

Phosphorus availability in particulate materials transported by urban runoff

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ONE OF THE ADVERSE EFFECTS OF URBANIZATION in the U. S. is the increase in the volume of urban stormwater runoff discharged to lakes and streams. Early studies¹⁻³ on urban runoff from a residential-light commercial area of Cincinnati, Ohio, demonstrated that urban runoff may contain concentrations of suspended solids (ss) that may exceed the concentrations found in raw domestic wastewater. In these studies, total phosphorus concentrations averaged 0.36 mg P/L, much higher than the critical threshold level of 0.01 mg P/L of soluble inorganic P, which was cited by Sawyer⁴ for algal nuisance conditions in lakes.

Because of the importance of phosphorus in the nutrition of algae, the phosphorus contributions from point sources, such as waste treatment plants, and also from diffuse sources, such as urban runoff, must be considered in nutrient budget calculations used for planning eutrophication control measures. Kluesener and Lee⁵ estimated that approximately 80 percent of the annual total P input to Lake Wingra, Madison, Wis., is from urban runoff. Owen and Johnson⁶ noted that, in one case, urban runoff produced a yield of total P that was seven times greater than the average yield from three agricultural watersheds in the metropolitan Toronto, Ont., Can., region.

The phosphorus transported by urban runoff occurs in both soluble and insoluble forms. Weibel *et al.*³ found that 62 percent of the total hydrolyzable P in their Cincinnati runoff samples was soluble hydrolyzable P. Similarly, Kluesener and Lee⁵ reported that about 58 percent of the total P in their samples was dissolved reactive P, as defined by the soluble orthophosphate colorimetric procedure of Murphy and Riley.⁷ Thus, about 40

percent of the total P in urban runoff may occur as particulate P. Much of this particulate P is apparently associated with the fine solids fraction of the particulate matter transported in the runoff. Sartor *et al.*⁸ reported that about 56 percent of the total P by weight in dry street contaminants was associated with very fine, silt-like material (< 43 μ). This fine material accounted for only 5.9 percent of the total solids by weight; thus, the small particles must have been relatively rich in phosphorus.

Because the availability to algae of the phosphorus in this particulate material is unknown, the availability of the total P loadings from urban runoff is also unknown, as is demonstrated by these equations:

$$TP = TSP + PP \quad (1)$$

$$\text{Available TP} = TSP \times (\text{percentage of TSP available}) + PP \times (\text{Percentage of PP available}). \quad (2)$$

in which

TP = total phosphorus,
TSP = total soluble phosphorus, and
PP = particulate phosphorus.

If it is assumed that essentially all of the total soluble P is eventually converted to soluble inorganic (orthophosphate-P) in the receiving water (and hence becomes 100 percent available to algae), then Equation 2 indicates that knowledge of the availability of the particulate P fraction of runoff allows estimation of the percentage of total P that should become available to algae. Such estimates would be more realistic inputs to nutrient budgets than would total P values. This study was undertaken to provide

estimates of the availability of runoff particulate P forms collected from a variety of urban land uses.

METHODS

Study area. Grab samples of urban runoff were collected at several locations in the city of Madison, Wis. (population 171,769 in 1970), from August 1972 to March 1973. Table I describes the areas drained by the runoff collected at each of the sampling stations, and Figure 1 shows the locations of these stations. Runoff was collected from low, medium, and high density residential areas; a university campus; the central commercial district; and areas of urban construction activity. No industrial land use areas were sampled, because these areas constituted only a small fraction of the total Madison urban area. The residential drainage basin around Station B (Manitou Way) has been described in detail by Kluesener and Lee.⁵

For runoff from urban construction activities, Station F was initially selected because of severe erosion from construction of an apartment complex. During the study, however, the exposed soil was covered with sod, and one sample (No. F-9) was taken after sodding for comparison with earlier samples. An alternate site at a nearby street

construction project (Station I) was then selected for the final sample of construction site runoff (No. I-12).

The samples were collected during 12 precipitation or snowmelt events when the storm sewer or street gutter flows were high enough for convenient collection of 1 gal (3.78 L) of sample in a plastic bottle. The samples were stored in darkness at 4°C within a few hours after collection and were maintained in cold storage until analysis.

Chemical analyses. The following phosphorus forms were determined by chemical analysis of urban runoff:

1. Dissolved reactive,
2. Total soluble,
3. Particulate,
4. Total, and
5. Particulate inorganic extracted by
 - (a) Acid,
 - (b) Base, and
 - (c) Anion exchange resin.

Dissolved reactive P was determined by the Murphy and Riley⁷ colorimetric procedure for soluble orthophosphate-P on samples filtered through 0.45- μ pore size membrane filters. Total soluble P was determined on the same filtered

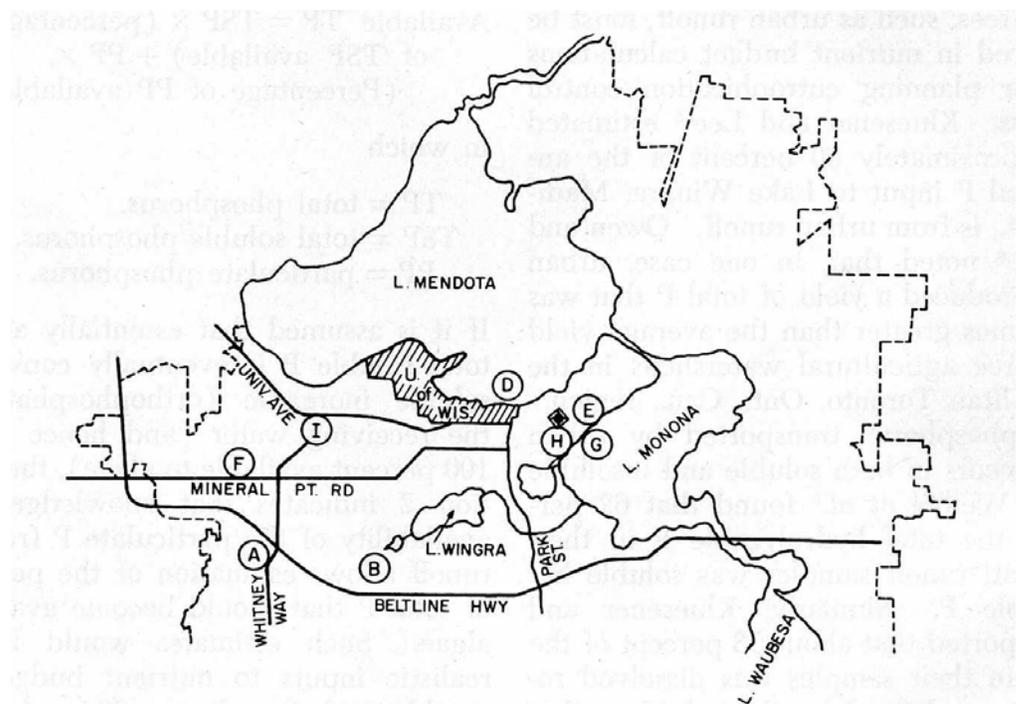


FIGURE 1.—Urban runoff sampling stations in Madison, Wis.

TABLE I.—Description of Areas Sampled for Urban Runoff

Sampling Station	Madison Zoning Code for Drainage Area	Description of Drainage Area
A	R1	Single family residential, with some low density multiple family dwellings
B	R2	Area like R1, except that less usable open space per dwelling is allowed
D	R5	The University of Wisconsin campus near Bascom Hill
H	R6	High density residential, located near the center of Madison, with low usable open space per dwelling unit
E and G	C4	Central commercial district around the capitol square
F	R1, R5, C1, C2	Residential-light commercial, with soil erosion from construction activity until sod was put down
I	R2	Residential, with soil erosion caused by construction activities

samples after H_2SO_4 -potassium persulfate digestion according to "Standard Methods."⁹ After digestion, the samples were neutralized and analyzed by the same procedure used for dissolved reactive P. Total P was measured on unfiltered runoff samples with the same procedure used for total soluble P. Before neutralizing the persulfate-digested samples, however, residual turbidity was removed by filtration. Particulate P was found either by calculation (total P - total soluble P), or by digestion of runoff particles that had been separated from the parent sample by 0.45- μ membrane filtration. The particles retained on the filters after passage of a known volume of

runoff were scraped into distilled water or phosphorus-free algal bioassay medium by using a metal spatula. The particulate suspension was then analyzed by the same procedure used for total P, and the particulate P concentration of the original runoff sample was computed from the volumes of runoff filtered and resuspension liquid used. The calculation method (total P - total soluble P) was used to quantitate the particulate P extracted by chemical methods, while the direct digestion procedure was used to measure the particulate inorganic P present in algal bioassay test flasks.

Particulate inorganic P was extracted from particles isolated on 0.45- μ pore size membrane filters and scraped into a solution containing acid, base, or anion exchange resin. For acid extraction, the particles and the membrane filter used for their isolation were placed into 20 ml of a solution containing 8.1 ml of concentrated HCl and 1.3 ml of concentrated H_2SO_4 /2 L of distilled water¹⁰ for 5 to 15 min at room temperature. The suspension was then filtered through glass fiber or membrane filters and analyzed by the dissolved reactive P procedure. Base extractions were performed with 0.1 N NaOH-0.1 N NaCl solution¹¹ in a similar manner, except that the membrane filter used to isolate the particles was removed from the extraction medium after the particles had been scraped off. The suspensions of particles in base were shaken overnight at 15° to 22°C on a wrist-action shaker before filtration and analysis by the dissolved reactive P procedure.

Particulate inorganic P extracted by resin was measured by resuspending runoff particles in 100 ml of water containing 1 g of air-dry, 20-50 mesh Dowex 1-X8 anion exchange resin* in the chloride form. The dry resin was sieved with a No. 60 (250- μ) wire sieve before use to remove small resin particles. The suspensions of resin and particulate matter were shaken for 24 hr at 15 to 22° C on a wrist-action shaker, the membrane filter used to isolate the runoff particles being left in each test flask. After the shaking period, the flasks were allowed to stand to effect the sedimentation

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of the resin beads, and a supernatant sample was decanted for filtration and dissolved reactive P analysis. The residue of resin and runoff particles was then poured through the No. 60 sieve to isolate the resin from the (smaller) runoff particles. The resin was scraped from the sieve into a long stem funnel, which was fitted with a plastic tube and pinch clamp on its stem and was filled with 1 N Na_2SO_4 solution. After soaking for 2 hr, the resin was eluted at about 3 ml/min with fresh Na_2SO_4 solution added to the funnel as required until 100 ml of leachate was collected. The leachate was analyzed by the dissolved reactive P procedure and corrected for the dissolved reactive P in the Na_2SO_4 and for the percentage recovery of orthophosphate spikes (added to 1 g of resin) by the Na_2SO_4 leaching procedure. The sum of the resin-bound inorganic P and the dissolved reactive P in the flask supernatant was termed the resin-extractable dissolved reactive P of the test flask. All chemical analyses and extractions were performed in duplicate or triplicate.

Bioassays of particulate P. Particles isolated by membrane filtration were resuspended in P-free algal assay procedure¹² medium, and five replicate 25-ml portions of the particulate suspension were placed into 50-ml Erlenmeyer flasks. One ml of water and 1 ml of a 27×10^4 cell/ml *Selenastrum capricornutum* suspension were added to give an initial cell population of 10^4 cells/ml. Standards and blanks were prepared in a similar manner, distilled water or KH_2PO_4 solutions being added to 25 ml of algal assay procedure medium. All flasks were stoppered with cotton and incubated for 19 to 22 days under algal assay procedure bottle test¹² conditions with daily swirling by hand. The cell yield in each test flask was determined by hemocytometer cell counting at the end of the incubation period.

Dark incubations. One hundred ml of unfiltered runoff were placed in each of three cotton-stoppered flasks and stored in darkness at 15° to 22°C for 21 to 50 days. The flasks were swirled daily by hand and aliquots were removed

twice during the incubation for dissolved reactive P determination. To six other portions of runoff was added 1 g of Dowex 1-X8 resin/flask. Twice during the incubation, three of the flasks were processed for resin-extractable dissolved reactive P analysis and their contents discarded.

In a similar manner, runoff particles were incubated in darkness after resuspension from membrane filters into Lake Mendota or Lake Monona water, with and without added resin. Lake water controls, with and without resin, were incubated along with the runoff particle suspensions so that the net dissolved reactive or resin-extractable dissolved reactive P from the runoff particles could be calculated.

Particulate P sorption of inorganic P. The sorption of soluble inorganic P by runoff particles was investigated by adding standard solutions to aliquots of runoff sample D-11 and shaking the spiked runoff for 24 hr. An aliquot was taken for dissolved reactive P analysis, and the remainder of the runoff was given 1 g of Dowex 1-X8 resin and shaken for 24 hr. The resin-extractable dissolved reactive P concentrations in the samples were then compared with the expected values of dissolved reactive P (Initial + added dissolved reactive P).

Particulate P concentrations. Concentrations of particulate P in Madison runoff samples varied widely, even among those collected from a given area (Table II). In the 44 samples collected for this study, the particulate P forms accounted for

TABLE II.—Particulate P Concentrations in Madison Urban Runoff Samples

Sampling Station	No. of Samples Collected	Particulate P Concentration Range ($\mu\text{g P/l}$)
A	9	33–223
B	9	99–421
D	10	85–561
H	4	69–262
E and G	7	14–145
F and I	4	365–2,850
F*	1	203

* Sample F-9 collected after construction site was sodded.

TABLE III.—Recovery of Particulate P from Urban Runoff by Membrane Filtration and Scraping

Sample	Particulate P Concentration ($\mu\text{g P/l}$)		Percentage Recovery $A/B \times 100$
	A Determined from Filtered, Scraped Particles	B Determined by Calculation (Total P - Total Soluble P)	
E-11	138	145	95
D-11	453	441	103
H-11	253	262	96
A-12	194	214	91
B-12	408	421	97
D-12	524	561	93
I-12	1,540	1,419	109

13 to 97 percent of the total P. Highest particulate P concentrations were found at actively eroding construction sites (Stations F and I, 365 to 2850 $\mu\text{g P/L}$), while sampling F-9, collected after sodding of a construction site, seemed to have a somewhat lower

particulate P level of 203 $\mu\text{g P/L}$. Lowest particulate P concentrations in this study were generally found in runoff collected from the central commercial district of the city, where most of the drainage area consisted of concrete surfaces (Stations E and G).

Comparison tests between particulate P concentrations calculated by difference (total P - total soluble P) and those determined by direct persulfate digestion of particles scraped off the 0.45- μ pore size filters showed (Table III) that the scraping technique used to isolate the particles for extraction or bioassay recovered about 91 to 109 percent of the calculated particulate P in the runoff.

Chemical extraction of inorganic P from particulate P. A summary of the particulate inorganic P extractable by acid, base, and resin is given in Figure 2. Because all of the extractions could not always be run on each sample, the extraction results from all samples collected from a given land use class were pooled for each method of extraction. The group ranges and mean

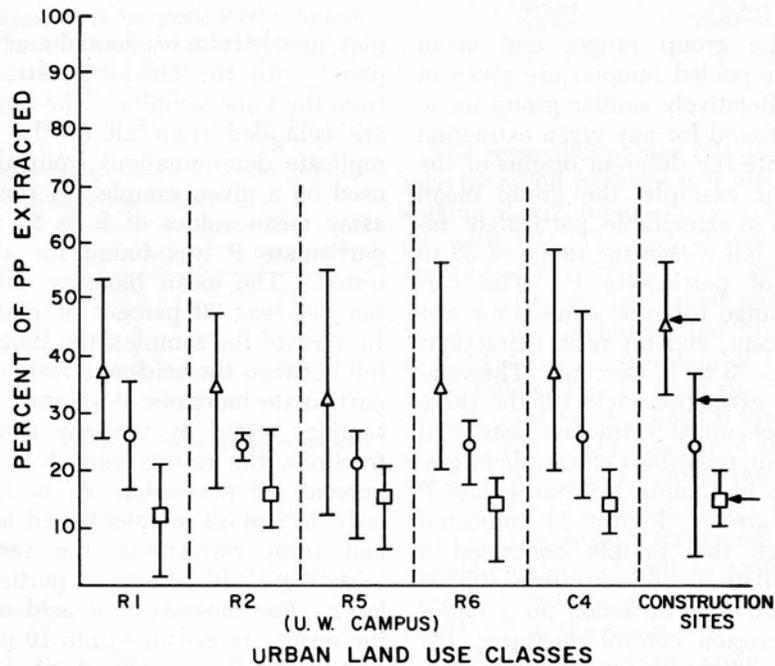


FIGURE 2.—Inorganic P extracted from runoff particles by acid (Δ), base (\circ), and anion exchange resin (\square), showing group mean values and group ranges. Arrows denote values from sample F-9, described in text.

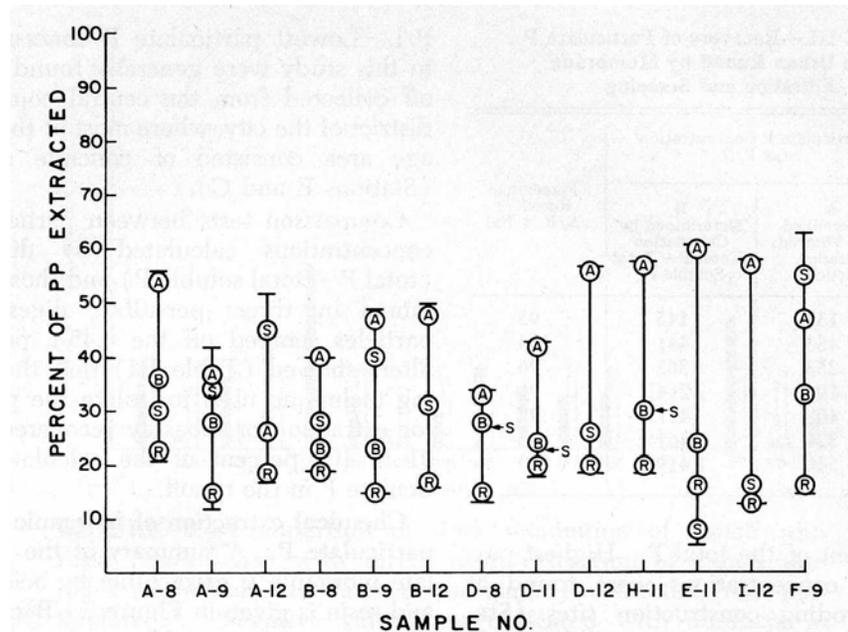


FIGURE 3.—Comparison of *Selenastrum* bioassays (S) of particulate P forms with chemical extractions of inorganic P from particulate P by acid (A), base (B), and anion exchange resin (R). Circled values are mean values; brackets denote ranges.

values for the pooled samples are given in the figure. Relatively similar group mean values were found for any given extraction method despite the different origins of the samples. For example, the group mean values for acid-extractable particulate inorganic P all fell within the range of 33 to 46 percent of particulate P. The corresponding range for base extractions was 22 to 27 percent, and for resin extractions the range was 13 to 17 percent. The relative order of extraction yield for the three methods of chemical extraction was acid > base > resin, regardless of sample origin.

The results of sample F-9 particulate P extractions (arrows, Figure 2) indicated that, although this sample contained a lower particulate P concentration (Table II) than the other construction site samples because of erosion control measures, the relative proportions of extractable particulate inorganic P in sample F-9 were comparable with those of other samples.

Algal bioassays. In Figure 3 the results of *Selenastrum* bioassays of 13 runoff samples,

mostly from residential areas, are compared with the chemical extraction data from the same samples. The ranges shown are compiled from all of the individual replicate determinations from all methods used on a given sample. A range of bioassay mean values of 8 to 55 percent of particulate P was found for all samples tested. The mean bioassay value for all samples was 30 percent of particulate P. In most of the samples, the bioassay value fell between the acid- and resin-extractable particulate inorganic P values. In 6 of 10 samples tested by bioassay and base extractions, the results agreed to within 10 percent (of particulate P) or less. Similarly, in 7 of 13 samples tested by bioassay and resin extractions, the results were fairly close (10 percent of particulate P or less). For bioassay and acid extractions, the results agreed to within 10 percent (of particulate P) in only 4 of 13 samples tested. No attempt was made to relate the bioassay results to sample origin because of the small number of samples tested from commercial and urban construction areas.

TABLE IV.—Net Mean Dissolved Reactive P Released from Runoff Particles to Lake Waters During Dark Incubations

Runoff Sample Particles	Particulate P incubated ($\mu\text{g P/l}$)	Net Mean Dissolved Reactive P ($\mu\text{g P/l}$) from Particles			
		Sample Particulate P only		Sample Particulate P + Resin	
		13 days	26 days	13 days	26 days
D-11 in Lake Mendota water	118	6	9	25	21
E-11 in Lake Monona water	158	-30	-20	7	12
H-11 in Lake Monona water	329	-35	-14	20	34

Dark incubation of particulate P in lake waters. The 26-day dark incubation of runoff particles in lake waters without added resin (Table IV) showed small posi-

TABLE V.—Recovery of Inorganic P from Spiked Urban Runoff Sample D-11 by Anion Exchange Resin

Dissolved Reactive P ($\mu\text{g P/l}$)		
Added in Spike*	Expected	Observed
0	212	191
50	262	246
98	310	281
192	404	363

Dissolved reactive P recovered by resin equilibration (24 hr)

Resin-extractable Dissolved Reactive P ($\mu\text{g P/l}$)		
Expected	Recovered	Percentage Recovered
212	213	100
262	280	107
310	344	111
404	428	106

* Four replicate flasks for each treatment; all data are mean values.

tive contributions of dissolved reactive P from sample D-11 particles and negative contributions from sample E-11 and sample H-11 particles. A negative dissolved reactive P contribution means that the runoff particles removed soluble inorganic P from the lake waters.

Addition of Dowex 1-X8 resin to the suspensions effectively dropped the dissolved reactive P levels of the lake waters from the initial values of 66 and 80 $\mu\text{g/L}$ for Lake Mendota and Lake Monona, respectively, to about 2 $\mu\text{g P/L}$. The computed resin-extractable dissolved reactive P contributions from runoff particles in these tests were positive for all three samples tested, in contrast to the experiments without the added resin. Comparison of the net mean resin-extractable dissolved reactive P values observed (in the incubations with resin) with the runoff particulate P concentrations incubated gave the following percentages:

Sample Particles	Maximum Percentage of Particulate P Observed as Net Mean resin-extractable dissolved reactive P
D-11	21
E-11	8
H-11	10

The reversible nature of inorganic P uptake by runoff particles was investigated by spiking an unfiltered sample (D-11) of runoff with KH_2PO_4 and allowing time for equilibration. Inorganic P was removed from solution by the runoff particles at all spike levels, including the unspiked controls (Table V). Addition of Dowex 1-X8 resin, followed by 24 hr of shaking, showed resin-extractable dissolved reactive P values of from 100 to 111 percent of the expected values. Apparently all of the soluble inorganic P lost to the particles in the spike test could be readily recovered in the resin extraction step, as well as some of the inorganic P initially associated with the particulate P in the sample.

Dark incubation of unfiltered runoff. Samples of runoff incubated in darkness without added anion exchange resin generally showed dissolved reactive P levels equal to or less than the resin-extractable dissolved

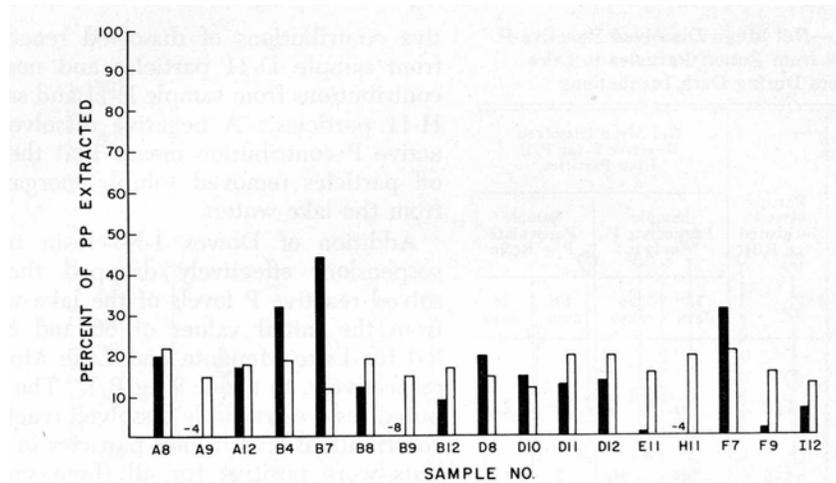


FIGURE 4.—Comparison of dark incubation of runoff plus resin (dark bars) with direct resin extraction of runoff particles (light bars) in terms of inorganic P extracted from particulate P. Negative values are indicated with numbers in place of bars.

reactive P values from flasks with resin. In the flasks with resin, the resin-extractable dissolved reactive P values at 50 days were generally close to the values at 25 days in the early tests. Consequently, samples from lake runoff events (Nos. 11 and 12) were incubated only 21 to 26 days. The estimated concentration of soluble inorganic P released from particulate P in flasks incubated with resin was computed with Equation 3.

$$\text{Estimated inorganic P released from PP} = \frac{\text{Maximum observed R-DRP} - \text{Initial Sample TSP}}{\text{Sample TSP}} \quad (3)$$

in which
 R-DRP = resin-extractable dissolved reactive phosphorus.

Values computed with Equation 3 were expressed as percentages of sample particulate P for comparison with the direct resin extractable particulate inorganic P values from the same samples (Figure 4). Equation 3 is only an estimate because it assumes that all of the total soluble P in the sample is present as soluble inorganic P (and measured as resin-extractable dissolved reactive P) by the end of the test, so that any resin-extractable

dissolved reactive P in excess of the initial sample, total soluble P must have come from the particulate P forms in the runoff. Calculated values found with Equation 3 ranged from -8 to 44 percent of particulate P. In only 3 of the 17 samples tested (B-4, B-7, and F-7) were the values from the dark incubations at least 10 percent of particulate P higher than the values from direct resin extraction of particulate P in distilled water. Nine of the 17 samples showed dark incubation values in essential agreement (within 10 percent of particulate P) with the direct resin extraction data, while five of the samples showed lower values for the dark incubations relative to the direct resin extractions of particulate P.

DISCUSSION

Particulate P concentrations. The wide range of particulate P concentrations found in runoff collected for this study could be attributed to several things. Among these are different street solids loading intensities found in different urban land uses^{8,13,14} and changes in ss concentrations as a function of time during the runoff event, including the effects of antecedent runoff events.^{3,5}

Also included are extra particulate inputs (such as autumn leaf fall), discharge of winter residues in spring snowmelt, and construction activities in the drainage basin.^{5, 13, 14} Regardless of the absolute concentrations of particulate P in the samples, however, the particulate P collected was expected to represent the qualitative nature of much of the particulate matter transported to the Madison lakes by urban runoff.

Inorganic P extracted from particulate P.

Comparison of group mean values of extractable particulate inorganic P from particulate P samples collected in different urban land uses indicated very little difference between the land uses for any given extraction method. Possibly, the dominant form of particulate P in all of the samples was derived from a common source input, such as dustfall or eroded soil. A 1969 study¹³ in Chicago showed that dust and dirt were generally the predominant forms of street litter in that city, except in October and November, when leaf litter became more important. Sather and Boyd¹⁴ found that, despite different loading intensities of total P in street surface contaminants from different urban land uses, the P content of the solids did not seem to differ appreciably among the various land use types (0.103 to 0.142 percent by weight).

In the study reported herein, group mean values of acid- and base-extractable particulate inorganic P ranged from 22 to 46 percent of particulate P, with considerable overlap between the two procedures (Figure 2). This overlap was expected, because the acid extraction should dissolve calcium phosphate completely and aluminum and iron-bound phosphate, considerably, while the base extraction should dissolve the aluminum and iron-bound phosphate, but not the calcium phosphate.¹⁵

Compared with acid or base treatments, the resin extraction was a relatively mild treatment, designed to measure the inorganic P on the particles, which was involved in relatively rapid exchange reactions between the solid and liquid

phases. Thus, this test was expected to produce lower values of extractable particulate inorganic P than either the acid or base procedures, as was actually the case for samples from all types of land use.

Comparison of chemical and bioassay data.

Because the chemical extractions of particulate inorganic P were essentially operationally defined procedures, comparisons with algal bioassays were desirable to establish which procedures best estimated algal-available particulate P. The data in Figure 3 indicated that the base and resin extractions seemed to estimate the algal-available fraction of particulate P more closely than did the acid extraction. The group mean values for all samples tested by the resin extraction method ranged from 13 to 17 percent of particulate P, while the bioassay average for all samples was 30 percent. These values bracket the range of group mean values (22 to 27 percent) for the base extraction. The studies of Golterman *et al.*¹⁶ and Fitzgerald¹⁷ have indicated that some relatively insoluble iron phosphates could be used for growth by *Selenastrum*, *Chlorella*, and *Scenedesmus* cells. Thus, some agreement between the algal growth assays and the base extraction, which dissolves iron-bound phosphate, is expected.

Fate of particulate P forms in receiving waters. The dark incubation of particles in lake waters for 26 days demonstrated that the release or uptake of inorganic P by the particles is dependent on the nature of the particles and on the soluble inorganic P concentration of the receiving water. This was noted by Taylor and Kunishi¹⁸ and Ryden *et al.*¹⁹ for agricultural and urban erosion, respectively in flasks without resin, two of the particulate P samples showed inorganic P uptake, while the third showed relatively low inorganic P release to the lake waters. In tests with resin, which lowered the dissolved reactive P level in the suspensions, all of the samples showed P release. Because of this dependence of phosphorus availability on the inorganic P concentration in solution, the tests with resin should be valid for

those periods when, in the receiving water, the dissolved reactive P levels are low and the algal demand for phosphate, as approximated by the anion exchange resin, is high.

The calculated contributions of dissolved reactive P from the particles in the resin lake water flasks (8 to 21 percent of particulate P) were close to the results obtained for the same particulate P samples in the resin-distilled water extraction of particulate P (16 to 20 percent; Figure 3). The relatively long, 26-day dark incubation of particulate P forms with resin in lake waters allowed time for microbial phosphorus mineralization of organic P compounds to inorganic P, as well as for the extraction of inorganic P from the particles via physical-chemical processes such as absorption-desorption and precipitation-dissolution. In contrast, the short, 24-hr resin extraction of particulate P in distilled water provided only a measure of the physical-chemical processes. The close agreement between the results of the two procedures indicated that the physical-chemical processes were more important than microbial mineralization reactions in regulating the release of inorganic P from the runoff particles. The quantitative recovery of immobilized inorganic P spikes from runoff sample D-11 by using anion exchange resin also indicated the importance of physical-chemical processes between inorganic P and runoff particles.

Dark incubations of unfiltered runoff. As in the dark incubations of particulate P forms in lake waters, the dark incubations of unfiltered runoff for 21 to 50 days allowed time for biological mineralization of organic particulate P forms. However, comparison of the results from the dark incubations (with resin) with the short-term (24 hr) direct resin extraction of particulate P in distilled water (Figure 4) showed that, in general, the short-term direct resin extraction values were greater than or equal to the long-term dark incubation values. Thus, the importance of physical-chemical reactions over biological processes was again indicated.

Applications of particulate P availability estimates. The assay procedure most likely to

predict the true availability of the runoff particulate P in receiving water cannot be definitely determined from only the data reported herein. The factors that will affect the eventual availability of particulate P to algae in the photic zone of a lake include the temperature and soluble inorganic P level of the receiving water, the steepness of the lake basin at the point of discharge, the rate of sediment deposition and mixing, and the density and diameter of the runoff particles.

The algal bioassays and dark incubations were performed at 15° to 22°C with adequate mixing and low inorganic P concentrations in solution. Hence, these conditions could be assumed as optimal for release of inorganic P from particulate P, and the results of these tests should be considered as upper bounds for particulate P availability in nature.

With the exception of the acid extractions of particulate inorganic P, all of the tests performed in this study showed on the average an estimated particulate P availability of 30 percent or less. Thus, for Madison urban runoff a value of 30 percent could be used as an estimate of the percentage of particulate P available term in Equation 2. As for the percentage of total soluble P available term in Equation 2, it should be noted that, in the samples collected for this study, the average percentage of total soluble P initially present as dissolved reactive P was 89 percent. Hence, the error in assuming that 100 percent of the total soluble P would eventually be available is probably not great, and Equation 2 could be simplified to give, for runoff samples from Madison, Available TP = TSP + 0.3 x PP. Such available total P concentration values could be multiplied by flow data to obtain urban runoff loading rates for nutrient budget calculations.

CONCLUSIONS

The following conclusions may be drawn from this study:

1. Particulate phosphorus of 0.45- μ pore size or larger, isolated from Madison urban runoff, showed group mean values of acid-extractable

inorganic P from particulate P (extractable particulate inorganic P) that ranged from 33 to 46 percent of particulate P. The corresponding range for base-extractable particulate inorganic P was 22 to 27 percent, and for anion exchange resin-extractable particulate inorganic P the range was 13 to 17 percent of particulate P.

2. Because the group mean values of the chemical extractions represented the chemical nature of particulate P from the various land uses sampled, the relatively narrow ranges of group mean values found for a given type of chemical extraction indicated that the particulate P forms transported by surface runoff from different land uses were similar. Possibly, the dominant type of particulate P in the samples was derived from a common source, such as dustfall or eroded soil. Land uses sampled for urban runoff included low, medium, and high density residential; institutional; commercial; and urban construction.

3. Dark incubations of runoff particulate P in lake waters or dark incubations of unfiltered runoff itself with anion exchange resin indicated that physical-chemical processes were most important factors in the release of inorganic P to solution than was microbial mineralization of particulate P. This conclusion was based on the fairly close agreement between resin-extractable particulate inorganic P in the relatively long-term as compared with short-term aqueous incubation systems containing particulate P and resin.

4. Bioassays of particulate P from Madison runoff generally showed availability values that were between the acid- and resin-extractable particulate inorganic P values for a given sample. The overall average for all samples was 30 percent of particulate P available to *Selenastrum* in 19 to 22 days. With the exception of the acid extractions, all of the tests performed in this study showed average particulate P availability estimates of 30 percent or less. Consequently, for Madison urban stormwater, a probable upper bound of the available total P in a sample of urban

runoff would be given by the sum of total soluble P and 0.3 x particulate P. The available total P concentrations in runoff samples could be multiplied by measured flow rates to give estimated available P loading rates from urban runoff.

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