Phosphorus Bioavailability and P-Cycling in Cannonsville Reservoir[1]

Martin T. Auer, Katherine A. Tomasoski[2], Mary J. Babiera[3]
and Melanie L. Needham

Department of Civil and Environmental Engineering
Michigan Technological University
Houghton, MI 49931-1295

Steven W. Effler
Upstate Freshwater Institute

Emmet M. Owens
Syracuse University

Jeff M. Hansen
University of Missouri - Rolla

ABSTRACT

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Algal bioassays and chemical fractionation analyses were applied in determining the bioavailability of phosphorus (P) discharged to Cannonsville Reservoir from its major tributary, the West Branch of the Delaware River (WBDR) and in reservoir bottom sediment. Soluble phase (soluble reactive and dissolved organic) P discharged by WBDR was found to be 100% bioavailable, in a single, dry-weather sample. Tributary particulate-phase P bioavailability varied with hydrologic conditions: 48% for a dry-weather sample and 25% for a wet-weather sample. The P-bioavailability of reservoir bottom sediments (24%) was comparable to that for the wet-weather tributary sample. Phosphorus released over the course of the tributary bioassays came from the Fe/Al-P and extractable biogenic-P pools, while that generated in reservoir bottom sediment bioassays originated entirely from the Fe/Al-P pool (despite the presence of a significant extractable biogenic-P fraction). WBDR sediment had approximately two times more total phosphorus (TP) and five times more bioavailable phosphorus (BAP) than did the reservoir's bottom sediment. Losses in particulate P between introduction and export occurred largely from the extractable biogenic-P fraction. Kinetic coefficients developed here (fraction bioavailable, solubilization coefficient) were used within the context of a nutrient-phytoplankton model to identify the sources of P ultimately realized by the algal community. Tributary soluble P accounted for 91-97% of the realized algal P. Tributary particulate P has a lesser impact due to its smaller loading contribution, lower bioavailability and because much of it is lost to sedimentation, adsorption following solubilization, and export. Depending upon the TDP:PP ratio in the tributary and bioavailability characteristics of the particulate phase P, soluble P contributes 4-7 times more P to the algal available pool than does the particulate phase.

Key Words: algae, eutrophication, lakes, nonpoint pollution, phosphorus, reservoirs.

The total phosphorus (TP) concentration of a waterbody has been widely used in defining trophic state and in developing the regulatory basis for eutrophication management. For example, TP-based total maximum daily loads (TMDLs) are now being developed for many lakes and reservoirs to assure attainment of eutrophication-related water quality standards (U.S. EPA 1991, Kane and Bader 1996) and water quality trading strategies are being explored as a means for managing those loads (U.S. EPA 1996). Total phosphorus is also the state variable most commonly used to

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represent nutrient conditions in the mathematical models which guide trophic state management. It is known, however, that TP is not necessarily an accurate indicator of trophic state. TP-chlorophyll correlations, developed for multiple systems across a gradient of trophic states, exhibit order of magnitude differences in the chlorophyll concentration predicted at a given TP concentration (cf. Chapra and Auer 1998).

The observed variability in empirical TP-chlorophyll relationships may, in part, be due to differences in the bioavailability of the phosphorus loaded to lakes and reservoirs, i.e., its capacity to support algal growth. The soluble reactive (SRP) and dissolved organic (DOP) P introduced to lakes and reservoirs are thought to be generally available for uptake by phytoplankton, perhaps following enzymatic hydrolysis of the organic component (Cotner and Wetzel 1992, Currie and Kalff, 1984). However, Young et al. (1982) reported that only ~72% of the soluble P in domestic wastewater effluent is bioavailable. Some high molecular weight or colloidal organic P, operationally defined as dissolved, may actually be unavailable for algal uptake (Hino, 1988). The pioneering efforts of DePinto (DePinto 1982, DePinto et al. 1981) and Young (Young et al. 1982, 1985) have demonstrated marked differences in the bioavailability of the particulate P loaded from different sources. For example, particulate P originating in wastewater effluent has been shown to be 2-3 times more effective in supporting algal growth than that originating from terrigenous sources (Young et al. 1982, 1985). Various investigators have utilized chemical fractionation schemes to identify the association of particulate phase P with characteristic chemical species, e.g., Fe and Al, $CaCO_3$, Ca-minerals and organic matter (Furumai and Ohgaki 1982, Hieltjes and Lijklema 1980, and Penn et al. 1995). Bioavailability has been strongly correlated with the presence of Fe/Al-P (Cowen and Lee 1976, DePinto et al. 1981, Dorich et al. 1985, Logan et al. 1979) and hydrolyzable organic-P is thought to be biologically available as well (Sommers et al. 1972, Penn et al. 1995). Biological and chemical transformations of particulate phase P (e.g., algal uptake, mineralization, precipitation, sorption/desorption), occurring in the water column, may alter speciation and thus influence bioavailability (cf. Tomasoski 1997, Penn and Auer 1997). Similarly, sedimented P may undergo diagenetic transformations which significantly change the bioavailability of the particulate phase P later reintroduced to the water column through wind action (resuspension).

Mechanistic nutrient-food chain models offer the potential to answer more detailed questions with greater precision than do empirical correlations and simple phosphorus budgets (Chapra and Auer 1998). As water quality managers increasingly turn to these more complex tools, it is necessary that the supporting science keep pace. In this paper, we describe a conceptual model for P-cycling in lakes which accommodates the bioavailability phenomenon and we outline the program of field measurements and laboratory experimentation required to support that model. Specifically, we apply algal bioassays to assess the fraction of a reservoir's external soluble- and particulate-P loads which are available to support algal growth. Additionally, we develop site-specific estimates for the rate coefficient describing water column desorption/mineralization of particulate-P. The analysis is applied to soluble- and particulate-P loads from the major tributary to Cannonsville Reservoir and to reservoir bottom sediments, i.e., particulate matter which may be resuspended in the water column. A chemical fractionation approach (sequential extraction) is explored as an alternative to the lengthy and involved bioassay protocol. Specific chemical fractions have been correlated with P bioavailability and thus a knowledge of their dynamics can provide insight into P cycling. Finally, bioavailability results are examined within the context of a partitioned (soluble/particulate) P model to examine the fate of externally-loaded P and its contribution to the P budget of the reservoir.

Study Site

Cannonsville Reservoir is the third largest (area = 19.3×10^6 m²; mean depth = 19 m) of the 19 reservoirs which comprise the New York City (NYC) drinking water supply system (Effler and Bader 1998). The reservoir is a dimictic, eutrophic (summer average TP = 24 μgP $\cdot$ L⁻¹), soft water system with a mean hydraulic flushing rate of 2.6 per year. Cannonsville Reservoir is fed by the West Branch of the Delaware River (WBDR; draining 79% of the reservoir's 1160 km² watershed), Trout Creek (draining 5% of the watershed) and several smaller tributaries (Owens et al. 1998). The WBDR is the major source of suspended sediment and nutrients, contributing 90% of the annual average total dissolved P (TDP) and 95% of the particulate P (PP) load (Doerr et al. 1998). Under base flow conditions, TSS and TP in WBDR average 5.3 mgDW $\cdot$ L⁻¹ and 39 μgP $\cdot$ L⁻¹, increasing to 93.4 mgDW $\cdot$ L⁻¹ and 176 μgP $\cdot$ L⁻¹ during wet weather events (Longabucco and Rafferty 1998). Substantial variations in the loads of these P fractions, and in their relative contribution to the overall TP load, are observed for WBDR, driven largely by natural variation in runoff (Longabucco and Rafferty 1998).

Several of the processes mediating soluble- and particulate-P dynamics have been characterized for

Cannonsville Reservoir, e.g., Effler and Brooks (1998) report on particle settling velocities and the flux of particulate-P to the sediment. Resuspension is known to occur, although the extent to which the reservoir's deep water sediments participate in this phenomenon remains unresolved (Effler et al. 1998). The direct release of dissolved-P to the water column from in-place reservoir bottom sediments is inhibited here by the presence of ferric iron, although a high potential for sediment exchange has been noted should the iron be reduced to the more soluble ferrous form, i.e., under conditions of extended anoxia (Erickson and Auer 1998).

Methods and Materials

Conceptual Framework

Doerr et al. (1998) developed a mechanistic nutrient-food chain model for the reservoir which partitions TP into SRP, DOP, and a particulate phase. The particulate phase is further partitioned into phytoplankton-P (PhyP), zooplankton-P (ZP) and available (ANLPP) and unavailable (UNLPP) non-living particulate-P. That framework is adopted here, with the following modifications (Fig. 1): (1) the SRP and DOP fractions are considered as their sum (total dissolved phosphorus, TDP) and (2) the potential for differences in the bioavailability of externally-loaded and resuspended NLPP is accommodated. Implementation of this conceptual framework requires specification of the bioavailable fraction (f) of the externally-loaded TDP and the externally-loaded and resuspended NLPP and of the rate coefficient (k) for conversion (desorption/mineralization) of ANLPP to TDP (Fig. 1). The experiments outlined below seek to provide site-specific estimates for the coefficients f and k.
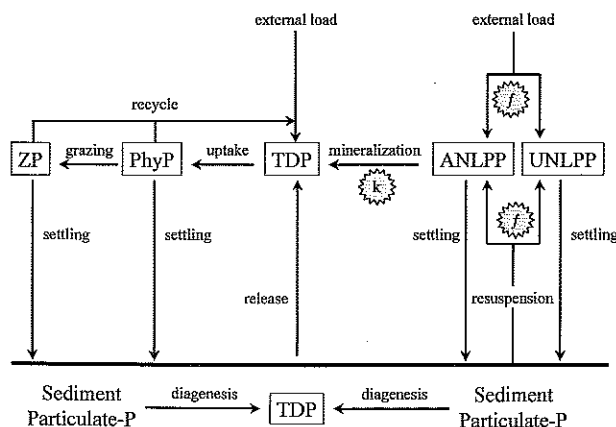

Figure 1.–Conceptual model for P-cycling.

Sample Collection and Processing

Samples were collected from WBDR and from the reservoir's bottom sediments for bioavailability determinations. Water samples (~10 L) from WBDR were passed through a 0.45 μm membrane filter to separate the soluble and particulate phases. Particulate phase samples were stored intact at 4 °C until assayed; soluble phase samples were analyzed immediately upon receipt in the laboratory. Reservoir bottom sediment was collected as intact cores at Stations 2, 4, and 5 (see Erickson and Auer 1998 for location, water depth, and sediment characteristics), extruded and sliced at 0.5 cm intervals. Chemical analyses were performed on slices from the top 15-20 cm and the surface 0.5 cm was removed for bioavailability assays. Oxygen was depleted at the sediment-water interface at the time of sediment collection, however, significant levels of nitrate-nitrogen (>500 :gN·L⁻¹) were present and redox conditions did not favor sediment P-release (cf. Effler and Bader 1998; Erickson and Auer 1998).

Algal Bioassays

Particulate phosphorus bioavailability was determined using a modification of the dual culture diffusion apparatus (DCDA) of DePinto et al. (1981), DePinto (1982), and Young et al. (1982). The ~1.6 L culture apparatus consists of a sediment vessel (dark: 0.5 μE·m⁻²·s⁻¹) and an algal vessel (light: 220-320 μE·m⁻²·s⁻¹) separated by a 90 mm, 0.45 μm, black mixed cellulose ester (MCE) membrane. Phosphorus released from the sediment diffuses across the membrane and is immobilized by P-starved algae, permitting direct measurement of P uptake.

Selenastrum capricornutum (Oregon State University, Corvallis, Oregon; APHA 1992) was used as the assay organism. Algae were initially cultured in the growth medium prescribed by APHA (1992) and then maintained under P-free conditions for a minimum of 7 days. Batch culture studies, conducted as part of methods development, indicate that the assay organism attains a stable (cellular P = 2.2±0.6 μgP · mgDW⁻¹), P-starved (<10% of the maximum cellular P) physiology after 7 days in P-free medium. P-starved algal cells (~10-50 μgChl·L⁻¹) and tributary or reservoir bottom sediment (30-125 mg·L⁻¹) were resuspended in P-free medium at concentrations which would lead to a measurable change in the phosphorus content of the algae (following uptake), without saturating the uptake mechanism (and thus leaving residual dissolved-P in the algal vessel). The algae and sediment suspensions were introduced to their respective vessels and incubated at 22-24 °C with continuous stirring for

30 days. Oxic conditions were maintained throughout the incubation. The algal vessels were harvested at 3-day intervals, the cell suspension filtered and the P content of the algae determined. The filtrate was inoculated with fresh P-starved algae (of known P content) and returned to the algal vessel.

The observed increase in algal PP (final less initial) over each incubation interval was taken as a measure of the incremental release of bioavailable P, i.e., that was released from the sediment, diffused across the membrane, and was utilized by the algae during this period. On occasion (~once per bioassay), algal PP would decrease. Given the P-starved nature of the algal cells, such occurrences were interpreted as reflecting analytical error and the associated change in algal PP was taken as zero. At the end of the 30-day incubation the filtrate was analyzed for TDP and SRP (APHA 1992) to account for soluble P released from the sediment but not consumed by the algae.

Bioavailable P is measured as the P sequestered by the algae and expressed per unit suspended solids (SS) originally introduced into the sediment vessel. Conversion of particulate phase to soluble phase P is assumed to follow first order kinetics:

$$BAP_t = BAP_{ult} \cdot (1 - e^{-k \cdot t}) \qquad (Eq. 1)$$

where BAP_t is the bioavailable P concentration ($\mu gP \cdot gSS^{-1}$) cumulatively sequestered in the algal vessel at time t, BAP_{ult} is the ultimately bioavailable P concentration ($\mu gP \cdot gSS^{-1}$), k is the first-order rate coefficient for conversion of particulate to soluble phase P (d^{-1}) and t is elapsed time (d). Estimates for BAP_{ult} and k were derived through nonlinear, least squares regression (SYSTAT 1992) of the times series of P accumulation (Eq. 1). The bioavailable fraction of particulate P (f, dimensionless) was calculated as BAP_{ult} divided by the PP concentration of the original sediment sample ($\mu gP \cdot gSS^{-1}$, measured as TP by persulfate digestion, APHA 1992). An estimate of the refractory P (RP) content of the sample is obtained by difference (PP-BAP_{ult}). This approach, curve-fitting of a time series to estimate an asymptote and a rate constant, is analogous to that routinely applied in surface water quality analysis for biochemical oxygen demand (APHA 1992).

Soluble phase P bioavailability was determined using a single vessel, aerated batch culture approach. A 2.5 L water sample was placed in a 5-L glass vessel and inoculated with ~10-50 $\mu gChl \cdot L^{-1}$ of P-starved algae. The culture was incubated at 20 °C and a saturating light intensity for 60 hours. Subsamples were collected at 0, 12, 24, 36, 48, and 60 hours and analyzed for SRP and TDP, with DOP determined by difference. The bioavailable fraction (f) of the soluble phase P was calculated as the mass of soluble P taken up by the algae

divided by the mass of TDP present in the original sample.

Chemical Fractionation

The chemical fractionation (sequential extraction) scheme utilized by Penn et al. (1995) was applied here (Fig. 2). Analytical techniques for P determination (SRP, TDP, and PP) were identical to those described previously for algal bioassays. The extraction method, essentially that of Hieltjes and Lijklema (1980), as modified by Furumai and Ohgaki (1982), identifies five operationally-defined-P fractions and describes their relationship with various chemical entities: calcium carbonate-associated phosphorus ($CaCO_3$-P), iron- and aluminum-bound phosphorus (Fe/Al-P), extractable biogenic phosphorus (extractable biogenic-P), calcium-mineral phosphorus (Ca-mineral-P), and residual phosphorus (residual-P). The $CaCO_3$-P fraction includes porewater P, loosely-sorbed P, and that associated with $CaCO_3$. It was not possible to determine the $CaCO_3$-P fraction here as it cannot be differentiated from Fe/Al-P in aerobic environments (sorption interactions). Solution chemistry considerations (i.e., a low alkalinity, low Ca^{2+} environment, Effler and Bader

PP = particulate phosphorus
TDP = total dissolved phosphorus
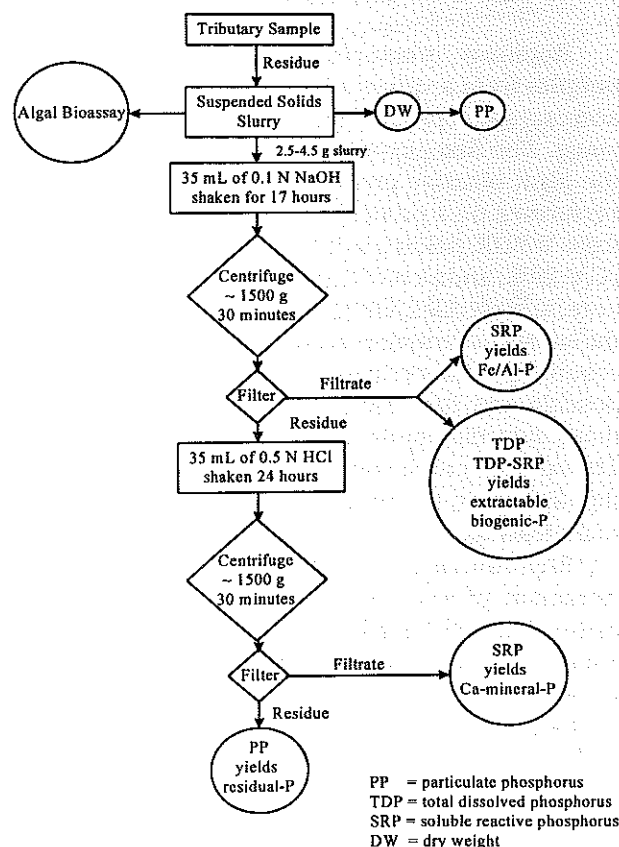SRP = soluble reactive phosphorus
DW = dry weight

Figure 2.–Chemical fractionation technique.

1998) and chemical characterization of particles in WBDR and the reservoir water column (Effler et al. 1998) indicate that the concentration of $CaCO_{3(s)}$ is extremely low in this system. Thus the P associated with $CaCO_3$ is almost certainly a small fraction of the total and porewater P and loosely-sorbed P are thought to be the primary contributors to the $CaCO_3$-P fraction. The Fe/Al-P fraction is that sorbed to iron and aluminum. Extractable biogenic P is composed of labile organic P and polyphosphates. Residual P includes refractory organic P and inert mineral P. The fractions are presented here in the approximate order of their lability. Several investigators (Cowen and Lee 1976; DePinto *et al.* 1981; Dorich *et al.* 1985; Logan *et al.* 1979) have reported a strong correlation between the Fe/Al-P fraction and bioavailable P. Penn et al. (1995) found that the particulate P available for solubilization in the sediments of a hardwater lake was contained within the $CaCO_3$-P, Fe/Al-P, and extractable biogenic-P fractions. Chemical extractions were performed on tributary and reservoir bottom sediment samples and on pre- and post bioassay particulate matter (to identify changes in phosphorus fractions over the course of the assay).

Reproducibility of Biological and Chemical Assays

Replicate measurements were performed on samples from a variety of sources to characterize the accuracy and reproducibility of biological and chemical assays. The first experiment defined the precision of the algal bioassay procedure. Triplicate assays were performed on a particulate phase P sample collected from WBDR yielding a BAP_{ult} of 1520 ± 435 $\mu gP \cdot gSS^{-1}$ (C.V. 29%) and a k of 0.13 ± 0.03 d^{-1} (C.V. 20%). Bioassays were, in most cases, limited to single determinations by the logistics of tributary sediment harvesting (volumes required). On occasion duplicate bioassays were possible and the results presented are averages for those determinations (as noted in figure captions). The variability in the replicate assays reported here was slightly higher, but comparable to that determined in trial bioassays.

Reproducibility of TP digestion and sequential extraction procedures is generally quite good, e.g., better than 5% for triplicate analyses on two WBDR samples, however spurious determinations occur. A second experiment was conducted to compare TP estimates for sediment samples made by direct digestion with those calculated as the summation of measurements of operationally-defined chemical fractions. Twelve samples, representing a variety of sources of particulate matter (tributaries, wastewater effluent, bottom sediments) were subjected to digestion

and sequential extraction. The average difference between the two approaches was 17%. There variation was not systematic, i.e., ~half of the digestions were higher than the extractions and half lower. Pre-bioassay digestions and extractions were conducted in triplicate, while post-bioassay extractions were limited to a single determination by the availability of particulate matter.

Due to limitations of sample size in post-bioassay samples, chemical fractionation results cannot be used to estimate P bioavailability, i.e., from the difference in pre- and post-bioassay determinations. Inefficiencies in recovering sediment from the bioassay chamber and losses of sediment during the particle separation steps of the extraction process are significant in relation to the small mass of sediment available for post-bioassay analysis. Particulate matter losses during sequential extraction are expected to be largely systematic, however, and thus not significantly influence estimates of the distribution of P among the various operationally-defined fractions.

Results and Discussion

Algal Bioassays

Soluble phase: A soluble phase algal bioassay was conducted on a sample collected from WBDR on July 29, 1997. SRP and DOP levels were reduced from initial concentrations of 57 $\mu gSRP \cdot L^{-1}$ and 46 $\mu gDOP \cdot L^{-1}$ to near the limit of analytical detection (~1 $\mu gP \cdot L^{-1}$) within the first 12 hours of incubation (Fig. 3). A small residual DOP concentration (~2 $\mu gP \cdot L^{-1}$) remained after the period of initial uptake. No differences in the rate, order or timing of SRP versus DOP utilization were apparent at the time scale of sampling employed here. These results indicate that essentially all of the SRP and DOP present in WBDR at the time of sampling
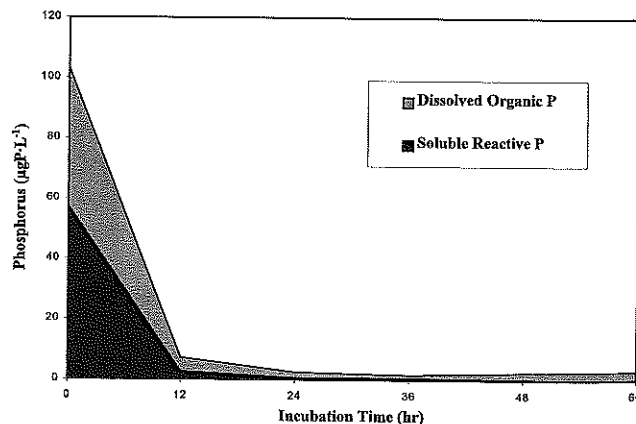

Figure 3.—Soluble phase bioassay results.

was available for algal uptake, i.e., $f = 1$. In bioassays of municipal wastewater samples, Young et al. (1982) observed that all of the SRP and a significant fraction of the DOP was bioavailable. The result of this assay supports the assumption, implicit in many modeling and management applications, that all of the soluble P delivered to a water body is ultimately available to support algal growth.

Particulate phase: Particulate phase bioassays were conducted on samples collected from WBDR on August 20, 1996 (dry weather conditions) and on December 1, 1997 (wet weather conditions) and on reservoir bottom sediment collected from Stations 2, 4, and 5 on August 30, 1995. In all five bioassays, a consistent and progressive increase in accumulated algal P was observed and, in some cases, an asymptote was approached within the 30-day incubation period (Fig. 4). A rapid increase in accumulated algal P (~1/3 of the total) was noted over the first 3 days of incubation for the wet weather WBDR sample and the surficial sediment samples. The results

of pre- and post-bioassay chemical fractionation measurements (discussed below) indicate that bioavailable P originates in the Fe/Al and extractable biogenic-P fractions. It is hypothesized that the initial increase in accumulated algal P corresponds to desorption of Fe/Al-P (a rapid, equilibrium process), with the balance of the release due to mineralization of extractable biogenic-P (a slower, kinetically-driven process) and continued desorption.

The total phosphorus content of the WBDR samples was quite high (2076 and 2929 $\mu gP \cdot gSS^{-1}$ for wet- and dry-weather conditions, respectively; Table 1), approximately double that for tributaries draining the rural portion of the Onondaga Lake, New York watershed (Tomasoski 1997) and 2.5 times that measured for five lower Great Lakes tributaries (DePinto et al. 1981). The BAP content of the dry-weather WBDR sample (TP = 1393 $\mu gP \cdot gSS^{-1}$, Table 1) was high as well: almost six times that of the average for the Great Lakes tributary data set of DePinto et al. (1981;
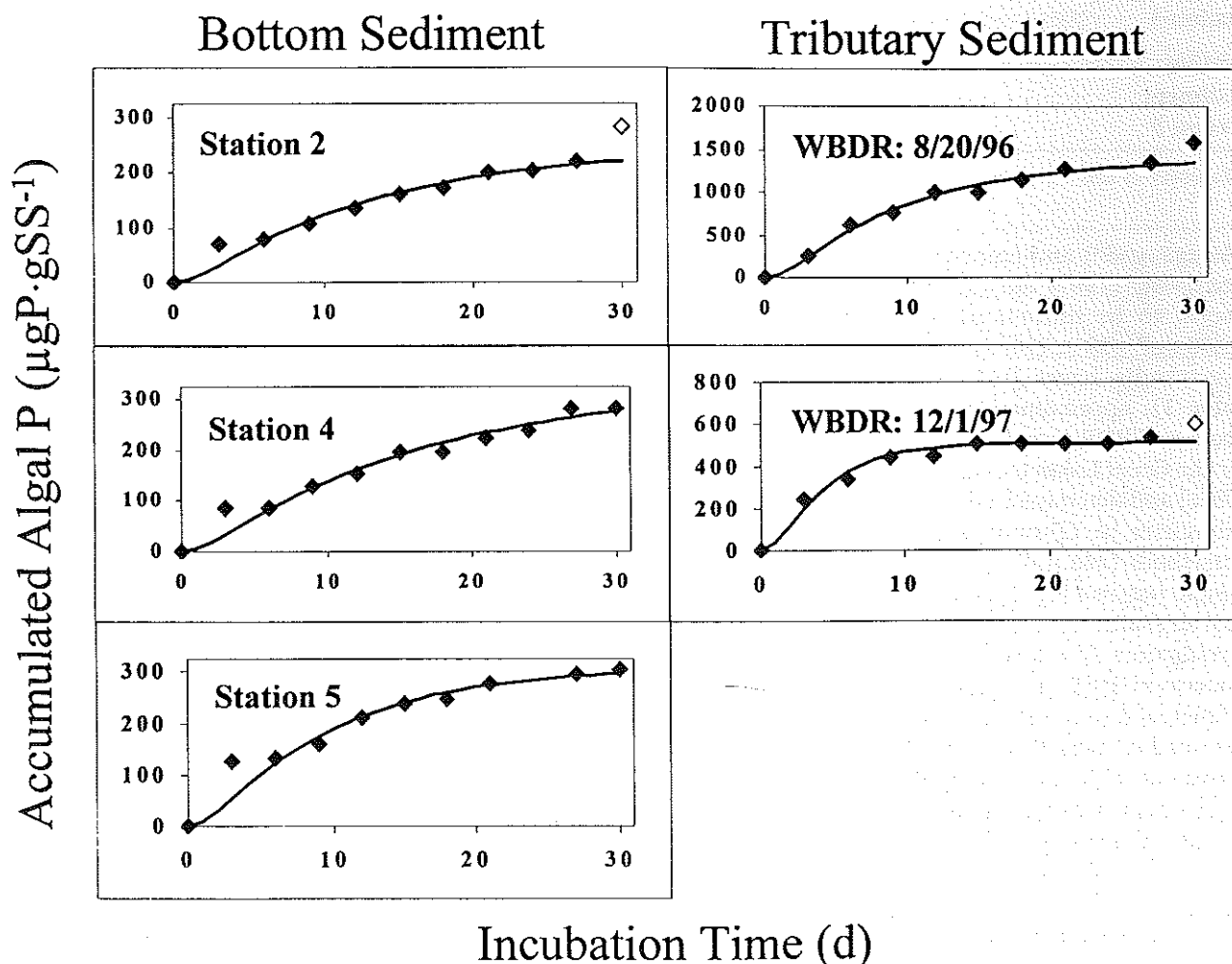

Figure 4.–Particulate phase bioassays. Results for bottom sediment Station 5 and tributary sediment on 12/1/97 are the average of replicate measurements. Open diamonds are data points considered to be outliers and not included in regression analysis.

Table 1.–Particulate phase bioassay results. TP is by direct digestion. BAP_{ult} and k are as determined through bioassays. Refractory P is determined by difference from TP and BAP.

Sample	Total P Concentration (TP, $\mu gP \cdot gSS^{-1}$)	Refractory P Concentration (RP, $\mu gP \cdot gSS^{-1}$)	Bioavailable P Concentration (BAP_{ult}, $\mu gP \cdot gSS^{-1}$)	Bioavailable P Fraction (f)	Rate Constant (k, d^{-1})
WBDR 8-20-96 (dry)	2929	1536	1393	0.48±0.04	0.11±0.03
WBDR 12-1-97 (wet)	2076	1565	511	0.25±0.01	0.30±0.11
Bottom Sediment Mean	1276	1029	294	0.24±0.06	0.08±0.05
Bottom Sediment Station 2	1508	1264	244	0.16±0.04	0.08±0.04
Bottom Sediment Station 4	1315	986	329	0.25±0.07	0.06±0.04
Bottom Sediment Station 5	1004	837	308	0.31±0.06	0.11±0.06

238 $\mu gP \cdot gSS^{-1}$) and comparable to that measured by Tomasoski (1997) for a tributary to Onondaga Lake known to be influenced by wastewater discharges (1650 $\mu gP \cdot gSS^{-1}$). The wet-weather WBDR sample had a markedly lower BAP content (511 $\mu gP \cdot gSS^{-1}$, Table 1): approximately one-third that of the dry-weather WBDR sample, but greater than the average for the Great Lakes tributary data set of DePinto et al. (1981) and that measured by Tomasoski (1997) for two tributaries to Onondaga Lake which drain rural watersheds (345 $\mu gP \cdot gSS^{-1}$). The dry-weather WBDR sample was also highly bioavailable (f = 0.48, Table 1) with an f value approaching that determined by other investigators (f = 0.60, Young et al. 1982; f = 0.58, Tomasoski 1997) for particulate P in effluent from municipal treatment plants. The bioavailability of the wet-weather WBDR sample (f = 0.25, Table 1) was consistent with measurements made on discharges from other rural watersheds (f = 0.22, Young et al. 1982, f = 0.27, Tomasoski 1997). The 'richness' of the dry-weather WBDR sample may reflect contributions from highly bioavailable P sources, such as those associated with treatment plant effluents, which become more prominent when dilution effects are less. The rate coefficients for mineralization of particulate P

(k = 0.30 and 0.11 d^{-1} for wet- and dry-weather conditions, respectively, Table 1) are comparable to those noted for other, similar systems (k = 0.08 – 0.28 d^{-1}, Young et al. 1982; k = 0.08 – 0.25 d^{-1}, Tomasoski 1997).

Reservoir bottom sediment samples were less rich (TP = 1276 $\mu gP \cdot gSS^{-1}$, BAP = 294 $\mu gP \cdot gSS^{-1}$) than the wet-weather WBDR sample, but similar in bioavailability (f = 0.24 d^{-1}), and markedly less rich than the dry-weather WBDR sample. One would expect similarities between bottom sediment and wet-weather tributary samples as runoff events account for nearly 90% of the PP load to the reservoir (Longabucco and Rafferty 1998). Post-discharge losses in sediment P content may reflect processes at work in the water column and in the surficial sediment. Water column soluble P and the portions of the particulate P pool released by desorption and mineralization become available for uptake by algae, i.e., conversion, at least in part, to extractable biogenic P. Soluble P may also be adsorbed to particulate matter. Ultimately, soluble and particulate P are lost from the water column to export (hydraulic flushing) and particulate P is routed to the lake bottom by sedimentation. Wind-driven resuspension events can reintroduce sedimented particulate P to the water column where it may once again participate in sorption reactions with a

potential attendant loss to export. Particulate P undergoes diagenesis in the sediments and may be released to the overlying waters (although this is thought to be a minor process in this system, Erickson and Auer 1998). The net effect of these phenomena is to 'work' sedimented particulate P, recycling a portion of that which settles with some attendant loss to export. This leads to impoverishment of sediment P relative to that loaded to the water column. It is noted here, therefore, that sediment introduced to the water column through resuspension may, on a per unit weight basis, play a lesser role in stimulating algal growth than that discharged from tributaries. This, despite the fact that reservoir bottom sediment is largely composed of material introduced through fluvial discharge (e.g., Effler et al. 1998). Additional insights regarding the transformations leading to losses of TP and BAP following the discharge of particulate P from tributaries may be gained from the results of chemical fractionation measurements.

Chemical Fractionation

Pre-bioassay chemical fractionation measurements can be used to characterize inputs of freshly discharged (tributary) and aged (reservoir bottom sediment) particulate P, shedding light on the role of water column transformations and sediment diagenesis in mediating the distribution of P among the various operationally-defined pools. For example, it is noted in Tables 1 and 2 that reservoir bottom sediments had a TP content ($\mu gP \cdot gSS^{-1}$) ~one-half that of the tributary (WBDR) samples. This is consistent with the widespread observation (see Reckhow and Chapra, 1983 for a summary) that approximately 20-50% of the phosphorus received by a lake is retained with the balance lost as soluble and particulate P in the outflow. Losses in PP between inflow and outflow in Cannonsville Reservoir were largely associated with the biogenic-P fraction (Table 2), as absolute levels of Fe/Al-P in reservoir bottom sediments differed little from those of the tributary discharge. The preferential loss of biogenic-P may reflect differences in the settling velocities of biotic and abiotic particles (cf. Chapra 1997), the rapid recycle of sedimented labile biogenic-P (Penn et al. 1995), and the potential for Fe to capture P released through mineralization of organic matter in the sediment (Erickson and Auer 1998).

A comparison of pre- and post-bioassay chemical

Table 2.–Results of pre- and post-bioassay chemical fractionation analyses. TP is the sum of the analytically-defined fractions. Bottom sediment mean is that for Stations 2, 4, and 5.

Sample	$\sum$TP Extracted ($\mu gP \cdot gSS^{-1}$)		Fe/Al-P ($\mu gP \cdot gSS^{-1}$)		Biogenic-P ($\mu gP \cdot gSS^{-1}$)		Ca Mineral-P ($\mu gP \cdot gSS^{-1}$)		Residual-P ($\mu gP \cdot gSS^{-1}$)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
WBDR 8-20-96 (dry)	2837	1387	930	124	1284	740	211	129	412	394
WBDR 12-1-97 (wet)	2631	1103	838	263	1356	286	45	193	394	361
Bottom Sediment Mean	1326	655	824	133	262	266	147	86	93	170
Bottom Sediment Station 2	1353	591	800	130	272	218	186	77	94	166
Bottom Sediment Station 4	1501	738	974	157	320	317	127	96	80	168
Bottom Sediment Station 5	1128	636	698	111	195	264	129	85	106	176

fractionation measurements (Table 2) permits identification of the operationally-defined P fractions contributing to the bioavailable P pool. Despite marked differences in the bioavailability of the wet- and dry-weather WBDR samples (*f* values, Table 1), the distribution of their PP among the various fractions in the original samples was quite similar (Table 2 and Fig. 5): biogenic-P accounted for ~one-half and Fe/Al-P for ~one-third of the sample TP. A significant residual-P fraction (15%, Table 2) was observed, but Ca-mineral-P levels were quite small. Both the Fe/Al-P and biogenic-P fractions contributed significant bioavailable P (gray bars in Fig. 6) in WBDR samples, with the Fe/Al-P fraction being more important under dry-weather conditions and the biogenic-P fraction being greater under wet-weather conditions. Substantial portions of the Fe/Al and biogenic-P fractions were solubilized over the course of the assay (compare black and gray bars in Fig. 6).

As discussed above, absolute levels of Fe/Al-P in reservoir bottom sediments were similar to, and biogenic-P levels significantly lower than, those for
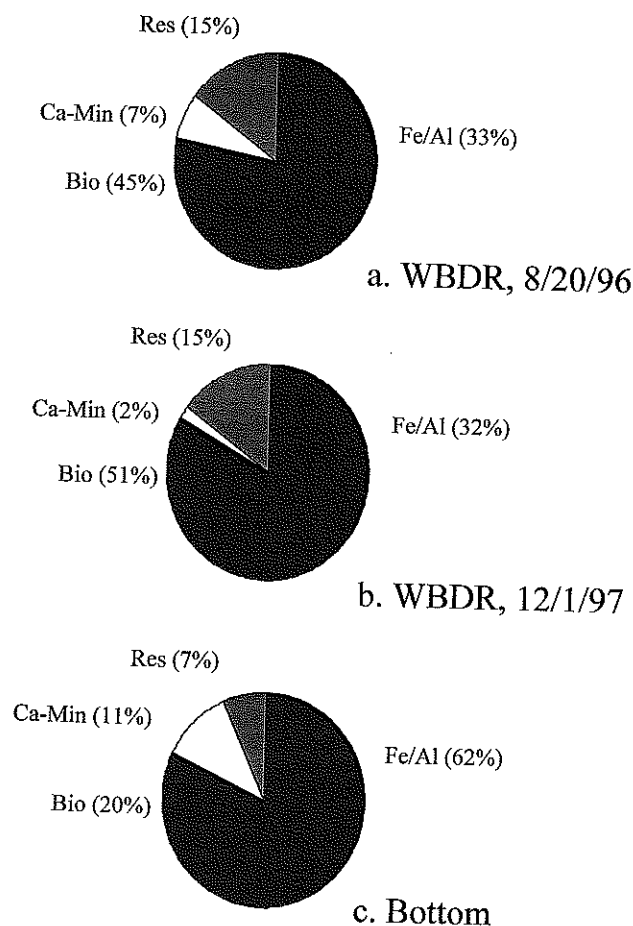

WBDR (dry): 8-20-96

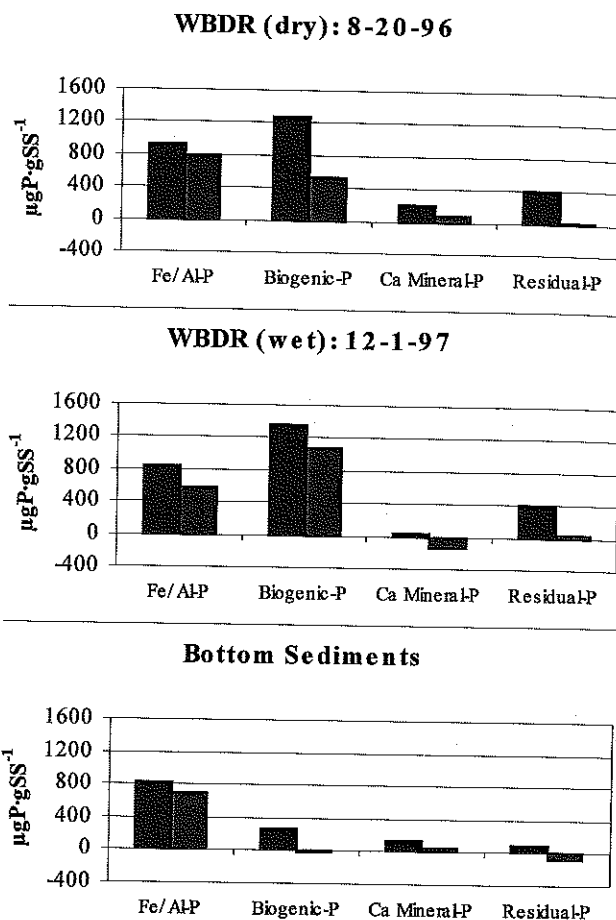WBDR (wet): 12-1-97

Bottom Sediments

Figure 6.–Changes in operationally-defined P fractions and contribution to the bioavailable-P pool. Black bars identify pre-bioassay levels and gray bars reflect the change over the course of the bioassay (pre - post). Differences in the magnitude of gray bars for a given sample reflect the relative contribution to the bioavailable-P pool. A comparison of black and gray bars for a given fraction indicates the portion of that fraction which became bioavailable over the course of the bioassay.

a. WBDR, 8/20/96

b. WBDR, 12/1/97

c. Bottom

Figure 5.–Distribution of operationally-defined P fractions in pre-bioassay samples.

tributary samples. Fe/Al-P was essentially the sole source of bioavailable P (Fig. 6), largely depleting Fe/Al-P pool over the course of the assay. The predominance of the Fe/Al-P fraction as a source of bioavailable P is especially striking here given the presence of significant levels of biogenic P in the reservoir bottom sediment sample (Table 2). In a study of Onondaga Lake, New York, Penn et al. (1995) noted the presence of 'fast' and 'slow' labile phosphorus fractions in lake sediments: the former having a half-life of 53 days and the latter having a half-life of ~7 years. Thus, depending on the balance and site-specific kinetics of the 'slow' and 'fast' fractions in Cannonsville Reservoir, the contribution of biogenic-P to the bioavailable pool from reservoir sediments might be expected to be small, at least over the time intervals associated with resuspension events. It is also likely that soluble P generated through

mineralization of the biogenic-P fraction is captured by Fe and then released as dictated by sorption kinetics (Erickson and Auer, 1998; see discussion above). In any case, it is clear that the biogenic P discharged by tributaries is more labile than that which accrues in reservoir bottom sediments. This observation also helps underscore the point that fractionation analysis alone does not provide conclusive evidence regarding bioavailability, i.e., the presence of a given phosphorus fraction is no guarantee of bioavailability.

Modeling Analysis

The relative importance of the soluble and particulate P delivered by WBDR as sources of algal available P is governed by the magnitude and bioavailability of their respective loads. Here we combine data from a tributary monitoring program (Longabucco and Rafferty 1998), the results of bioavailability studies (this manuscript), and the capabilities of a mass balance model (Doerr et al. 1998), to quantify the contributions of externally-loaded soluble and particulate P to the algal available P pool in Cannonsville Reservoir. Loading calculations are for the May to September period of 1994 and 1995, wet and dry intervals, respectively. Model simulations were made for comparable periods for those years (May-November, 1994; April-November, 1995). Conclusions drawn are limited to those periods.

The WBDR TP loading was dominated by soluble forms, with TDP comprising 60 and 76% of the input for the wet and dry years, respectively (Table 3). The

Table 3.—Phosphorus loads from WBDR for the May-September period. For %BAP and %RBAP, results, bold face type corresponds to the kinetics of the wet-weather WBDR sample ($f = 0.25$, $k = 0.20$) and standard face type corresponds to the kinetics of the dry-weather WBDR sample ($f = 0.61$, $k = 0.08$).

a. TDP Loading Contribution

Year	TDP Load ($MT \cdot yr^{-1}$)	% of TP Load	% of BAP Load	% of RBAP Load
1994 (wet)	10.4	60	**71-86**	**91-94**
1995 (dry)	5.1	76	84-93	95-97

b. PP Loading Contribution

Year	PP Load ($MT \cdot yr^{-1}$)	% of TP Load	% of BAP Load	% of RBAP Load
1994 (wet)	6.8	40	**14-29**	**6-9**
1995 (dry)	1.6	24	7-16	3-5

contribution of BAP can be calculated by applying the bioavailability factor (f, Table 1) to the TDP and PP loads. The dissolved fraction of the P loading accounts for 71-93% of the bioavailable P (Table 3), again dependent upon the contribution of PP to the TP load and the fraction of the PP load which is bioavailable (f, Table 1).

Contributions of algal available phosphorus are not, however, rigorously described through a simple accounting of BAP inputs. While soluble P is immediately accessible for algal uptake, available particulate P must undergo desorption and/or mineralization in the water column. Because particulate matter is lost to settling and export as desorption/mineralization proceeds, not all of the bioavailable particulate P entering the reservoir is realized by the algal pool. The model may be used (through the coefficient, k, in Table 1) to partition available particulate P into that lost to settling as PP, that lost to export as PP, and that converted to SRP. The soluble P resulting from the latter category may be further partitioned into that lost to adsorption as SRP, that lost to export as SRP, and that ultimately realized by the algae. As shown in Fig. 7, 65% of the TDP and 26-39% of the PP (depending on the value of k and related sink terms) are ultimately realized by the algae, with the balance lost to adsorption, export, and settling. Applying these percentages to the BAP loads calculated in Table 3, yields an estimate of the contributions to the realized bioavailable phosphorus (RBAP) load from the soluble and particulate fractions. As shown in Table 3, the TDP loading accounts for 91-97% of the BAP load ultimately realized by the algae, varying as a function of the ratio of TDP:PP in the tributary discharge and the bioavailability coefficients (f, k) associated with the PP fraction. Stated in another way, soluble P has 4-7 times more impact as algal available P than an equivalent quantity of particulate P, again for the values of f and k determined here.

This analysis could be extended to internal loads as well. Although no soluble P is released from the surficial sediments of the reservoir under existing redox conditions (iron binding), resuspended sediment has the potential to desorb P upon mixing with the water column. One would expect that, on a per unit mass basis, resuspended particulate P ($f = 0.20$) would make a contribution to algal available P comparable to that discharged from WBDR during wet-weather conditions. However, the magnitude of the solids load from the lacustrine zone during resuspension events is potentially greater than from tributary inputs (Effler et al. 1998) and thus resuspension may contribute significant quantities of BAP. Calculations relating to resuspension are not included here, as the model framework of Doerr et al. (1998) has not been extended to accommodate resuspension.

a. TDP

Realized (65%)
Loss to export (2%)
Loss to adsorption (34%)

b. PP (12-1-97, wet): $f = 0.25$, $k = 0.3$

Loss to export (2%)   Mineralized (60%)
Loss to settling (38%)
Realized (39%)
Loss to adsorption as SRP (20%)
Loss to export as SRP (1%)

c. PP (8-20-96, dry): $f = 0.48$, $k = 0.11$

Loss to export (4%)   Mineralized (40%)
Loss to settling (56%)
Realized (26%)
Loss to adsorption as SRP (13%)
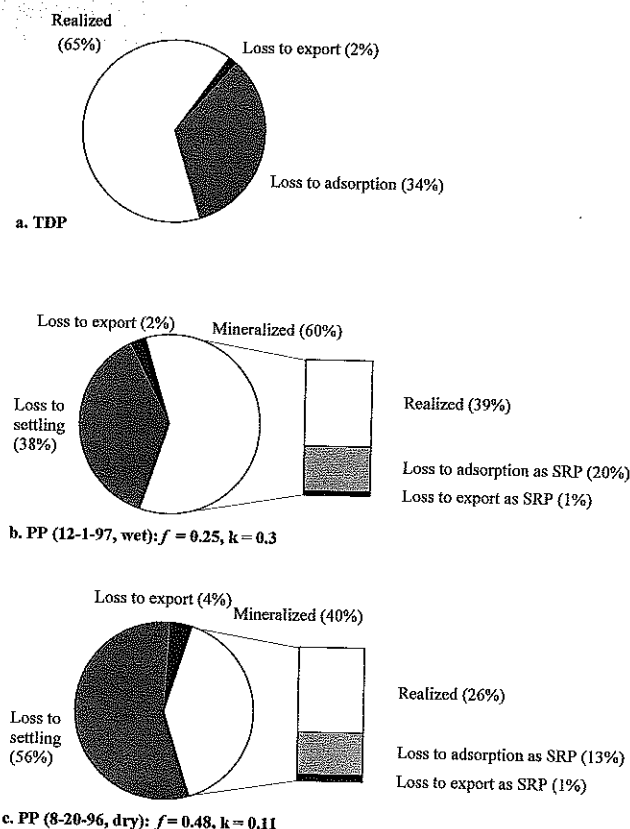Loss to export as SRP (1%)

Figure 7.–Contributions to the TP, BAP, and RBAP pools from WBDR.

Summary, Conclusions, and Management Considerations

Algal bioassays and chemical fractionation measurements were used to identify and characterize the bioavailability of soluble- and particulate phase phosphorus in the major tributary discharge and bottom sediments of Cannonsville Reservoir. An algal bioassay of a single, dry-weather WBDR sample indicated that soluble phase (DRP and DOP) phosphorus was completely available to support algal growth ($f = 1$). Particulate matter collected from the tributary (WBDR) water sample was enriched in both total and bioavailable phosphorus compared with that collected from the reservoir bottom sediment. The bioavailability of tributary particulate P varied with hydrologic conditions ($f = 0.48$ for a dry-weather sample and $f = 0.25$ for a wet-weather sample) and that of the bottom sediments was most similar to WBDR PP under wet-weather conditions.

Tributary particulate P solubilized during algal bioassays originated from the Fe/Al-P and extractable biogenic-P pools, while that released in reservoir bottom sediment bioassays came exclusively from the Fe/Al-P pool (i.e., reservoir bottom sediment extractable

biogenic-P was not bioavailable). This finding calls into question the value of chemical fractionation procedures in defining a bioavailable P analyte. The TP content of reservoir bottom sediment samples was significantly lower than that for tributary samples, a finding consistent with reported retention coefficients for P in lakes and reservoirs. Reductions in TP content could be ascribed to the extractable biogenic-P fraction as the Fe/Al-P content of tributary and bottom sediments was similar.

Modeling analysis, applying these findings within the context of a comprehensive nutrient-phytoplankton framework, has demonstrated that soluble P inputs to Cannonsville Reservoir are the most significant source of algal available P, contributing 95-97% of the P realized by the algal pool. The contribution of tributary particulate P to the realized algal P pool is small by comparison because it represents a lesser fraction of the TP load, has a lower bioavailability (f) and because a significant fraction of the PP solubilized is lost to adsorption and export. While acknowledging that the conclusions drawn here evolve from a limited number of measurements, it is noted that: (1) the two particulate phase bioassays bracket flow conditions for the system's dominant tributary and (2) the apparent dominance of soluble phase P as a source of realized algal available P is uninfluenced by the range in coefficient (f and k) values observed for wet and dry years. Nonetheless, applications of these findings in selecting management strategies for particulate and soluble P loads may profit from additional assays to better resolve seasonal variability, especially in soluble phase P bioavailability.

The results of this analysis have immediate value in their contribution to the development of a reliable and mechanistically sound mathematical model for nutrient-phytoplankton dynamics in Cannonsville Reservoir. Beyond this immediate impact, these findings suggest that bioavailability should be considered in developing load management strategies for lakes and reservoirs (e.g., TMDLs and discharge trading protocols). Soluble P discharged by WBDR was found to contribute 4-7 times more phosphorus to the algal pool than did the PP fraction. It is recommended that the defining features of bioavailability (f and k) be accommodated through a program of bioassay measurements in equating P loads from various sources. Finally, it is cautioned that bioavailability characteristics will likely change from source to source and basin to basin and that intersystem application of these concepts need be accompanied by site-specific determination of the attendant kinetic coefficients.

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