearly 3.5 hrs. However, even though the FR^{32}P is not free, it is still responsive to the acid molybdate test, and is only partially available to the plankton. Up to 60% of FR^{32}P is removed by binding from the utilizable pool of orthophosphate. Thus, one-half to two thirds of the total molybdate response is not biologically available

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to the plankton within the time period of my experiments.

Since this is a nutrient deficient system which would emphasize the importance of the colloidal fraction, the actual importance of "bound" phosphate would certainly be less important in eutrophic or nutrient sufficient systems, especially those systems low in CO₂ or iron or calcium. In those systems the FRP test may well give a very reliable estimate of free DIP.

APPENDIX



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