



Project Summary

Biological Availability of Sediment Phosphorus Inputs to the Lower Great Lakes

Scott C. Martin, Joseph V. DePinto, and Thomas C. Young

In this study, river water samples were collected from several major tributaries to the Lower Great Lakes during storm runoff events in the spring and early summer of 1980 and 1981. Suspended sediments from these samples were subjected to a chemical fractionation sequence of NaOH-CDB-HCl, as well as algal bioassay analyses of sediment P bioavailability using the Dual Culture Diffusion Apparatus (DCDA) technique of DePinto. Sediments from several of the bioassay experiments were reconcentrated after the bioassays and resubjected to the chemical fractionation sequence. Several other forms of P inputs to the Lower Great Lakes were also analyzed for chemical composition and/or bioavailability.

This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Since April, 1972, when the governments of Canada and the United States signed the Great Lakes Water Quality Agreement, extensive efforts have been made to curb eutrophication in the Lower Great Lakes. This attention has been focused primarily on the Lower Lakes (Erie and Ontario), where the most severe problems exist. Reductions in the phosphorus (P) loadings to these lakes are generally considered to be the most effective

means of controlling eutrophication. Accordingly, target total P loads were established based on the reduction of treatment plant effluent P concentrations to 1.0 mg/l. These were later revised through the use of water quality models to predict the load reductions necessary to achieve the desired water quality for the Great Lakes (Task Group III, 1978). Billions of dollars were committed to improving P removal at wastewater treatment facilities discharging to the Lower Lakes basin. Although municipal loads have decreased considerably, the revised target loads of 11,000 metric tons/year for Lake Erie and 7,000 metric tons/year for Lake Ontario cannot be met via the present programs. In addition, improvements in the water quality of the lakes resulting from these load reductions have, to date, been less than anticipated. Future courses of action being considered include further reductions in municipal treatment plant effluent P concentrations to 0.5 mg/l and improvement of land management practices (e.g. implementation of conservation tillage programs) in order to reduce diffuse (runoff) sources of P to the lakes (U.S. Army Corps of Engineers, 1982).

Consideration of these options has caused the utility of target loads based on total P to be questioned. It is now recognized that the relative availability of P from different sources for supporting algal growth must be carefully evaluated in developing a cost-effective management scheme for the control of eutrophication. Nearly 50% of the total P load to Lake Erie and 40% of the Lake Ontario load are from diffuse sources. A large fraction of this P is in a sediment-bound

form and may, therefore, not be readily available for an algal uptake. Studies of several Great Lakes tributaries have indicated that generally 40% or less of suspended sediment total P is potentially bioavailable. However, the kinetics of conversion of unavailable allochthonous P to available forms have not been adequately quantified. It is possible that particulate material may settle out of the water column before all of its potentially available P is released. In addition, the rate of P release from allochthonous particulate material in the water column may differ considerably from the regeneration rate for autochthonous particulate P.

As P associated with suspended particulate material enters the receiving water environment, it may become available for algal uptake via desorption, dissolution, and microbial decomposition of organic matter. The degree of particulate P availability depends on the physical, chemical and biological characteristics of the particles and the receiving water. Among the most important factors are the lake's productivity level, soluble inorganic P concentration in the water column, temperature, lake morphometry, hydrology and mixing dynamics, size, shape, and density of the particles, and the chemical forms of P in the particles. A more thorough understanding of the relationships between these factors and the bioavailability of particulate P, in order to predict P release for a wide variety of sediment and receiving water conditions, was the overall goal of this study.

The specific objectives of the experimental program were:

1. to determine the rate and extent of sediment P bioavailability for a variety of tributaries to the Lower Great Lakes under receiving water conditions using a bioassay procedure;
2. to physically and chemically characterize the tributary suspended sediments with respect to factors influencing phosphorus bioavailability;
3. to develop a methodology that may be used to estimate the rate and extent of available P release from suspended sediments based on the characteristics of the sediments; and
4. to compare the P bioavailability and chemical characteristics of tributary suspended sediments to other potential sources of sediment P to the Lower Great Lakes.

Experimental Approach

River water samples were collected from six Lower Great Lakes tributaries

(Maumee, Sandusky, Cuyahoga, and Genesee Rivers, and Honey and Cattaraugus Creeks) during storm runoff events. Over 50 tributary suspended sediment samples were collected during March-June, 1980 and April-June, 1981. Suspended sediments from these samples were concentrated and algal bioassays of sediment P availability were conducted using the Dual Culture Diffusion Apparatus (DCDA) method of DePinto (1982). In addition, a variety of chemical and physical analyses were performed, including sediment particle size distribution (results presented in the full report) and a chemical fractionation sequence for sediment P. Kinetic coefficients (rate and amount) for the release of sediment P were determined and correlations between these values and the physical and chemical parameters were examined. This was done to develop a means of predicting the kinetics of sediment P bioavailability based on a more convenient analytical procedure than the sediment P bioassays.

Results

Tributary Suspended Sediments

The P fractionation procedure used in this study consisted of the sequential measurement of reactive (R-NaOH-P) and nonreactive (NR-NaOH-P) sodium hydroxide extractable P, citrate-dithionite-bicarbonate extractable phosphorus (CDB-P), HCl extractable P (HCl-P) and the residual fraction after the above sequence. A summary of the P fractionation results for the tributary suspended sediment samples is shown in Table 1. Concentrations of most of the extractable fractions were consistent among the samples for a given tributary. Greater variability was seen between tributaries than among samples from any one tributary. Thus, it appears that temporal variations in the forms of P bound to suspended sediments in streams are of minor importance compared to differences in soil type and land use, at least for periods of high flow associated with stormwater runoff.

The chemical fractionation results in Table 1 can provide insights into the forms and mobility of P associated with suspended sediments from the different tributaries. The sum of R-NaOH-P and CDB-P fractions may be considered to represent the concentration of non-apatite inorganic P (NAIP) in the suspended sediments, while HCl-P provides an estimate of apatite P. Thus, the Ohio tributaries

contained high levels of NAIP and small amounts of apatite P, while Cattaraugus Creek sediments were rich in apatite P and low in NAIP. Samples from the Genesee and Detroit Rivers contained intermediate levels of both NAIP and apatite P.

The release of available P from river sediments in the DCDA reactors was measured by monitoring P uptake by *Selenastrum capricornutum* in the assay vessel. An example of a plot of cumulative P release versus time obtained from bioassays on two samples (#19 and #20) is shown in Figure 1. The form of these release curves is typical of the results observed for the majority of samples analyzed. In Figure 1, the error bars about each data point represent one standard deviation for triplicate bioassays, while the solid lines illustrate the amount of sediment P release predicted by the first-order equation:

$$P_{rel}(t) = P_{ult}[1 - \exp(-K_r t)] \quad (1)$$

where $P_{rel}(t)$ = the amount of sediment P released at time t ($\mu\text{gP/g sed}$), P_{ult} = the total amount of sediment P ultimately available for algal uptake ($\mu\text{gP/g sed}$), and k_r = the first-order P release rate coefficient (day^{-1} , base e).

A summary of the tributary mean values calculated for the first-order release coefficients, P_{ult} and k_r are presented in Table 2. The order of mean bioavailable sediment P concentrations for the tributaries was Cuyahoga > Maumee > Honey > Sandusky > Genesee > Cattaraugus. These results confirm that the ultimately available fraction of tributary suspended sediments is much less than that of autochthonously produced particulate P (e.g. phytoplankton), while its release rate is much faster.

The implications of not distinguishing between external ultimately available P and that produced within the lake in phytoplankton models have been reported elsewhere. When sediments of tributary origin remain suspended in the water column of a lake for longer than about 7 days, the current modeling approach would tend to overestimate the input of soluble P to the lake. For models calibrated primarily on the basis of algal biomass, this would likely cause an overprediction of soluble P concentrations in the water column. In turn, this might lead to either an overestimation of the P retention time, or an unrealistic adjustment of other model coefficients in order to effect a calibration. It might also lead to inaccurate conclusions about the relative con-

tributions of the various P sources to biological productivity in the lake.

In order to investigate the possibility of using a chemical method as a surrogate measure of bioavailable P, simple product-moment correlation coefficients (*r*) were determined between all chemically extractable sediment P fractions (Table 1) and the one-component P release coefficients, P_{ult} and k_r (Table 2).

All of the chemical fractions except Residual P were significantly correlated ($\alpha < 0.05$) with P_{ult} . The highest correlation coefficient obtained was between P_{ult} and non-apatite inorganic P (NAIP = R-NaOH-P + CDB-P); however, the inorganic component of base-extractable sediment P (R-NaOH-P) is more closely linked to bioavailability than any other single chemical fraction measured in this study. Correlation coefficients and regression equations are presented in the full report.

Observation of the changes in sediment P fractionation during DCDA bioassays confirmed that the major contribution of the various chemically extractable forms of sediment P to the release during bioassays came from R-NaOH-P. This was accomplished by reconcentrating the sediments after a DCDA run and resubjecting them to the same chemical fractionation sequence used for initial characterization. Seventeen of the 52

tributary samples were analyzed in this manner. The most noticeable feature of the data from this analysis is that decreases in R-NaOH-P during the bioassays consistently exceeded the changes in all other chemical fractions. A large and relatively constant percentage of the R-NaOH-P initially present in the DCDA was released for all of the samples analyzed. This percentage ranged from 66.0 to 80.1%, with a mean of 70.8% and a coefficient of variation of only 6.5%. In addition, Δ R-NaOH-P was very closely correlated ($r = 0.896$) with the amount of sediment P taken up by the assay culture in the bioassays.

Shoreline Bluff and Bottom Sediment Samples

The erosion of shoreline (bluff) sediments and the resuspension of lake bottom sediments during high winds both may result in substantial inputs of particulate P into the water column of Lake Erie. The biological availability of sediment P in samples from these sources was investigated using chemical fractionation and bioassay analyses. The results are presented in Table 3. These data are especially interesting since they encompass much wider extremes of sediment P fractionation and bioavailability than the tributary data.

The eroding bluff material contained extremely low levels of NaOH- and CDB-extractable P. In addition, the T-Sed-P concentrations of the Port Stanley and Rondeau Park samples were well below the lowest value measured for tributary sediments. A large percentage (mean = 78.3%) of T-Sed-P in the bluff samples was removed in the HCl extraction step and, therefore, was most likely present in the form of apatite P. By comparison, although concentrations (in $\mu\text{gP/g}$ sediment) were similar for Cattaraugus Creek sediments, HCl P made up only 47.9% of T-Sed-P. In DCDA bioassays on these samples, none of the sediment P became available to algae during the course of the experiments. This is consistent with the assertion made by other researchers that apatite P is virtually unavailable to aquatic organisms and that recessionary shoreline sediments contain very low levels of bioavailable sediment P.

The Monroe bottom sediment samples represent the opposite extreme from the bluff sediments. All concentrations of T-Sed-P, T-NaOH-P, and CDB-P in the Monroe #2 sample were more than twice as large as the highest values observed for tributary suspended sediments. Bioassays showed that P_{ult} for both Monroe samples was also over twice the largest value measured for tributary sediments. The percentage of T-Sed-P available to

Table 1. Summary of P Fractionation Results for Tributary Suspended Sediments

Tributary T-SED-P	Concentrations in $\mu\text{gP/g}$ sediment						
	(TP-TSP) SS	T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P
Maumee River (n = 9):							
Mean	1,259	1,244	403 (32.0)*	273 (21.7)	131 (10.4)	238 (18.9)	174 (13.8)
C.V. (%)	14.3	18.9	32.4	20.9	61.9	17.5	42.2
Sandusky River (n = 25):							
Mean	1,188	1,193	449 (37.7)	298 (25.1)	151 (12.7)	237 (20.0)	194 (16.3)
C.V. (%)	11.7	13.6	20.8	20.8	31.1	21.0	42.5
Cuyahoga River (n = 4):							
Mean	1,315	1,246	575 (43.8)	442 (33.6)	133 (10.1)	280 (21.3)	73 (5.6)
C.V. (%)	6.2	9.9	13.4	21.4	29.6	16.6	63.9
Cattaraugus Creek (n = 5):							
Mean	637	588	76 (11.9)	46 (7.2)	30 (4.7)	82 (12.9)	48 (7.5)
C.V. (%)	11.0	12.0	33.2	27.2	46.5	22.7	8.7
Honey Creek (n = 4):							
Mean	1,189	1,218	505 (42.5)	356 (30.0)	149 (12.5)	203 (17.1)	265 (22.3)
C.V. (%)	16.5	14.5	19.1	23.5	11.3	22.2	21.7
Genesee River (n = 1):							
	957	994	240 (25.1)	170 (17.8)	69 (7.2)	187 (19.5)	77 (8.0)
Detroit River (n = 1)†:							
	1,424	—	596 (41.9)	305 (21.4)	291 (20.4)	177 (12.4)	170 (11.9)

*Values in parentheses are means expressed as a percentage of T-Sed-P.

†Sediments composited from four sampling locations.

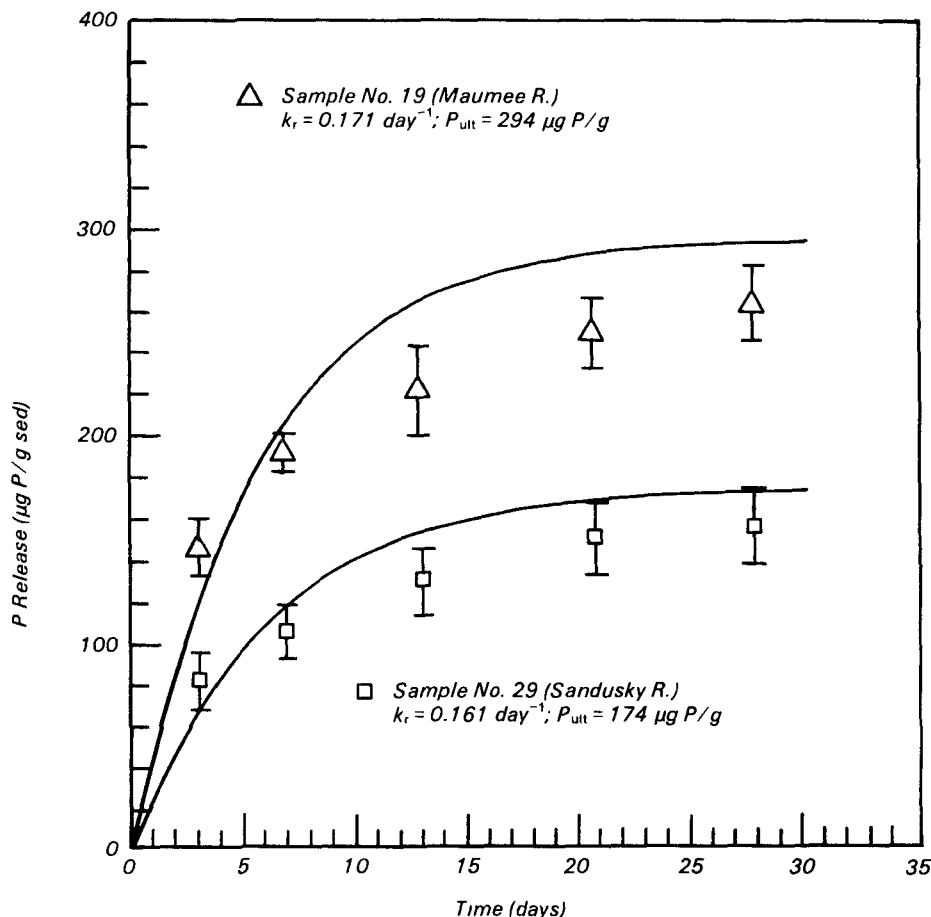


Figure 1. Cumulative release of sediment P versus time measured in DCDA bioassays on Samples #19 (Maumee R.) and #20 (Sandusky R.).

algae (over 50%) was greater as well. Bottom sediments from the Toledo sites, on the other hand, exhibited chemical fractionation and bioavailability characteristics well within the ranges measured for tributary suspended sediments.

Sandusky River Bottom Sediment Samples

The effect of a point source of P on the sediment P chemistry was also briefly examined. Our chemical fractionation sequence was applied to bottom sediment samples from three sites each upstream and downstream from the Bucyrus, Ohio wastewater treatment plant discharge (on the Sandusky River). The results are given in Table 4. Substantial increases in the R-NaOH-P and CDB-P fractions occurred downstream of the point source. The NR-NaOH-P, HCl-P, and Residual P fractions increased by smaller amounts. This movement of P into the sediments is consistent

with the finding that soluble reactive P concentrations decreased rapidly with distance downstream from the Bucyrus treatment plant discharge. The data in Table 4 indicate that, although much of the point source P may be in relatively unavailable forms such as CDB-P, HCl-P, and Residual P, a sizable amount is also present as R-NaOH-P, and is therefore potentially bioavailable should these sediments become resuspended and carried into the receiving water body. Never-

theless, these data suggest that the P discharged from an indirect point source undergoes a reduction in bioavailability in transit to the receiving water body relative to that discharged from a direct point source.

Conclusions

An analytical program combining the accuracy of bioassay measurements with the efficiency of chemical fractionation studies has been shown to be an effective means of quantifying sediment P bioavailability. The information gathered in this study can, therefore, serve as a preliminary basis for evaluating the impact of P management strategies on bioavailable P loads to the lower Great Lakes. It also provided the necessary process experimental information for implementing changes in phytoplankton model structures to permit differentiation of allochthonous and autochthonous sources of bioavailable P.

The results presented in the full report indicate that bioavailability remains relatively constant for a given set of soil type (i.e. geochemistry and texture) and land use conditions. Evidence is seen in the similarity between the bioassay and fractionation results for the Maumee and Sandusky Rivers. Also, Cattaraugus Creek sediments, which were much higher in apatite content, showed a distinctly lower level of P availability. The Cuyahoga River, which experiences a greater anthropogenic influence, displayed a higher level of sediment P bioavailability. Little fluctuation in sediment characteristics was observed over time for any given tributary. Based on these findings, it is felt that future monitoring programs should concentrate on identifying differences between regions of distinct soil type and land use. This can be accomplished most readily by using routine chemical extraction analyses on sediments transported during storm runoff events supplemented by less frequent bioassay measurements of sediment P bioavailability.

Table 2. Mean First-Order Release Coefficients Calculated from Bioassay Data

Tributary	T-Sed-P* in DCDA's (µgP/g sed)	Ultimately Bioavailable Sediment P P _{ult} (µgP/g sed)	P _{ult} as a % of T-Sed-P	Release Rate, k _r (day ⁻¹)
Maumee River	1308	337.3	25.0	0.182
Sandusky River	1145	247.1	21.4	0.177
Cuyahoga River	1314	449.2	33.9	0.188
Genesee River	900	173.8	19.3	0.264
Cattaraugus Creek	559	38.8	7.7	0.131
Honey Creek	1198	298.0	24.9	0.214

*The T-Sed-P values listed in this table are based on TP and SS analyses performed on the sediment suspensions placed in the DCDA's.

Table 3. Chemical Fractionation and Bioassay Results for Shoreline Erosion (Bluff) and Lake Bottom Sediment Samples

A) Chemical Fractionations (Values in = gP/g sed.):

Sample (Type)	T-Sed-P	T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P
Monroe #1 (bottom)	2266	1321	1226	95	475	258	44
Monroe #2 (bottom)	3551	1863	1796	67	612	315	43
Toledo #1 (bottom)	926	208	156	53	156	248	105
Toledo #2 (bottom)	935	226	187	40	167	227	99
Port Stanley (bluff)	279	13	8	5	94	228	25
Rondeau Park (bluff)	396	8	6	2	22	326	28
L. Superior (bluff)	771	15	13	2	32	543	88

B) DCDA Bioassays (One-Component Release Coefficients Calculated by Thomas Method):

Sample	T-Sed-P in DCDA's ($\mu\text{gP/g sed.}$)	Sediment P Released in DCDA's ($\mu\text{gP/g sed.}$)	Ultimately Bioavailable Sediment P, P_{ult} ($\mu\text{gP/g sed.}$)	P_{ult} as a % of T-Sed-P	Release Rate, k_r (day^{-1})
Monroe #1	2656	964.2	1435.0	54.0	0.42
Monroe #2	3044	1341.3	1482.4	48.7	0.080
Toledo #1	947	99.3	99.3	10.5	0.140
Port Stanley	662	0	0	0	—
Rondeau Park	557	0	0	0	—

Table 4. Effects of a Point Source Discharge on Phosphorus Fractionation in Sandusky River Bottom Sediments

Site no.	Miles from point source	Concentrations in $\mu\text{gP/g sediment}$							Sandusky River Flow	Point Source Discharge
		T-Sed-P	T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P		
1	9	777	284	215	69	214	125	107	●	
2	7	644	226	177	49	160	123	91	●	
3	3	470	55	43	12	92	263	54	●	
4	0.5	1510	528	434	94	452	249	132	●	
5	5	1039	397	320	77	308	165	119	●	
6	10	1404	596	305	291	177	323	170	●	

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S. C. Martin, J. V. DePinto, and T. C. Young are with Clarkson College of Technology, Potsdam, NY 13676.
W. L. Richardson is the EPA Project Officer (see below).
 The complete report, entitled "Biological Availability of Sediment Phosphorus Inputs to the Lower Great Lakes," (Order No. PB 85-121 036; Cost: \$17.50, subject to change) will be available only from:
 National Technical Information Service
 5285 Port Royal Road
 Springfield, VA 22161
 Telephone: 703-487-4650
 The EPA Project Officer can be contacted at:
 Large Lakes Research Station
 Environmental Research Laboratory—Duluth
 U.S. Environmental Protection Agency
 Grosse Ile, MI 48138

