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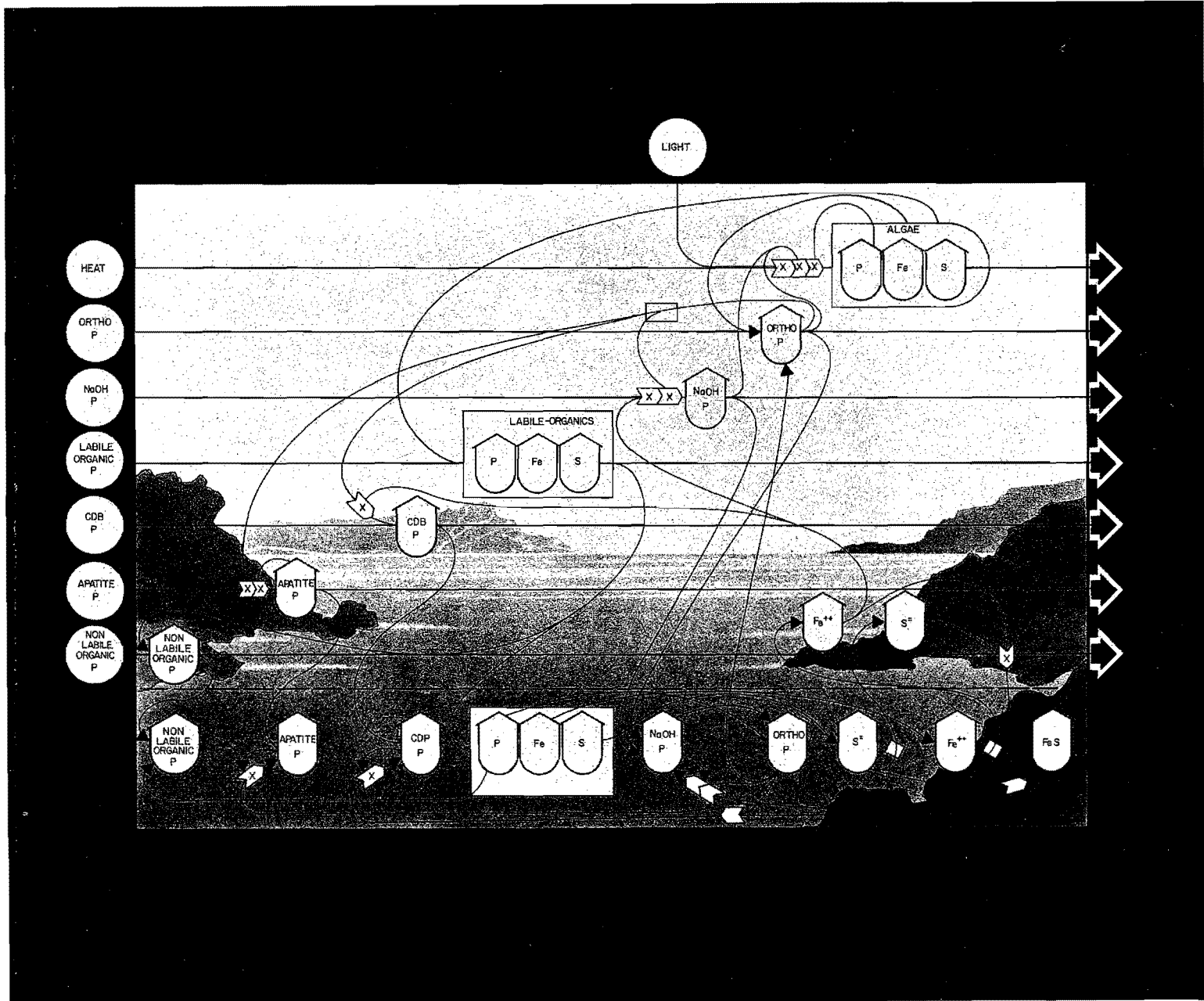
RECONNAISSANCE OF SEDIMENT-PHOSPHORUS RELATIONSHIPS IN UPPER FLAMING GORGE RESERVOIR

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EXECUTIVE SUMMARY

A reconnaissance-level study was conducted in Flaming Gorge Reservoir, Wyoming, during the late summer of 1982 in order to determine the possible importance of the sediments in exacerbating the blue-green algal blooms that occur in summer in the upper reservoir. Sediments can affect phytoplankton dynamics in reservoirs on an annual basis by delaying the availability of particulate P associated with spring runoff until late summer, when the warm water temperatures and the light climate favor the growth of blue-green algae. Over the longer term, however, sediments that historically have served as a trap for part of the annual phosphorus load entering the system may release some of this stored P in response to decreased P concentrations in the overlying water. The decreased concentrations may result from unusually wet water years or, more importantly from a management standpoint, from restoration strategies aimed at reducing inputs of P from the watershed. The resulting internal P loading can delay the anticipated recovery of a reservoir for many years, relative to the recovery rate that would be predicted in its absence. The study of lacustrine sediments is helpful in predicting the potential for internal P loading from a particular sediment, as well as the factors most important in controlling P release in situ.

Phosphorus in reservoir sediments may be associated with clays, with short-range order hydrous iron oxide gels, with apatite, or with organic matter. According to the operational definitions used in this study, $\text{NH}_4\text{Cl-P}$ is associated with clays and interstitial water; NaOH-P and CDB-P is associated with Fe gels (either on their surfaces or occluded within, respectively); HCl-P is associated with apatite; and the residual P is assumed to be associated with organic matter. Although any of these fractions may control P binding and release from a particular sediment, NaOH-P has been shown in several studies to be most closely associated with internal P loading from sediments, either through migration out of anaerobic sediments, or through contact of suspended sediments with phytoplankton in the water column. Also, paleolimnological studies have indicated that P associated with Fe complexes often can be seen to have increased in sediment profiles in conjunction with historical increases in the anthropogenic P loadings to the corresponding lakes. Similar increases have not been noted for other forms of sediment P.

Sulfur has been suggested as being important in controlling P release from such Fe-P complexes, by acting as a competing ligand for supplies of reduced iron. Sediments high in sulfide, or sulfuretums that form as a result of sulfur-rich detritus decomposing on the sediment surface, may enhance P release by keeping the concentration of reduced iron low due to equilibrium with metastable 1:1 FeS minerals. Thus the Fe:Fe-P:S ratio has important implications with regard to the release of P from such sediments.

The chemistry of the surficial 13 cm of cores taken on three dates from five locations in the reservoir demonstrated there to be a significant difference in the sediment chemistry of the two upper arms. The apparent concentrations of the various P fractions in the sediments were found to be highly dependent on the

extraction protocol used. Neither the wet extraction used routinely during this study, nor the extraction method used most frequently by previous investigators resulted in a quantitative extraction of the NaOH-P in the sediment.

The Blacks Fork arm of the reservoir, which drains an arid plateau, is characterized by low concentrations of NaOH-P, Fe, and total sulfur. Conversely, the Green River arm, which originates in the Wind River Range and is subject to more anthropogenic influences, exhibits significantly higher concentrations of all of these species. Both Fe and NaOH-P increase in a downstream direction in each arm, and the sediment below the confluence of the two arms reflects some combination of the two upper arm sediment types. Although apatite-P accounted for the majority of the P in the sediments (43 to 55 percent of the total P present) the concentrations were virtually identical at all stations. Organic P, occluded Fe-P, and NH_4Cl -exchangeable P concentrations were lower than NaOH-P or apatite P at all of the stations, and NaOH-P accounted for most of the variability in the total P content. NaOH-P concentrations in the sediments of the Blacks Fork arm were lower than the values typical of hardwater eutrophic lakes, and would be expected to release P at a much lower rate than the Green River sediments, which exhibited NaOH-P concentrations in the range expected to result in substantial rates of P release under anaerobic conditions. The CDB-Fe:NAI-P ratios in the lower arms of the reservoir and below the confluence were low (6-7), indicating some overloading of the P-binding capacity of the reactive iron in the sediment. The CDB-Fe:total S ratios were also lowest at these stations (1.8 -2.5), but were sufficiently high to ensure a stoichiometric excess of Fe to bind substantial P as vivianite under anoxic conditions.

The NaOH-P content of the sediments was found to be highly correlated with both aerobic and anaerobic release rates of P from August cores in laboratory incubations. Also, the chemistry of the water overlying the sediment cores confirmed the importance of Fe in controlling P release and the relative paucity of sulfur in the incubated sediments. The relative magnitudes of the release rates from sediments collected at the different study sites closely followed the "equilibrium" concentrations of P maintained by the anaerobic sediments. Release rates generally decreased over the course of the 44 day incubation. The rates ranged from virtually insignificant to $>25 \text{ mg P/m}^2\text{-day}$ in the lower Green River arm. Average rates for the entire incubation period ranged from 0.1 to $11.1 \text{ mg/m}^2\text{-day}$. Very crude calculations indicated that rates of $>5 \text{ mg/m}^2\text{-day}$ in the lower Green River arm, and $>1 \text{ mg/m}^2\text{-day}$ in the Blacks Fork arm, may be sufficient to exacerbate algal blooms during the late summer months in the upper reservoir. The close relationship between P release rates from sediment cores and their NaOH-P content, together with the finding that this P fraction corresponds most closely to algal available P from suspended sediments, suggests that Fe:P complexes should serve as the focus for future studies of internal P loading in the reservoir. The relative importance of recycling of algal detritus versus inputs of P originating in spring runoff or from prior yearly inputs of P to the sediments is not known at this time. A hypothesis presented in the text suggests that surficial supplies of non-occluded Fe:P complexes may be more important in supporting algal blooms than historically older P diffusing up from sediments deposited in earlier years. However, this assumption may depend to some extent on the length of the anoxic period following stratification (which was unusually short during the summer of 1982) and requires substantiation in further laboratory and field studies.

One of the objectives of the study, to determine the water column P loading by mass balance of P on the surficial sediments, was not possible due to the small

P flux relative to the large pool of reactive P stored in the sediments. There did appear to be a decrease in the NaOH-P fraction in the surface sediments during the course of the summer, but the lack of replication precluded establishing statistical significance. It is likely that a longer period of stratification, with a correspondingly greater P release, would be necessary to calculate P loadings to the water column by this method in the upper reservoir.

We emphasize that the work reported here is preliminary in nature, and that its primary purpose was to establish guidelines for future sediment-water quality studies in the upper reservoir. Emphasis thus was placed on breadth of sampling in time and space, and examination of different sampling and analytical techniques, rather than on replication. Consequently, few statistical comparisons of temporal changes versus spatial variability were possible. These results thus should best be treated as hypotheses to be tested in future studies. However, many of the patterns observed were both consistent and intuitively reasonable, based on our present knowledge of sediment biogeochemistry. We emphasize that the true importance of P release from the sediments in situ depends on the complex hydrodynamic interplay between thermal stratification in the reservoir, the density and chemistry of riverine inputs, and light climate in the water column. These considerations represent a high priority for future studies, but were beyond the scope of this investigation.

An important goal of the study was to formulate a conceptual model that could be used to effectively guide future investigations on the reservoir. Such a model is presented in the text, along with some suggestions for mathematically describing and quantifying the fluxes represented. Subsequent research should be aimed at determining which of these pathways are most important. Refinements of the mathematical equations and input data hopefully will provide a management model that could suggest the most effective ameliorative strategies for reducing the problem of nuisance algal blooms in the upper reservoir.

Suggestions for specific research topics include the following, all of which are important to the construction and calibration of the model:

1. Quantify the inputs of the various P fractions to the upper arms of the reservoir via surface inflows (e.g. NaOH-P, CDB-P).
2. Repeat the 1982 study to determine the effects of the unusual 1982 summer on sediment P, Fe, and S chemistry. Determine effects of longer periods of anoxia on NaOH-P/NAI-P, Fe/NAI-P, and Fe/S ratios.
3. Perform extractions on a long core (>1 m) to determine whether the P or Fe fractions have shown changes in recent years. Such analyses should be performed in conjunction with ^{137}Cs or ^{210}Pb dating in order to determine the annual storage of the P forms in the sediment profile.
4. Section a core according to visual appearance, and compare the core chemistry with the mineralogical characteristics.
5. Perform pore water analyses to determine saturation ratios for various mineral species and ion exchange ratios.
6. Perform P release simulations on intact sediment cores taken at two-week intervals from the reservoir to determine initial (<7 day) release rates.

This is important in order to determine the importance of recycling of labile detritus in P release rates.

7. Perform laboratory P release simulations using sediment cores of different lengths (<20 cm), in order to determine the depth of active involvement of sediment P with the overlying water column.
8. Perform further experiments on the effects of temperature and stirring rate on P release from intact cores, and relate stirring rates to sediment-water interface shear forces in situ.
9. Perform P release simulations using a flow-through incubator (chemostat) in order to determine the importance of the ortho-P concentration in the overlying water, relative to that in the interstitial water, in driving P release from anoxic sediments.
10. Perform more P release simulations with benthic invertebrates present, and determine the probable importance of benthos in enhancing P release from aerobic sediments in the reservoir.
11. Determine the spatial distribution of the various sediment types in the reservoir. A combination of sonic probes with frequent coring to establish "ground truth" will probably be necessary.
12. Determine the nature and importance of P transport across the thermocline as a function of flow and stability parameters in the arms of the upper reservoir.
13. Perform further bioassays to refine the relationship between NaOH-P and algal availability of surficial sediment P.
14. Run balanced statistical designs on the effects of extraction ratios and wet versus dry extraction on the apparent concentrations of extractable P and Fe species in the sediments.
15. Confirm, reject, or refine the hypothesis that NaOH-P forms preferentially to CDB-P in aerobic water columns through laboratory experiments with freshly prepared Fe gels and aged gels in both water and artificial sediment profiles. Confirm the relative availability of the two forms in algal assays.
16. Determine the lability of organic P with season in the water column and surficial sediments.
17. Determine the relative importance of clay minerals versus Fe hydrous oxide gels in maintaining "equilibrium concentrations" of P in contact with intact or suspended sediments.
18. Determine the importance of coprecipitation of P on calcite during algal blooms as a result of increasing pH.
19. Determine detrital delivery rates to the sediment during the spring and summer using sedimentation traps.

20. Based on literature searching and laboratory simulation, determine the kinetic rates for the various solution-solid reactions of the P model presented in the text.

All of the above recommendations are aimed at refining and providing quantitative input to the conceptual model presented in this report. We recommend that any research plan be sufficiently flexible that attention can be focused on the pathways that are shown to be important in preliminary experiments, and that less fruitful pathways receive less attention.

CHAPTER 1

INTRODUCTION

Phosphorus inputs to lakes and reservoirs from tributary streams and nonpoint sources are widely known to contribute to nuisance algal growths that degrade water quality in lakes and reservoirs. However, phosphorus inputs to the euphotic zone may also occur from within the lake itself, as a result of release from both oxic and anoxic sediments. The phosphorus may originate from inputs to the lake or reservoir during high runoff periods in the previous winter or spring, or it may represent phosphorus trapped in the sediment during previous years or decades, during which phosphorus contributions from natural or anthropogenic sources were higher than at present. Whatever its origin, phosphorus loading from sediments may exacerbate the eutrophication process and delay the recovery of eutrophic lakes following reductions in external P loading aimed at restoration. This phenomenon has been graphically likened to the "memory" of a lake for its previous trophic state: oligotrophic lakes tend to trap phosphorus in their sediments, thus remaining oligotrophic, while eutrophic lakes may mine their sediments for phosphorus during summer stratification and thus further contribute to the production of late summer and fall phytoplankton blooms.

Virtually no information is available on the extent to which internal phosphorus loading is important in Colorado River Basin reservoirs or on the factors controlling phosphorus uptake or release. Indeed, there remains considerable debate over the universal applicability of the simple paradigm outlined above. Under certain circumstances, oxic release rates of phosphorus from some sediments can be substantial, while anoxic release rates may be relatively low. Furthermore, the availability of phosphorus associated with sediments in transport in the Colorado River Basin may be greatly restricted, relative to tributaries in the East that derive much of their phosphorus load from wastewater or agricultural runoff. The goals of this study were to determine the degree to which sediments in upper Flaming Gorge Reservoir, Wyoming, might contribute to the nuisance algal blooms that occur in the reservoir, to establish a basis for providing useful management guidelines for minimizing sediment phosphorus inputs, if they could contribute significantly to the eutrophication of the reservoir, and to determine the most promising and cost-effective directions for future research.

The specific objectives of the sediment-phosphorus study were to:

1. Determine the spatial distribution of algal-available P in the surface sediments of the upper arms of the reservoir over the summer season and, if possible, to estimate the internal P loading based on the mass balance of the P lost from the sediments.
2. Define the reasons for, and possible magnitude of, P release from the sediments based on the mole ratios of iron, manganese, phosphorus, and sulfur species in the sediments, and the degree of aeration of the overlying water column.

3. Determine phosphorus release rates from intact sediment cores in the dark through laboratory incubations of cores taken from the reservoir during the period when the upper reaches of the reservoir are normally stratified and algal blooms reach nuisance proportions.
4. Relate biologically available P to total P measures based on the concordance of different extraction procedures with P availability based on the EPA Algal Assay Procedure (AAP).
5. Develop a conceptual model for P release from the sediments based on allochthonous and autochthonous detrital P inputs, chemical stoichiometry, and physical factors such as temperature and turbulence at the benthic boundary layer.

The organization of this report follows the basic outline of the objectives stated above. Wet chemical extractions were performed on cores taken from the reservoir on three dates in the late summer of 1982, for purposes of comparing the P chemistry between stations and dates. Dried sediments, extracted at a higher extractant:sediment ratio than the wet cores to insure virtually quantitative extractions of the P and metal species, were analyzed on one set of cores to determine mole ratios of relevant chemical species, and to compare the concentrations of these species with similarly analyzed cores from other lakes and reservoirs. P release studies on intact cores are described, and the release rates related to some chemical parameters in the cores, followed by a similar presentation of algal assay data. Finally, a conceptual sediment phosphorus model is presented.

We emphasize that the results reported here are preliminary, and primarily represent an attempt to delineate and prioritize research goals and objectives for future field seasons. A decision was made early in the study, based on the preliminary results, that attention would be focused on sampling many stations as often as possible, rather than emphasizing repetition in order to provide power for statistical hypothesis testing. The degree of difference noted in the various stations in the upper reservoir made this approach possible, although future work should, of course, confirm these casual observations statistically, and for more hydrologically "normal" water years, when summer anoxia is more widespread and long-lasting. Nonetheless, the hypotheses generated by the experiments reported here, as well as the observations made on problems with "standard" extraction procedures, will undoubtedly save many false starts in future field seasons, both on upper Flaming Gorge and, hopefully, on other lakes and reservoirs.

CHAPTER 2

PHOSPHORUS AND LAKE SEDIMENTS

Studies of the interactions of phosphorus in lake sediments with overlying water have generally fallen within three categories; laboratory simulations, inference based on sediment composition, and mathematical modeling based on field observations. Studies in the first category were pioneered by Einsele (1936) and Mortimer (1941, 1942), who demonstrated that the release of P by anoxic lake sediments was related to the redox cycle of iron. The use of sediment chemistry data to infer the trophic history of a lake received great impetus from the work of Mackereth (1966) in the English Lake District, who found that the history of anoxia in the hypolimnion of a lake was recorded in the ratios of iron to manganese with depth in the sediments. More recent work by the late J.D.H. Williams and his colleagues at the University of Wisconsin aimed at categorizing the forms of P in sediments using various extraction techniques, and trying to conceptually relate differences in the relative concentrations of these various fractions to historical changes in lake trophic state or to differences in trophic state between lakes. The modeling approach applied to whole-lake P budgets provides a basis for the empirical phosphorus retention coefficient (R_p) employed in various input/output models used to predict steady state P concentrations in lakes as a function of P loading, morphometry, and hydraulic residence time (e.g. Reckhow 1979). Simulation models that deal directly with the biogeochemical reactions controlling P release from lake sediments also have been applied with some success to field data (e.g. Kamp-Nielsen 1977).

Some results of these previous sediment studies will be summarized below in order to provide a context for interpreting the results of the Flaming Gorge sediment studies and to suggest directions for future research. Because the chemical analyses of the Flaming Gorge sediments are based upon the techniques developed by Williams and his colleagues, the discussion of the P chemistry of sediments will be organized around the forms of P extracted by the various reagents in their scheme. The availability of these various forms of P to algae will also be discussed, as well as the relationships thus far discovered between the quantitative presence of the various P forms and lake trophic state. A brief review of some field and laboratory P release studies will be followed by a discussion of some of the more promising mathematical modeling techniques for describing P interchange with sediments.

Sediment P Chemistry

Characterization and comparisons of the phosphorus chemistry of lake sediments historically has been based either on the chemical fractionation techniques developed by Chang and Jackson (1957) for agricultural soils, or upon inferences regarding minerals thought to be in thermodynamic equilibrium with ion concentrations found in interstitial waters (e.g. Emerson 1976). The chemical fractionation techniques are based on the ability of certain extractants to

quantitatively recover P added to soils in known chemical or mineralogical form. These fractions then could be correlated with the ability of crop species to take up that particular form of P to meet their growth requirements. The latter techniques evolved in the field of low-temperature geochemistry, in which workers were originally concerned with deep sediment systems that had been buried for a sufficiently long time to approach thermodynamic equilibrium. The extent to which equilibrium is actually reached in recent lake sediments depends to a great extent on the mineral in question (e.g. Jones and Bowser 1978).

Williams et al. (1971a,b, 1976) modified the original soil-oriented P extraction techniques in order to account for certain peculiarities of lacustrine sediments. The techniques in the fractionation scheme separate sediment P into three major groupings: non-apatite inorganic P, apatite P, and organic P. This division is operationally defined, and knowingly ignores minor amounts of P that are probably unimportant from a lake management standpoint. The various fractions and their limnological significance are described below, and detailed extraction schemes are presented in Chapter 3.

Non-apatite inorganic P. This P fraction (NAI-P) actually is comprised of two fractions from the original scheme of Williams et al. (1971a): NaOH-P, which is extractable in cold NaOH/NaCl solution during an 18 hr incubation period, and CDB-P, which is extractable with hot (85°C) citrate/bicarbonate/dithionite solution in 30 min. The former extraction is thought to include Fe-bound forms of P that are not occluded within the matrices of crystalline oxides and hydrous oxides of Fe, as well as small amounts of ortho-P dissolved in the interstitial water. The latter fraction includes P that is covered by such coatings and thus not extractable with the NaOH alone.

Statistical analysis of their data led Williams et al. (1971c) to conclude that CDB-extractable iron was highly correlated with NaOH-P and CDB-P in both calcareous and non-calcareous lake sediments. This led them to conclude that a "short-range order Fe-inorganic P complex," in which P was covalently bound to the amorphous iron oxyhydroxide, was primarily responsible for the presence of NaOH-P and CDB-P in the sediments. They also concluded that neither Mn, Al, or Ca were important in controlling the concentration of these P fractions of their study lakes. Williams et al. (1971a,b) found that the CDB-P fraction was often small compared to the NaOH-P fraction in non-calcareous sediments, but was often considerably larger than the NaOH-P fraction in the calcareous Wisconsin lakes that they studied. These fractions were combined in subsequent studies (Williams et al. 1976), and thus it is not clear whether this pattern was followed in other lake sediments.

The importance of non-apatite inorganic P in lake sediments is related to the relatively dynamic Fe cycle in lakes that develop anoxic hypolimnia. Iron is delivered to lakes in several forms, the relative predominance of which is controlled by watershed geochemistry. Highly crystalline clastic iron minerals (eg. hematite) do not affect the cycling of phosphorus in lakes to a significant extent (Stauffer 1981), while amorphous hydrous oxides of Fe which form coatings on clay minerals exhibit a great deal of reactivity. This reactivity results from their high specific surface area and is affected by the pH and the zero point of charge of the particles (Jenne 1977). Phosphorus associated with these coatings can have several origins.

Phosphorus associated with hydrous Fe oxide gels may be input directly from soils in the watershed. Lindsay (1979) indicated that amorphous Fe hydroxides are

the most common repositories of iron in soils, and McLaughlin and Syers (1978) have shown that such hydrous oxides readily remove P from crystalline phosphate minerals such as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), upon which they form a coating. Erosion of such particles could provide an allochthonous source of NAI-P to lake or reservoir sediments. Particles containing such coatings can also sorb soluble P from surrounding water. Shukla et al. (1971) found that removal of the iron associated with hydrous oxides in sediments greatly reduced or eliminated their ability to sorb orthophosphate. Reddy (1979, 1980) found that the NaOH-extractable P of suspended sediments in the Genesee River in New York increased with distance downstream, despite the absence of a concomitant changes in soluble or total P concentrations. Although this phenomenon could have resulted from input patterns alone, the results led Reddy to suggest that iron hydroxide coatings on fine suspended particles may have been controlling the concentrations of both soluble Fe (below the detection limit of 50 $\mu\text{g}/\text{l}$) and orthophosphate in the river.

Once the particles containing the short-range order Fe-P complex reach a lake or reservoir sediment, several alterations can occur. If the sediment surface is oxygenated, the complex may continue to sorb P either from the overlying water or from deeper sediment layers. Sources of P from the water column could include P mineralized from decomposing plankton populations or fecal pellets, as well as autochthonous detritus from the watershed. Sources of P from within the sediments could include the release of orthophosphate from iron complexes undergoing reduction, from mineralization of organic P, and perhaps from dissolution of apatites in the case of mildly acidic sediments receiving inputs from calcareous watersheds. The likelihood of organic P mineralization and apatite dissolution will be discussed in the sections dealing with these P forms, and the sources of Fe-associated P will be dealt with here.

Upon attaining a reduction potential of approximately 0.2 eV, Fe^{+++} is reduced to Fe^{++} , and the hydrous iron oxide gel begins to decompose (Mortimer 1941, 1942). The fate of the associated P then depends on the stoichiometry of Fe, orthophosphate, and sulfide in the interstitial water. Sulfide in lake sediments originates either from the anoxic decomposition of organic sulfur compounds, or from sulfate that is reduced by the respiratory activities of bacteria such as Desulfovibrio. If the resulting sulfide concentration exceeds a 1:1 stoichiometric ratio with Fe^{++} , the P that was released from the Fe-P complex will be free to migrate upward in the sediment column until it encounters an oxidized Fe gel. In sediments overlain by oxygenated water, this encounter will occur in the so-called oxidized microzone at the surface of the sediment, and P release to the overlying water will be minimal (e.g. Mortimer 1941, 1942). If the 0.2 eV Eh isopleth moves above the sediment surface as in an anoxic lake hypolimnion, however, P will be released to the overlying water column.

If the sulfide concentration fails to reach the 1:1 stoichiometry described above, the excess Fe^{++} will be free to form a variety of phosphate minerals including vivianite ($\text{Fe}_3(\text{PO})_2 \cdot 8\text{H}_2\text{O}$) and anapatite ($\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$). Vivianite has been found to be both present and thermodynamically stable in the sediments of Lake Greifen, Switzerland (Emerson 1976, Emerson and Widmer 1978), and in the North American Great Lakes (Nriagu and Dell 1974). Williams et al. (1980a) found that vivianite and rockbridgite, an iron hydroxyphosphate, are both represented quantitatively in the NAI-P extraction procedure. The appropriateness of the 1:1 Fe-S stoichiometry was determined by Nriagu (1968) and Doyle (1968), who found

that mackinawite (FeS) was the stable reduced Fe-S phase in most lacustrine sediments, rather than greigite (Fe₃S₄) or pyrite (FeS₂) which are more common in marine sediments. The reason for the failure of FeS to convert to the more stable 1:2 stoichiometry is apparently the absence of insufficient elemental S in lake sediments to catalyze the transformation (Emerson and Widmer 1978). Stauffer (1981) raises the point that if the source of P to the overlying water derives primarily from mineralizing detritus on the surface of the sediment, the Fe:S stoichiometric ratio may be relatively lower in at the sediment-water interface than in the bulk sediment below because of the correspondingly low Fe:S ratio in biomass. If allochthonous Fe inputs are also low, then such lakes may experience relatively heavy P loading from sediments, even under oxic conditions.

Once P is released from anoxic sediments, it may migrate toward the thermocline, where it either may be entrained into the epilimnion as a result of storms (Stauffer 1982) or spring or fall overturn. If Fe⁺⁺ is also present when the water containing the P is oxygenated, the P may be very effectively scavenged from the water by formation of a complex with the freshly precipitated hydrous iron oxide floc or gel. Such a freshly formed Fe floc may be considerably more effective at scavenging P from water than the aged gels present as coatings on soil or mineral particles described above (Lijklema 1980). These freshly formed Fe-P complexes then become another source of NAI-P to sediments. P in Fe gels formed under such conditions has been shown to be extractable immediately after formation, but as much as 10-12 percent may become resistant to NaOH extraction within 7 to 10 days (McLaughlin et al. 1977).

Apatite P. Apatite P (AI-P) is that fraction extracted in cold 0.5N HCl in 16 hr. Sources of apatite P inputs to lake sediments include detrital input of clastics eroded from the watershed and diagenetic formation within the sediment. There is also evidence that phosphate may coprecipitate on calcite in lake or river water (Otsuki and Wetzel 1974, Reddy 1979), and thus may be transferred to the sediments in this way.

There appears to be little doubt that much of the apatite-P in lake sediments is of detrital origin. Williams et al. (1976) found the apatite-P in Lake Erie to derive from erosion of the apatite-rich bluffs on the north shore of the lake. Similarly, Allan and Williams (1978) found that apatite-P concentrations decreased in sediment cores from Canadian prairie lakes in response to increasing anthropogenic P inputs as a result of dilution with other P forms. Thus, although apatite-P (or at least Ca-P forms) may result from the fertilization of agricultural land, anthropogenic activities in a watershed probably favor inputs of NAI-P over AI-P.

Williams and Mayer (1972) proposed that phosphate delivered to the surface of Great Lakes sediments would undergo diagenetic transformation to apatite at depth in the sediment, whereupon the decreased surface area of the resulting crystalline material would make it relatively resistant to subsequent dissolution. Nriagu and Dell (1974) subsequently showed that mixed iron-calcium phosphates, such as anapatite would be the stable Ca-P phases in these sediments, rather than apatite itself. Williams et al. (1980) demonstrated that all of the Ca-P minerals that they investigated (fluorapatite, chlorapatite, and dahllite, among others) were extracted quantitatively by the HCl treatment except for fish bones, that contain a significant percentage of organic P.

Although pore water thermodynamics can be a useful technique in sediment chemistry, the presence of interfering ions such as Mg^{++} or F^- at nucleation sites and the relative concentration of Ca^{++} versus $PO_4^{=}$ can render the kinetics of calcium-phosphate mineral phases extremely complex (e.g. Nancollas et al. 1979). Also, organic material can greatly hinder the kinetics of formation of such complicated crystals. Whatever their origin, however, their low bioavailability renders them a P sink, as will be described below.

Organic P. Organic P (O-P) is that fraction usually obtained by the difference between an acid digestion of a sediment and the sum of the ortho-P concentrations in the various extracts. While this fraction can contain nucleic acids and other relatively labile P forms, except for surficial sediment strata, it probably consists of a combination of relatively refractory inositol phosphates and humic and fulvic acids (Cosgrove 1977). Although a certain fraction of this pool undergoes mineralization, the rate is probably low compared to inorganic P transformations associated with Fe and the redox cycle of anoxic sediments (Kamp-Nielsen 1975). This author has determined through laboratory studies that the mineralization rate for detrital O-P is zero-order and strongly affected by temperature. One of the principal difficulties surrounding the determination of the importance of organic P in contributing to P release from sediments is the difficulty of obtaining samples of autochthonous detrital P representative of that actually reaching a lake sediment in quantities sufficient to study. Golterman (1973) reviewed some of the major arguments, and on the basis of earlier literature, concluded that algal inputs of labile P to the sediments of most deep lakes was quantitatively unimportant.

Availability of P Forms to Algae

A great deal of research has been done during the past decade on the bioavailability of various forms of P to lake phytoplankton. The principal impetus for this research was elucidating the probable effectiveness of reducing wastewater inputs of P (including banning P detergents) to the North American Great Lakes in reversing the cultural eutrophication of these water bodies. The results of these studies have been reviewed recently by Lee et al. (1980), Williams et al. (1980), and Sonzogni et al. (1982). The results of all studies performed on midwestern lake and river sediments that were allowed to come into contact with the test algae during an incubation have indicated that the P extracted by the NaOH/NaCl procedure of Williams et al. (1971a) comes closest to representing the P in sediments that is potentially available to algae.

Williams et al. (1980b) found that the amount of P taken up by Scenedesmus in a 14-day incubation corresponded almost exactly with the amount of NaOH-P added to the culture medium, in the form of lacustrine and fluvial sediments or clastics collected from erosional bluffs on the north shore of Lake Erie. NAI-P over-estimated the amount of available P by an average of 43 percent, and in no case was all of the NAI-P available. AI-P was found to be virtually unavailable to the test algae, in contrast to the findings of Smith et al. (1977). Williams et al. attributed the availability of AI-P in the Smith study to incubation times and conditions conducive to mineralizing apatite. Messer and Mok (unpublished data) have shown very close agreement between NaOH-P and algal available P as determined by the AAP procedure (Miller et al. 1978) on turbid water collected during the winter from the White River in eastern Colorado. Although other P

fractionation techniques such as NTA extraction (Golterman 1977) or weak anion exchangeable P (Cowan and Lee 1976, Sagher 1976, Huettl et al. 1979) have also been used to predict algal available P, these techniques have tended to produce over-predictions. This may result in part from the ability of chelators and ion-exchange resins to solubilize calcium associated with apatite.

Lee et al. (1980) emphasize that bioavailability studies should be interpreted in light of their intended application. For example, the availability of P in a sediment sample that must be in intimate contact with an algal cell over a 14-day incubation period for uptake to occur would be of little interest if the sediment particle were removed from the photic zone in one to two days. In the case of sediments that have already been deposited in a lake or reservoir, especially below the photic zone, the principal interest in bioavailability would be in the event that the sediment would be suspended into the overlying water column. However, given the fact that bioavailability appears to correspond to the degree of protection of P covalently bonded to amorphous iron hydroxides, it seems reasonable to expect that this P fraction would also be the most readily released when the ambient Eh dropped below the reduction potential for iron.

Relationships Between Sediment P Chemistry and Lake Trophic State

Although several earlier workers investigated the effects of lake trophic state on sediment chemistry (reviewed by Syers et al. 1973), differences in extraction schemes make many of these results difficult to compare with the studies based on the extraction scheme developed by Williams. A sense of the overall conclusions based on the work of Williams and his colleagues can be gained from Allen and Williams (1978) and Allan et al. (1980), and a critical review of the midwestern lake data by Stauffer (1981). A representative sampling of these data, along with some data collected by other workers, is summarized in Table 2.1.

Data on NaOH-P are restricted for the most part to Fe-rich lakes in Wisconsin and Minnesota, and values greater than 400 mg/kg are common. In the calcareous lakes for which NaOH-P data have been reported, even the culturally eutrophic Yahara lakes (Mendota, Monona, and Wingra) have concentrations of less than 400 mg/kg. CDB-P values are likewise higher in the non-calcareous lakes, but an important difference is seen in the relative concentrations of the NaOH-P and CDB-P fractions. In the non-calcareous lakes, CDB-P is virtually identical to NaOH-P, while in the calcareous sediments, NaOH-P usually represents less than one half of the CDB fraction. This pattern would suggest that occluded NAI-P is quantitatively unimportant in the non-calcareous lakes, but that it represents an important NAI-P pool in calcareous lake sediments. The absence of occluded P in short-range order iron complexes might result if 1) the stoichiometric Fe:P ratio was low during the formation or subsequent aging of the complex, or 2) if the formation of non-occluded P is typical of in situ formation of the complex, but not of its formation in soils in the watershed. The high Fe:P ratios in the non-calcareous lakes would tend to render the first possibility unlikely, and the second has thus far apparently not been considered by Williams' colleagues.

The CDB-Fe:CDB-P ratios in Table 2.1 were originally proposed by Williams et al. (1971c) to be an important factor in controlling the retention of P by sediments. These authors found that a wide range of sediments from Wisconsin

Table 2.1. Concentrations of various P and Fe fractions and P release rates from some lake sediment cores.

Lake	Trophic State	NaOH-P ($\mu\text{g/g}$) mg/kg	NAI-P ($\mu\text{g/g}$) mg/kg	CDB-Fe (mg/g)	Atomic Fe:P	P Release Rates ^a ₂ (mg P/m ² -day)
<u>Noncalcareous lakes</u>						
Devils (WI) ¹	O-M	906	822	12	7.8	
Little John (WI) ¹	E	414	383	18	27	0-0.9
Trout (WI) ¹	O-M	102-5,080	100-5,040	9-50	5.5-49	
Crystal (WI) ¹	O	333-604	285-497	4-5	5.6-8.7	
Plum (WI) ¹	M	167	144	2	6.5	
Little Arbor Vitae (WI) ¹	M	757	720	22	17	
Minocqua (WI) ¹	M-E	1,720	1,750	27	8.7	0.3-1.4
	O-M	5,800	6,040	22	2.1	
Tomahawk (WI) ¹	O-M	114-2,950	95-2,970	4-53	9.8-26	
Shagawa (MN) ²	E	3,350	3,810	-		6.2-10.3
Finjasjön (SWED) ³	HE	1,960	1,960			
Sodra Bergundasjön (SWED) ^{3,4}	HE	4,250	4,250		3.6	
Burley Griffen (AUS) ^{5,6}	E	200		26	3.2-4.5	
<u>Calcareous lakes</u>						
Wingra (WI) ⁷	E	47	207	17	4.5	0.9-2
Monona (WI) ⁷	E	245	621	6	5.0	
Mendota (WI) ⁷	E	380	722	8	6.4	7.2-11
Delevan (WI) ⁷	E	62-83	312-396	2-3	3.0-3.1	
Geneva (WI) ⁷	M	74	233	4	9.3	
Erie (Ont) ^{7,8}	E	202	155-424	7-13	15-25	7.4
Crooked (Sask) ⁹			690			
Round (Sask) ⁹			508			
Mission (Sask) ⁹	H		434	5	5.9	10
Katepwa (Sask) ⁹	H		301	7	9.4	10
Echo (Sask) ⁹	H		380	5	7.9	12
Pasqua (Sask) ⁹	H		308	6	11	4
Cooking (Alb) ⁹	E		247	3	6.8	
Wabamun (Alb) ⁹			218			
Winnipeg (Man) ⁹	M		209	10	28	
Okanagan (BC) ⁹			334			
Skaha (BC) ⁹			177			
Osoyoos (BC) ⁹			149			
Wood (BC) ⁹			143			
Kalamalka (BC) ⁹			130			
Fysingen (SWED) ³	O	328	328			
Vallehtunasjön (SWED) ³	E	400	400			

Table 2.1. Continued.

^aAll release rate data from Holdren and Armstrong (1980) except Shagawa (Larson et al. 1981) and Saskatchewan lakes (Allan and Williams 1978).

^bAssuming release occurs only 6 months of the year.

- ¹Williams et al. (1971a)
- ²Larson et al. (1981)
- ³Boström (1982)
- ⁴Bengtsson (1978)
- ⁵Rosich and Cullen (1980)
- ⁶Rosich and Cullen (1981)
- ⁷Williams et al. (1971b)
- ⁸Williams et al. (1976b, 1980a)
- ⁹Allan and Williams (1978)

lakes maintained an extractable Fe:P ratio of 5-10, regardless of whether or not they were calcareous. This common ratio suggested to these authors that a ratio of approximately 6 was typical of the short-range order Fe:P complex that controls the solubility of orthophosphate in oxic sediments. Stauffer (1981) concluded from a review of the work of Einsele, that such a ratio is typical of the amorphous Fe:P complex that results when P is allowed to sorb onto a fresh hydrous oxide Fe floc. It is important to note that this ratio can be much lower (1.8 or above) if orthophosphate is present along with the Fe at the time that it is oxidized (Stauffer 1981).

The extractable Fe:P ratio of another group of non-calcareous sediments studied by Williams et al. (1971c) ranged from 21 to 85. Although there was nothing unusual about the magnitude of the Fe or P concentrations in any of the corresponding sediments, Williams et al. noted that they were typically collected in shallow water, and he hypothesized that the nature or stoichiometry of the Fe-P complex may differ with grain size or oxidation state of the sediment.

Subsequent studies on Lake Erie sediments by Williams et al. (1976a,b) revealed NAI-P concentrations to be 109-424 mg/kg in the surficial sediments, with the lower concentrations occurring at the less-polluted western end of the lake. Extractable Fe:P ratios in the top 10 cm of the sediment column, calculated from data presented by Allan and Williams (1978), were higher than those in the calcareous Wisconsin lakes, with the highest ratios occurring at the midlake stations. Williams et al. (1976b) suggested that these high ratios were associated with the high P retention coefficient ($R_p=0.8$) in the lake.

Further work on Canadian prairie lakes (Allan and Williams 1978, Allan et al. 1980) demonstrated high levels of NAI-P (generally > 250 mg/kg) in these hypereutrophic lakes. Lower values were associated with the sediments of Lake Winnipeg, which is mesotrophic to eutrophic, and four lakes in British Columbia. Extractable Fe:P ratios in the eutrophic prairie lakes ranged from 6 to 11, with Lake Winnipeg exhibiting a ratio of 28.

Allan and Williams (1978) and Allan et al. (1980) attempted to relate changes in extractable P fractions with depth in sediment cores to changes in anthropogenic changes in P loading in the watersheds of the respective lakes. They found that pre-settlement NAI-P values in Lake Erie were less than 100 mg/kg, while post-settlement concentrations (Table 2.1) were greater than 100 mg/kg. Extractable Fe:P ratios were also on the order of 30-100 in the pre-settlement sediments, compared to the lower ratios in Table 2.1. Similar changes in NAI-P concentrations were observed in the depth distribution of Fe and P in the prairie lake sediments, although pre-settlement NAI-P concentrations in these sediments were all greater than 200 mg/kg. The higher concentrations led the authors to conclude that the prairie lakes had always been eutrophic.

Unlike the Lake Erie cores, the Canadian lake sediments (except Lake Winnipeg) showed increasing Fe:P ratios toward the surface. Both Lake Erie and the Canadian lakes exhibited increasing extractable Fe concentrations which increased between 20 cm and the surface, which Allan and Williams (1978) attributed to the mobilization of Fe in the reducing zone of the sediment and its subsequent precipitation in the oxidized microzone. The difference in Lake Erie and the Canadian lake sediments would thus appear to be less effective Fe mobilization in the latter, relative to the NAI-P supply to the surficial sediment. Lake Winnipeg, unlike the other Canadian lakes, had extractable Fe:P ratios similar to the pre-cultural sediments of Lake Erie, which probably results from its less eutrophic condition. As stated above, Allan et al. (1980) found that the relative content of apatite P decreased in the surficial sediments of the prairie lakes, apparently as a result of dilution by NAI-P resulting from agricultural and wastewater inputs to these lakes following settlement of the watersheds.

If NAI-P concentrations of extractable Fe:P ratios are closely related to the presence and nature of the short-range order complex that controls P solubility, it would appear likely that one or more of these data could be related to internal loading of P from the sediments. Unfortunately, very few comparisons of sediment release rate estimates and the concentrations of NaOH-P or NAI-P have been published. However, Table 2.1 includes some internal loading estimates for some of the lakes studied by Williams and his coworkers.

The release rates from Shagawa Lake, Lake Mendota, and Lake Erie represent estimates based on both laboratory or field studies and whole-lake P budgets, and thus are probably representative of actual in situ loadings during periods of anoxia in the hypolimnion. The values for the Canadian prairie lakes are estimates based on very rough P budgets, while the values from the remaining lakes represent laboratory studies only. The latter are particularly difficult to extrapolate to field conditions, as will be explained in the next section.

For the calcareous lakes, all but Lake Wingra appear to have relatively high NAI-P concentrations corresponding to high P release rates. Release rates from the non-calcareous sediments also occur in the same order as the NAI-P concentrations, but the ratio of release rate to NAI-P concentration appears to be considerably lower. However, the paucity of available data suggest caution in making any such extrapolation to a wider range of lakes at this time.

One other study deserves mention in the context of relating the P chemistry of sediments to the P chemistry of the water column. Wildung et al. (1974) traced changes in the total P, N, and organic C content of the surficial sediments

of Lake Klamath, Oregon, with season. The lake is non-calcareous and naturally eutrophic, and inorganic P (mostly NAI-P) ranged from 295 to 474 mg/kg in the surficial sediments. They found that decreases in these sediment components accompanied periods of maximum phytoplankton growth in the late spring and early summer. Subsequent increases in concentrations accompanied the decline of algal populations during late summer and early fall. Inorganic P was responsible for most of the change in sediment total P, and the authors suggested that the inverse correlation between sediment inorganic P and water column TOC was indicative of internal supply of P to the overlying water column during the summer. They gave no indication whether the sediment surface was anoxic during this period.

Stauffer (1981) emphasized the importance of sulfur in the Fe-Pe relationships in lake sediments. In a sulfuretum, i.e. a sediment that is rich in reduced S species (H_2S and HS^-), if the stoichiometric ratio of S to Fe exceeds unity, P will be released from the reduced Fe complex. Such a scenario would result if the decomposition of S-rich phytoplankton (relative to Fe) at the sediment surface created a sulfuretum at the sediment water interface. This scenario has been termed the "sulfide intercept model" by Stauffer, and it provides a mechanism whereby P in anoxic sediments is not controlled by the solubility of vivianite.

It is therefore necessary to consider not only the Fe:P ratios of sediments, as has been the practice of Williams and his associates, but also the Fe:S ratio. In so doing, however, Stauffer points out the importance of distinguishing between Fe associated with the relatively labile 1:1 FeS species, vivianite, and perhaps Fe-Ca-P metastable minerals, and the relatively inert pyrite, FeS_2 . CDB extracts Fe from pyrite, and thus any consideration of Fe:S stoichiometry should distinguish between FeS_2 and other Fe compounds, especially if the sulfide analysis fails to include S associated with pyrite. Unfortunately, very little work seems to have been done on the simultaneous distribution of the various Fe and S fractions in a sediment column. Most of the work available has dealt either with total element concentrations (e.g. Bortleson and Lee 1974) or interstitial ion concentrations (e.g. Emerson 1976).

P Release from Sediments

Studies of the interaction between P and lake sediments fall into two basic categories. The first category of experiment is designed to investigate solid-solution interactions with a minimum of interference from slow diffusion rates and heterogeneous microenvironments not directly associated with the particles themselves. Examples of this type of study include the investigations of Li et al. (1973) on the exchange rate of ^{32}P on 1 percent suspensions of lake sediment, and sorption/desorption studies in shaken flasks such as those of Shukla et al. (1971) and Kuo and Lotse (1974). More recent variations on this theme include the studies of Lee et al. (1977), McAllister and Logan (1978), and Mayer and Gloss (1980). Such experiments have been very useful in demonstrating that P exchange with sediment surfaces is highly labile (Li et al. 1973), that the ability of suspended sediments to absorb P is dependent on factors such as short-range order Fe concentration (Shukla et al. 1971) and ions such as silica that can compete with P for ion exchange sites on suspended clays (Mayer and Gloss 1980).

Lee et al. (1977) demonstrated that, in sediment suspensions, the mineralization of organic P under oxic conditions can result in higher P release over longer periods of time than if the same sediments were held under anoxic conditions. While such studies contribute to our understanding of individual components of the overall relationships between P and sediments in situ, it is very difficult to make quantitative predictions regarding P release rates from bottom sediments on the basis of the results. Such results are of considerable utility, however, in understanding the interactions of P with suspended sediments in the water column during storms or spring runoff.

The other approach to sediment-water P interactions is simulation of the sediment water interface in the laboratory, or isolating the interface in the field so that P flux can be measured. Such P release simulations are particularly informative, provided that certain conceptual and procedural safeguards are taken. Conceptually, P release from sediments depends on the supply of P from internal pools within the sediment, the effective diffusion coefficient for transport of P to the sediment surface, and the maintenance of a "representative" orthophosphate concentration in the overlying water.

Providing a representative P supply in the sediment may entail providing reducing conditions sufficient to release P from short-range order Fe complexes or supplying a source of organic P of similar lability to that normally settling onto the sediment surface from the overlying water column. Maintaining a realistic diffusion coefficient in a relatively homogeneous or well-mixed sediment may be possible by artificially constructing a core from a dredged sediment. In varved sediments that exhibit significant vertical inhomogeneities, however, it is probably necessary to work with an intact sediment core with a minimum of compaction. Three representative P-release studies described below illustrate the importance of the factors outlined above.

Kamp-Nielsen (1974) investigated the effects of certain sediment parameters on the exchange rates of P, Fe, Ca, and N species between sediment cores from four Danish lakes and the water overlying these cores in laboratory simulations. The release of P under anaerobic conditions was highly correlated with the P concentration gradient, as measured by the difference between ammonium chloride-extractable (ion exchangeable) P in the sediments and the orthophosphate concentration in the overlying water. Release rates varied from 0.8 to 17.3 mg P/m²-day. Fe was released in all cases, but not in proportion to the P released. Under anaerobic conditions, P was released from the oligotrophic and dystrophic lake sediments, but absorbed by the eutrophic lake sediments. The degree of sorption was highly correlated with the P concentration in the overlying water, and the crossover concentration (at which net sorption equals zero) was 30 µg P/l. The highest aerobic P release rate was 0.6 mg P/m²-day.

Kamp-Nielsen also investigated the effects of microorganisms, pH, and sediment P chemistry on release rates. Decreasing microbial activity by applying antibiotics decreased the sorption of P by the two eutrophic lake sediments, but had no effect on P release from anaerobic sediments. In the calcareous lake sediment, aerobic P exchange was thought to be controlled by a combination of sorption processes and apatite formation, while anaerobic release was concluded to result from apatite dissolution in the pH range of the sediments (pH 7.6-8.5). In the non-calcareous lake sediment, the solubility of iron phosphate was felt to be important.

Kamp-Nielsen also found that the greatest change in concentration of the P fractions in the non-calcareous sediment under anaerobic incubation was in the apatite P fraction, which was sufficient to account for the total loss of P from the core. The CDB-P fraction decreased by approximately 36 percent, and the organic P fraction increased by the same amount. The apatite-P:CDB-P ratio was found to be approximately constant below 6-7cm depth in the cores and to decrease toward the surface. Kamp-Nielsen concluded that this pattern resulted from a relative increase in the CDB-P fraction in the surficial 6-7 cm because of a favorable pH and redox potential for the stability of some Fe-P complex. The dissolution of apatite P, which accounted for more than 50 percent of the P in this "non-calcareous" lake sediment, would suggest that changes in the chemistry of this lake in the recent past have occurred. If so, then this sediment may be atypical of a non-calcareous lake sediment.

The sediment P-release studies of Holdren and Armstrong (1980) focused on the effects of collection date, stirring rate, aeration, and benthic fauna on cores from several Wisconsin lakes. Observed release rates during 2-27 day incubation periods ranged from 0.02 to 83 mg P/m²-day (see Table 2.1), depending on the incubation conditions. Bioturbation was found to greatly increase the rates of P release from these epilimnetic sediments. Increasing temperature and low O₂ were found to increase P release rates, while sediment suspension and decreasing temperature often resulted in the sorption of P by sediments. Redox was found to be more important in controlling release from non-calcareous sediments, while temperature was more important in calcareous sediments.

It is noteworthy that release rates were quite high from cores collected during the summer, when phytoplankton were abundant, while rates were often 5-100 times lower from cores collected from the same lake during the winter. These results suggest that labile organic P pools from senescent phytoplankton or macrophyte detritus may be a significant source of P release from epilimnetic lake sediments. This highlights the need to incubate freshly collected, intact cores in P release simulations. It is not known whether organic P is as important in deep lake sediments (cf. Golterman 1973).

The results of in situ P release studies by Sonzogni et al. (1977) on the eutrophic, non-calcareous Shagawa Lake, Minnesota, are especially interesting in light of the confirmatory P budget calculations of Larsen et al. (1980). Using benthic release chambers, Sonzogni et al. (1977) determined release rates of P from profundal sediments to range from 6.2 to 8.3 mg P/m²-day. Mass balance calculations led Larsen et al. (1980) to calculate a mean annual release of 10.2 mg P/m²-day from these sediments. Although not identical, the similarity of these estimates suggests that simulations can be a useful source of information on actual P release rates. Larsen et al. also calculated that the upper 10 cm of profundal sediments in the lake contained 15-25 times the calculated annual internal P loading in the form of NaOH-P. This internal loading has been the cause of the relatively slow response of this lake to restoration by reduction of P inputs (Larsen et al. 1975).

Mathematical Modeling of P Release

Internal P loading to lakes is accounted for in the popular input/output eutrophication models developed by Vollenweider (1975) and subsequent workers, in

the form of the net P sedimentation coefficient, R_p . This term includes both P removal to the sediments and its subsequent regeneration and release as an empirical function of the mean depth and hydraulic loading of a lake. If the P mass balance of the lake is calculated on an annual basis, the model does not take into account the fact that sediments that act as a P sink on an annual basis may be important contributors to water column P concentrations during the summer season, when algal blooms are most likely to reach nuisance proportions (e.g. Bengtsson 1978). However, if P mass balances are constructed for the hypolimnion during stratification, or for a lake that is undergoing restoration via P reduction or flushing, meaningful sediment P release rates may be obtained.

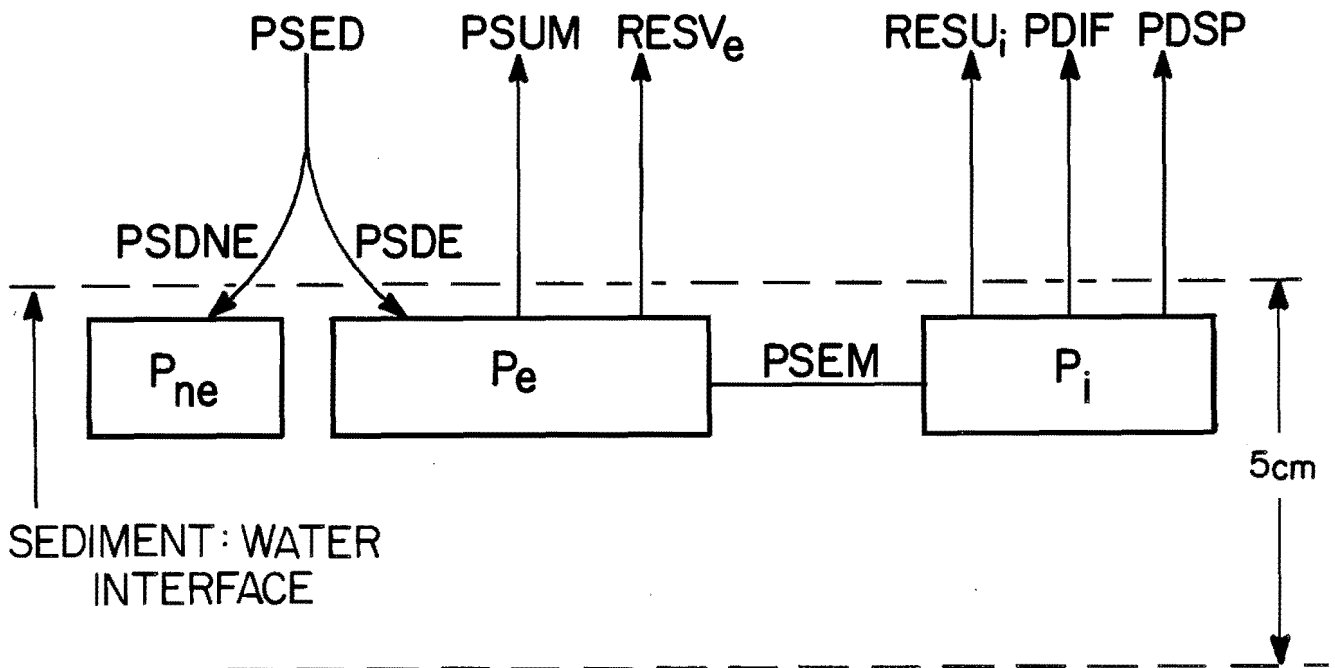
In the previous section, the results of a summertime hypolimnetic P mass balance on Shagawa Lake were summarized (Larsen et al. 1980), and in Table 2.1, the results of similar calculations on some Canadian prairie lakes were presented (Allan and Williams 1978). The latter authors present a summary of some previous P budgets, primarily on European lakes, that indicate release rates of 7-50 mg P/m²-day have been observed. The result of such loading depends on transport rates of P across the thermocline (Stauffer 1981), but is generally acknowledged to result in the causation or maintenance of summer and fall blue-green algal blooms in eutrophic lakes (e.g. Lee et al. 1977, Ahlgren 1977, Bengtsson 1978, Larsen et al. 1980).

Several aspects of whole lake or hypolimnetic P budgets are notable. The first is that, despite the fact that sediment P pools may be enormous in a historically eutrophic lake (e.g. Larsen et al. 1980), internal P release rates from the sediments are often seen to decline with time in lakes receiving reduced P inputs. For example, Ahlgren (1977) found that sediment P release in Lake Norrviken, a eutrophic lake in Sweden, decreased from 9.2 mg/m²-day following sewage diversion in 1971, to 1.6 mg/m²-day in 1976, with a concomitant reduction in water column total P at fall overturn of from 470 to 150 µg/l. This observation suggests that labile forms of P are gradually depleted from surficial sediments, providing inputs from the overlying water column are reduced.

Another point that may be worthy of note involves the value of R_p in whole lake P input/output models. This constant has been predicted empirically on the basis of lake mean depth and hydraulic residence time. Although these coefficients have proven generally acceptable in their application to lakes (e.g. Rast and Lee 1978), the empirical formulae used to predict R_p in lakes have not been equally successful when applied to reservoirs (Higgins and Kim 1981, Thornton and Walmsley 1982, Mueller 1983). In the latter case, they tend to under-predict R_p , thus indicating that either sedimentation is more efficient than in lakes or that P mineralization and release may be less efficient in reservoirs than in lakes with corresponding P loadings and morphometric parameters. The reasons for this apparent phenomenon do not appear to have been studied in the field or laboratory.

In addition to lakewide mass balance models, mathematical simulations of P release from sediments have been suggested as being critical to the understanding of whole lake P dynamics (Jorgensen 1977). One of the best developed and tested of such models is that of Kamp-Nielsen (1977). This model is depicted in Figure 2.1, and includes three state variables, although only two are actually modeled. P_i includes interstitial and dissolved P, and is measured as that extracted with ammonium chloride. This fraction thus includes P on ion exchange sites, but apparently does not include short-range order Fe:P complexes. The P_e compartment

contains what Kamp-Nielsen calls "exchangeable-P", and is measured as the difference between the total P minus P_i in the upper 5 cm of the sediment column, and the total P at 5-10 cm depth. The latter value is assumed to represent "stabilized P" (P_{ne} in Figure 2.1) that is no longer capable of interacting with the overlying water on a time scale relevant to the model. The P_e pool may represent labile organic P, vivianite, and the Fe:P complex extracted by NaOH and/or CDB. Sedimented in tripton is divided into four possible paths. A constant fraction of the tripton (PSDNE) is assumed to represent P_{ne} based on the concentration of P_{ne} present in the 5-10 cm depths in the sediment. The remaining P_e in the tripton is allowed to enter the sediment (PSDE), to be resuspended without mineralization ($RESU_e$), or mineralized to P_i and released to the overlying water without diffusion limitation. The fraction of P_e mineralized within the sediment (PSEM) can enter the water column through desorption (PDSP), diffusion (PDIF), or resuspension of the sediment ($RESU_i$).



Pools:

- P_e = the exchangeable, sedimentary phosphorus
- P_{ne} = the non-exchangeable, sedimentary phosphorus
- P_i = the interstitial and sorbed phosphate

Rates:

- PSDE = the exchangeable fraction of the sedimentating phosphorus
- PSDNE = the non-exchangeable fraction of the sedimentating phosphorus
- PSUM = the exchangeable phosphorus mineralized on the sediment surface and released without transport limitation to the bottom water
- PSEM = the exchangeable phosphorus mineralized within the sediment
- $RESU_e$ = the exchangeable phosphorus removed from the sediment by resuspension
- PDSP = the desorption of interstitial and sorbed phosphate
- $RESU_i$ = the interstitial and sorbed phosphate removed by resuspension
- PDIF = the interstitial and sorbed phosphate removed by diffusion to the overlying water

Figure 2.1. Model of P interactions between water and sediment in Lake Esrom, Denmark (based on Kamp-Nielsen 1977).

The differential equations describing the changes in the state variables P_i and P_e are based on earlier experimental work done on sediment cores from Lake Esrom in Denmark. In all of the equations, only the value of the first order rate constant for the mineralization of PSEM was calibrated using model data, and the temperature coefficient for the same reaction was taken from the literature. All other terms in the equations were derived from laboratory simulations on sediment cores.

The resulting model, when applied to the lake data, showed excellent agreement with observed values of P_i , but P_e pools were poorly represented. Although Kamp-Nielsen proposed some improvements to the model to alleviate this discrepancy, he noted that a similar model had been adequate to describe internal P loading rates to Lake Lyngby, and thus that internal loading estimates may not be especially sensitive to the high frequency changes in the P_e pool. Continued refinement of such models would appear to be a valuable heuristic exercise, even if their predictive power were limited by experimental difficulties.

Summary

Sediment P studies have fallen into the categories of 1) identification of forms of P, Fe, and S responsible for the control of P release from sediments, 2) simulation studies of P release in the laboratory, and 3) mathematical models of P release at both macroscopic and microscopic scales. Studies of sediment chemistry suggest that the relative concentrations of Fe, S, and P associated with vivianite, short-range order ferroso-ferric P complexes, and 1:1 Fe-S minerals interact to determine whether and when P might be released from lake sediments as a result of anoxic conditions at the sediment-water interface. There is evidence to indicate that apatite P may be responsible for some P uptake or release from sediments under conditions of extreme super- or undersaturation, but that crystalline apatites are not usually associated with P availability to algae or the overlying water column. Organic P in lake sediments is generally refractory, except perhaps for fresh tripton at the sediment surface. There is evidence that eutrophic lakes have CDB-P concentrations exceeding 200-250 mg/g, and that the preservation of this P form in deep sediments can be used to assess the past trophic state of lakes.

Laboratory simulations are useful in defining exchange mechanisms for P between water and sediment, for relating exchange rates to sediment chemistry and physical processes, and for generating coefficients for mathematical simulations of P behavior in lakes. Although simulations must be conducted with conditions such as availability of labile detritus and realistic concentration gradients in mind, there is frequently reasonable agreement between the results of such simulations and P release rates based on whole-lake or hypolimnion P mass balances. Such balances have indicated the importance of P release from sediments in promoting or maintaining blue-green algal blooms in lakes, even following lake restoration measures. The construction of realistic sediment P simulation models provides a useful heuristic tool and has also proven useful in a management context.

CHAPTER 3

METHODS

Sample Collection

Sediment cores were collected from the reservoir on three dates during the summer of 1982: July 27, August 17, and September 21. The sampling plan that was originally envisioned called for collection of replicate cores at five stations representing the Blacks Fork and Green River arms of the reservoir and a point below their confluence. These stations are shown in Figure 3.1, along with their assigned abbreviations for this study and the corresponding Bureau of Reclamation station designations. Problems with equipment precluded sampling station BC on the July trip, and station UBF was abandoned on the September trip to focus more attention on the remaining sites.

The cores were collected using a gravity corer equipped with a 61 cm acrylic core liner with an internal diameter of 44-47 mm (Tapp Plastic Co., Salt Lake City). Core liners were prewashed with 6N nitric acid and thoroughly rinsed with reagent grade (MILLEQ, Millipore Corp.) water in the laboratory. Cores to be used for release experiments were pre-soaked in 2 mg/l NaHPO_4 solution for 48 hr prior to use to prevent sorption of P by the tube walls during the incubation. Although this technique was found to be necessary for glass tube liners by Holdren and Armstrong (1980), experiments in our laboratory indicated that this treatment was unnecessary for the plastic liners used in this study. The tubes were rinsed in lake water immediately prior to collecting the cores.

At most of the stations it was possible to collect the core by lowering the coring device into the sediment gradually, thus preserving the integrity of the sediment-water interface. At stations LGR and BC it was generally necessary to drop the device from 1-2 meters above the sediment surface. These cores were discarded if the characteristic "fluffy" layer could not be observed at the interface. While it is impossible to tell whether the entire interface was sampled, the firmer texture of the interface at these sites, together with the observation of an intact benthic community in one of the cores, suggests that the interface was recovered more or less intact. Upon bringing the cores to the surface, the bottom was stoppered with a rubber stopper, and both ends of the core covered with a plastic cap. The cores were returned to the laboratory within 10 hr of collection, and placed in a 4°C cold room in the dark.

On the following day, a physical description was made of each core, and the cores to be sectioned were frozen at -14°C. On the July and August trips, the cores were frozen solid for sectioning. Although this technique allowed more precise sectioning than would have been possible with unfrozen cores, some distortion of the cores and migration of pore water along the sides of the core tube were noted. Although neither of these problems was likely to seriously affect the chemical profiles, the September cores were put in the freezer for only 4-5 hr. This practice resulted in a relatively firm core with no evidence of distortion or interstitial water channeling along the walls of the tube. The

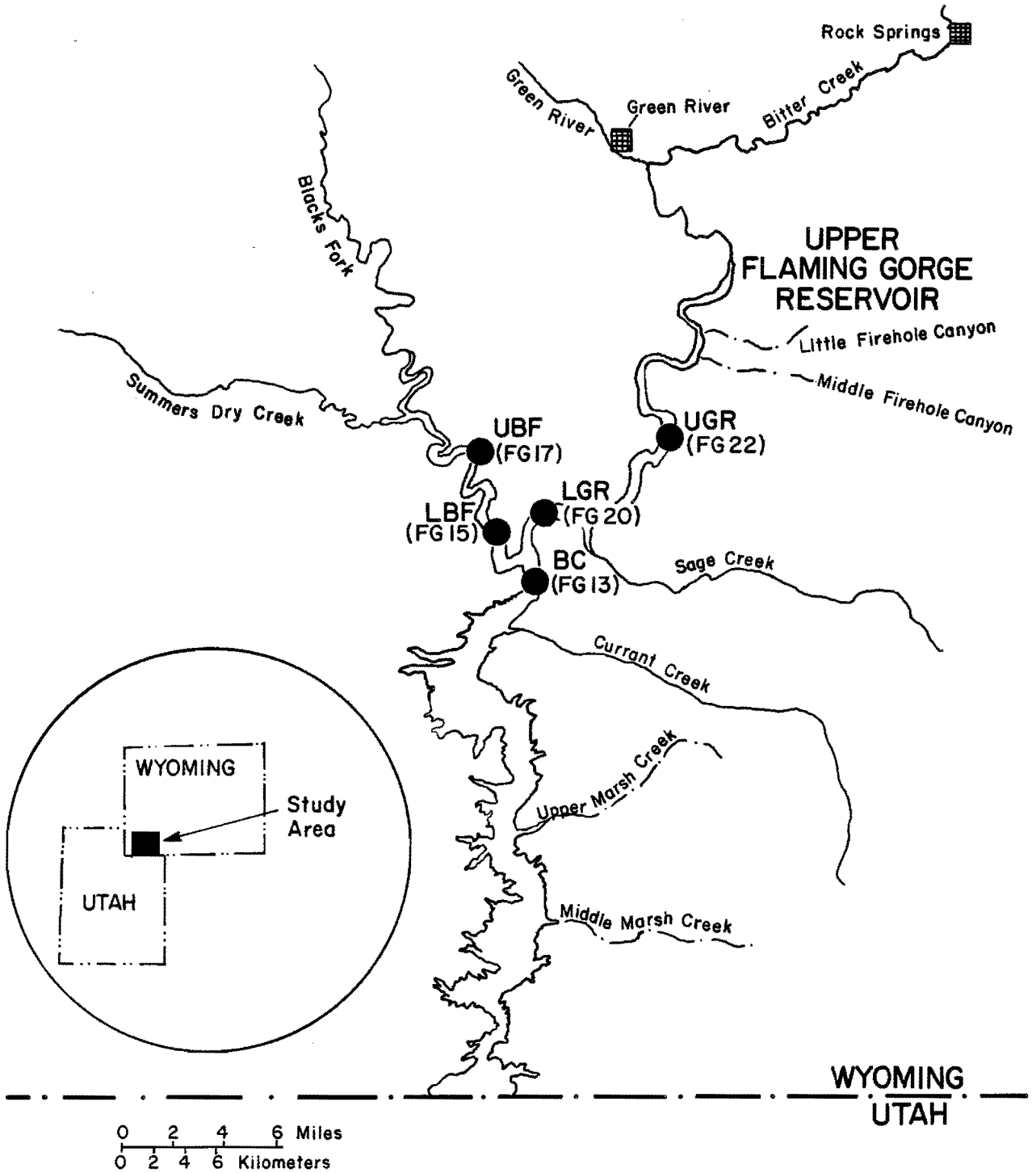


Figure 3.1. Upper Flaming Gorge Reservoir, Wyoming, showing the coring station (letters) and the corresponding Bureau of Reclamation water sampling station numbers in parentheses.

cores were extruded from the tube liners by pushing from the bottom, and sections were taken representing 0-2, 2-4, 4-7, 7-10, and 10-13 cm from the surface, respectively. Each section was placed in a polyethylene beaker and homogenized to produce a paste or slurry for subsampling for the various extraction and determination procedures. In most cases, the remainder of the core was frozen for possible future use.

Chemical Analyses-Wet Extractions

Percent dry weight. It has been customary in previous studies to express all core chemistry data on a dry weight basis. Although such studies have also tended to work with air-dried or oven-dried sediments, it was reasoned that drying may have adverse (or at least unknown) effects on sediment chemistry. Therefore, routine extractions were done on wet sediments, and the concentration of the various chemical parameters on a wet basis divided by the wet weight:dry weight ratio to convert the values to a dry weight basis. The wet weight:dry weight ratio was obtained by comparing the wet weight of a sediment subsample (approximately 2-3 g) with its weight obtained by drying to a constant weight in a 105°C oven.

NaOH-P. NaOH-extractable P was determined according to Williams et al. (1976a) on the July samples, and according to Sagher (1976) on the August and September cores. These techniques differ only in the addition of a 1 M NaCl wash following the initial NaOH-NaCl treatment in the Williams et al. procedure. This second wash did not release a large amount of P from the sediments in this study. Two to three grams wet weight (\approx 1 g dry weight) of sediment was extracted in 25 ml of 0.1 N NaOH/1 N NaCl solution for 18 hr on a reciprocating shaker table. The suspension was then centrifuged and filtered through a Gelman 0.45 μ m filter and, following neutralization of the filtrate, soluble molybdate-reactive P was determined on a Technicon AutoAnalyzer following the manufacturers instructions. Standards carried through the entire procedure were used to determine the standard curve for all extraction procedures.

CDB-P. CDB-P was determined following Williams et al. (1976a) on the July cores. Again 2-3 g wet weight of sediment was extracted in 30 ml 0.22 M Na citrate/0.11 M Na bicarbonate for 15 min in an 85°C water bath. One gram of Na dithionite was added and the solution was heated for an additional 15 min, following which the suspension was centrifuged and the supernatant removed. The pellet was then extracted with 25 ml of 1 N NaOH for 18 hr on a shaker table, centrifuged, and the supernatant combined with that of the citrate-bicarbonate supernatant for analysis. The concentration of P in the NaOH wash was found to be quite small, however, and thus it was decided to forego the second NaOH extraction on the August and September cores.

Orthophosphate was determined on the CDB extracts following Mayer and Williams (1981), using the colorimetric finish of Weaver (1974). One ml of 1 M FeCl₃ was added to each extract, and the solution was bubbled with wet air for 4 hr to oxidize the dithionite, which would otherwise interfere with color development in the phosphomolybdate complex. A 15 ml aliquot of this sample was diluted to 50 ml, and an aliquot of this solution was analyzed for P. Standard curves were prepared from standards carried through the entire extraction procedure.

CDB-Fe and CDB-Mn. CDB extractable iron and manganese were determined on an aliquot of the CDB extracts, acidified to $\text{pH} < 2$ with NH_3 , by atomic absorption spectrophotometry on an IL Model 357 spectrophotometer. The standard curve was prepared using standards carried through the entire extraction procedure.

Chemical Analyses-Dry Extractions

Sagher (1976) and Williams et al. (1980) noted that the recovery of NaOH-P was affected to a small extent by the sediment:extractant ratio. Because of the heterogeneity of the wet sediments used in this study, a wide sediment:extractant ratio was felt to be necessary and thus 2-3 g wet weight of sediment was commonly extracted in 50 ml of extractant. However, an initial experiment with the Flaming Gorge sediments (Appendix B) indicated that the relatively low extractant:sediment ratio being used seriously underestimated both P and metal forms, compared to the wider ratios used by Williams et al. (1976a). Therefore replicates of the September samples were analyzed using 60 mg aliquots of the 105°C dry sediments in 30 ml of the various extractants. This resulted in an extractant:sediment ratio of 500, rather than the ratio of 30-50 used for the wet extractions. The phosphorus analyses were performed following the general outline of Mayer and Williams (1981), on one set of replicates. The second set of replicates were preceded by an NH_4Cl extraction following Hieltjes and Lijklema (1980). Total P and S were also analyzed on aliquots of the dried sediment, as detailed below.

$\text{NH}_4\text{Cl-P}$. A 60 mg aliquot of dried sediment was first extracted in 2 consecutive 30 ml volumes of 1 M NH_3Cl for 2 hr periods on a shaker table at room temperature (22°C). The extractants were centrifuged, filtered through a Whatman GFC filter, and ortho-P was determined on the combined filtrates using the ascorbic acid technique (APHA 1981).

NaOH-P. The pellet then was extracted in 30 ml cold 0.1 N NaOH/1 N NaCl solution for 18 hr on a reciprocating shaker table. The resulting suspension was centrifuged and filtered through a Whatman GFC filter, and ortho-P was determined on the neutralized filtrate by the ascorbic acid method.

CDB-P. The pellet was subsequently extracted in 30 ml of 0.22 M Na-citrate/0.11 M NaHCl_3 for 15 min in an 85°C water bath. One gram of Na-dithionite was then added, and the solution was incubated for an additional 15 min. Orthophosphate was determined on the extracts using the colorimetric finish of Weaver (1974), as outlined above. The sum of the NaOH-P and CDB-P is referred to as non-apatite inorganic phosphorus (NAI-P), following the practice of Williams.

Apatite-P. The sediment pellet was then extracted in 30 ml 1.0 N HCl at room temperature on a shaker table for 18 hr. The supernatant was centrifuged and filtered, and ortho-P determined on the neutralized filtrate using the ascorbic acid method (APHA 1981).

Total P. Total P was determined by the persulfate digestion method (APHA 1981) on a separate 60 mg aliquot of each sediment added to 30 ml of deionized water. The difference between total P and the sum of NAI-P and apatite-P is assumed to represent organic-P by Mayer and Williams (1981).

CDB-Fe and CDB-Mn. CDB extractable iron and manganese were determined on an aliquot of the CDB extracts, acidified to pH<2 with HNO₃, as outlined above.

Total S. Total S analyses were performed on 1 g aliquots of the oven-dried, powdered sediments by a Leco induction furnace method by Rocky Mountain Geochemical Corp., Salt Lake City, UT.

Phosphorus release studies. In order to compare aerobic and anaerobic release rates of phosphate from the sediments, two cores taken from each reservoir station were incubated in the laboratory. Incubations were begun on cores that had been held at 5 C overnight following collection. Prior to incubation, all cores were pushed toward the top of the core tube using the rubber stopper in the bottom as a piston, so that the sediment surface was approximately the same distance from the top of the core tube in each core. This was done to minimize differences among cores in turbulence or microbial biomass growing on the exposed surface of the core tube.

The aerobic cores were incubated with an open headspace, into which was inserted a paddle attached to a jar test apparatus to provide mechanical stirring. The paddles were painted with an epoxy resin that has been determined to be inert to surface chemical reactions in experiments conducted at this laboratory (D. Selby, unpublished data). The two stirring regimes investigated were 4 and 8 rpm. Before each sampling, deionized water was added to each core to make up for evaporation, and after 2 min of stirring, an 8 ml aliquot of water was withdrawn into an acid-washed flask containing a drop of 5 N nitric acid (inclusion of the acid acted as a control for the anaerobic cores, where acid was added to prevent the oxidation of iron and the subsequent precipitation of phosphate when the sample was aerated during filtration). The aliquot was filtered immediately through a 0.45 µm Gelman membrane filter prior to analysis for ortho-P using the manual ascorbic acid method (APHA 1981). All aerobic incubations were carried out at 20-22°C in the dark.

Anaerobic cores were incubated by sealing the top of the core with a three-hole rubber stopper through which passed two glass tubes that extended into the water overlying the sediment, and one tube that extended only into the 5 mm air space between the water and the stopper. The glass tubes were each attached to a length of tygon tubing secured with a pinch clamp. Before each sampling, reagent grade nitrogen gas (99.995% purity subsequently passed through an Alltech gas purifier) was bubbled into the water for 4-5 min to provide thorough mixing of the water column (but no sediment suspension). This was done by passing the gas into the long inlet tube and out through the short tube connecting to the headspace. The short exhaust tube was then sealed and the gas pressure was increased to force a 15 ml aliquot of water out of the long exhaust tube into a flask containing a drop of citric acid. A 15 ml aliquot of deionized water was added through the short tube to replace that withdrawn for the sample, and the tube then was bubbled for 10 minutes with N₂ to remove any O₂ inadvertently admitted during sampling. Toward the end of the experiment, the replacement water was bubbled with N₂ to further assure anoxic conditions following sampling. However, no significant change in P release was observed as a result of this added precaution. Anaerobic incubations were carried out in the dark at two different temperatures, 22-24°C and 5°C.

Midway in the core incubations, the overlying water was sampled for iron, manganese, and sulfide. Fe and Mn were determined on acidified samples by atomic absorption spectrophotometry. Sulfide was determined by ion specific electrode (Orion 1977). The overlying water was immediately replaced with an artificial water made up to resemble the water in each arm of the reservoir on the August sampling trip, except without phosphate. The composition of this water was; UBF and LBF: 218 mg/l CaSO₄, 252 mg/l NaHCO₃, 102 mg/l MgCl₂·6H₂O, 185 mg/l MgSO₄·7H₂O, and 85 mg/l NaNO₃; UGR, LGR, and BC: 170 mg/l CaSO₄, 77 mg/l MgCl₂, 147 mg/l NaHCO₃, and 65 mg/l MgCO₃.

Algal Assay. In order to determine the availability of the phosphorus forms in the sediment to algae, an AAP bioassay (Miller et al. 1978) was run on suspensions of sediment from the top 2 cm of cores taken at stations LBF and LGR on the September sampling trip. On the day following the trip, each sediment core was put in a freezer for 3 hr to firm the core for sectioning, and the cores were subsequently extruded. The top 2 cm of each core was slurried into 300 ml of deionized water for subsampling. Five ml of the slurry was put into each of 15 bioassay flasks containing 95 ml of AAP medium. Triplicate flasks received additions of 50 µg/l P, 1.0 mg/l N, 50 µg/l P + 1.0 mg/l N, or 1.0 mg/l EDTA, and one set of triplicates received no nutrient or EDTA spike. All flasks then received an inoculum of the test alga Selenastrum capricornutum (10³ cells/ml), except for a set of triplicate control flasks that acted as a blank for fluorescence readings. Growth measurements were made almost daily by reading the fluorescence of the culture (excitation wavelength = 430 nm, emission wavelength = 663 nm). This method of growth measurement is rapid and precise, and is effective in the absence of toxicants.

In order to avoid altering the form of phosphorus present in the sediment in an unknown way, it was desirable not to autoclave the samples prior to introducing the test alga. After 1.5 days of incubation, however, visual examination of the cultures showed that growth of native algal forms was going to present a problem. Measuring growth by fluorescence requires that the relationship between chlorophyll a fluorescence per unit cell biomass is constant. This may not be the case in mixed cultures. Therefore, all flasks were autoclaved and reinoculated with the test alga. The low biomass present at 1.5 days was assumed not to alter the availability of P or N to the algae in the subsequent test period.

The slurry used to inoculate each flask was tested for the presence of various forms of P analyzed for in the cores. These tests involved adding either the NaOH/NaCl or CDB extractant reagents to the aliquots of the slurry to give a final concentration equal to that used in the sediment extracts. Following the appropriate extraction time, the sample was filtered through a 0.45 µm membrane filter, and ortho-P determined on the filtrate by the procedures outlined above. In addition, soluble reactive P was determined on the raw slurry using the ascorbic acid procedure (APHA 1981).

CHAPTER 4

RESULTS AND DISCUSSION

The results of the reconnaissance-level survey of the upper Flaming Gorge sediments can best be presented in three categories, based on differences in experimental procedures: core chemistry, P release simulations, and bioavailability assays. Core chemistry is discussed in terms of differences between wet and dry extraction results, and of the bearing of these results on the most probable geochemical mechanisms operating to control the binding and release of P by the sediments. The extraction data are then compared to the results of P release simulations under a variety of incubation conditions and also with the bioavailability of the various P species based on algal bioassay results. A final section of this chapter relates the results of these studies to a conceptual model for P release from the reservoir sediments and to their possible management implications for the reservoir.

Sediment Chemistry

Heterogeneity of sediments. Before dealing with the chemistry of the sediment cores themselves, it is important to note that a substantial degree of vertical heterogeneity was occasionally observed in the gross physical structure of cores taken from the same reservoir location. Figure 4.1 diagrammatically illustrates the appearance of four replicate cores collected from site LBF on the

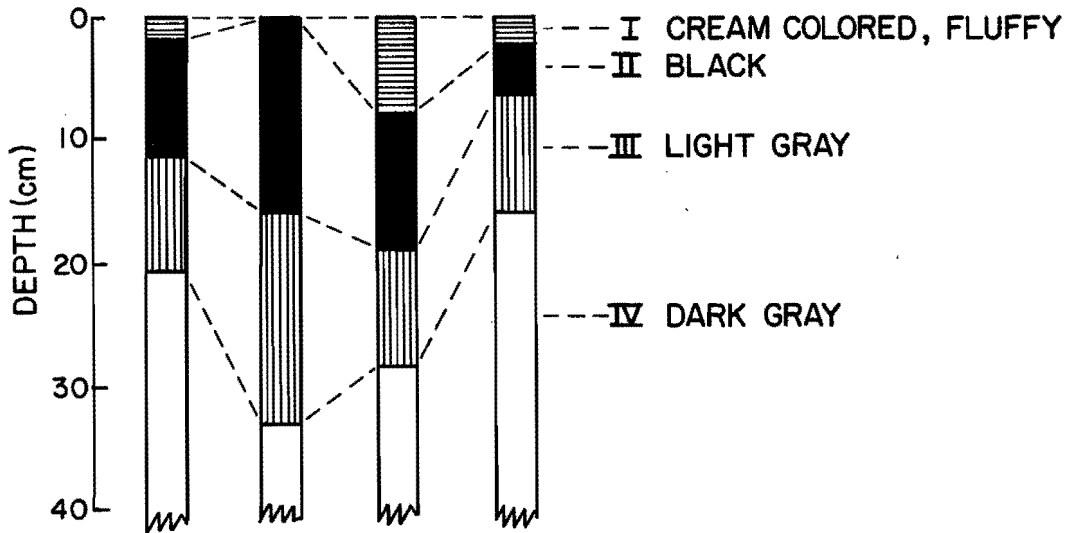


Figure 4.1. Visual appearance of four replicate sediment cores collected at site LBF in August 1982.

August sampling trip. Visually, the cores from this site could be divided into four distinct zones. A creamy-white flocculent layer (I) was present at the sediment-water interface in all of the cores, but its thickness ranged from 0.3-2.5 cm. A black and probably highly reducing zone (II) of sediment 3-5 cm thick occurred beneath the oxidized interface, below which was a light gray layer (III) 3-5.5 cm in thickness. A darker gray layer (IV) ranged from zone III to 23-300 cm below the interface, where a slightly lighter gray layer began. Replicate cores from all of the coring sites showed some degree of variation, and the patterns observed were different from site to site.

The variations in the gross appearance of replicate cores taken at the same station indicate that patterns in chemical concentrations brought about by diagenetic reactions may be superimposed upon more general patterns resulting from the gross physical composition of the sediments themselves. Although such differences may derive from core compression or loss of the surface layer during sampling, it is more likely that the differences among the cores studied here resulted from short-range differences in sedimentation or erosion patterns caused by bottom currents in the riverine arms of the reservoir. In the discussion below, the possibility that a given core section (e.g. 2-4 cm) may represent fundamentally different layers in replicate cores should be considered when interpreting differences in average chemical composition among cores taken at different stations or on different sampling dates.

Wet extractions. A summary of the concentrations of the various constituents found in the sediment cores on the three sampling dates is presented in Table 4.1. Station locations are shown in Figure 2.1. The concentrations of the constituents in the core sections have been volume-weighted to give overall mean values for the top 13 cm of each core. Aggregation of the data at the whole-core level enables comparisons to be made more easily between dates and between arms of the reservoir. Concentrations of the constituents in each individual core section are presented in Tables A.1-A.3 of the Appendix, and vertical patterns within the cores are discussed below.

The July samples revealed a striking difference in the sediment chemistry of the two arms of the upper reservoir. The Blacks Fork arm was characterized by lower concentrations of NaOH-P and CDB-Fe, although the CDB-Mn concentrations did not appear to differ appreciably among stations. The analytical coefficient of variation for NaOH-P in the wet extraction, based on replicate analyses of two homogenized sediment cores, was approximately 20 percent (Appendix B). An idea of the sampling variability can be gained by comparing the results of duplicate cores collected at the various stations (July cores, Table 4.1). There do not appear to be significant overlaps between the concentrations of NaOH-P at the different stations, relative to the increasing concentrations in a downstream direction in each arm.

In August, NaOH-P appears to have decreased slightly in the Blacks Fork arm, and to have increased somewhat in the Green River arm. NaOH-P appears to have decreased below the confluence of the two arms of the reservoir, relative to the concentrations at the Lower Green River station, probably as a result of dilution of the Green River sediment or water by low-P inputs from Blacks Fork. The CDB-P concentrations also were low in the Blacks Fork sediments and high in the Green River sediments, although the concentration of this P form appears to have increased below the confluence in the August cores.

Table 4.1. Average extractable species concentrations (0-13 cm) in upper Flaming Gorge sediment during summer, 1982 (all values in mg/kg except % CaCO₃).

Reser- voir Station	July			August				September			
	NaOH-P ^a	CDB-Fe	CDB-Mn	NaOH-P	NAI-P	Total-S	% CaCO ₃	NaOH-P	NAI-P	CDB-Fe	CDB-Mn
UBF	0.53/1.4	1210	110	0.75	50	410	7.5	-	-	-	-
LBF	5.1/7.0	1510	150	3.2	87	580	5.9	2.3	68	1020	140
UGR	7.4/8.6	4420	150	9.8	140	790	8.1	7.9	79	1700	100
LGR	22/35	4500	130	36	155	1210	8.7	26	192	2540	310
BC	-	-	-	23	192	2280	9.2	13	126	1790	280

^aValues for duplicate cores.

Total sulfur (S) and percent CaCO_3 contents were determined on oven-dried sediments from the August sampling trip. The results revealed the sediments to be relatively low in both S and CaCO_3 , relative to calcareous Wisconsin sediments (Williams et al. 1971c, Nriagu 1974). Both species exhibited higher concentrations in the Green River arm than in the Blacks Fork arm, although unlike the P species, concentrations of CaCO_3 and total S increased below the confluence. Deposition of CaCO_3 may have been brought about by the replacement of gypsum by photosynthetically induced precipitation of calcite by phytoplankton blooms in the upper arms of the reservoir, as has been suggested by Bolke and Waddell (1975). The higher S concentrations may have resulted from the deposition of S-rich algal detritus (e.g. Stauffer 1981) or from trapping of S by sediments with an oxidized water interface, inasmuch as the bottom water at station BC failed to become anoxic during the summer of 1982.

NaOH-P in the September cores followed the same pattern observed in the cores collected earlier in the summer, although the concentrations appear to have decreased again. NAI-P concentrations decreased in all of the cores except at the lower Green River site, and CDB-Fe decreased in all of the cores sampled. The CDB-Mn concentrations appear to have increased in the lower Green River arm and below the confluence, which would be consistent with its mobilization from anoxic sediments upstream and its subsequent deposition in the aerated downstream sediments, which were overlain by oxygenated water on the September sampling date.

The data presented above suggest that NaOH-P, together with reduced Fe and Mn, are lost from the sediments in the upstream reaches of the reservoir arms during the late summer. These reduced species were probably returned to the sediments downstream, either upon oxidation in the water column, in the case of the metals, or through sedimentation of algal detritus or coprecipitation with Fe, in the case of P. It is not clear from the limited amount of data collected in this study whether Fe and Mn were returned to the sediments by the time they reached the station below the confluence in September. However, NaOH-P does appear to have been mobilized out of the study reach. If so, the role of blue-green algae in "rafting" P out of the study reach, despite the oxidizing conditions in the water column, may be more important in controlling downstream transport of P than is the coprecipitation mechanism.

Dry extractions. Although Williams et al. (1980b) reported only minor effects of extractant:sediment ratios on P recovery, some preliminary experiments suggested that the wet extraction procedure was yielding considerably lower concentrations than some extractions of oven-dried sediments using wider extraction ratios. Also, Hieltjes and Lijklema (1980) reported that, contrary to the findings of Williams et al. (1971b), not all of the P precipitated in calcareous sediments during the NaOH/NaCl extraction was recovered in the subsequent CDB extraction. Although the relatively low CaCO_3 content of the Flaming Gorge sediment originally suggested minimal problems with such precipitation, it was decided to compare two dry extraction techniques with the wet procedure used routinely in the study.

The first procedure is essentially scheme "D" of Williams et al. (1971b), which consists of a single NaOH extraction followed by a single hot (85°C) CDB extraction. This scheme was chosen because of our interest in the NaOH-P fraction, which has been shown by many workers to be closely related to the P available to algae in bottle bioassays (see Chapter 2). The technique of Hieltjes and Lijklema (1980), in which the NaOH/NaCl extraction procedure is preceded by an

NH_4Cl extraction which removes anion-exchangeable P along with any CaCO_3 present was also investigated. Both techniques were tested using a 500:1 extractant:sediment ratio on aliquots of the September cores that previously had been analyzed using the wet extraction procedure. Although no systematic investigation of the reproducibility of the latter two techniques has been conducted by us, some 20-25 samples that have been rerun for various reasons have shown agreement to within 5 percent in 90 percent of the cases.

It is apparent from the data in Table 4.2 that the extraction scheme employed has an important effect on the interpretation of the chemical data. NaOH-P and NAI-P were 8.3 and 2.1 times larger, respectively, in the "D" procedure of Williams than in the wet extractions. The latter ratio is derived from the sum of the NaOH/NaCl and CDB extracts in scheme D. The proportion of NAI-P represented by NaOH-P also increased in scheme "D", with the largest increases corresponding to the lowest NaOH-P concentrations. However, despite the increases in both the magnitude and proportion of the NaOH-P fraction, the relative ranking of concentrations among the various sampling sites remained similar. CDB-Fe and CDB-Mn concentrations showed smaller, but nonetheless substantial increases amounting to 3.3 and 1.7 times the wet extraction concentrations, respectively. The relative Fe concentrations observed among the stations showed the same patterns as the data from the wet extractions, although for Mn the relative order of stations LGR and BC were reversed.

The extraction scheme of Hieltjes and Lijklema (1980) indicated that a large loss of NAI-P to calcium had occurred during the NaOH extractions, with most of the loss occurring from the NaOH-P fraction. The NH_4Cl extract removed relatively little P, compared to the total P present, but it resulted in increasing the NaOH-P fraction markedly. If it is assumed that the NaOH/NaCl extract should include all exchangeable and non-occluded Fe-P, then the sum of the NH_4Cl -P and NaOH-P fractions should equal the NaOH-P fraction in the Williams "D" procedure. Instead, this fraction averaged 3.3 times higher in the Hieltjes and Lijklema procedure, thus indicating that a substantial loss of this P fraction occurred by precipitation. Furthermore, the P subsequently redissolved by the CDB extract was quite small, contrary to the results of Williams et al. (1971b), who found virtually complete recovery. The resulting NAI-P concentrations averaged 1.7 times those determined using the Williams "D" procedure, and now accounted for the majority (60-76 percent) of the NAI-P present in the sediments.

This result was confirmed by analyzing the BC core a second time using the Hieltjes and Lijklema procedure; the results of the second extraction were virtually identical to the data presented in Table 4.2. Of the metals, only Fe was rerun on five samples from station BC. The resulting average concentration was 11 percent higher, but there was no consistent pattern among the core sections, which suggests that the error was randomly distributed rather than systematic.

The majority of the P in the cores was in the apatite-P (HCl-P) fraction, which is probably of little significance to algal growth in the reservoir (Syers et al. 1982). This factor is significant if much of the apatite is detrital rather than diagenetic because management programs aimed at reducing apatite-P loadings are likely to have little effect on water quality in the reservoir, even though they may represent a significant fraction of the P inputs. Conversely, reduction in the more available P fractions, while small, may actually have a disproportionately beneficial influence.

Table 4.2. Average concentrations (0-13 cm) of various constituents in Flaming Gorge sediment cores collected in September 1982, using different extraction techniques (all values in mg/kg).

Reservoir Station	Wet Extraction				Williams et al. "D" (1971b)				
	NaOH-P	NAI-P	CDB-Fe	CDB-Mn	NaOH-P	CDB-P	NAI-P	CDB-Fe	CDB-Mn
LBF	2.3	68	1020	140	43	129	172	3600	290
UGR	7.9	79	1700	100	86	133	219	7300	280
LGR	26	192	2540	310	169	129	298	6800	380
BC	13	126	1790	280	113	172	285	5700	440
Hieltjes and Lijklema (1980)									
	NH ₄ Cl-P	NaOH-P	Σ-P	CDB-P	NAI-P	HCl-P	ORG-P	Total-P	CDB-Fe
LBF	83	216	299	60	359	510	50	919	-
UGR	22	216	238	81	319	498	27	844	-
LGR	39	396	435	85	520	464	86	1070	-
BC	65	325	390	82	472	506	60	1038	6300

It is also notable that the CDB-P and apatite-P fractions appear to vary little between the arms of the reservoir. Organic P, which is calculated by the difference between total P and the sum of the inorganic P fractions, appears to be quite low, with the highest concentrations appearing in the lower Green River arm. Total P content exhibited patterns similar to NaOH-P and was, in fact, controlled by differences in this fraction. Taken together, these factors are important, because they suggest that the differences in P chemistry in the arms of the reservoir are controlled principally by the fraction of P referred to here as NaOH-P. This point takes on added significance in the discussion of the P release experiments below.

It was hypothesized in Chapter 2 that Fe-P short-range order complexes formed by the sorption of P on freshly formed Fe gels in an aerated hypolimnion, or in the vicinity of the oxycline, would be characterized by a low ratio of NaOH-P to CDB-P. This would be so because ample opportunity would exist for P to be occluded by the rapidly forming Fe gel. Such a scenario might also be expected if Fe and P were simultaneously migrating toward an oxidized sediment-water interface. However, if P were being sorbed onto older, preformed Fe gels, as might be the case for P being released from aerobic sediments in the absence of a stoichiometric amount of Fe, then the NaOH-P:CDB-P ratio might be expected to be relatively high.

The data in Table 4.2, based on any of the extraction procedures, indicate that the NaOH-P:CDB-P ratios are highest in the Green River sediments and also are higher in the downstream than in the upstream reaches of both arms. The extraction procedures differ considerably, however, in predicting the actual ratios. Based on the observation of McLaughlin et al. (1977) that oven-drying does not affect the extractability of P from freshly formed Fe gels by the NaOH extractant, it must be assumed that the values from the Hieltjes and Lijklema procedure most accurately represent the distribution of P in the Flaming Gorge sediments. If the hypothesis regarding the formation of NaOH-P versus CDB-P outlined above is correct, then scavenging of P from an oxygenated water column by preformed Fe oxyhydroxide gels must be an important process in the upper reservoir, and may be somewhat more important in the Green River arm than in Blacks Fork. Further field and laboratory studies would be helpful in testing the utility of the NaOH-P:CDB-P ratio as an indicator of recent Fe-P interactions in lakes and reservoirs.

Comparison with other lake sediments. The concentrations of the various P and metal species in the Williams extraction procedure D in Table 4.2 can be compared with values obtained on other lake and reservoir sediments using a similar technique. The wide range of values noted for lakes of similar trophic state (Table 2.1) preclude the simple application of sediment P concentrations as trophic state "indicators". Bostrom and Pettersson (1982) have provided an interesting case study illustrating the difficulties with such an application. Nonetheless, as is demonstrated below, NaOH-P may provide an indication of the driving force behind P release from sediments under anoxic conditions. Also, Messer and Ihnat (1983) have demonstrated that the NaOH-P fraction in the sediment of Panguitch Reservoir in southern Utah has provided a useful record of historical changes in the trophic state of the reservoir since construction of the dam there in 1892.

A comparison of the concentrations of the various P species in the sediments of several Intermountain reservoirs is shown in Table 4.3. NaOH-P concentrations

Table 4.3. Summary of chemical analyses and P release rates for sediment cores taken from several reservoirs in the Intermountain West.

	P Concentrations (mg/kg)				Mole Ratios		Release Rates (mg/m ² -day)	
	NaOH-P ¹	NAI-P ²	Apatite-P	Total P	Fe:NAI-P	Fe:S	Aerobic	Anaerobic
Deer Creek Reservoir								
Upper (1) ³	224	355	507	934	9	2.1	1.2 (0.3) ⁴	9.9 (4.0)
Upper middle (10)	18	208	337	782	2	0.8	1.5 (0.3)	5.7 (2.3)
Lower middle (13)	212	418	429	912	11	2.2	3.7 (0.9)	7.7 (3.1)
Lower (18)	211	444	385	874	13	1.6	2.8 (0.6)	13.7 (5.5)
Flaming Gorge Reservoir								
Lower Blacks Fork (14)	43	359	510	901	6	2.5	0.5	1.7
Upper Green River (4)	86	319	498	843	13	5.6	0.2	1.8
Lower Green River (9)	169	520	464	1090	7	2.4	2.1	11.1
Below Confluence (19)	113	472	506	1038	7	1.8	1.2	8.2
Panguitch Reservoir								
Middle (PLO-1) ⁵	281	510	176	726	5	2.2	-	3.1
Clear Creek (C.K.)	33	192	345	656	6	1.6	-	-
Blue Spring Creek (B.S.)	169	260	325	752	10	3.4	1.0	-
Scofield Reservoir								
	192	345	680	1160	17	5.3	-	-

¹Based on scheme "D" of Williams et al. (1971b).

²Based on technique of Hieltjes and Lijklema (1980) on cores 4, 9, 14, 18, 19, PLO-1 and Scofield.

³Numbers in parentheses represent core designations.

⁴Corrected to 25°C; numbers in parentheses represent 9.5°C (aerobic) and 7.2°C (anaerobic).

⁵Average for 2 cores.

in the Blacks Fork arm are among the lowest reported (Table 2.1), and they are similar to the concentrations found in Lake Erie bluff material that showed little tendency to support algal growth in bioassays (Williams et al. 1980b). The NaOH-P concentrations in the Green River arm are higher, although still below the values typical of many eutrophic lakes (Table 2.1) and Intermountain reservoirs (Table 4.3).

Other workers have concentrated on the entire NAI-P fraction, rather than the NaOH-P concentrations alone. Allan and Williams (1978) and Allan et al. (1980) have demonstrated that increases in the former fraction correspond to the cultural eutrophication of Lake Erie and also of some Canadian prairie lakes. NAI-P concentrations in the Flaming Gorge cores range from 319 to 520 mg/kg, based on the Hieltjes and Lijklema extractions, which are higher than the values believed by these authors to represent the onset of eutrophic conditions in Lake Erie (100-150 mg/kg). This also appears to be in the range of values cited for the eutrophic lake sediments in Canadian prairie lakes that exhibit significant internal P loading (290-420 mg/kg in the top 14 cm). The latter lakes have estimated internal P loadings under anoxia in the hypolimnion of 4-12 mg/m²-day (Table 2.1) (Allan and Williams 1978). Apatite-P is present in similar concentrations to those in Deer Creek and Scofield Reservoirs in the Flaming Gorge sediments. The lower concentrations in the Panguitch Reservoir sediments are the result of the relatively low erosion rates from a basaltic watershed.

CDB-Fe concentrations are typical of calcareous Wisconsin lake sediments at the Green River and BC stations, while the Blacks Fork arm stations are somewhat Fe-poor. Shukla et al. (1971) found that lake sediments with a low CDB-Fe content (1676 mg/kg) showed the least tendency of all of the sediments that he studied to sorb Fe from solution. CDB-Mn concentrations are more typical in the Flaming Gorge sediments, when compared to values for Wisconsin lakes ranging from 165 to 660 mg/kg (Williams et al. 1971c). Total S can be compared to values of 1500-2800 mg/kg in the surface sediments of the calcareous eutrophic Lake Mendota, Wisconsin (Nriagu 1968), 1200-4200 in the deep sediments of Deer Creek Reservoir, 450-1400 mg/kg in Panguitch Reservoir, and 1000 in Scofield Reservoir. The resulting Fe:P and Fe:S ratios are discussed below. The CaCO₃ concentrations are somewhat low, compared to Wisconsin hardwater lake sediments, which typically have carbonate concentrations ranging from 40 to 60 percent (Williams et al. 1971c). The low value probably results from dilution of biogenically precipitated and detrital carbonates by non-carbonate clastics from the highly erodible watershed.

In summary, the sediments of Blacks Fork arm appear to be typical of an Fe- and Fe-P poor calcareous lake sediment, whereas the sediments in the Green River arm and below the confluence are more typical of a moderately eutrophic calcareous lake sediment. The reasons for the differences in the two arms undoubtedly stem from the nature of the geochemistry of the watersheds that they drain, as much as from the trophic state of the reservoir arms themselves. Indeed, the sediment geochemistry may be an important factor in controlling the trophic state of the two arms. In any case, the Green River arms would appear to support more active Fe-related internal P cycling than the more Fe-P-poor Blacks Fork arm.

Geochemical controls on sediment P. As a first step in unravelling the behavior of P, Fe, and S in the Flaming Gorge sediments, correlation coefficients were computed for the various parameters measured on the sediment cores. Coefficients were computed on the basis of each core section on which analyses for the corresponding constituents had been performed, for both wet and dry

extractions, and also on whole-core weighted averages for each constituent on all sampling dates on wet extraction data alone. All calculations were run using the PEARSON CORR subprogram of SPSS (Nie et al. 1975).

Correlations based on whole core data (Table 4.4) were quite high for many of the constituents analyzed. CDB-P was highly correlated with CDB-Fe ($r=0.95$), NaOH-P ($r=0.85$), total S ($r=0.91$), and NaOH-S ($r=0.83$). Similar values were obtained by Williams et al. (1971c) for CDB-P and CDB-Fe correlation coefficients ($r=0.90$), based on values obtained on different types of sediment dredged from a number of Wisconsin lakes. These results are thus most comparable to those reported in Table 4.4, in which different sediment types are being compared. CDB-Fe showed lower correlation with NaOH-P and virtually none with CDB-Mn.

On a section-by-section basis (Table 4.5) significance levels were lower than for the whole-core statistics, which is to be expected because of variations in the Fe to P ratio in the Fe-P complex within a particular sediment. The coefficients were higher for the dry extractions using the Williams extraction

Table 4.4. Pearson correlation coefficients (r) and probability levels for correlations between chemical parameters on a whole core basis for sediment cores taken from upper Flaming Gorge Reservoir during summer, 1982. Numbers in parentheses refer to the number of core sections compared.

Parameter	Parameter					
	CDB-P	CDB-Fe	CDB-Mn	NaOH-P	NaOH-S	Total S
CDB-P	1.0000 (9) P<0.001					
CDB-Fe	0.9250 (4) P=0.038	1.0000 (11) P<0.001				
CDB-Mn	*	0.2038 (4) P=0.398	1.0000 (4) P<0.001			
NaOH-P	0.8493 (9) P=0.002	0.4744 (11) P=0.070	0.0204 (4) P=0.490	1.0000 (16) P<0.001		
NaOH-S	0.8303 (4) P=0.041	*	*	0.6360 (5) P=0.124	1.0000 (5) P<0.001	
Total S	0.9116 (5) P=0.016	*	*	0.6816 (5) P=0.103	0.9833 (5) P=0.001	1.0000 (4) P<0.001

*Not computed

Table 4.5. Pearson correlation coefficients (r) and probability levels for correlations between chemical parameters on a section-by-section basis for sediment cores taken from upper Flaming Gorge Reservoir during September 1982. Subscripts: 1 = Scheme "D", Williams et al. (1971b), 2 = Hieltjes and Lijklema (1980).

Parameter	Parameter									
	NaOH-P ₁	CDB-P ₁	CDB-Fe ₁	CDB-Mn ₁	Total P	Total S	NH ₄ Cl-P ₂	NaOH-P ₂	CDB-P ₂	HCl-P ₂
NaOH-P ₁										
CDB-P ₁	0.4813 (19) P=0.018									
CDB-Fe ₁	0.5883 (19) P=0.004	0.3273 (19) P=0.086								
CDB-Mn ₁	0.6460 (19) P=0.001	0.6391 (19) P=0.002	0.4047 (19) P=0.043							
Total P	0.7759 (19) P<0.001	0.5603 (19) P=0.006	0.1224 (19) P=0.309	0.7649 (19) P<0.001						
Total S	0.3684 (19) P=0.060	0.7588 (19) P<0.001	0.1409 (19) P=0.283	0.5442 (19) P=0.008	0.5381 (19) P=0.009					
NH ₄ Cl-P ₂	-0.2308 (19) P=0.171	0.2191 (19) P=0.184	-0.5035 (19) P=0.014	0.2091 (19) P=0.195	0.1576 (19) P=0.260	0.1352 (19) P=0.291				
NaOH-P ₂	0.8970 (19) P<0.001	0.5615 (19) P=0.006	0.3292 (19) P=0.084	0.6056 (19) P=0.003	0.8941 (19) P<0.001	0.4979 (19) P=0.015	-0.0556 (19) P=0.411			

Table 4.5. Continued.

Parameter	Parameter									
	NaOH-P ₁	CDB-P ₁	CDB-Fe ₁	CDB-Mn ₁	Total P	Total S	NH ₄ Cl-P ₂	NaOH-P ₂	CDB-P ₂	HCl-P ₂
CDB-P ₂	0.7764 (19) P<0.001	0.4172 (19) P=0.038	0.7608 (19) P<0.001	0.5442 (19) P=0.008	0.4254 (19) P=0.035	0.4227 (19) P=0.036	-0.3643 (19) P=0.063	0.5895 (19) P=0.004		
HCl-P ₂	-0.4506 (19) P=0.026	-0.2804 (19) P=0.122	-0.3274 (19) P=0.086	-0.1870 (19) P=0.222	-0.2698 (19) P=0.132	0.0396 (19) P=0.436	-0.2920 (19) P=0.113	-0.4668 (19) P=0.022	-0.4071 (19) P=0.042	

than for the corresponding wet extractions. This result is to be expected because the wet NaOH/NaCl and CDB extractions were performed on different aliquots of sediment, while the Williams procedure involves sequential extraction of the same aliquot of sediment. Only the correlations for the dry extraction data will be presented. Table 4.5 includes data from the Williams procedure (subscript = 1) and the Heiltjes and Lijklema procedure (subscript = 2) for comparison.

The upper right hand corner of Table 4.5 contains the correlation coefficients between parameters in the Williams extraction technique. NaOH-P is highly correlated ($P < 0.005$) with CDB-extractable metal species and with total P. CDB-P is highly correlated only with CDB-Mn. In all cases, however, the correlation coefficient fails to exceed 0.8. Within the Heiltjes and Lijklema procedure data (lower right), NaOH-P is highly correlated only with total-P and CDB-P. Between the extraction procedures it can be seen that the corresponding NaOH-P fractions are highly correlated ($r = 0.90$), in spite of the large discrepancy in their absolute values. The correlation coefficients between the wet procedure and the dry extraction procedures were $r = 0.96$ and $r = 0.91$ for the Williams and the Heiltjes and Lijklema procedures, respectively. This result suggests that NaOH-P in these sediments represents a relatively robust measure of the comparative concentrations of the P pools represented by this extraction procedure in different sediments, irrespective of the absolute amounts of P extracted.

Geochemical controls on P release from sediments, in which the redox cycle of Fe (rather than ion exchange reactions with aluminosilicates) is the principal controlling factor, involve the atomic ratios of Fe, P, and S, as discussed in Chapter 2. Table 4.6 presents the ratios of these constituents in the Flaming Gorge sediments, based on Fe concentrations in the September cores, and total S concentrations in the August cores. CDB-Fe:NAI-P ratios based on all three extraction methods are presented for comparison. It is assumed that the CDB-Fe concentrations are the same for both of the dry extraction procedures.

Except at UGR, the CDB-Fe:NAI-P ratios in Table 4.5 are only slightly higher than the value of 7 suggested by Williams et al. (1971c) as the lower limit for effective control of aerobic release of P by lake sediments. They are also in the range typical of the eutrophic Canadian prairie lakes studied by Allan and Williams (1978) and, except at the upper Green River station, they are lower than the ratios for the deep-water sediments of eutrophic Deer Creek Reservoir (Table 4.3). This observation holds regardless of the extraction procedure used, although the Williams et al. (1971c) data correspond most closely to the wet extractions in this study, and the Allan and Williams (1978) data to the scheme D extraction of Williams et al. (1971b). The low CDB-Fe:NAI-P ratios in Table 4.6 may represent the cultural "overloading" of the Fe-related P binding capacity of these sediments, as was suggested for the Canadian lake sediments studied by Allan and Williams (1978). In any event, the low ratios suggest that control of anaerobic P release by vivianite or other Fe(II) minerals is relatively inefficient, once the sediment surface becomes anoxic.

The CDB-Fe:total-S ratios presented in Table 4.6 are typical of most of the reservoir sediments in Table 4.3, and they indicate that Fe is present at well above the 1:1 stoichiometric ratio of the metastable Fe-S species that are commonly formed in anoxic freshwater sediments (Nriagu and Dell 1974). Only at station BC does the atomic ratio fall below 2, and thus this station may be expected to maintain a somewhat higher "equilibrium" P concentration than the

Table 4.6. CDB-Fe:NAI-P and CDB-Fe:S atomic ratios with depth based on different extraction techniques in sediment cores collected in September from upper Flaming Gorge.

Reservoir Station	Depth (cm)	CDB-Fe:NAI-P Ratio			CDB-Fe:S Ratio
		(1)	(2)	(3)	
LBF	0-2	6.9	11	5.7	2.8
	2-4	-	11	4.3	2.2
	4-7	9.8	11	4.9	3.8
	7-10	14.3	11	5.3	5.9
	10-13	<u>6.9</u>	<u>11</u>	<u>6.0</u>	<u>3.5</u>
	Average	8.6	11	5.3	3.8
UGR	0-2	7	24	16	6.7
	2-4	12	14	9	4.4
	4-7	10	15	12	4.5
	7-10	18	15	10	3.7
	10-13	<u>16</u>	<u>18</u>	<u>13</u>	<u>6.1</u>
	Average	12	18	12	5.0
LGR	0-2	8.9	-	-	-
	2-4	1.5	10	5.7	2.3
	4-7	9.4	10	6.2	4.3
	7-10	7.4	11	7.3	2.6
	10-13	<u>8.3</u>	<u>12</u>	<u>7.8</u>	<u>3.3</u>
	Average	7.3	11	8.2	3.7
BC	0-2	8.6	12	8.0	2.4
	2-4	7.9	10	6.6	1.4
	4-7	6.4	10	5.8	1.4
	7-10	8.1	10	5.3	1.5
	10-13	<u>10.3</u>	<u>10</u>	<u>6.0</u>	<u>0.8</u>
	Average	7.9	11	6.2	1.4

1 - Based on (30:1) wet extraction

2 - Based on Williams et al. (1971b) scheme "D" technique

3 - Based on Hieltjes and Lijklema (1980) technique

others, relative to the amount of NAI-P present. The ratio in Table 4.6 may actually underestimate the true labile Fe:S ratio by including some pyrite-S which would not be accompanied by the associated pyrite-Fe in the CDB extraction (Stauffer 1981). There is also no evidence of low Fe:S ratios in the surface 2 cm of sediment caused by decomposition of relatively S-rich algal detritus, as proposed by Stauffer (1981), and his sulfide intercept model apparently does not apply to these sediments.

Vertical profiles of Fe and P species also have been used by previous workers as indicators, both of mobility of the species near the sediment-water interface and of historical changes in the trophic state of the overlying body of water. Vertical profiles of CDB-P and NaOH-P concentrations in one of the August cores described above are shown in Figure 4.2. As in the cores from Canadian lakes described by Allan and Williams (1978), concentrations of CDB-P increase toward the sediment-water interface. The cores from the upper Green River, lower Blacks Fork, and below the confluence stations showed the largest gradients, while the cores from the lower Green River and upper Blacks Fork indicated little change in concentration with depth. NaOH-P concentrations exhibited generally lower values below 5 cm depth than in the surface 4 cm. Similar patterns were observed in the September cores, and the basic patterns were not altered by dry versus wet extraction methods.

Increasing CDB-P and NaOH-P concentrations toward the sediment-water interface in a core could result from increasing deposition of Fe-P complexes on the sediment surface over the period of time represented by the core sections studied. Similar NAI-P profiles have been observed in Canadian prairie lakes (Allan et al. 1980) and in Lake Erie (William et al. 1976b), where they also

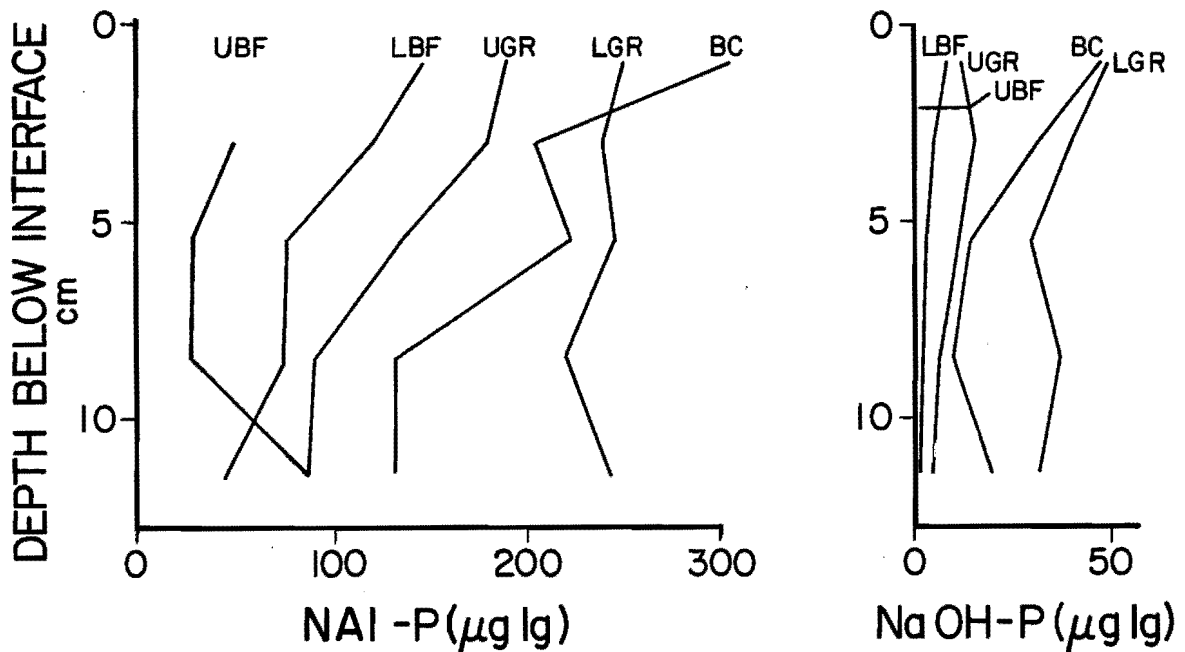


Figure 4.2. Concentration profiles of CDB-P and NaOH-P in sediment based on wet extractions of cores collected from upper Flaming Gorge Reservoir in August 1982.

were attributed primarily to increases in P deposition following settlement of the respective lake watersheds. At the present time, it is not known whether the time scale represented in the profiles in Figure 4.2 is measured in months or years.

Alternatively, if within the zone of active diagenesis, such a profile could result from the mobilization of P from the reducing zone deeper in the sediment, and subsequent trapping of the mobilized P by hydrous ferrosiferrous compounds in the oxidized interfacial zone. Fe and Mn concentrations also appear to increase toward the sediment-water interface, however, (Tables A.1, A.3, and A.4) and the CDB-Fe:NAI-P ratio does not decrease near the sediment-water interface (Table 4.6). These observations suggest that the increasing concentrations of NAI-P near the interface result from migration, rather than from recent increases in P loading to the sediment surface.

It is important to note, when interpreting these data, that the summer of 1982 was atypical of previous summertime conditions in the reservoir. While a substantial period of stratification, accompanied by zero dissolved oxygen and low Eh, typifies most late summertime conditions in the upper arms, in 1982 dissolved oxygen concentrations of < 1 mg/l were only observed during the August sampling trip at the lower Blacks Fork station (0.7 mg/l) and the lower Green River site (0.3 mg/l). Therefore, inferences based on 1982 concentration profiles may not be applicable to years in which low Eh conditions persist in the hypolimnion for two or more months.

Summary. In conclusion, the chemistry of the sediment cores collected from upper Flaming Gorge during the summer of 1982 are indicative of a calcareous sediment with a relatively low affinity for phosphorus. Although the numerical values are dependent on the extraction procedures used, all of the chemical data suggest a similar scenario. NAI-P concentrations are low in the Blacks Fork arm, but suggest the potential for moderate levels of P release from the sediments in the Green River arm and below the confluence. NAI-P concentrations are highly associated with labile Fe in all of the sediments, with considerably higher concentrations of Fe in the Green River arm of the reservoir. CDB-Fe: CDB-P ratios are similar to those found in deep Wisconsin lake sediments, and are somewhat lower than those found in other Intermountain reservoirs. The sediments are characterized by a labile Fe:S ratio of 1.8 to 2.5, which suggests moderately inefficient control of P by Fe under anaerobic conditions. In summary, the sediments in the Green River arm and below the confluence would be expected to readily release P from pools of NAI-P stored in the surface sediments as a result of inputs from spring runoff or senescing phytoplankton blooms. Lower internal loading rates would be expected in the Blacks Fork arm of the reservoir.

P Release Experiments

Factors affecting P equilibrium concentrations. Duplicate intact cores collected on August 17, 1982, from each of the sampling sites were incubated in the laboratory in order to determine the effects of various physicochemical parameters on the release or sorption of P by the reservoir sediments. Changes in the concentrations of soluble reactive P (SRP) with time in the water overlying the cores are shown in Figure 4.3. Aerobic cores are represented by solid lines and anaerobic cores by dotted lines. The symbols along the abscissa represent changes in incubation conditions, described below.

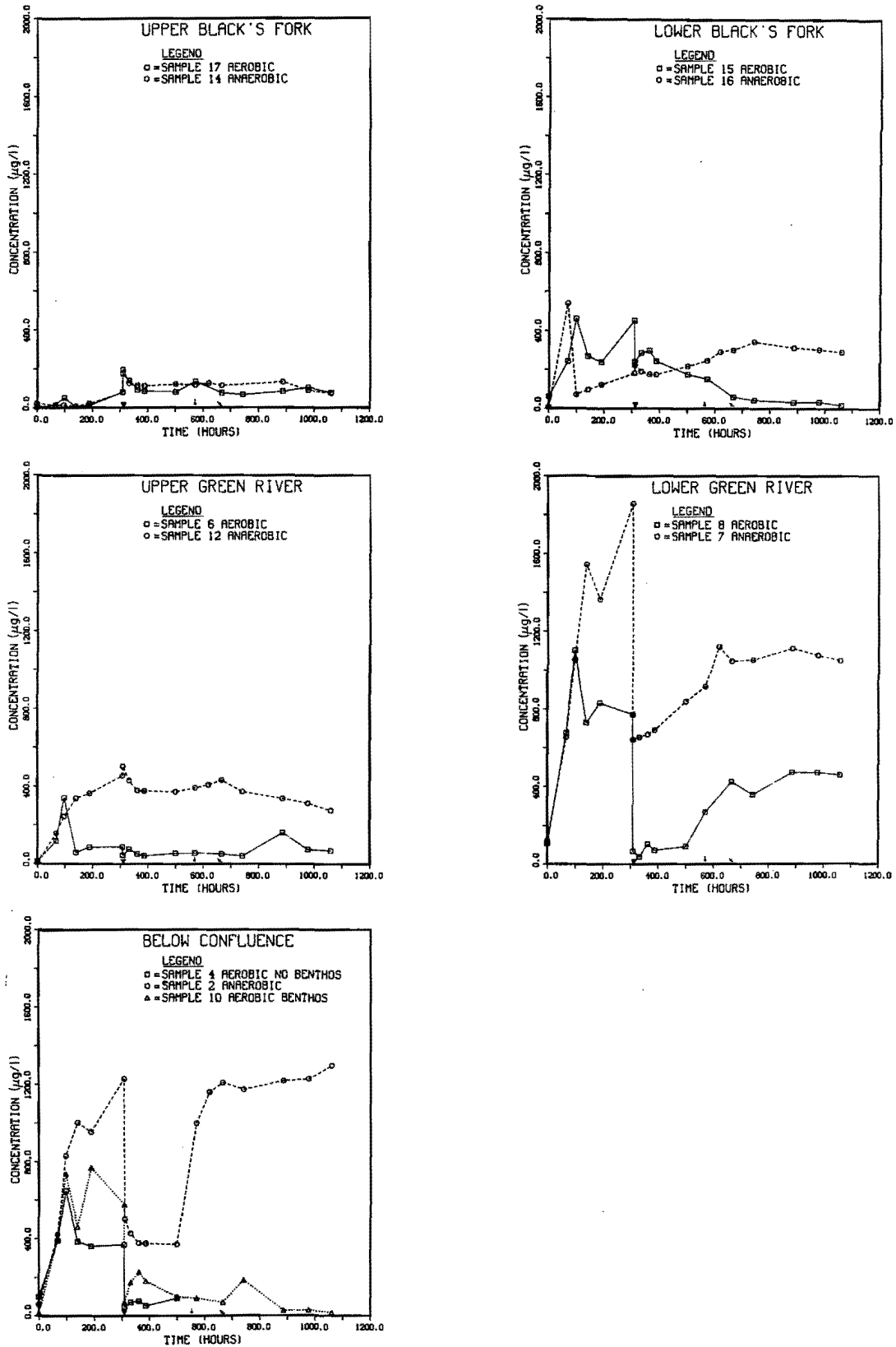


Figure 4.3. Changes in ortho-P concentrations with time in the water overlying August sediment cores incubated in the laboratory. (See text for an explanation of the symbols.)

Throughout the following discussion, it is important to note that at each sampling point, 6 to 10 percent of the SRP was removed from the system for analysis and the corresponding volume replaced with deionized water. Therefore, a constant concentration of P in the overlying water does not indicate the absence of P release, but rather the tendency of the sediment to maintain an "equilibrium" or "crossover" concentration in the overlying water (sensu Mayer and Gloss 1980). Although true equilibrium may not have been reached during the incubations described below, the term "equilibrium concentration" will be used for convenience. Rates of P release will be discussed below.

During the course of the incubations, several perturbations took place. In order to determine whether P accumulation in some of the systems was inhibiting P release, the original reservoir water in each of the cores was replaced with a synthetic water made up to resemble the late summer major ion chemistry of either the Blacks Fork arm (UBF and LBF) or the Green River arm (UGR, LGR, and BC) of the reservoir. Nitrate (2.4 mg N/l) was included in the Blacks Fork water but not in the Green River water, inasmuch as no nitrate was found in field samples from the Green River during the summer of 1981. The presence of nitrate has been shown to inhibit P release from anoxic sediments by poisoning the redox potential above that required for Fe(III) reduction (Bostrom and Pettersson 1982, Andersen 1982). The artificial water contained no phosphorus. Other perturbations included changing the incubation temperature of the anaerobic cores from 21° to 4°C at 570 hr, and increasing the stirring rate from 4 to 10 rpm in the aerobic cores at 665 hr.

The most striking aspect of the P concentrations in the water overlying the cores was the difference between the Blacks Fork cores and those from the other stations. P concentrations in the UBF system were typically below 200 µg/l, and aeration had virtually no effect on P concentration. The LBF cores maintained a P concentration of generally less than 400 µg/l, with the concentration decreasing with time in the aerobic core and increasing in the anaerobic system. The UGR aerobic core maintained a low concentration of P throughout the incubation (50-100 µg/l), but the anaerobic core maintained a relatively constant 400 µg/l concentration. The cores from LGR and BC showed considerably greater equilibrium P concentrations than those from the other stations. In the LGR cores, P concentrations ranged as high as 1860 µg/l in the anaerobic cores and 1100 µg/l in the aerobic cores. The concentrations in the paired cores followed very similar patterns, but with the anaerobic core maintaining a concentration approximately twice that in its aerobic counterpart. The P concentration in the anaerobic BC core was similar to that in LGR system, except during the initial 308 hr period, during which it was somewhat lower.

Two cores from below the confluence were incubated aerobically. Core 4 is a true duplicate of the anaerobic Core 2, and maintained a P concentration of somewhat less than half of its anaerobic counterpart. Core 10 was actually taken downstream from the other two cores and was unique in that it contained tube-building benthos at its surface. The sediment surface was much more consolidated at this location than at the slightly upstream site, which from sonar traces appeared to represent sediment trapped by a submerged sill. Although Core 10 is not, therefore, a true replicate of Core 4, it appears that the benthic fauna were capable of increasing the equilibrium P concentration relative to its macroinvertebrate-free counterpart. This would echo the findings of Gallep (1979), Holdren and Armstrong (1980), and Gardner et al. (1981), who found that benthic macroinvertebrates greatly enhanced P release rates from oxic sediments.

Replacing the natural water with the P-free artificial water had little effect on the Blacks Fork or upper Green River systems. The absence of a drastic drop to very low levels of P probably is attributable to the inability to exchange the water in the systems without entraining part of the sediment-water interface. Such behavior suggests that equilibration between the sediments and overlying water would be quite rapid in the presence of moderate turbulence at the interface. Exchange of the water in the LGR and BC cores resulted in a substantial initial decrease in P concentrations, but only in the case of the aerobic cores did the concentration return to the low initial values typical of the start of the experiment. In the LGR core, the equilibrium P concentration never returned to its high level of the first 308 hr of incubation. Although the same was true for the BC aerobic cores, the anaerobic core regained the 1200 µg/l concentration typical of the initial incubation period.

The final two perturbations appeared to have had little, if any, effect on the equilibrium P concentrations. Based on the work of Holdren and Armstrong (1980) it was anticipated that lowering the incubation temperature to 4°C would greatly decrease the equilibrium P concentrations, especially in the UGR and BC cores, where the P concentration in the water was high. Although a small decrease in the equilibrium concentration may have occurred in UBF, LBF, and UGR, the equilibrium concentrations appear to increase, if anything, in the LGR and BC cores. Stirring rate over the range examined here appeared to have no effect on P concentrations. The higher rate used here was insufficient to suspend sediment in the water column, unlike the higher rates used by Holdren and Armstrong (1980).

In addition to the P data collected on a routine basis during the incubations, Fe, Mn, and S data were collected on the water removed from above the various cores at 308 hr. These data are presented in Table 4.7. There were substantial concentrations of Fe in the water overlying the anaerobic core from the Green River arm, while the concentrations in the water overlying the Blacks Fork arm cores were quite low. The concentration was intermediate in the BC anaerobic core. The Mn concentration patterns were similar to those exhibited by the Fe concentrations, except that the order of the concentrations in the BC and UGR cores were reversed, and substantial increases occurred between aerobic and anaerobic cores, even in the Blacks Fork arm cores. These results could indicate that the Eh at the sediment-water interface was sufficiently low in all of the anaerobic cores to release Mn, but only low enough to release Fe in the Green River arm cores. Alternatively, the low concentrations of Fe in the UBF and LBF cores may simply represent the lower availability of extractable Fe in these sediments (cf. Table 4.1).

No sulfide was detectable with a silver/sulfide ion-selective electrode in the water overlying any of the cores. If the water in the anaerobic cores had an insufficiently low Eh to maintain sulfide in solution, any sulfide that was released could have been oxidized and thus escape detection. However, there was also no evidence for increased sulfate concentrations in the aerobic cores relative to their anaerobic counterparts (Table 4.7). The sulfate concentrations in the water overlying the cores generally decreased in conjunction with the corresponding total S concentrations characteristic of the sediments at the various sites (Table 4.1), with the exception of the site below the confluence. These data suggest that sulfate concentrations in the overlying water are controlled by equilibrium with sulfate in the interstitial water, but that any sulfide formed is maintained within the sediments by the stoichiometric excess of

Table 4.7. Concentrations of various constituents in the water overlying sediment cores from Upper Flaming Gorge 308 hr after beginning the incubations.

Core Station	Constituent Concentration ($\mu\text{g/l}$)				
	Iron	Manganese	Sulfide	Sulfate	SRP
UBF					
Aerobic	20	10	0.00	18,100	81
Anaerobic	40	200	0.00	520	78
LBF					
Aerobic	20	10	0.00	6,000	183
Anaerobic	20	420	0.00	7,500	453
UGR					
Aerobic	60	10	0.00	4,200	89
Anaerobic	380	640	0.00	2,500	455
LGR					
Aerobic	30	60	0.00	3,200	772
Anaerobic	550	>1600	0.00	4,700	1,858
BC					
Aerobic	60	30	0.00	10,500	370
Anaerobic	110	920	0.00	7,600	1,230

Fe noted in the discussion of Table 4.6. The differences in sulfate between aerobic and anaerobic cores from UBF, UGR, and BC may be the result of sulfate production.

P release rates. Rates of P release from the various cores under the different incubation conditions are tabulated in Table 4.8. The rates are expressed on the basis of $\text{mg P/m}^2\text{-day}$ for comparison with the data of other workers. The data have also been aggregated on the basis of the first two incubation periods (before and after changing the overlying water) and the entire 1058 hr incubation period.

The relative magnitudes of the release rates are similar to the corresponding equilibrium concentration data presented in the previous section. Oxidic release rates ranged from 0.47 to 4.47 $\text{mg P/m}^2\text{-day}$, with the highest rates associated with LGR and BC. The benthic invertebrates in BC raised the release rate by a factor of 2 over the BC core without invertebrates during the initial incubation period. Aerobic release rates decreased with time during the second and third incubation periods in all cores, becoming very near zero for all but the LGR core. It is not known whether the decrease in activity in the BC core containing the invertebrates resulted from their death, or from depletion of the labile P pool in the sediment. It appears likely that any change in release rate during the final incubation period was brought about by depletion in the labile P pool in all of these sediments, rather than by the concomitant change in the stirring rate.

Table 4.8. Ortho-P release rates from intact cores from Upper Flaming Gorge Reservoir incubated in the laboratory under aerobic and anaerobic conditions (mg P/m²-day).

Reservoir Station	Averaging Interval (hr)									
	Aerobic					Anaerobic				
	0-308	308-665	665-1059	0-665	0-1059	0-308	308-570	570-1059	0-570	0-1059
UBF	0.47	-0.23	0.24	0.09	0.10	0.61	-0.33	0.14	0.18	0.16
LBF	2.1	-0.13	-0.05	0.89	0.53	2.85	1.24	1.22	2.11	1.70
UGR	0.56	-0.14	0.19	0.18	0.17	4.78	0.73	0.46	2.92	1.78
LGR	4.47	1.65	0.72	2.96	2.11	25.55	7.22	4.12	17.12	11.1
BC ¹	2.45	0.60	*	1.46	1.46 ³	13.74	7.45	5.19	10.8	8.24
BC ²	4.45	0.28	-0.13	2.21	1.23					

¹No benthos

²Benthos present

³Core sacrificed, value for BC² 665-1059 hr period used to calculate 0-1059 hr mean

Anaerobic release rates were generally much higher than the corresponding aerobic release rates, especially in the Green River arm and below the confluence. During the initial incubation period, P release decreased in the order LGR>BC>UGR>LBF>UBF. This pattern was similar to the order observed for aerobic release, except that LBF and UGR were reversed. Some possible reasons for the differences in release rates are considered in the following section. Release rates declined during the second and third incubation periods, but not as sharply as in the aerobic simulations. LGR and BC continued to exhibit substantial release rates into the final incubation period. Although it is difficult to separate the effects of P depletion and temperature, it appears that the P release rate may have declined somewhat in response to the decreased temperature.

The release rates observed during the simulations fall into the low to medium range of the rates observed in the laboratory simulations of Holdren and Armstrong (1980), who found rates as high as 83 mg P/m²-day in short (2 day) incubations. These authors generally observed lower release rates (1-10 mg P/m²-day) in longer (10-27 day) incubations of sediments from the same lake. Actually, long term incubations may be more appropriate for determining release from sediments more or less isolated from detrital inputs following stratification, while short term incubations may be more useful in estimating dynamic regeneration rates from a sediment receiving inputs of senescent phytoplankton from the epilimnion. The relationship between release rates during an incubation and internal loading from reservoir sediments depends on the factors driving P release in situ.

If internal P release is driven primarily by relatively labile detritus settling on the sediment surface, then release rates are best measured using short incubations. However, these releases represent P already accounted for in whole-lake mass balance, at least on an annual basis. In this case, short incubations would be misleading in estimating the internal loading that would occur if P inputs to the lake or reservoir were decreased. If the supply of P to the water column from external sources were decreased, less biomass would sediment out, and the pool of P available for internal loading would decrease. Such releases may be important, however, in delaying the availability of P in spring runoff until warmer water favors the growth of blue-green algae in late summer.

Conversely, if water column inputs of detritus were minimized during an incubation, internal P loading from the sediments would be limited to the pool of labile P stored in the sediments during previous periods when the lake acted as a P trap. In the latter case, a long term incubation, with detrital P supplies excluded, would offer a more meaningful estimate of internal P loading following reduction of upstream P inputs. This is the approach aimed for in the simulations reported here. Unfortunately, we were forced to begin with a finite detrital P pool at the beginning of the incubation because the summer algal bloom was already underway when the sediment cores used for the incubations were collected. If the sediments were collected earlier, however, the detrital P pool may have originated largely from inputs of organic P associated with spring runoff, and thus already may have been accounted for in the P loading budget of the reservoir. Similar incubations comparing release rates as a function of season would be helpful in revealing the relative importance of detrital P of recent origin versus sediment P derived from inputs from previous years.

If the entire incubation period is considered to represent the release of P from an initial detrital P supply plus some historical P available in the

sediment, the values in Table 4.8 can be compared to summertime internal P loading measured by seasonal P budget for other lakes. As pointed out in Chapter 2, rates of approximately 6-8 mg P/m²-day have been responsible for the continuation of eutrophic conditions in Shagawa Lake, Minnesota, despite the virtual elimination of P loading from the municipal wastewater input to the lake (Larson et al. 1981). The importance of the release rate in terms of the total P budget must be interpreted in light of the contributing sediment surface area, the lake volume and residence time, and the effectiveness of P transport across the thermocline (e.g. Stauffer 1981). Nonetheless, the anoxic P release rates from LGR and BC of 8-11 mg P/m²-day are sufficiently high to justify their consideration in a P budget for the reservoir, especially if the effectiveness of a management scheme to lower summertime, rather than annual, P inputs to the upper reservoir is to be considered.

Two factors in these experiments may result in some underestimation of the true rate of P release in situ by decreasing the concentration gradient of ortho-P between the interstitial water and the overlying water column, relative to that in the bottom waters of the reservoir. Typical values for dissolved P and Fe species during summer stratification at stations LGR, LBF, and BC (based on 1981 data) are displayed in Table 4.9. Concentrations of ortho-P in the bottom water were highest in August, with the highest value (530 µg/l) occurring at LBF. Otherwise, typical concentrations were on the order of 10-200 µg/l. These values are in

Table 4.9. Concentrations of dissolved Fe, Mn, and ortho-P (mg P/l) in bottom water overlying the sediments of Upper Flaming Gorge Reservoir during summer, 1981.

Date		Reservoir Station			
		BC	LBF	UGR	LGR
Aug. 1981	Fe	0.30	0.60	0.30	
	Mn	0.25	0.26	0.06	
	Ortho-P	0.33	0.53	0.18	
Sept. 1981	Fe	0.20	0.70	0.80	0.90
	Mn	0.08	0.05	0.04	0.52
	Ortho-P	0.09	0.07	0.17	0.21
Oct. 1981	Fe	0.40	0.30	0.50	
	Mn	0.04	0.05	0.07	
	Ortho-P	0.08	0.01	0.08	

contrast to the 450-1860 µg/l equilibrium P concentrations attained by the cores under anaerobic incubation (Table 4.7). Although the incubations consequently underestimate P release rates later in the incubations, when P concentrations in the overlying water approach the equilibrium concentration for the particular sediment, it is not known how depletion of the labile pool of P driving the release may affect the rate. Experiments are now under way to design a chemostatic incubator that will maintain a desired concentration of ortho-P in the overlying water.

Another potential problem is uptake of P from the water overlying the cores by attached microbial communities growing on the sides of the core tubes. P release of the magnitude measured in these experiments could have resulted in a standing crop biomass of approximately 150 to 750 mg wet weight, assuming the

biomass was 0.1 percent P on a wet weight basis (Jorgensen et al. 1981, Messer et al. 1983). No visible growths were observed on the tube walls during the experiment, however, and thus the calculations above suggest that any such uptake could only account for a small fraction of the total P released.

Relationships between sediment chemistry and P release rates. Because of the problems with extrapolating P release rates determined in laboratory simulations to field conditions, the information that is ultimately sought in studies such as those reported here is identification of the sediment P pools that drive P release from a particular sediment. Correct identification should lead to an understanding of how factors such as temperature and redox conditions will likely affect release rates, and consequently, which reservoir management practices are most likely to reduce internal P loading. It also would be extremely useful to have an easily analyzed "indicator" fraction of sediment P that could be used to predict whether a particular sediment is likely to act as a significant source of P to the overlying water under a given set of conditions.

It is important to note at the outset that a P-release "indicator" need not be universally applicable to be useful. Bostrom and Pettersson (1982) found several distinct "types" of sediments in the Scandinavian lakes that they studied, based on their behavior in binding and releasing P in laboratory studies. It is likely that some sediments control P release primarily through the redox-associated binding by Fe oxyhydroxide gels, as discussed above (e.g. Shukla et al. 1971). In other sediments, P release may be controlled by the rate of biological oxidation of organic P (e.g. Kamp-Nielsen 1977), while in still others, release may be controlled by ion-exchange reactions with clays (Mayer and Gloss 1980) or the solubility of calcium phosphate minerals (Williams and Mayer 1972). However, it is logical to expect the sediments within a particular lake or drainage basin to have similar geochemical controls operating on P binding and release, at least as an initial hypothesis. Therefore, the approach taken here was first to search for correlations between the P release rates measured in the laboratory simulations, and the various P fractions found in the different extraction techniques described above.

Pearson correlation coefficients were calculated for P release rates and P fractions determined using wet extractions of cores taken from the same station. Coefficients were calculated for all three release periods (cf. Table 4.8) and aggregations of these periods using the PEARSON CORR subprogram of SPSS (Nie et al. 1975). The choice of the release period was not found to significantly affect the correlation coefficients, and so only the coefficients for the entire 45 day release experiment are presented (Table 4.10). For station BC the value for P release of the core without benthic invertebrates was used for the first two incubation periods, and the results from the core with invertebrates were used for the final incubation period because the former core was sacrificed at the end of period two.

High correlations were observed between both aerobic and anaerobic release rates and the NaOH-P concentrations in the cores from the different stations ($P < 0.01$). Because extractable P in the surficial layers of sediment could be expected to control the release rates more than the deeper strata, correlations also were calculated for the upper 2 cm and the upper 4 cm of sediment. Changes in the correlation coefficients were minimal, however, probably because the variability among sediment layers in a single core was small relative to the

variability among cores. These results thus should not necessarily be interpreted as close involvement of deep (>4 cm) strata in P release. Correlations between the NAI-P concentrations and P release rates were considerably lower than those for NaOH-P. Whole-core values gave higher correlations than did 0-2 or 0-4 cm averages, and anaerobic release was much more highly correlated with NAI-P than were the corresponding aerobic release rates. Phosphorus data from all cores were combined because CDB-P was not measured on the August cores, themselves, and because the small changes observed in the NaOH-P cores on the three dates was felt to be small enough to justify the resulting increase in precision gained by pooling data. In fact, the correlation coefficient for anaerobic P release was identical ($r=0.98$) for NaOH-P determined on the August cores alone to the value shown in Table 4.10.

Table 4.10. Pearson correlation coefficients (r) for aerobic and anaerobic P release from Flaming Gorge sediment cores as determined in 45 day laboratory incubations and selected extractable P concentrations based on wet extractions. (n=5 for all cases.)

Phosphorus Parameter	Release Rates	
	Aerobic	Anaerobic
NaOH-P:		
Upper 13 cm	0.9517 P=0.006	0.9829 P=0.001
Upper 2 cm	0.9501 P=0.007	0.9812 P=0.002
Upper 4 cm	0.9430 P=0.008	0.9828 P=0.001
CDB-P:		
Upper 13 cm	0.7304 P=0.081	0.8095 P=0.048
Upper 2 cm	0.7269 P=0.137	0.8152 P=0.092
Upper 4 cm	0.6530 P=0.116	0.7283 P=0.081

Unfortunately, only the September cores were analyzed for all of the fractions in the Hieltjes and Lijklema procedure. However, the high between-station variation in the cores, relative to the within-station variation, may allow realistic conclusions to be drawn based on correlations between P release from the August cores and the P concentrations based on the more complete extractions of the September cores. The resulting correlations, based on the data in Table 4.2, are shown in Table 4.11. Only correlations with a probability value of 0.05 or less are shown. Again, high correlations were found between P release rates under both aerobic and anaerobic conditions and NaOH-P and its associated parameters. The relationship holds for both extraction procedures, although the correlations are higher for the Hieltjes and Lijklema technique. As in the correlations based on the wet extractions, correlations with anaerobic release were higher than with aerobic release. Although the small number of data points prevents a conclusive analysis, the correlations based on NaOH-P alone are higher than those based on NaOH-P plus $\text{NH}_4\text{Cl-P}$ (exch-P), NAI-P, or the sum of organic P added to any of the above fractions. Correlations based on $\text{NH}_4\text{Cl-P}$, organic P, or apatite P were considerably lower for anaerobic release than were those based on

the Fe-P fractions. Aerobic release rates correlate more closely with organic P, as would be expected, but the correlation coefficient is still higher for the NaOH-P fraction in the Hieltjes and Lijklema extraction procedure.

The results of the various NaOH-P/P-release correlations are displayed graphically in Figure 4.4. It is apparent that there is a decreasing, negative Y-intercept associated with the wet, scheme "D", and Hieltjes and Lijklema P values, respectively. It is tempting to speculate that the value of NaOH-P at the X-intercept represents the value for this P pool in the sediment that would have been in equilibrium with the overlying water in the core tubes during the release experiments. The corresponding value would have been 0.10, 34, and 182 mg/kg for the wet, scheme "D", and Hieltjes and Lijklema procedures, respectively.

Table 4.11. Pearson correlation coefficients (r) between various P fractions in the dry extraction procedures and P release rates in laboratory simulations. Only coefficients with $P < 0.05$ are shown; $n=4$ for all cases.

	Aerobic Release	Anaerobic Release
NaOH-P ₁	0.8803 P=0.060	0.9189 P=0.041
NAI-P ₁	0.8298 P=0.085	0.9348 P=0.033
NaOH-P ₂	0.9822 P=0.009	0.9967 P=0.002
Total P	0.9392 P=0.030	0.9467 P=0.027
EXCH-P	0.9130 P=0.044	0.9261 P=0.037
NAI-P ₂	0.9293 P=0.035	0.9620 P=0.019
ORG-P ₂	0.9539 P=0.023	

1 = Scheme "D", Williams et al. (1971b)

2 = Hieltjes and Lijklema (1980).

The poorer correlations between P release and some of the other P fractions probably result, to some extent, from the higher coefficient of variation associated with the corresponding analytical determinations. For example, the coefficient of variation was 6 percent for high-P cores using the wet extraction, compared to 23 percent for CDB-P (NAI-P), Appendix B. Similarly, CDB-P was near the lower detection limit in the Hieltjes and Lijklema extraction, and organic P is based on the difference between total P and the sum of several values, each with their own uncertainty. Nonetheless, it would seem reasonable to expect that non-occluded P (measured by the NaOH/NaCl extraction procedure) would be more easily released from an Fe-P complex than would its occluded (CDB-extractable) counterpart, and also that the Fe-P fraction, rather than the relatively small counterpart, and also that the Fe-P fraction, rather than the relatively small amount of organic P in these sediments, would be the primary factor controlling P release from the upper Flaming Gorge sediments, regardless of their location in the reservoir. It would also seem reasonable to expect that the NaOH-P fraction maintain an equilibrium interstitial P concentration that drives the Fickian diffusion of P out of the sediment. This relationship is apparently not reflected

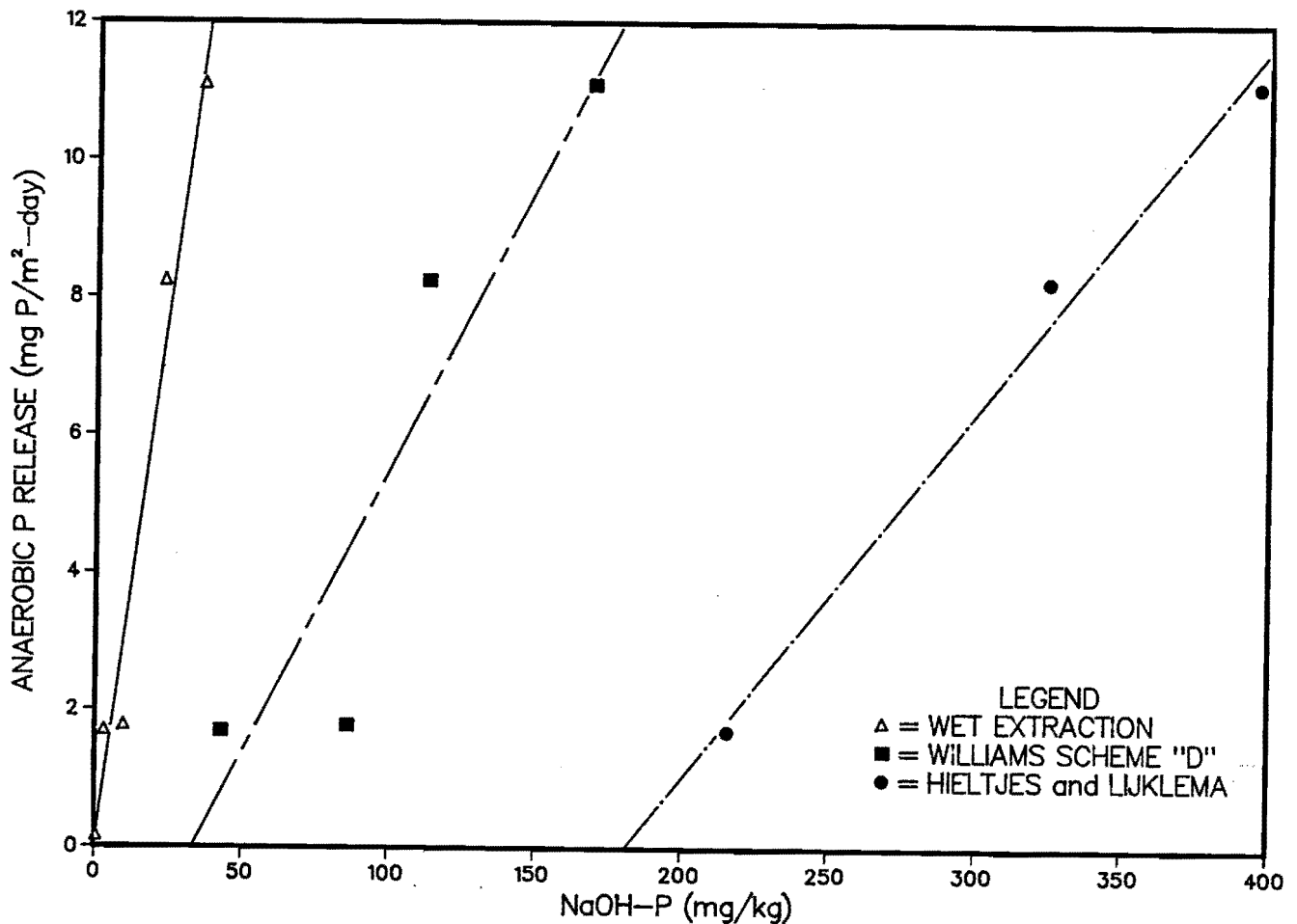


Figure 4.4. Best fit linear regression models for the relationship between NaOH-P concentrations determined using various incubation procedures and anaerobic P release (25°C) from intact sediment cores taken at the same reservoir stations.

in the "exchangeable P" represented by the NH_4Cl extraction, however. It is not clear whether the organic P, rather than the Fe-P fraction, controls aerobic release, as might be expected from the immobility of hydrous oxide Fe gels under aerobic conditions. In any event, the rates of the corresponding aerobic release are apparently low from these sediments.

If the concept of NaOH-P, or non-occluded Fe-P, as the driving force behind anoxic P release can be extended to similar sediments, it is even more useful than release estimates based on interstitial P concentrations. Problems with sampling interstitial water (e.g. Emerson 1976) and with choosing the appropriate end members for a Fickian diffusion model (e.g. Kamp-Nielsen 1977) often make such release calculations difficult, if not unreliable (Messer and Brezonik 1983). Prentki (1976) has speculated that the removal of different P forms by the reagents used in the various extraction procedures may not identify discrete mineral fractions, as much as it identifies a continuum of binding sites of increasing strength on the same amorphous and heterogeneous sediment-P complex. The results reported here neither contradict nor confirm that hypothesis, but they

do suggest that the majority of the Fe-associated P in the upper Flaming Gorge sediments belongs to the P fraction normally associated with non-occluded Fe-P, and that P release from these sediments is enhanced by anaerobic conditions and accompanied by the loss of Fe, according to the classical model of Mortimer (1941, 1942). This conclusion holds, somewhat surprisingly, despite variations in the apparent concentration of the NaOH-P fraction in the sediment based on the different extraction schemes (e.g. Figure 4.4).

Finally, it is important to note that this pool of NaOH-P probably should not be thought of as a "tank" of P to be emptied before a reservoir can be spared from internal P loading, but as a compartment providing the driving force for the diffusion of P into the overlying water. This is important, because the top 2 cm in the sediments represented in the laboratory release studies contain approximately enough P to supply the overlying water with phosphorus equivalent to a year of release at the rates reported in Table 4.8. It is likely, however, that the release rate will decrease as the size of the NaOH-P pool in the sediment decreases, even if the P in the overlying water is well below the "equilibrium" concentration.

Summary. The laboratory simulations indicated that the sediments of the Green River arm of Flaming Gorge Reservoir are capable of maintaining a higher equilibrium P concentration and releasing more P per unit time and area than their Blacks Fork arm counterparts. Within a given arm, equilibrium P concentrations and release rates increased in a downstream direction, with the station below the confluence appearing to show intermediate characteristics between the two arms. Equilibrium P concentrations were greater than 1 mg/l under anaerobic conditions, and release rates higher than 8 mg/m²-day at the lower Green River and below-confluence stations.

Release rates were strongly affected by the presence of oxygen, NaOH-P concentrations in the sediment cores, and the presence of benthic invertebrate fauna. Anaerobic release rates were 3-10 times higher than aerobic rates, and a core containing a benthic invertebrate fauna collected below the confluence exhibited release rates almost twice as high as its counterpart without benthos during the first 2 weeks of incubation. Both aerobic and anaerobic release rates were highly correlated with NaOH-P concentration in the cores, regardless of the extraction procedure used. Correlations with CDB-P and organic P were lower, but correlations with exchangeable and apatite P were insignificant. These observations suggest that P release is controlled by short-range order Fe-P complexes in which P is held primarily in surficial positions on the complex, at least under anaerobic conditions. Organic P may be more important in regulating P release under oxygenated conditions at the sediment-water interface.

Bioavailability of P Forms

Bioavailability of sediment P can be thought of in two different but related ways. Ortho-P released from the sediments via diffusion or bioturbation is readily available to phytoplankton as soon as it can be transported to the euphotic zone. Alternatively, P bound to sediment particles can be transported to the euphotic zone by turbulent transport of the surficial sediments. Once in contact with the phytoplankton community, some fraction of this P becomes available via mechanisms that are, as yet, poorly understood. The bioassay work of Sagher (1976) and Williams et al. (1980b), among others, has indicated that

the NaOH-extractable P corresponds most closely to the particulate fraction of this bioavailable P (Syers et al. 1982). It would also seem reasonable that the P nearest the surface of particles and least occluded by oxyhydroxide coatings would be the most readily available fraction for reaction with the phosphatases produced by the phytoplankton.

Because much of the sediment P in calcareous sediments may play an insignificant role in phytoplankton growth (eg. Williams et al. 1980b), it would be worthwhile to identify the fraction most closely associated with algal availability. Both aspects of bioavailability noted above are of interest. Availability of particulate P is likely to be more important during spring runoff and during high discharge periods associated with summer thunderstorms, while P release across the sediment-water interface is of more significance during summer stratification. Bioavailability in the first sense can be approximated through the use of algal bioassays in which the sediment is allowed to remain in contact with the test alga. Bioavailability in the second sense has been demonstrated to be closely associated with NaOH-P in the previous section.

Algal bioassays were conducted following the EPA AAP protocol (Miller et al. 1978) using the surficial 2 cm of sediment from each of two sediment cores collected on the August sampling trip from stations LBF and LGR. The sediments were slurried into 350 ml of deionized water, and aliquots of the slurry introduced into triplicate bioassay flasks inoculated with Selenastrum capricornutum Printz. We initially hoped to avoid autoclaving the sediment extract in order to prevent any unforeseen conversions in sediment P fractions. However, after 36 hr of incubation, microscopic examination of the cultures indicated that native diatoms might be successfully competing with the test algae. Consequently, the cultures were autoclaved and reinoculated with Selenastrum. The small amount of growth in the cultures at 36 hr was insufficient to have significantly affected the pool of bioavailable P in the cultures. The results of the two bioassays, with $t=0$ associated with the reinoculation following autoclaving, are presented in Figure 4.5.

Several differences are apparent in the two bioassays. The first is the significantly higher standing crop of algae produced by the LGR sediment. Even the unamended sediment slurry from LGR produced a higher standing crop than the LBF sediment amended with 50 $\mu\text{g}/\text{l}$ of ortho-P. The second difference is that, although both slurries indicated P-limitation of standing crop, the LBF sediment responded to amendment with nitrate and with EDTA. The nitrate response indicates a better stoichiometric balance of available N and P in the LBF sediments than the LGR sediment. Although enhanced growth in the EDTA-amended cultures is frequently attributed to detoxification of heavy metals in the water sample (Miller et al. 1978), it is also likely that EDTA increases the availability of apatite-P by complexation of the calcium ions associated with the mineral. Such a scenario would be consistent with the geochemistry of the Colorado Plateau drained by Blacks Fork, which includes the apatite-rich Park City Formation (Wardlaw et al. 1980). Apatite-P is apparently less significant in the Green River arm of the reservoir.

Although there are several methods of calculating the availability of P in the AAP procedure, all are fraught with some experimental difficulty. The preferred approach is to determine the maximum biomass of the cells produced and to convert this to standing crop P on the basis of the empirically derived P fraction of P-starved algae. This procedure entails either an ash-free dry weight

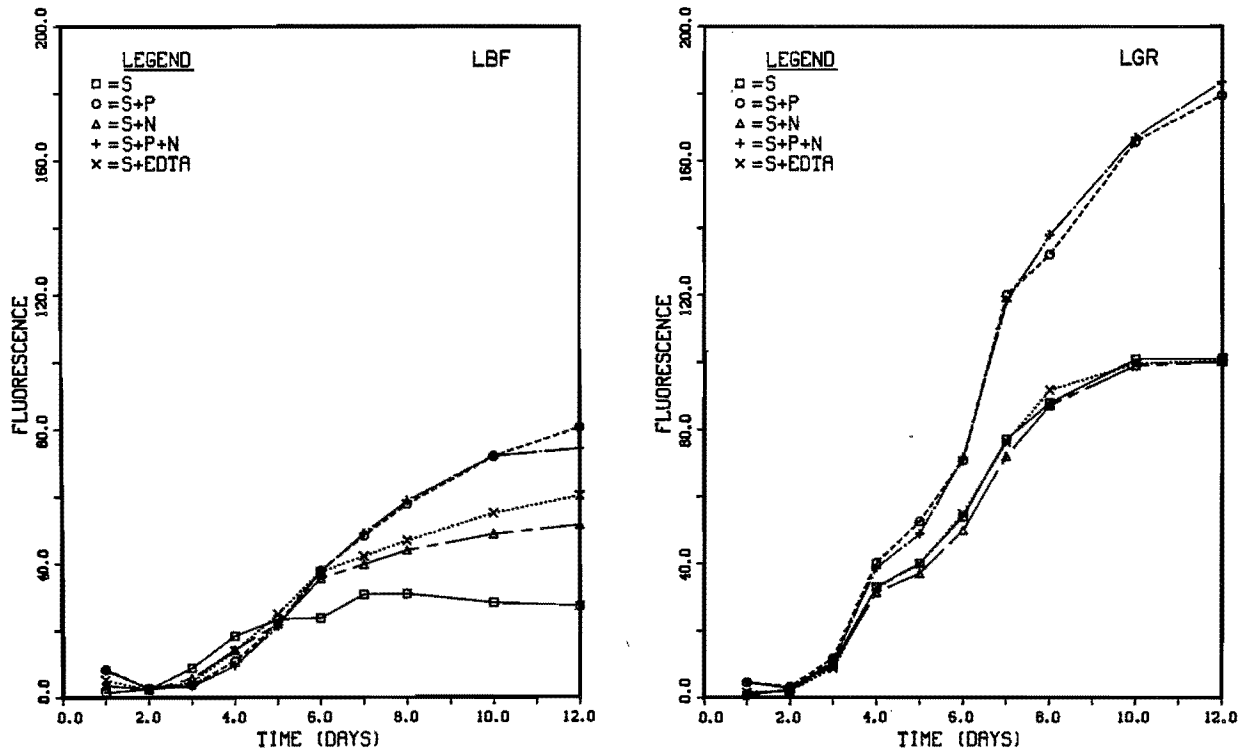


Figure 4.5. Growth of *Selenastrum* as measured by corrected fluorescence in response to a slurry of surficial sediments (S) collected from sites LBF and LGR in August 1982, and to amendment of the slurry with P, N, and EDTA.

determination on each culture at the time of maximum standing crop, or determination of the biovolume by solid geometric calculations based on microscopic examination or particle counting. The first technique is unsatisfactory for cultures containing a substantial fraction of the suspended solids in the form of the test sediment. The latter technique is crude and time-consuming. We have found that the *in vivo* fluorescence of the culture offers a reasonably fast and accurate proxy for standing crop biomass, at least within a given experiment and in the absence of toxic substances that depress the chlorophyll:biomass ratio or the specific fluorescence of the chloroplasts themselves.

The standing crop P in biomass can thus be calculated (for the case of P-limitation) by solving two simultaneous equations for the relationship between P concentration and relative fluorescence for the sample alone and the sample

amended with 50 µg/l ortho-P at the time of maximum standing crop. The resulting equations for the two incubations are:

$$\begin{array}{l} .i \ 10 \\ \quad P \quad \quad 27.2 \quad \text{LBF} \quad \quad \quad (4.1) \\ .i \ 10 \\ 0.05 + P = 80.5 \end{array}$$

$$\begin{array}{l} .b \\ .i \ 10 \\ \quad P \quad \quad 101 \quad \text{LGR} \quad \quad \quad (4.2) \\ .i \ 10 \\ 0.05 + P = 179 \end{array}$$

Solution of the above equations leads to the results shown in Table 4.12. Also shown are the concentrations of ortho-P, NaOH-P, and CDB-P in the unamended sediment suspensions as determined by wet extraction of the respective sediment slurries.

It is apparent that the bioavailability of the sediment P to the test alga is greater than the ortho-P and much less than the CDB-P fraction. In each case, however, the bioavailable P appears to be in excess of the NaOH-P by a factor of 55-120 percent. Although this finding would appear to be in contrast to the close correspondence between NaOH-P and bioavailability found by Sagher (1976) and Williams et al. (1980), the discrepancy is undoubtedly due to the low extraction ratio used to determine NaOH-P, which was determined to be approximately 1:30 on a dry-weight basis. This ratio has been shown to underestimate NaOH-P and NAI-P by severalfold, compared to the procedure normally used by Williams et al. (1980b). Therefore, the "true" NaOH-P concentrations may have been closer to 125 and 250 µg/l for the LBF and LGR cores, respectively. Similar values for the NAI-P

Table 4.12. Concentrations of various forms of P in algal assay cultures of surficial sediment slurries from Upper Flaming Gorge Reservoir.

Reservoir Station	P Form	Concentration µg P/l
LBF	Ortho-P	8
	NaOH-P	12
	CDB-P	148
	Available AAP-P	26
LGR	Ortho-P	21
	NaOH-P	42
	CDB-P	340
	Available AAP-P	65

fraction may have been approximately 230 and 700 µg/l, respectively. Although the higher values suggest that NaOH-P overestimates the P available to phytoplankton through sediment suspension, the proportional relationship between this fraction and algal-available P in the bioassays suggest that NaOH-P may control aerobic P release, as well as anaerobic release, as suggested by the laboratory simulations discussed above.

Summary. EPA AAP bioassays conducted on slurries of the surficial 2 cm from sediment cores collected at LBF and LGR indicated closest correspondence between available P and NaOH-P. However, the finding that the 30:1 extraction ratio

underestimates the "true" NaOH-P concentration in the sediment suggests that algal-available P is some fraction of the NaOH-P concentration. The bioassays also indicated available N was adequate to support the additional algal growth resulting from the 50 µg/l ortho-P amendment in the LGR culture, but that the LBF core indicated a closer stoichiometric ratio of available N to P, and perhaps more significant inputs of apatite-P. The proportionality between NaOH-P in the sediments and both particulate P bioavailability and ortho-P release from intact cores, lend support to the utility of this parameter in tracking temporal changes in P in the reservoir sediments, as well as indicating a potential causal link between P bioavailability and the chemical nature of the Fe:P complex.

A Conceptual Model for P Interactions with Sediments in Upper Flaming Gorge Reservoir

Although incomplete and tentative in nature, the studies reported here allow us to conceptualize a hypothetical model to describe the interaction of P with sediments in upper Flaming Gorge Reservoir. The purpose of this conceptual model is not necessarily to present the facts as they occur in the reservoir, but to suggest hypotheses to be tested and to guide future sampling programs in the direction of the most cost-effective spatial and temporal directions. Although the model presented below is primarily conceptual, some suggestions will be made for the development of some of the transfer equations needed. The preliminary nature of the experiments reported here preclude drawing conclusions regarding the exact quantitative importance of the sediments in the P budget of the reservoir. However, some order-of-magnitude calculations will suggest the potential importance of the sediments as a P source for the overlying water. Specific suggestions for further research based on this conceptual model are presented in the executive summary at the beginning of this report.

As noted previously, P release experiments and the sediment bioassays both strongly implicate the NaOH-P fraction as the most labile and dynamic fraction in the sediments. The work of Williams and his coworkers has identified this fraction with non-occluded, short-range order Fe:P complexes in the sediments. Although we have found a high correlation between P and Fe extractable with CDB reagent in the sediments of upper Flaming Gorge, the correlation between NaOH-P and CDB-Fe is much weaker (e.g. Table 4.3). A probable explanation is that the formation of the non-occluded complex is tied closely to certain water column conditions under which ortho-P is able to sorb onto preexisting ferrosiferrous hydroxide gels. Such a scenario could result when ortho-P encounters the Fe gel in an already aerobic environment. This situation would more likely result from release of P by mineralization of phytoplankton or allochthonous detritus in the water column or at the oxidized sediment-water interface, or from ortho-P being introduced from an upstream point source not associated with stoichiometric amounts of Fe. Conversely, comigration of reduced Fe and P from depth in the sediment, or from sudden oxidation of P in the hypolimnion at the time of overturn or hypolimnetic entrainment would seem more likely to increase the ratio of CDB-P to NaOH-P in the sediments.

Turning to the specific case of upper Flaming Gorge Reservoir, the Blacks Fork arm appears to be impoverished with Fe, and consequently there is little opportunity for ortho-P to complex with Fe gels. The result is a sediment low in

both P and Fe, and especially in NaOH-P (Tables 4.1 and 4.2). Fe is considerably more abundant in the Green River arm, and consequently both CDB-P and the NaOH-P:CDB-P ratios are higher. While the concentration of CDB-Fe shows little change between the upstream and downstream stations in either of the reservoir arms, both CDB-P and NaOH-P increase in a downstream direction. This observation suggests interaction between ortho-P and Fe in situ, rather than the transport of preformed Fe:P gels from upstream in the watershed. The station below the confluence appears to represent a comingling of contributions of sediment Fe and P from both arms of the upper reservoir. The consequence of the difference in the Fe-P chemistries of the various sediments is that internal loading should be several times more important in the Green River than in the Blacks Fork arm, and also more important in the upper than in the lower reaches of both arms.

A conceptual model, presented in Figure 4.6, may help to demonstrate the relationships between the various P fractions in the surficial sediments and water column of a reservoir reach. Although the symbols used for the various inputs (circles) and storages (tanks) are those used in the "Energy Circuit Language" of Odum (1983), all fluxes (arrows) represent mass transfers, and thus no entropy sinks are shown for the various reactions. Such sinks are embodied in the model, however, in the form of conversions of labile P to non-labile organic P or P minerals that are ultimately buried in the sediments. The same is true for Fe and S.

The primary feature of the model is the inputs of various P materials from upstream in the reservoir. Inputs of Fe not associated with either CDB-P or NaOH-P are probably negligible, and thus have not been included. A certain fraction of these inputs move downstream, and the remainder interact with dissolved or suspended species in the water column or are removed to the sediments. Non-labile organic P (e.g. humics, inositol P) and apatite-P represent examples of relatively unreactive P species in the last category. Ortho-P and some fraction of the NaOH-P are available for algal uptake, which represents a self-catalyzed cycle (e.g. higher biomass leads to more rapid uptake). Fe and S are present in stoichiometric ratios to P in the phytoplankton, but neither is ever likely to limit growth, and so there is no connection shown between these constituents and their dissolved counterparts. Labile organic P may be derived from senescence of the phytoplankton community within the reservoir reach, or it may represent detritus from upstream. In Flaming Gorge, the latter source may be important during the spring, when aquatic macrophytes are scoured from the Green River below Fontanelle Reservoir, 200 km upstream. Such a source may also be important in several closely spaced reservoirs operating in series. CDB-P is assumed not to be available to phytoplankton under aerobic conditions.

Once ortho-P is released from the phytoplankton community, it can be rapidly recycled (Nalewajko and Lean 1980), or it may sorb onto a solid phase. These pathways are represented by a "switch" in the recycle pathway from the water column ortho-P compartment. In aerobic water, the P may form non-occluded adducts with NaOH-P or apatite-P (here used to represent all calcareous P phases), depending on the pH and crystallization kinetics (Nancollas et al. 1979, Lijklema 1980). If the ortho-P migrates into anaerobic water, it may coprecipitate with hydrous Fe oxide gels to form CDB-P and some NaOH-P, according to the hypothesis outlined above. The latter reaction is shown to depend on the concentration of reduced Fe in the water column.

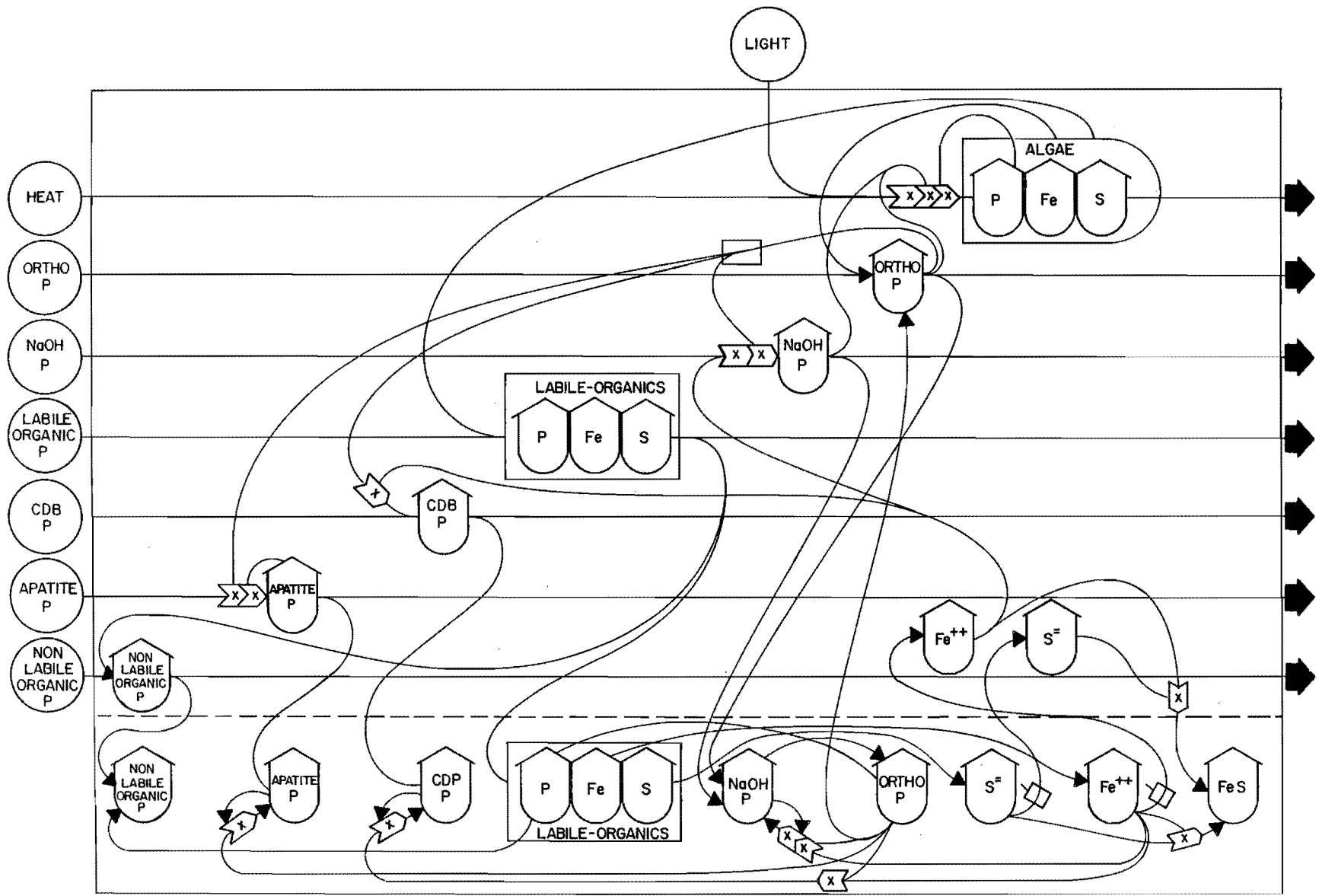


Figure 4.6. A conceptual model of sediment-water P interactions in upper Flaming Gorge Reservoir. Tanks represent storages, arrows represent fluxes, and squares represent switches. See text for further explanation.

The sediment P, Fe, and S compartments are driven by sedimenting fluxes of the corresponding P species from the water column, and from diagenetic fluxes of the dissolved ions from deep within the sediment. Labile detritus decomposes into dissolved ions, which migrate toward their respective compartments, and non-labile organic P which represents a sink for P over geologic time. Ortho-P may follow several competitive pathways, depending on the relative concentrations of "nucleation sites" (autocatalytic arrows), Eh, pH, and kinetic factors. The reactions with Fe are also interactive with the Fe concentrations, which are in turn affected by the sulfide concentration driven by decomposition of labile detritus and deep diagenetic fluxes of sulfide. This is essentially the sulfide model of Stauffer (1981). Fe and S are also capable of being released to the water column, where their concentrations depend on Eh and solubility criteria (Emerson 1976). The switches are "on" only when the water overlying the sediment is anaerobic.

Each of the flow paths in Figure 4.6 can be described by some differential equation with respect to time, provided that the factors most important in governing the particular flux are known or can be determined. The model of Kamp-Nielsen (see Figure 2.1) provides tentative equations for some of the pathways. For example, P mineralization from the labile detritus pool has been described as a first order reaction

$$P_{\min} = k P_l 0^{T-20} \quad (4.3)$$

where P_l is the P in the labile P pool, T is the Celsius temperature, and k and 0 are constants (Jorgensen et al. 1975), whose values may be determined by model calibration or in the laboratory. Diffusion of interstitial P into the overlying water has been described by the equation

$$P_d = (1.21 \left(\frac{P_i - 0.004 - P_w}{.0157} \right) - 1.7) \quad (4.4)$$

where P_i and P_w are the ortho-P concentrations in the interstitial water and on ion exchange sites, and in the bottom water, respectively (Kamp-Nielsen 1977). This equation only holds when D.O. in the bottom water falls below 0.5 mg/l, the P sedimentation rate is sufficiently high to provide an anoxic sediment surface, and the bottom temperature exceeds 12°C in Kamp-Nielsen's model. The assumptions that affect such a switching action may well differ from lake to lake (cf. the small effect of T in Table 4.8). Transfer of ortho-P in the bottom water to interstitial anion exchange sites was assumed to follow the equation

$$P_s = -(0.6 \ln P_w + 2.27)(0.001) \quad (4.5)$$

by Kamp-Nielsen (1975). The parameter values for such an equation probably depend to a significant extent on the nature of the ion exchange sites (i.e. ferrosferric gels, calcium compounds, or clays), and most likely need to be determined for each individual sediment.

The remaining terms in the model presented in Figure 2.1 were obtained by field determinations of algal sedimentation rates and by mass balance considerations by Kamp-Nielsen (1977). The resulting model is quite empirical relative to the conceptual model outlined in Figure 4.6, however, and would appear to offer more in the way of predictive ability than in understanding of

system function. One conceptual improvement would be to include geochemical kinetic models for the precipitation and dissolution of the ferrosiferrous gels, iron sulfide, and the various Fe-P complexes (e.g. Sung and Morgan 1980, Emerson and Widmer 1978, Nancollas et al. 1979). Accurate determination of the kinetics of these reactions under ambient environmental conditions is a high priority pursuit for such a modeling effort, although a considerable body of information exists upon which to build. The same approach would apply to the kinetics of algal growth and decomposition (e.g. Scavia 1979), sedimentation rates, and the like. The remaining tasks simply involve creating mass balances for the various splitting pathways and inserting the proper functions into the pathway "switches," that is, the pH, Eh, or turbulence conditions under which the various alternative pathways are constrained to operate. Only by following such a rational approach to sediment P control can one be assured of discarding the truly superficial pathways from a model, while including the pathways that may be responsive to proposed restoration techniques.

Returning to the specific case of upper Flaming Gorge Reservoir, the important input pathways must be identified by intensive field sampling. Such an effort should partition reservoir inputs, not just into total and ortho-P and total Fe, but into the various forms in Figure 4.6. The high involvement of CDB-P with CDB-Fe may result more from the importance of the input and sedimentation of occluded Fe:P complexes within a reservoir reach than from in situ diagenesis. The relative importance of coprecipitation of P with calcium carbonates during algal blooms should be investigated, as well as the relative importance and biogeochemical pathways of in situ formation of occluded versus nonoccluded Fe:P complexes and clay minerals. The latter difference is important considering the variable degree of availability of the various P forms to phytoplankton (e.g. Figure 4.5). It would also be useful to be able to distinguish between the importance of upstream inputs of labile P from decomposing macrophytes (e.g. Hill and Webster 1982) and those resulting from the senescence of algal blooms supported by P originating, at least in part, from recycling of sedimentary P within a reservoir reach. Short (2-7 day) P release experiments conducted on cores taken at frequent intervals following spring runoff would be useful in this regard. Perhaps the most interesting follow-up study to the work reported here would be to determine whether the patterns noted for the unusually wet 1982 water year, with its relatively short period of stratification, would be repeated in a normal water year with longer and more intense stratification and anoxia.

Although further refinements would be desirable, a crude calculation suggests the potential importance of P release from the reservoir sediments. If, in a typical year, 1.83×10^6 m³ of water flows past LGR during the late summer months (Madison and Waddel 1973), and the reach is 19 m deep and 300 m wide at the station, and the average aerobic release rate is 2.11 mg/m²-day (Table 4.8), then the resulting input to the water column would be 0.11 mg P/m³-day. If the 6 km reach between Sage Creek and station BC is representative of station LGR, then internal P loading to the water column could increase the P concentration by approximately 2 µg/l, which corresponds approximately to 2 µg/l of chlorophyll a under P limitation (Jorgensen et al. 1981, Messer et al. 1983). This clearly would not be an alarming rate of increase.

However, the anaerobic release rate from LGR sediment (11.1 mg/m²-day) is sufficient to increase the average P concentration by 11 µg/l, which would be sufficient to produce bloom conditions in itself, provided that the P could be efficiently transported into the overlying water. It is important to note that P

release rates of $>25 \text{ mg/m}^2\text{-day}$ were noted for this station early in the incubations, and that there is a possibility that the true release rates were underestimated, as discussed above. The interpretation of the initial release rates depends on the relative importance of labile P from senescing phytoplankton, relative to "historical" inputs of P to the sediment during previous months (spring runoff) or years. It is clear, however, that sediment P releases of $>5 \text{ mg/m}^2\text{-day}$ would be a cause for concern in the lower Green River arm of the reservoir. Although release rates in the lower Blacks Fork arm may be lower by a factor of approximately 4-5, the late summer flow in this arm is an order of magnitude lower than in the Green River arm (Madison and Waddell 1973), and thus the impact may be no less severe. Future studies should attempt to refine these calculations, as well as to determine the extent and timing of entrainment of hypolimnetic water into the euphotic zone (e.g. Stauffer 1981).

Summary. Conceptually, P cycling between the sediments and the overlying water in upper Flaming Gorge Reservoir can be thought of in terms of the inputs of various P fractions to the upstream region of the reach, and the interactions of these constituents with phytoplankton, suspended matter, and the interstitial water of the sediment, subject to constraining influences of pH and Eh. Each important pathway can be included in a flow diagram, which can in turn be used to direct a search for useful mathematical relationships between the compartments. This search can include both field measurements and laboratory experiments. Subsequent simulations can be used to identify important pathways that may be sensitive to ameliorative measures or restoration programs, and to identify unimportant pathways in order to avoid wasting costly time and effort in their manipulation. One such tentative model is presented, along with some suggestions for the mathematical structures appurtenant to the various pathways.

The experiments and field work described throughout this report suggest a strong involvement between P and Fe in the reservoir sediments. The closer involvement between occluded P and Fe than between Fe and non-occluded P may indicate that Fe:P complexes formed upstream in the watershed, or through the oxidation of Fe in the presence of ortho-P in interstitial water or upon aeration of hypolimnetic water, are more important than the sorption of ortho-P on preformed hydrous Fe gels in an oxic water column. However, it may be the latter P fraction that plays the dominant role in the subsequent availability of sediment P to algae, whether by anaerobic release from intact sediments or suspension of surficial sediments into the euphotic zone. The lower correlations also may suggest that clays or calcium carbonates play some role in the control of P concentrations in the sediments, although the fact that NaOH-P and CDB-Fe were determined on different subsamples of sediment may be the cause of this lower correlation. Nonetheless, the P release experiments, together with the P:Fe:S stoichiometry of the sediments in upper Flaming Gorge, strongly suggest that Fe controls both the oxic and anoxic release of ortho-P from the sediments.

Approximate calculations regarding the potential importance of sediment P releases indicate that, in both arms, the sediments could support considerable algal standing crops during the late summer. Although release rates are higher in the Green River arm than in the Blacks Fork arm, the longer hydraulic residence time in the latter may result in similar temporal P increases. Further work needs to be done to determine how much of the P release in the early periods of incubation represents P recycled from the water column by a senescing algal bloom, and how much represents P loading from some historical (months or years) P inputs

to the sediment. Hydrodynamic modeling of the transport of P released to anaerobic bottom water into the euphotic zone is also necessary for a thorough interpretation of the probable success of reducing upstream P inputs to the reservoir. Specific recommendations for further research are presented in the executive summary at the beginning of this report.

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APPENDIX A
SEDIMENT CHEMISTRY - RAW DATA

Table A-1. Chemical parameters based on wet extraction cores collected on July 27, 1982. P in $\mu\text{g/g}$ dry weight, metals in mg/g dry weight.

Station	Core #	z #	NaOH-P	CDBFe	CDBMn
UGR	1	1	21.4	4.27	0.190
	1	2	9.1	4.60	0.187
	1	3	9.2	4.30	0.163
	1	4	5.7	3.74	0.148
	1	5	1.9	2.16	0.086
UGR	2	1	8.8	4.25	*****
	2	2	7.8	5.02	*****
	2	3	11.9	6.52	*****
	2	4	4.5	5.16	*****
	2	5	4.6	4.70	*****
LGR	3	1	16.9	4.28	*****
	3	2	15.4	4.74	*****
	3	3	30.5	5.46	*****
	3	4	45.9	4.79	*****
	3	5	51.9	3.32	*****
LGR	4	1	39.7	3.44	0.126
	4	2	26.9	5.53	0.185
	4	3	28.4	4.71	0.160
	4	4	18.3	3.42	0.094
	4	5	6.5	5.69	0.094
LBF	5	1	2.4	1.09	*****
	5	2	5.5	1.55	*****
	5	3	4.5	1.25	*****
	5	4	2.9	1.28	*****
	5	5	3.1	2.08	*****
LBF	6	1	6.1	2.04	0.191
	6	2	6.9	1.65	0.180
	6	3	6.0	1.11	0.145
	6	4	4.8	1.98	0.164
	6	5	2.6	1.22	0.109
UBF	7	1	****	1.06	*****
	7	2	****	1.08	*****
	7	3	****	1.85	*****
	7	4	1.3	1.33	*****
	7	5	1.0	1.17	*****
UBF	8	1	2.6	1.07	0.113
	8	2	2.5	0.99	0.111
	8	3	0.6	1.07	0.109
	8	4	0.6	1.00	0.100
	8	5	1.4	1.29	0.124

Table A-2. Chemical parameters based on wet extraction cores collected on August 17, 1982. P in $\mu\text{g/g}$ dry weight; S in mg/g dry weight.

Station	Core #	z #	NaOH-P	CDB-P	Total-S
UGR	3	1	12.3	189.0	0.76
	3	2	16.0	180.1	0.70
	3	3	11.4	136.8	0.86
	3	4	6.0	93.1	0.92
	3	5	5.7	91.4	0.68
LBF	5	1	8.4	145.3	1.00
	5	2	4.2	121.2	0.88
	5	3	2.2	79.2	0.52
	5	4	1.8	78.5	0.30
	5	5	1.5	42.0	0.44
UBF	11	1	0.8	*****	0.28
	11	2	1.0	49.0	0.40
	11	3	0.6	30.4	0.32
	11	4	0.4	28.6	0.28
	11	5	0.9	91.9	0.72
LGR	13	1	50.4	251.7	1.40
	13	2	40.6	138.7	1.40
	13	3	29.4	147.5	0.80
	13	4	36.9	120.2	1.50
	13	5	30.7	143.0	1.20
BC	4	1	48.5	303.6	1.80
	4	2	31.9	204.0	2.70
	4	3	15.3	223.7	2.00
	4	4	10.5	134.7	1.70
	4	5	20.3	134.0	3.20

Table A-3. Chemical parameters based on wet extraction cores collected on September 21, 1982. P in $\mu\text{g/g}$ dry weight; metals in mg/g dry weight.

Station	Core #	z #	NaOH-P	CDBFe	CDBMn	CDB-Ca
LBF	14	1	8.2	125.1	1.58	0.235
	14	2	1.6	*****	0.62	0.108
	14	3	1.2	63.1	1.12	0.133
	14	4	1.3	42.2	1.08	0.140
	14	5	0.9	62.1	0.77	0.103
UGR	4	1	6.4	136.4	1.76	0.137
	4	2	5.0	75.2	1.64	0.109
	4	3	6.7	92.6	1.74	0.102
	4	4	11.3	46.6	1.45	0.075
	4	5	8.7	63.8	1.88	0.077
LGR	9	1	28.5	171.6	2.76	0.411
	9	2	34.6	209.2	0.56	0.382
	9	3	39.7	200.8	3.40	0.373
	9	4	16.8	209.6	2.82	0.242
	9	5	15.5	170.7	2.55	0.185
BC	19	1	26.7	186.9	2.91	0.501
	19	2	24.6	140.9	2.02	0.343
	19	3	10.1	170.5	1.97	0.287
	19	4	10.6	95.0	1.39	0.185
	19	5	3.1	60.4	1.12	0.180

Table A-4. Concentrations of constituents determined on oven-dried (105°C) aliquots of Flaming Gorge sediments collected in September 1982, using technique "D" of Williams et al. (1971b). All concentrations are in mg/kg; and ratios are on mole basis.

Station	NaOH-P	CDB-P	CDB-Fe	CDB-Mn	NAI-P	CDB-Fe: NAI-P
LBF	93.	158.	4800.	360.	251.	10.6
	33.	135.	3300.	290.	168.	10.9
	40.	127.	3400.	230.	167.	11.3
	32.	123.	3100.	230.	155.	11.1
	29.	114.	2700.	260.	143.	10.5
UGR	75.	127.	8900.	330.	202.	24.5
	78.	135.	5300.	210.	213.	13.8
	86.	165.	6800.	260.	251.	15.1
	98.	120.	6000.	220.	218.	15.3
	89.	127.	7200.	290.	216.	18.5
LGR	184.	125.	5500.	430.	309.	9.9
	184.	150.	6000.	410.	334.	10.0
	162.	170.	6800.	330.	332.	11.4
	150.	154.	6800.	280.	304.	12.4
BC	170.	181.	7600.	680.	351.	12.0
	144.	202.	6400.	520.	346.	10.3
	114.	179.	5000.	360.	293.	9.5
	103.	138.	4300.	280.	241.	9.9
	65.	172.	4400.	350.	237.	10.3

Table A-5. Concentrations of constituents determined on oven-dried (105°C) aliquots of Flaming Gorge sediments collected in September 1982, using Hieltjes and Lijklema (1980). All concentrations are in mg/kg; and ratios are on mole basis.

Station	NH ₄ Cl-P	NaOH-P	CDB- HCl-		T-P	NO-P	NAI-P	Σ P	ORG-P	CDB-	
			P	P						Fe:	CDB-Fe:
										NAI-P	Total-S
LBF	98.	311.	61.	466.	1032.	409.	470.	936.	96.	5.7	2.8
	162.	196.	66.	428.	882.	358.	424.	852.	30.	4.3	2.2
	61.	256.	66.	494.	930.	317.	383.	877.	53.	4.9	3.8
	93.	180.	55.	531.	851.	273.	328.	859.	-8.	5.3	5.9
	34.	163.	55.	587.	926.	197.	252.	839.	87.	6.0	3.5
UGR	3.	215.	88.	500.	842.	218.	306.	806.	36.	16.2	6.7
	42.	187.	83.	510.	836.	229.	312.	822.	14.	9.4	4.4
	34.	214.	77.	482.	861.	248.	325.	807.	54.	11.6	4.5
	24.	233.	77.	512.	830.	257.	334.	846.	-16.	10.0	3.7
	7.	221.	83.	491.	849.	228.	311.	802.	47.	12.9	6.1
LGR	44.	398.	94.	478.	1139.	442.	536.	1014.	125.	5.7	2.3
	26.	433.	83.	476.	1097.	459.	542.	1018.	79.	6.2	4.3
	50.	383.	88.	442.	1030.	433.	521.	963.	67.	7.3	2.6
	36.	372.	78.	464.	1036.	408.	486.	950.	86.	7.8	3.3
BC	94.	340.	91.	496.	1138.	434.	525.	1021.	117.	8.0	2.4
	67.	379.	93.	467.	1076.	446.	539.	1006.	70.	6.6	1.4
	60.	338.	83.	486.	1028.	398.	481.	967.	61.	5.8	1.4
	54.	316.	81.	486.	1012.	370.	451.	937.	75.	5.3	1.5
	61.	274.	71.	579.	982.	335.	406.	985.	-3.	6.0	0.8

APPENDIX B
EFFECTS OF EXTRACTION PROCEDURE
ON APPARENT CONSTITUENT CONCENTRATIONS

Williams et al. (1980) and Sonzogni et al. (1982) have noted the effect of extraction ratio on the apparent concentrations of NaOH-P in sediment samples. In this study, we desired to work with undried sediment, and in order to work with a sufficiently large subsample to avoid non-representative sampling, we used wet sediments at an extraction ratio equivalent to 1g sediment:30 g extractant. In order to compare our values with those of Williams and his colleagues, who generally used a 1:100 extraction ratio, we performed the following comparative extractions on two homogenized surficial sediment cores. It should be noted that Williams et al. (1980) used a 1:1000 extraction ratio when determining algal P availability, and found the lower ratio gave values approximately 10 percent lower than the wider ratio.

The top 13 cm of two fresh sediment cores collected in August, 1982, from LGR and LBF, respectively, were removed and homogenized in a Waring blender for 20 min to provide an apparently uniform slurry. Six aliquots of approximately 2 g equivalent dry weight were extracted separately in 30 ml aliquots of NaOH/NaCl or CDB extractant as described in the Methods section of this report (Chapter 2). Identical extractions were performed on three 300 μ g aliquots of the sediment suspensions that were dried for 48 hr in a 103°C oven. The results of the analyses for NaOH-P, CDB-P, and CDB-Fe are presented in Table B.1.

Coefficients of variation for most of the wet extractions (1:30) were on the order of 20 percent, except for NaOH-P in the LBF sediment (6 percent) and CDB-Fe in the LBF core (53 percent). Contrary to expectations, the coefficients of variation were generally the same or smaller for the dry extractions at the wider sediment:extractant ratio. The wet extraction procedure resulted in values 55-58 percent low relative to the dry procedure for all but the CDB-Fe value, which was only 38 percent of the wet value. The relatively high standard deviation for the LBF CDB-Fe value may indicate that this value is in error.

Table B.1. Comparison of two different extraction ratios on NaOH-P, CDB-P, CDB-Fe, and various ratios of constituents. See text for details of extraction techniques.

Parameter	Core #	
	LBF 11	LGR 13
NaOH-P (1:30 wet)	3.61 ± 0.81 (n = 6)	71.5 ± 4.2 (n = 6)
CDB-P (1:30 wet)	46.4 ± 9.3 (n = 6)	143 ± 33 (n = 6)
CDB-P (1:100 dry)	84.6 ± 20.7 (n = 3)	261 ± 16 (n = 3)
CDB-P (dry:wet)	1.82	1.83
CDB-Fe (1:30 wet)	992 ± 530 (n = 5)	2774 ± 492 (n = 5)
CDB-Fe (1:100 dry)	1718 ± 17 (n = 3)	6255 ± 206 (n = 3)
CDB-Fe (dry:wet)	1.73	2.63
CDB Fe:P (wet)	21.3	16.6
CDB Fe:P (dry)	20.3	24.0