

Callahan Reservoir: II. Inflow and Outflow Suspended Sediment Phosphorus Relationships

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ABSTRACT

THE inflow and outflow of Callahan Reservoir, located in an agricultural area near Columbia, Missouri, was studied for 1 yr to understand the sediment and solution phosphorus (P) relationships. The solution phase was analyzed for dissolved organic, hydrolyzable, and ortho-P and the sediment was analyzed for total, inorganic, and organic P. The discharge weighted mean solution phase concentration of dissolved organic, hydrolyzable, and ortho-P for the inflow was 0.008, 0.002, and 0.059, mg/l, respectively, as compared with 0.011, 0.005, and 0.021 mg/l for the outflow. The outflow sediment had a larger concentration ($\mu\text{g/g}$) of total, inorganic, and organic P than did the inflow sediment. However, because of sediment deposition within the reservoir, there was a 4-fold decrease in outflow suspended sediment P volume concentrations (mg/l). Isotopic dilution techniques with ^{32}P were used to estimate the portion of sediment- P^{31} in equilibrium with solution- P^{31} . The quantities of isotopically exchangeable sediment- P^{31} in the inflow and outflow sediments were 30 and 41 $\mu\text{g/g}$, respectively.

INTRODUCTION

Several hundred flood control structures are built within the United States annually, many in agricultural areas. While the primary purpose of these structures is flood control and sediment entrapment, the quality of water within these reservoirs and released is also important because of an increased demand for recreation and downstream uses. Since the quality of water downstream from a reservoir depends not only on the quality of the inflow, but also on the physicochemical relationships within the reservoir, a better understanding of inflow-outflow sediment nutrient relationships is needed to improve the management of streams and impounded waters.

Both the chemical and physical properties of reservoir water and subsequent downstream releases are influenced by suspended sediment (Holt, 1971). Suspended sediment influences light penetration and, hence, algal production (Ganf, 1974; Leving and Fish, 1956). Suspended sediments also influence the chemical

composition of water, because of associated sorbed chemicals, like phosphorus (P). However, the biological significance of suspended-sediment sorbed P is unclear (Holt, et al. 1973), although there is no doubt that the availability of P, associated with suspended sediment, depends upon the mechanism of P sorption, as well as the P form (Golterman, 1973). Thus, only a small fraction of the total P associated with sediment is probably biologically important (Golterman, 1973). Although seasonal decreases in the inorganic P content of Klamath Lake, Oregon sediments corresponded with the exponential growth period of bluegreen algae (Wildung, et al. 1974), culture tests indicate that some lake muds support little or no algal growth (Fitzgerald, 1971). Suspended sediments have been described as buffers with respect to phosphate content of water, releasing P from sediments that sustain growth of an algal bloom, although the soluble P content could only have supported the observed photosynthesis rate for 1 day (Martynova, 1971). Many limnologists consider P as the key element causing accelerated eutrophication in most freshwater (Lee, 1973). To predict algal blooms on the basis of the nutrient status of waters, the chemistry of P in lakes and reservoirs must be understood (Lee, 1973). Since the turnover rate of P in eutrophic lakes can be rapid, it is important to know the P status of both suspended sediments and inflow water in a reservoir, and how the P status of the suspended sediments changes as they move through the reservoir and downstream.

The quality of water downstream from agricultural reservoirs is important, since water may be utilized by municipalities, industry, agriculture, and by the public for recreation. Callahan Reservoir, because it is located in an agricultural area near Columbia, Missouri, offered an opportunity to determine the influence of an agricultural reservoir on outflow water quality with respect to sediment and solution phase P. Specific objectives of this research were (a) to determine the P enrichment of outflow suspended sediments relative to inflow suspended sediments, (b) to determine the differences in the concentrations and forms of inflow soluble P compared with outflow soluble P, and (c) to develop relationships between P (sediment and/or solution) and suspended sediment in the inflow and outflow of Callahan Reservoir.

MATERIALS AND METHODS

Reservoir Description

Callahan Reservoir, a flood retarding structure, receives runoff from a 1,460 ha watershed, 40 percent of which is cropland, 36 percent pasture, and 24 percent forest. Soil textures of the watershed soils ranged from clay loam to silt loam. The reservoir length, width, mean depth, and maximum depth are 1,270, 70, 2, and 5 m, respectively, with a 8.2 ha permanent pool surface area.

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TABLE 1. SEDIMENT PHOSPHORUS CONCENTRATIONS IN THE INFLOW AND OUTFLOW OF CALLAHAN RESERVOIR.*

	Mass basis			Volume basis†		
	Total	Inorganic μg/g	Organic	Total	Inorganic mg/l	Organic
Inflow	402	253	149	1.47	0.92	0.55
Outflow	841	464	377	0.32	0.18	0.14
Enrichment‡	2.1	1.8	2.5	0.22	0.20	0.25

*Discharge weighted mean values for the 1973 water year

$$\dagger \text{Sediment P} = \frac{\text{mg P}}{\text{g sediment}} \times \frac{\text{g sediment}}{\text{l, runoff}}$$

‡Outflow concentrations/inflow concentrations.

Sample Collection

Samples of inflow and outflow were collected by automatic pumping samplers. Inflow was sampled with a PS-66 pumping sampler (developed by the Federal Inter-Agency Sedimentation Project, St. Anthony Falls Hydraulic Laboratory, Minneapolis, MN) with a 800 ml sample taken every 8 min to 2.5 hr, depending on the rate of rise in stage. Samples representative of the storm hydrograph were selected, packed in ice, and shipped via air freight to the USDA Sedimentation Laboratory, Oxford, MS, for chemical analysis. Phosphorus concentrations from these samples were used to compute storm loads and discharge-weighted nutrient concentrations. Unless otherwise indicated, chemical concentrations will represent storm discharge-weighted values.

Outflow from the reservoir was sampled at the discharge end of the spillway pipe with a Columbia spillway sampler (Rausch and Haden, 1974). Samples were taken automatically every 2 hr, when flow was greater than 0.57 m³/s, and manually at lower flows. A storm period was defined as the beginning of a rise in reservoir stage in one storm to the beginning of a rise in reservoir stage for the next storm (Rausch and Schreiber, 1977). Inflow included in a storm period was offset in time by the volume of water stored in the reservoir, so inflow and outflow water were the same. Both rainfall and runoff during the study period, November 1972 to October 1973, were above normal. Rainfall was 152 cm as compared with a 70 yr mean of 97 cm, whereas runoff (inflow) was 62 cm as compared with a 5 yr mean of 25 cm.

Chemical Analysis

Sediment concentrations were determined by oven drying a 50 to 60 g portion of the runoff sample overnight at 105 °C to obtain by weight the dissolved and suspended solids (total solids). Another portion of the same runoff sample was filtered through a 0.45-μm Millipore* filter. A 50 to 60 g portion of the resulting clear filtrate was also oven dried overnight to obtain dissolved solids. The concentration difference between total and dissolved solids was considered to be sediment concentration. Another portion of the filtrate was used to determine the concentration of dissolved organic, hydrolyzable, and ortho-P (PO₄-P) (FWPCA, 1969).

*Names of products are given for information purposes only and do not constitute an endorsement or preferential use by the U.S. Department of Agriculture over similar products.

Sufficient sample was filtered to collect at least 0.1-g suspended sediment for analysis of total, inorganic, and organic P. Phosphorus was extracted from the sediment by a series of HCl and NaOH extractions, using the procedure developed by Mehta, et al. (Mehta, 1954). Total sediment P was determined by HC10₄ digestion of a portion of the acid-base extract. Inorganic P was determined on an aliquot of the acid-base extract, following centrifugation to remove organic matter. Organic P associated with the suspended sediment was considered as the difference between the total and inorganic P.

Dissolved PO₄-P was measured by a direct colorimetric procedure, whereas dissolved hydrolyzable P was PO₄-P present (after a sulfuric acid hydrolysis of the sample) minus predetermined PO₄-P (FWPCA, 1969). Dissolved organic P was PO₄-P present (after a sulfuric acid and ammonium persulfate digestion) minus predetermined dissolved hydrolyzable and dissolved PO₄-P. Orthophosphorus was determined using the procedures of Murphy and Riley (1962), as discussed by Watanabe and Olsen (1965) and measured at 715 nm, using a Cary 16 spectrophotometer equipped with 10-cm path length cells.

Isotopic dilution techniques with ³²P (carrier free as NaH₂PO₄) were used to estimate the quantity of exchangeable P associated with the suspended sediment. A 50 g portion of the runoff sample was spiked with 0.01 microcuries of ³²P, shaken overnight, centrifuged, and the supernatant was analyzed for ³²P activity and PO₄-P. A series of blanks, consisting of a 50 g portion of runoff filtered through a 0.45 - μm Millipore filter, was similarly spiked, equilibrated, and analyzed for ³²P activity. With a knowledge of PO₄-P in solution, ³²P solution activity (blanks and sediment samples), and sediment concentration, it was possible to calculate on either a mass (μg/g) or volume basis (mg/l) the quantity of exchangeable P associated with the sediment.

RESULTS AND DISCUSSION

Sediment Phosphorus Enrichment

On a mass basis, concentrations of total, inorganic, and organic P in the outflow suspended sediments of Callahan Reservoir were greater than those in the inflow suspended sediments (Table 1). This apparent enrichment of P in the outflow sediments can be attributed to processes of selective coarse sediment deposition within the reservoir. For the study period, 87 percent of all sediment entering the reservoir was trapped (Rausch and Schreiber, 1977). The yearly inflow discharge weighted

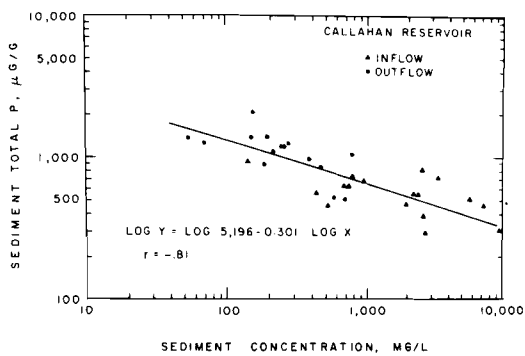


FIG. 1 Sediment total phosphorus concentration [mass] as related to sediment concentration for storms during the 1973 water year.

mean suspended sediment concentration was 3,663 mg/l as compared with 386 mg/l in the outflow. Thus, sediment deposition decreased 10-fold the sediment concentration in the outflow. Coarse sediment deposition within the reservoir effectively increases the clay proportion (<2 μm) in the outflow suspended sediments. Since P is largely associated with clay, an apparent enrichment of P in the outflow suspended sediments is to be expected. Outflow suspended sediments were enriched in total P by a factor of 2 (Table 1). Also, outflow suspended sediments contained 55 and 45 percent of the total P as inorganic and organic P, respectively, as compared with 63 and 37 percent in inflow suspended sediments (Table 1).

On a mass basis, storm mean sediment total P concentrations were inversely related to the sediment concentration as a log transformed power function with a slope of -0.30 (Fig. 1). This is attributed to higher clay concentrations at very low sediment concentrations. Similarly, concentrations of inorganic and organic P in bottom sediment cores from near the outlet of Callahan Reservoir were 1.2 to 3.0 times greater than P concentrations near the inlet (Olness and Rausch, 1977). Clay content of the same bottom sediment cores increased from the reservoir inlet to the outlet by a factor of 2.5 and correlated significantly with the increase in sediment P content. Similar enrichment in organic matter and nutrients of lake bottom sediments as compared with contributing watershed soils have also been observed (Frink, 1969). Even though Callahan outflow suspended sediments had a higher P concentration on a mass basis, 72 percent of the total sediment P entering the reservoir was trapped (Rausch and Schreiber, 1977). Thus, both the quantity of sediment trapped in the reservoir, as well as its P content, were important in sediment-P trapping efficiency.

Fig. 2 shows the relationship between sediment total-P yields and sediment yield for individual storms. These data partly support a conclusion by Olness, that P is accumulating in the bottom sediments of Callahan at a rate nearly proportional to the sediment accumulation rate (Olness and Rausch, 1977). The regression slope of 0.84 indicates apparent P enrichment at low sediment yields. Sediment transport of nutrients from watersheds in northern Mississippi also indicated that loss of plant nutrients is not linearly related to sediment concentration or soil loss, but rather, to clay loss in the runoff (Holt, et al. 1973).

Assuming that a part of the P associated with the suspended sediment is biologically important, suspended

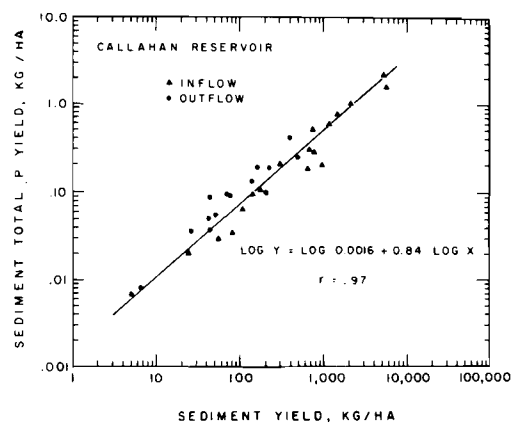


FIG. 2 Inflow-outflow total sediment phosphorus yield as related to sediment yield for Callahan Reservoir.

sediment-P concentrations are more meaningfully expressed on a volume basis. Sediment P per volume of runoff is the product of mgP/g of sediment and g sediment/l of runoff. Mean annual suspended sediment concentrations for the inflow and outflow were 3,663 and 386 mg/l, respectively. Utilizing these data, along with the sediment total P data (Table 1), volume sediment total P concentrations for the inflow and outflow are 1.47 and 0.32 mg/l, respectively. Thus, the concentration of inflow sediment total P on a volume basis is over 4 times more than that for the outflow (Table 1). On a volume basis, storm mean concentrations were related to sediment concentrations as a log transformed power function (Fig. 3). The slope of 0.66 indicates a non-linear relationship. Values of suspended sediment total P ranged from 0.07 to 3.00 mg/l. The relative position of inflow sediment P to outflow sediment P is reversed in Figs. 1 and 3; i.e., on a volume basis the outflow has a smaller concentration of suspended sediment total P than does the inflow, which could be important with respect to downstream eutrophication. Similar relationships were developed for inorganic and organic P (Table 2, equations [3], [4], [5], and [6]).

Sediment - ^{32}P Relationships

While suspended sediment total P values were as

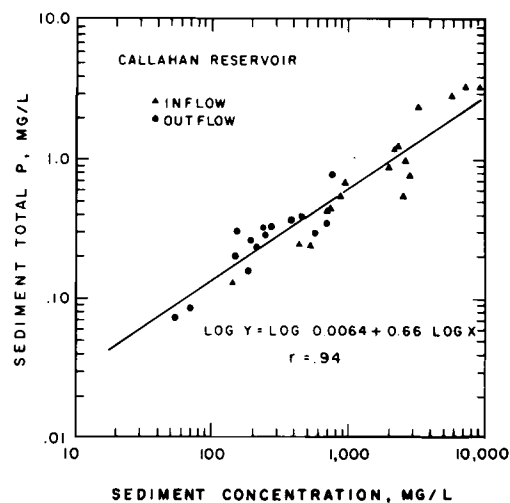


FIG. 3 Sediment total phosphorus concentration [volume] as related to sediment concentration for storms during the 1973 water year.

TABLE 2. SEDIMENT PHOSPHORUS RELATIONSHIPS FOR CALLAHAN RESERVOIR.

Regression equation	Y equals	X equals	r
[1] $Y = 5.196X^{-0.30}$	Sediment total P ($\mu\text{g/g}$)	Sediment conc. (mg/l)	-0.81
[2] $Y = 0.0064X^{0.66}$	Sediment total P (mg/l)	Sediment conc. (mg/l)	0.94
[3] $Y = 2.376X^{-0.26}$	Sediment inorganic P ($\mu\text{g/g}$)	Sediment conc. (mg/l)	-0.74
[4] $Y = 0.0035X^{0.67}$	Sediment inorganic P (mg/l)	Sediment conc. (mg/l)	0.94
[5] $Y = 2.315X^{-0.32}$	Sediment organic P ($\mu\text{g/g}$)	Sediment conc. (mg/l)	-0.75
[6] $Y = 0.0020X^{0.69}$	Sediment organic P (mg/l)	Sediment conc. (mg/l)	0.89
[7] $Y = 586.6X^{-0.34}$	Clay, percent	Sediment conc. (mg/l)	-0.94*
[8] $Y = 0.00079X^{1.07}$	Total P (clay) (mg/l)	Clay conc. (mg/l)	0.99*

* Derived from point samples of selected hydrographs; data are not discharge-weighted.

large as 900 $\mu\text{g/g}$ for the inflow and 2,080 $\mu\text{g/g}$ for the outflow, these data do not imply that all of this P is available for desorption and subsequent biological activity. There is general agreement that only a small portion of the sediment is able to undergo exchange with ortho-P in solution. The quantity of exchangeable sediment P is important because biological depletion of ortho-P could result in desorption of sediment P to maintain the solution P-sediment P equilibria. Various methods, like P-adsorption isotherms, resin extractions, and isotopic dilution with ^{32}P have been used to estimate the sediment pool of exchangeable P. In this study, sediment-aqueous samples were equilibrated with ^{32}P to quantitatively define the loosely bound sediment P, which could undergo exchange with P in solution. Conceivably, this same loosely-held sediment P could be utilized by algae, if the sediment-solution P equilibria were shifted toward P desorption during an algal bloom, when soluble P might decrease in concentration.

At equilibrium, P^{31} solid, the readily exchangeable P can be calculated by the following equation:

$$P^{31}\text{solid} = \frac{^{32}\text{P solid}}{^{32}\text{P soln}} \times P^{31}\text{soln}$$

P^{31} solid = exchangeable sediment P in equilibrium with the solution-phase P,

^{32}P solid = ^{32}P associated with the sediment phase at equilibrium,

^{32}P soln = ^{32}P associated with the aqueous phase at equilibrium, and

P^{31} soln = non-radioactive ortho-P ($\text{PO}_4\text{-P}$) associated with the aqueous phase at equilibrium.

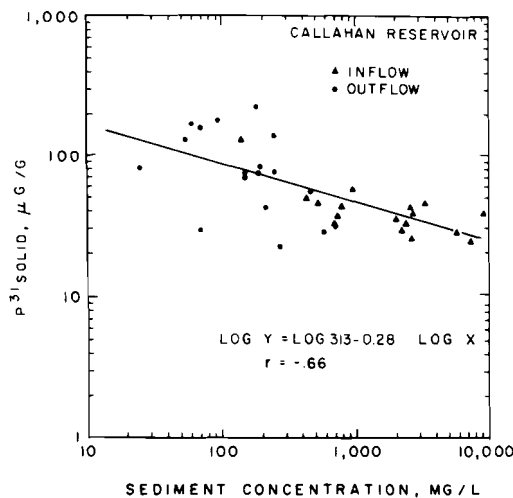


FIG. 4 Exchangeable phosphorus concentration [mass] as related to sediment concentration for storms during the 1973 water year.

The ^{32}P -equilibration data reflect the sediment P enrichment processes, as sediment moves through the reservoir (Fig. 4, Table 3). Mean annual concentration of exchangeable P in the outflow suspended sediments (41 $\mu\text{g/g}$) was larger than that in the inflow suspended sediments (30 $\mu\text{g/g}$). On a mass basis, exchangeable sediment P was inversely related to sediment concentration (Fig. 4). High exchangeable P concentrations ($\mu\text{g/g}$) in the outflow suspended sediments can probably be attributed to the greater proportions of clay in the suspended sediment. Increased sorption of solution phase ortho-P by progressively finer sediments as suspended sediment moves through the reservoir could also account for increased exchangeable P per unit of sediment. The mean annual concentration of ortho-P in the outflow was only 0.021 mg/l compared with 0.059 mg/l in the inflow (Table 4). The inorganic P fraction of sediment in other studies responded to changes in lake conditions which affected total sediment P content (Wildung, et al. 1974). Also, much of the recently adsorbed P is usually adsorbed in some labile form (Harter, 1968). Since exchangeable P is associated with suspended sediment inorganic P, the quantity of exchangeable P was expressed as a percentage of the inorganic P (Table 3). Considering both inflow and outflow, only a small portion, about 11 percent, of the inorganic sediment P (about 6 percent of the sediment total P) could undergo exchange with P in solution (Tables 1 and 3). Furthermore, the percentage of exchangeable P was nearly the same in inflow and outflow sediments and was independent of sediment concentration.

Anion resin extraction of suspended sediments from an agricultural watershed indicated that about 6 percent of the P sorbed by the sediments was extractable (Kunishi, et al. 1972). Equilibration studies with ^{32}P on Wisconsin bottom sediments indicated that 19 to 43 percent of the inorganic P was exchangeable and that a substantial portion of inorganic P in sediments should be available to organisms in close contact with the

TABLE 3. SEDIMENT EXCHANGEABLE PHOSPHORUS IN THE INFLOW AND OUTFLOW OF CALLAHAN RESERVOIR.*

	Exchangeable sediment phosphorus†			Labile phosphorus‡
	mg/l	$\mu\text{g/g}$	percent §	mg/l
Inflow	0.109	30	12	0.168
Outflow	0.016	41	9	0.037

* Discharge weighted mean values for the 1973 water year

† Exchangeable phosphorus as determined by ^{32}P equilibration

‡ Labile P = exchangeable P (mg/l) + soluble orthophosphorus (mg/l)

§ $\frac{P^{31}\text{solid, } \mu\text{g/g}}{P_{\text{inorganic, } \mu\text{g/g}}} \times 100 = \text{percent exchangeable.}$

TABLE 4. SOLUBLE PHOSPHORUS CONCENTRATIONS IN THE INFLOW AND OUTFLOW OF CALLAHAN RESERVOIR.*

	Organic	Hydrolyzable	Ortho
	-----mg/l-----		
Inflow	0.008	0.002	0.059
Outflow	0.011	0.005	0.021

*Discharge weighted mean values for the 1973 water year, expressed as elemental P.

sediments (Armstrong, et al. 1971). On a volume basis, there was an 85 percent decrease in exchangeable P as the sediment moved through the reservoir (Table 3). Likewise, labile P [P^{31} solid, (mg/l) + PO_4 -P, (mg/l)], the total P in the system which undergoes isotopic exchange, was much lower in the outflow, 0.037 mg/l, as compared with the inflow, 0.168 mg/l. Exchangeable P concentrations (mg/l) increased as a nonlinear function of sediment concentration (Fig. 5).

Clay-Phosphorus Relationships

Since sediment P is associated with the more chemically active clay, information on the clay content of the inflow and outflow would aid in understanding the movement of P through the Callahan Reservoir system. Due to the limited sample size, storm discharge weighted clay data were not obtainable; however, clay concentrations were determined in individual point samples from various storm hydrographs, when sample size permitted. These same samples were analyzed for sediment P (total, inorganic, organic, ^{32}P exchangeable) and soluble P. In total, 84 individual hydrograph point samples were analyzed for clay content (< 2 μ m) from January through July 1973, when there was the most runoff. Clay content was inversely related to the sediment concentration with a correlation coefficient of -0.94 (Table 2, equation [7]). Clay percentages were constant at 87 percent in the outflow, but ranged from 22 to 58 percent in the inflow samples.

While the clay data represented only specific point samples from various storms, the data add strength to explanations regarding P movement through the reservoir. For example, the relationship between sediment total P (clay-volume basis) and clay concentration shows that the slope of the regression was nearly equal to 1.00 (Table 2, equation [8]).

Inflow and Outflow Soluble Phosphorus

Ortho-P was the dominant form of soluble P (86 and 57 percent in the inflow and outflow, respectively). The mean annual weighted concentration of ortho-P in the inflow (0.059 mg/l) was nearly three times greater than that in the outflow (0.021 mg/l; Table 4). This decrease in ortho-P concentration could be due to utilization by algae and/or adsorption to sediment with subsequent deposition within, or transport out of, the reservoir.

Concentrations of dissolved organic and hydrolyzable P were higher in the outflow than in the inflow, which may have been caused by P released from dead algae and decomposing bottom organic matter. Of the total dissolved P, the reservoir outflow contained 30 and 14 percent organic and hydrolyzable P, respectively, as compared with only 12 and 3 percent, respectively, for

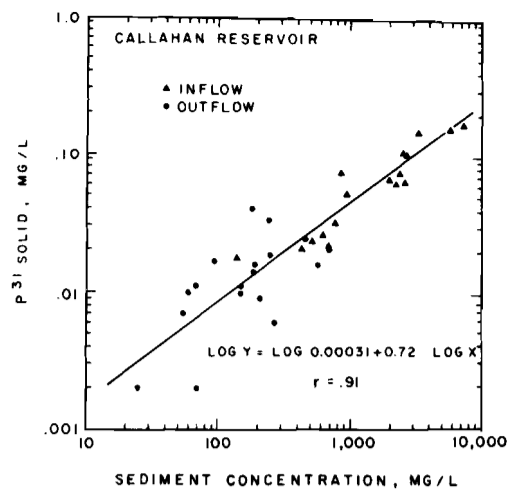


FIG. 5 Exchangeable phosphorus concentration [volume] as related to sediment concentration for storms during the 1973 water year.

the inflow (Table 4). While inorganic P (ortho-P) is the form most readily utilized by phytoplankton, they can excrete soluble organic P compounds during biosynthesis (Gumerman, 1970; Lean, 1973). Also, some enzymes can break down and release organic phosphorus forms from bottom sediments (Golterman, 1973). Dissolved organic-P compounds in natural waters can account for a significant part of the total P present (Minear, 1972).

CONCLUSION

Chemical and physical analyses of the inflow and outflow of a midwest reservoir indicated a reduction in the P concentration of the outflow relative to the inflow. Although outflow suspended sediments were enriched severalfold in sediment P, the concentrations of total, inorganic, and organic P on a volume basis were considerably lower in the outflow as compared with the inflow. Also, the most readily available forms of P, (ortho-P and sediment exchangeable P) were decreased both in volume concentrations and outflow loadings, even though the quantity of inflow (runoff) into Callahan Reservoir was 148 percent above normal.

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