Kinetics and Modeling of Dissolved Phosphorus Export from a Tile-Drained Agricultural Watershed

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ABSTRACT

Agricultural runoff can be a source of P, a limiting factor for freshwater eutrophication. To develop a simple method to estimate P export from the cropland, we studied 1.2-μm filtered dissolved phosphorus (DP) output from four tiles draining areas ranging from 8 to 25 ha, and from a river draining a 48 173 ha watershed in east-central Illinois during 1993 to 1996. The land was under maize (*Zea mays* L.)-soybean (*Glycine max* L.) rotation. The tiles were estimated to contribute more than 86% of the river flow and 65 to 69% of the river DP export during 1995 to 1996. The DP load from tiles followed consecutive pseudo first-order kinetics in terms of tile flow (DP load depended on the amount of DP remaining in the soil matrix). The kinetic curves indicated a soluble-inorganic-P pool that was quickly depleted and replenished. In contrast, for DP export from the river at the watershed scale we observed pseudo zero-order kinetics based on river flow (DP export was independent of how much DP remained in the watershed). The contribution from numerous tiles and surface runoff to the river may have stabilized DP export at the watershed scale and therefore could explain the different kinetic orders. For the study watershed, a one parameter equation could estimate watershed-wide DP export: k' × (surface water discharge from the watershed) × (watershed area), with k' being 3.94×10^{-6} mg P L^{-1} ha^{-1}. Our approach should be tested in watersheds with different geographic and agricultural characteristics.

Phosphorus is known to be a limiting factor in fresh water eutrophication. Because point sources have generally been controlled, increased attention is being directed at the impact of nonpoint P sources from agricultural runoff on the quality of receiving water bodies (Sharpley et al., 1994; Tiessen, 1995).

Various models have been constructed to estimate P export from agricultural runoff (Dillon et al., 1991; Frink, 1991; Sharpley and Smith, 1992). However, many of these prediction models require numerous parameters and variables that are not readily available. For example, some regression models require geological, hydrological, and meteorological parameters. Examples of these parameters include humidity, slope, peat area percentage, minor till plain area, carbonate till area, exposed bedrock, flow in spring, and area of small open waters (Dillon et al., 1991); the determination of these parameters is tedious. As a result, Sharpley et al. (1995) pointed out that the practical usefulness of these complicated models is often limited.

First-order kinetics have been used to describe the export of pollutants such as chemical oxygen demand and total P from residential, commercial, and highway land (Wanielista et al., 1997):

$$-dX/dt = k X \qquad [1]$$

where X is the amount of a pollutant remaining in a domain, t is time, and k is a constant independent of X or t. By analogy, P export from agricultural land might follow the same kinetics. When the output rate of X from a domain is small as compared to the amount of X in the domain, X could in fact remain constant with respect to time. Then the k X term in Eq. [1] could be combined as k'. Some studies have found weak or no relationships between soil P content and P concentration in runoff (Daniel et al., 1993), and between P loss from leaching and fertilization (Vighi et al., 1991). Therefore, we considered zero-order kinetics for P export as a possibility:

$$-dX/dt = k' \qquad [2]$$

The two kinetic models are illustrated in Fig. 1, where the variable t in Eq. [1] and [2] has been substituted by flow simply because there will be no P export without flow. For the zero-order kinetics in Fig. 1, a straight line results because the export rate of X is the constant k' (Eq. [2]), whereas the first-order kinetic curve in Fig. 1 reaches a plateau because the amount of X remaining in the land is proportional to the export rate and when X is depleted the output rate diminishes (Eq. [1]).

The objectives of this investigation were therefore to (i) elucidate the pattern of P export as related to flow from a typical Midwest tile-drained agricultural watershed; and (ii) estimate P output from the cropland using simple and easily measured parameters. We focused on 1.2-μm filtered DP, because DP is immediately available for algal growth (Steenbergen et al., 1993).

MATERIALS AND METHODS

Camargo Watershed

The upper segment of the Embarras River drains a 48 173 ha watershed with a U.S. Geological Survey (USGS) gauging station located at Camargo, IL, (39°47′30″N, 88°11′10″W). The watershed was under a maize and soybean rotation in east-central Illinois. Besides farmland, 4.5% of the watershed is urban, 0.6% woodland, 0.5% grassland, 0.6% water bodies, 0.3% home sites, and 2.9% roads. There was no large source of sewage effluent into the river. The Mollisols in the area formed in 100 to 150 cm of loess over medium to fine-textured till. Drummer (fine-silty, mixed mesic Typic Haplaquolls) silty clay loams and closely related soils (Flanagan-Catlin) are dominant in the nearly flat watershed where tile drainage is essential for agricultural production. Subterranean drainage tiles

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Abbreviations: DP, dissolved phosphorus passed through 1.2 μm filter; NTS, non-tile seepage; PR, precipitation; SR, surface runoff; TD, tile drainage.

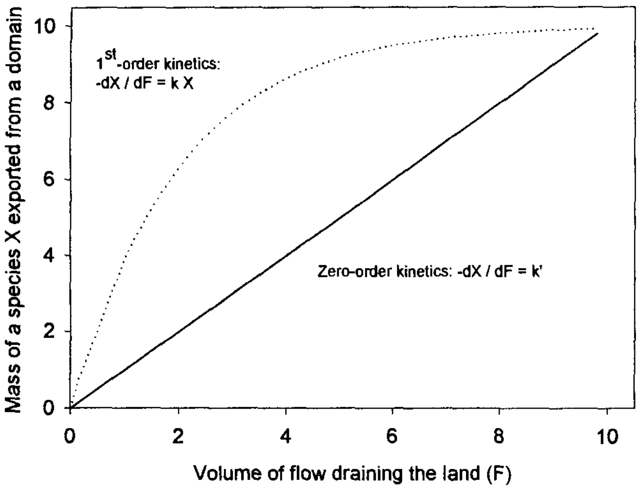

Fig. 1. First- and zero-order kinetic models for the export of a species from a domain.

are estimated to be present in 75 to 80% of the watershed. (See David et al. [1997] and Gentry et al. [1998] for a map and additional information on the watershed.)

Three Hundred North Watersheds

The field-size watersheds were located 15 km upstream of Camargo along the east side of the Embarras River between the roads 200 N and 300 N in south-central Champaign County. There were four drainage tiles located in adjacent agricultural fields draining an estimated total of 65 ha (see David et al. [1997] and Gentry et al. [1998] for detail and a map). All field watersheds as well as the entire Camargo watershed were located in the medium P-supplying region of Illinois where it is recommended that P fertilizer be applied to achieve a minimum Bray P value of 50 kg ha^{-1} (Illinois Agronomy Handbook, 1997–1998). Phosphorus fertilizer (triple super phosphate that contains 46% P) was applied in the fall after crop harvest in the 300 N watersheds. From 1993 to 1996, the average application rate was 42 kg P ha^{-1} yr^{-1}. In the fields drained by tiles A, B, and C, 12 soil sampling locations were positioned as described in Gentry et al. (1998). In December 1994, soil was sampled at each location and extractable P was determined at different depths (the top 30 cm and top 100 cm) using air-dried soils by Bray analysis (Olsen and Sommers, 1982).

River/Tile Flow and Dissolved Phosphorus Analysis

Runoff from the watershed was continuously monitored at the Camargo USGS station on the Embarras River. We monitored water flow and DP concentration in four tiles within the watershed and at the USGS station. Tile A drains 15 ha, tile B 8 ha, tile C 17 ha, and tile D 25 ha. Tile flow was determined on 15 min intervals by fitting each tile outlet with a weir, pressure transducer, and data logger (detail in David et al. [1997] and Gentry et al. [1998]).

For chemical analysis, weekly or biweekly water samples were collected from the Camargo location, whereas frequency of sample collection from the four tile outlets increased with increasing tile flow. Using automated water samplers (ISCO, Inc., Lincoln, NE), tile samples were collected to completely characterize each rain-event hydrograph associated with DP export (David et al., 1997; Gentry et al., 1998). Samples were taken on a USGS water year basis which is from 1 October of the previous calendar year to 30 September of the year. No tile samples were taken when tile flow stopped during the dry season. For instance, tile flow ceased during periods of low precipitation and high evapotranspiration in summer. Water samples were first filtered (Whatman glass fiber filter, 1.2 μm) and then analyzed by ascorbic acid colorimetric technique for dissolved P concentration (APHA, 1995). Dissolved P transport was calculated in terms of concentration (mg P L^{-1}) times flow (L s^{-1}). Flow-weighted concentration was calculated by dividing the sum of instantaneous concentration × corresponding instantaneous flow by the sum of instantaneous flow using the field measured flow values and the measured DP concentrations in the water samples taken from the field by automated water samplers.

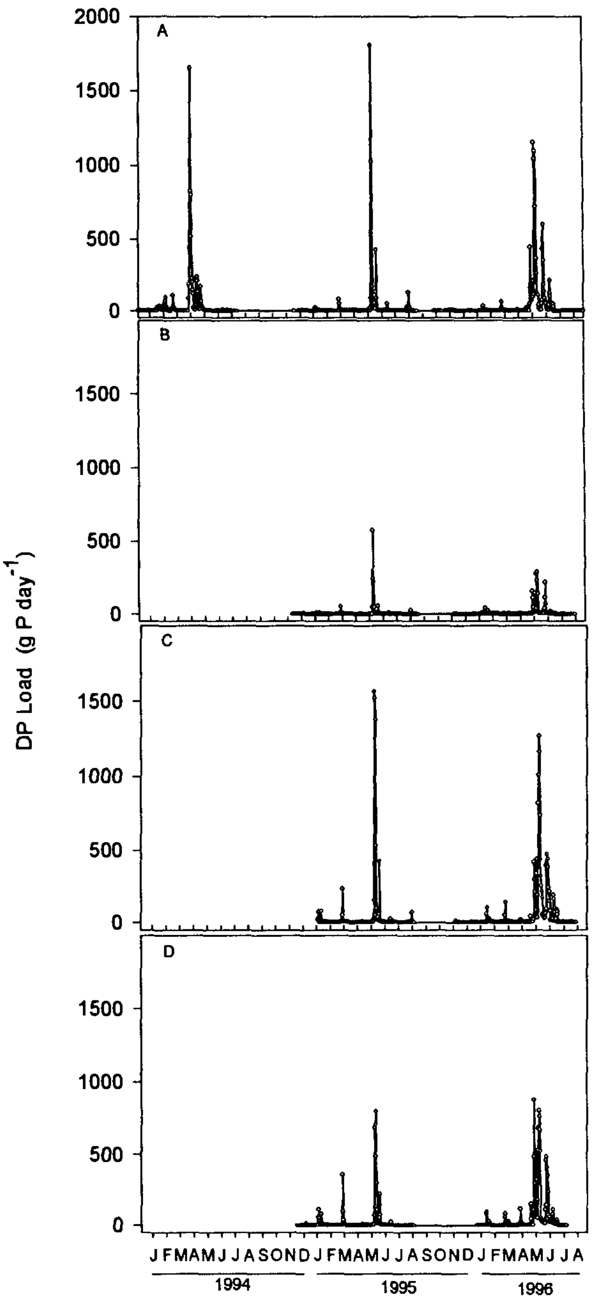

Fig. 2. Loadographs for 1.2-μm filtered dissolved phosphorus (DP) from tiles draining agricultural land under a soybean-corn rotation in east-central Illinois. A: tile A, B: tile B, C: tile C, D: tile D.

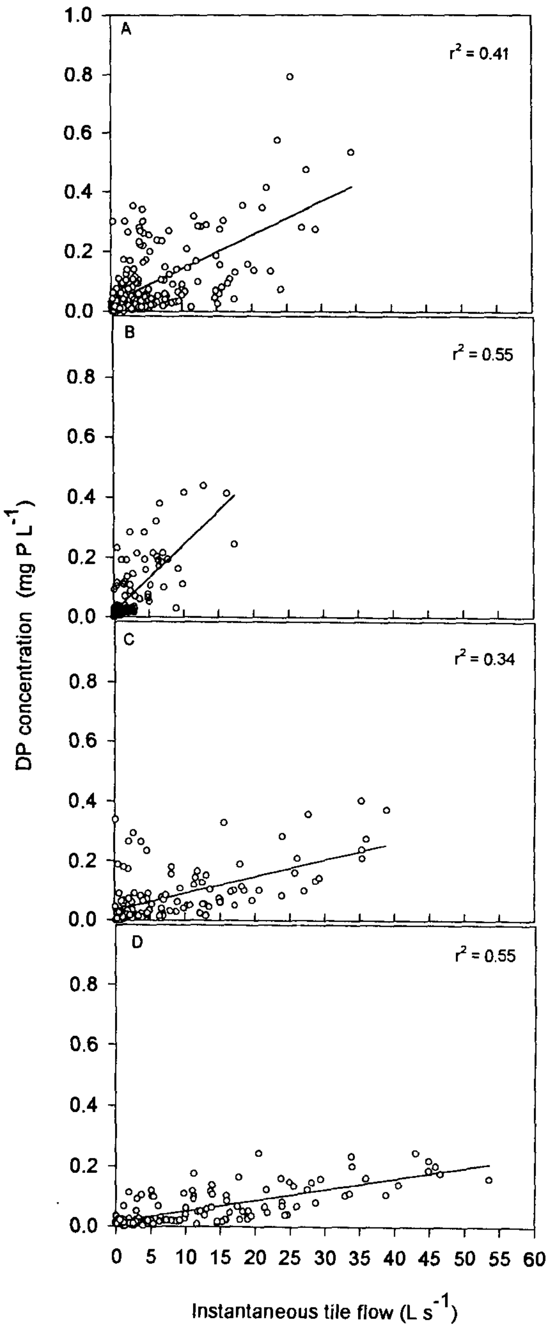

Fig. 3. Correlation between tile flow and 1.2-μm filtered dissolved phosphorus (DP) concentration. A: tile A, B: tile B, C: tile C, D: tile D.

RESULTS AND DISCUSSION

Patterns of Dissolved Phosphorus Export

Loadographs in Fig. 2 (defined as load vs. time) showed that DP export was not constant over time from each of the tiles. The clustered peaks corresponded to intense rains with high tile flow. Because the area under the curves in Fig. 2 represent DP output, a great part of the yearly export could occur in a few days. David et al. (1997) have demonstrated that NO_3^- export from this agricultural watershed was characterized by irregular pulses; Fig. 2 shows that DP output followed a similar pattern. There was a significant but weak correlation between instantaneous tile flow and tile water DP concentration (Fig. 3). Based on coefficients of determination r^2, 34 to 55% of the increase or decrease in DP concentration was due to changes in tile flow (Fig. 3). During heavy rains and high tile flow, DP concentrations in tile water were >0.2 mg P L^{-1}.

Table 1. Export of dissolved phosphorus (DP) from tiles and the river in a watershed under corn-soybean rotation.†

Site	n‡	Water year§	Flow weighted concentration	Flow intensity	DP export
			mg P L^{-1}	$\times 10^3$ m^3 ha^{-1} yr^{-1}	kg P ha^{-1} yr^{-1}
Embarras	44	1993	0.19	6.62	1.24
River at	49	1994	0.21	4.87	1.00
Camargo	44	1995	0.15	2.60	0.40
	48	1996	0.21	3.97	0.84
Yearly average:			0.19	4.52	0.87
Tile A	104	1994	0.18	5.30	0.52
	80	1995	0.17	1.94	0.34
	92	1996	0.17	3.85	0.66
Tile B	78	1995	0.11	1.59	0.18
	71	1996	0.12	2.37	0.30
Tile C	57	1995	0.20	3.23	0.39
	93	1996	0.14	5.54	0.79
Tile D	76	1995	0.08	2.25	0.19
	85	1996	0.11	4.09	0.45
Yearly average of all tiles:			0.14	3.35	0.42

† Camargo is at the outlet of the river that drains the 48 173 ha watershed. Tiles A, B, C, D are within the watershed, draining 15, 8, 17, and 25 ha, respectively.
‡ Number of samples analyzed.
§ From 1 October of the previous year through 30 September of the year.

The yearly average flow-weighted DP concentration at Camargo station on the Embarras River was 0.19 mg P L^{-1}, higher than the tile flow-weighted average 0.14 mg P L^{-1} (Table 1). From the water quality standpoint, total P concentrations above 0.03 mg P L^{-1} in lake waters are considered hypereutrophic (Grobbelaar and House, 1995). The water in the river came from tile drainage (TD), nontile seepage (NTS), surface runoff (SR), and precipitation (PR). A water balance for the watershed is:

$$RO = TD + NTS + SR + PR \quad [3]$$

where RO is the runoff at the Camargo gauging station, the units for the five variables are m^3 yr^{-1}. Equation [3] will hold true when both sides are divided by 48 173 (the area of the study watershed in ha). The PR term, which is the direct precipitation onto the river, was negligible as compared to TD or SR terms in Eq. [3]. If we assume NTS was small as opposed to TD or SR because the study watershed was mostly an artificially drained cropland, the following is derived:

$$RO' = TD' + SR' \quad [4]$$

where the units for all three terms become m^3 ha^{-1} yr^{-1}. We assume our four tiles were representative of all tiles in the watershed. Based on the average flow values for the river and tiles in Table 1 and Eq. [4], we could estimate the contribution of the surface runoff to the river: (2.60 − 2.25)/2.60 = 13.5% for 1995 water year and (3.97 − 3.96)/3.97 = 0.3% for 1996 water year; in the calculation, 2.25 is the average flow of the four tiles for 1995 water year (1.94 + 1.59 + 3.23 + 2.25)/4 and 3.96 is the average flow of the four tiles for 1996 water year. For water years with heavy rains that occur in short periods of time, there will be more surface runoff and therefore a higher surface runoff contribution to the river flow.

Applying this method for DP export and using the average DP export values in Table 1, the contribution of the DP in the surface runoff to the river DP export was (0.40 − 0.275)/0.40 = 31% for 1995 water year and (0.84 − 0.550)/0.84 = 35% for 1996 water year; in the calculation, (0.34 + 0.18 + 0.39 + 0.19)/4 = 0.275 is the average DP export of all four tiles for 1995 water year and 0.550 is the average DP export of all four tiles for 1996 water year. Thus, as a first approximation, surface runoff contributed <14% to the river flow, yet about 31 to 35% of the river DP came from the surface runoff.

These estimates indicate that due to P adsorption the ability of the subsurface water movement to transport DP was smaller than the surface water movement. Our analysis is consistent with Baker et al. (1975) who observed that P loss through subsurface drainage is less than through surface runoff.

Apparent Rate Laws of Dissolved Phosphorus Output

Dissolved P export from cropland is a direct function of water flow and the availability of DP for leaching. Absent of either, DP export will not occur. Seasons, fertilization, soil conditions, and mineralization all affect the availability of flow and DP in the soil matrix. Figure 4 and 6A indicate that DP export was directly driven by flow events because flow curves closely corresponded to DP export curves. Because fertilization occurred during the low flow periods, it did not directly relate to DP export (Fig. 4). Figure 5 shows plots of cumulative DP export vs. cumulative flow for four tiles, and was calculated using measured flow and measured DP concentration values. The curve for each of the tiles in Fig. 5 could be described by connecting several first-order kinetic curves in Fig. 1. Thus, DP export depended on how much P was readily available for output within a short-time period for the small land area drained by each tile. This pool of soluble-soil-inorganic-P (defined as available for leaching) was depleted quickly as the plateaus in Fig. 5 suggest. Because of mineralization, fertilization, and atmospheric deposition inputs, however, the pool of soluble-soil-inorganic-P was soon replenished so another first-order kinetic export could occur.

Soil mineralization of organic P may be an important source of soluble-soil-inorganic P. In temperate regions, only 1 to 2% of soil organic P mineralizes annually; in addition, application of fertilizer P reduces mineralization (Sharpley et al., 1995); thus, fertilization and mineralization complement each other to maintain a certain amount of soluble-soil-inorganic-P in the land. There was a large stock of total P in the soil but only a small portion of the total-P stock was available for leaching. In December 1994, the average extractable soil Bray P measurements (Olsen and Sommers, 1992) from 12 locations in the 300 N watersheds indicated the existence of a P stock: the top 30 cm soil contained 167 kg P ha^{-1} whereas the top 100 cm contained 195 kg P ha^{-1}.

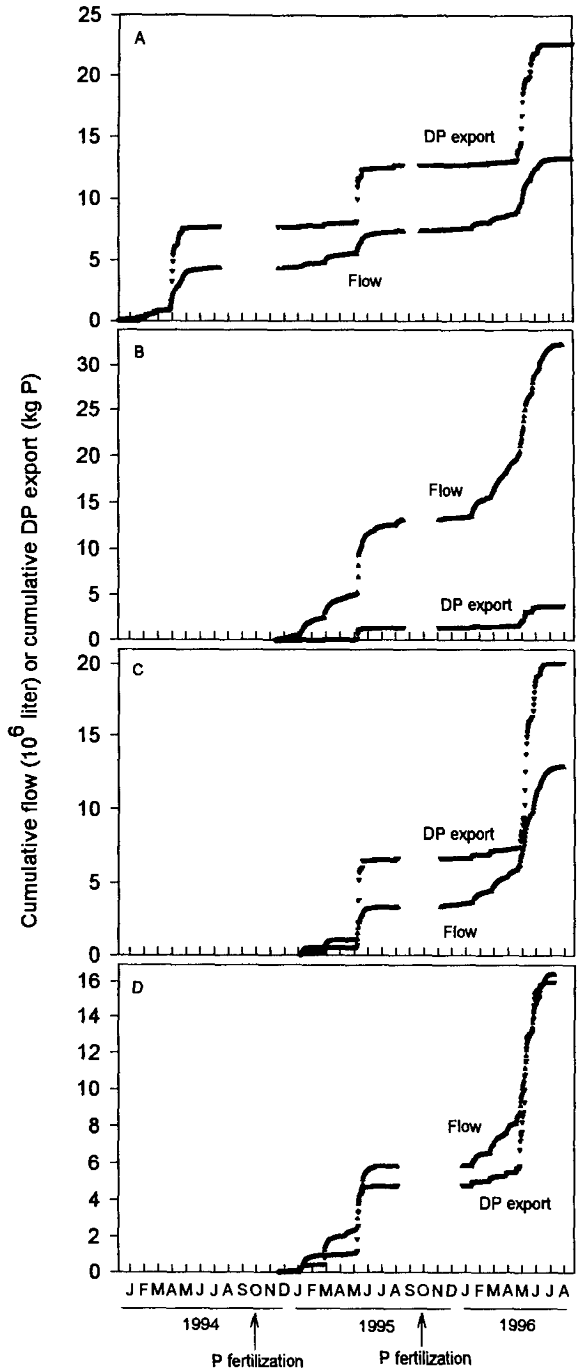

Fig. 4. Patterns of flow and 1.2-μm filtered dissolved P (DP) export. Lines are not continuous when tile flow stopped. A: tile A, B: tile B, C: tile C, D: tile D.

However, <2 kg DP ha^{-1} yr^{-1} was exported from the tiles or watersheds (Table 1). The abundant P stock could serve as a long-term source for DP export. This may explain the apparent consecutive first-order kinetics in Fig. 5. Weaver et al. (1988) used the term "rapidly released P" to describe dissolved inorganic P contained in soil solution after soil incubation. They found that rapidly released P decreased in successive supernatants of the soils they evaluated. Our data revealed a similar effect of "rapidly released P" in drainage tiles.

In contrast to the tile DP export, the DP export from the watershed through the Embarras River followed an

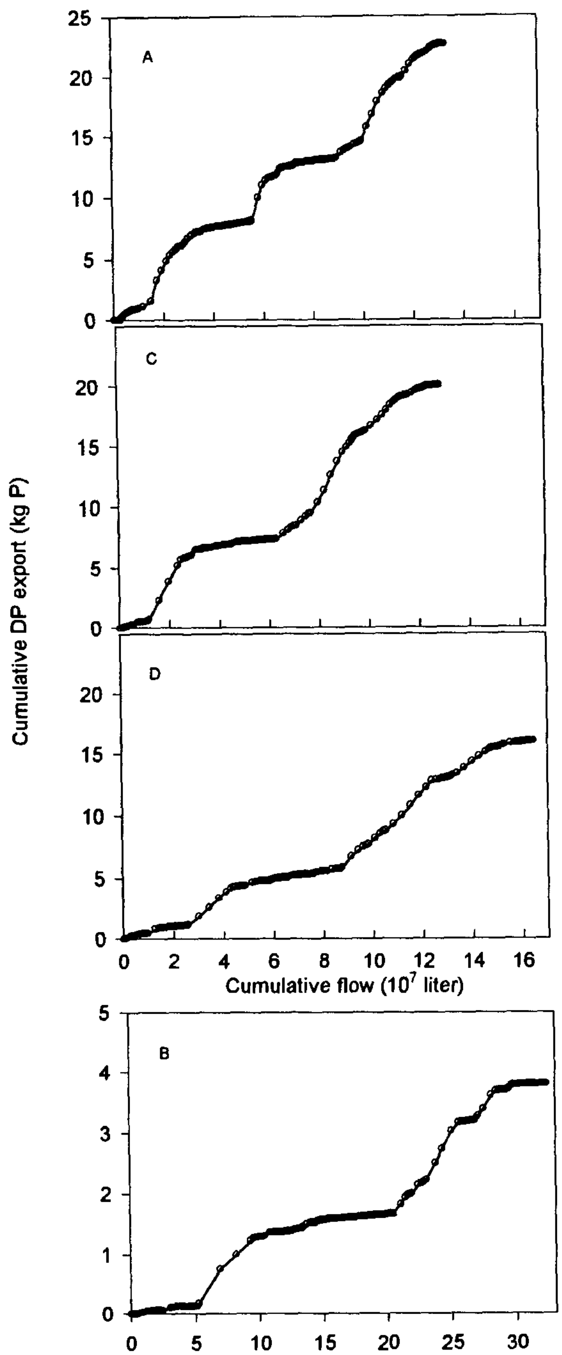

Fig. 5. Export of 1.2-μm filtered dissolved phosphorus (DP) from tiles draining cropland under soybean-corn rotation. A: tile A, B: tile B, C: tile C, D: tile D. (Top three graphs share same horizontal axis.)

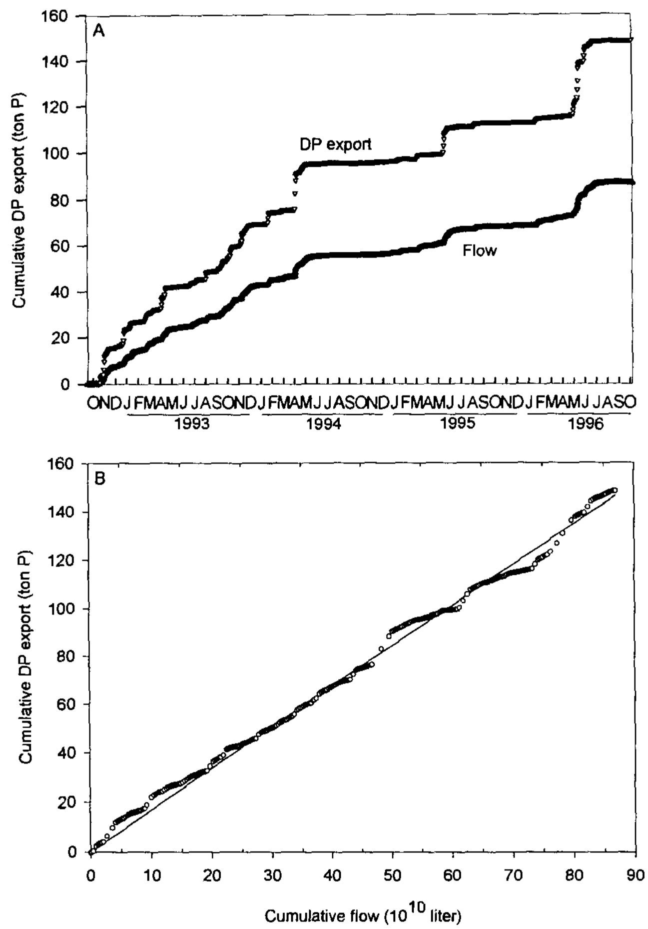

Fig. 6. A: Flow and export of 1.2-μm filtered dissolved phosphorus (DP) from Embarras River at Camargo, Illinois. B: Watershed DP export through river = 3.94×10^{-6} (mg P L^{-1} ha^{-1}) × discharge × watershed area.

apparent zero-order rate law (Fig. 6B), which suggests that DP export at a watershed scale was not dependent on the amount of DP that remained in the watershed. Because hundreds of tiles and surface runoff contributed to the overall river flow, the sum of all these sources may have resulted in the zero-order export kinetics at the watershed level. Cosser (1989) empirically found that P load per unit runoff per unit area was constant for an Australian watershed. Based on dimensional comparison, this constant was in fact the slope or zero-order rate law constant in Fig. 6B.

We wish to note the "pseudo" nature of the rate laws we used in this study. Several processes such as dissolution, chemical reactions, adsorption, and transport, influence P export, and these processes were not evaluated individually. Thus, the apparent rate laws represent the overall P export process. Because of the "apparent" approach we were using, input and output due to fertilization, mineralization, atmospheric deposition, plant uptake, and microbial uptake were not included in the kinetic equations in Fig. 1. In an elementary kinetic analysis, these processes must be individually considered and the analysis is expected to be substantially less tractable without resorting to the "pseudo kinetics" approach (Steinfeld et al., 1989).

Because the rate law of DP export on the watershed scale observed zero-order, a linear equation with one parameter could estimate DP output to the receiving water body (Fig. 6B):

DP export from a watershed =

$$k' \times \text{discharge} \times \text{watershed area} \qquad [5]$$

where discharge is the total surface runoff leaving the watershed, and k' is a constant. In the study watershed, k' was 3.94×10^{-6} (mg P L^{-1} ha^{-1}).

In the study watershed, the DP export patterns from tiles were different from the river. The short-term export pattern for a tile was also different from the long-term pattern for the tile. It appears that our zero-order/first-order kinetic analysis has unified these themes to help understand the DP export from this agricultural watershed. Our approach might provide a simple way to determine the export of P to surface waters in agricultural areas dominated by tile drainage. Future research may focus on export kinetics and modeling of tile-drained watersheds in different geographic regions, under different crop regimes and field management practices.

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