

Sampling Procedures for Nitrogen and Phosphorus in Runoff

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ABSTRACT

THE nitrogen and phosphorus content of surface runoff from two watersheds in southwestern Iowa was analyzed for a 5-year period (1969-1973). Sampling procedures were evaluated for quantifying discharges of water-soluble $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and inorganic P and sediment-associated Kjeldahl N and NaHCO_3 -extractable P. The arithmetic mean nutrient concentration of samples collected during major runoff (defined as greater than $0.28 \text{ m}^3/\text{sec}$), multiplied by the quantity of water or sediment discharged, compared favorably with a standard integration procedure for determining N and P discharges associated with surface runoff. Also, the arithmetic mean nutrient concentration of three samples collected during major runoff was adequate for determining storm discharges of water-soluble $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ and of Kjeldahl N associated with sediment. Nitrate-nitrogen concentrations showed a progressive decrease from storm to storm, indicating that each storm should be sampled or an accounting made for this decrease to determine the storm quantity discharges of $\text{NO}_3\text{-N}$ during the cropping season. This storm-to-storm effect was not as evident for $\text{NH}_4\text{-N}$, inorganic P, total Kjeldahl N, and NaHCO_3 -extractable P, indicating that sampling of every

event would not be required to determine cropping season quantity discharges of these nutrient constituents.

INTRODUCTION

Public attention has been focused recently on water quality as influenced by agricultural practices. The pollution of some surface waters has been attributed to the movement, by runoff and erosion processes, of chemicals from agricultural land into streams and lakes (Biggar and Corey 1969). In the mid-1960's, when pollution became a worldwide concern, information was inadequate for assessing the cause and severity of the problem.

A variety of sampling and analytical methods has been used to characterize the quality of water in streamflow. Frequently, comparisons were made by observing chemical concentrations, with no consideration of the volumes of water represented. Thus, large changes in chemical concentrations were observed sometimes with little or no change in the total quantity of the chemical. Concurrent changes in the chemical concentration and water discharge with time are prime factors of concern in establishing frequency of sampling required. If the chemical concentration changes significantly with time, however, the quantity of the chemical must be determined by joint consideration of (a) temporal changes in concentration of the constituent and (b) change in water flow. The number of samples needed to determine the quantity of the constituent may differ greatly depending upon the relative variation of these two values. Frere (1971) reported that the concentrations of nitrate-nitrogen ($\text{NO}_3\text{-N}$), ammonium-nitrogen ($\text{NH}_4\text{-N}$), potassium (K), chloride (Cl), and dieldrin in surface runoff from agricultural land remained constant within sampling variation and that the quantity of these constituents transported could be estimated adequately as the product of the mean concentration of a few samples collected at peak water flow multiplied by the total

water flow. This conclusion was derived from runoff samples collected from 36 different storm events on five watersheds ranging in size from 0.49 to 3.12 ha at the North Appalachian Experimental Watershed Station, Coshocton, Ohio. The purpose of this paper is to provide additional information on sampling-calculation requirements for determining quantity discharge of N, P, and sediment movement during surface runoff events from a 30.2- and a 33.5-ha, corn-cropped watershed.

EXPERIMENTAL PROCEDURES

Surface runoff samples were collected from 1969 through 1973 from two adjacent watersheds continuously cropped to corn since 1964. The watersheds are located in southwestern Iowa in Pottawattamie County near Treynor. The watersheds are within, and typically represent, the Iowa and Missouri deep loess hills region. The area is characterized by a deep loess cap over glacial till. The loess cap depth on the watersheds ranges from about 35 m on the ridges to less than 5 m in the valleys. Most main and upland valleys have moderately to deeply incised channels. A water-saturated zone above the till-loess interface causes seepage into these channels throughout the year. Soils on the watersheds are of the Marshall-Monona-Ida-Napier series. In the new soil classification system, the Marshall and Monona soils are typic hapludolls, and the Ida and Napier soils are typic haplorthents and cumulic hapludolls, respectively. The soils are fine, silty mixed mesics and have moderate to moderately rapid permeability. Average landslope of research watersheds 1 and 2 is 9 and 8 percent, respectively. Although contour-farming has been followed on the watersheds and the surrounding area, erosion is serious under row-cropping practices (Piest and Spomer 1968). Conventional preplanting tillage operations, consisting of moldboard plowing, disking, and harrowing, were performed on the watersheds in the

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TABLE 1. FERTILIZER TREATMENTS FOR 1969-1973.

| Watershed no. | Area hectares | Year | N fertilization | | P fertilization‡ |
|---------------|------------------------------------|-------------------|-------------------------|--------------------|-------------------------|
| | | | Application rate, kg/ha | Source of N | Application rate, kg/ha |
| 1 | 30.2 (27.9 hectares cultivated) | 1969 | 405 | Anhydrous ammonia* | 112 |
| | | | 74 | Ammonium nitrate† | |
| | | 1970 | 291 | Anhydrous ammonia | 101 |
| | | | 136 | Ammonium nitrate | |
| | | 1971 | 408 | Anhydrous ammonia | 39 |
| | | | 36 | Ammonium nitrate | |
| 1972 | 383 | Anhydrous ammonia | 40 | | |
| | 36 | Ammonium nitrate | | | |
| 1973 | 442 | Anhydrous ammonia | 39 | | |
| | 35 | Ammonium nitrate | | | |
| 2 | 33.5 (31.1 hectares cultivated) | 1969 | 185 | Anhydrous ammonia | 44 |
| | | | 150 | Anhydrous ammonia | |
| | | 1970 | 146 | Anhydrous ammonia | 39 |
| | | | 36 | Ammonium nitrate | |
| | | 1971 | 143 | Anhydrous ammonia | 39 |
| | | | 36 | Ammonium nitrate | |
| 1972 | 141 | Anhydrous ammonia | 39 | | |
| | 35 | Ammonium nitrate | | | |

*All anhydrous ammonia was injected 25 to 36 cm deep. Injector spacing on watershed 1 was 51 cm; on watershed 2, injector spacing was 99 cm.

†All ammonium nitrate was broadcast before plowing.

‡All P fertilizer was concentrated superphosphate and broadcast before plowing.

spring for seedbed preparation. Mechanical and chemical weed control operations were performed as needed. The fertilizer applications for 1969 through 1973 are described in Table 1.

The watersheds were instrumented to measure precipitation and the quantity and quality of streamflow. The sediment portion of the runoff included mineral soil material and organic particles. The samples were collected at the outlet of each watershed and represent runoff from the cropland areas. The number of samples obtained and the frequency of sampling varied among runoff events. Samples of storm flow were collected during the rising, peak, and recession stages for most events. Samples collected for nutrient analysis were stored at 4 C to minimize chemical and microbiological conversions. For chemical analysis, the liquid and sediment portions of streamflow samples were separated by centrifugation and (or) filtration through Whatman No. 42* filter paper.

Nitrate-nitrogen and $\text{NH}_4\text{-N}$ of the supernatant liquid were determined by steam distillation procedures (Bremner 1965a) from 1969 through June 1970. For the rest of the study period, continuous-flow colorimetric

procedures (Bolleter et al. 1961, Henriksen and Selmer-Olsen 1970) were used to determine $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$. Inorganic P content of the water and NaHCO_3 -extractable phosphorus of the sediment (1:20 ratio of sediment to NaHCO_3) were determined by the ascorbic acid method (Murphy and Riley 1962, Olsen et al. 1954) and will be referred to henceforth in this paper as inorganic P and NaHCO_3 -extractable P, respectively. Total N of the sediment and associated material was determined by using micro-Kjeldahl procedures (Bremner 1965b). Soluble

$\text{NH}_4\text{-N}$ in the sediment was negligible. The sediment concentration of the sample was determined by gravimetric procedures.

The basic method for calculating nutrient discharge effectively integrated runoff and sediment with nutrient concentrations. This integrated method assumed a smooth curve between nutrient sample concentration points. The nutrient discharge for each small successive time interval was computed throughout the event. The integrated method will be referred to in this report as method no. 1. Nutrient discharge data reported herein include only storm events with sufficient nutrient sample coverage to adequately define a continuous nutrient concentration curve throughout the event.

Three additional calculation procedures were considered for comparison with the integrated method to obtain information on the number of samples required for determining nutrient discharges in surface runoff. The first of these three methods will be referred to as the "all-sample arithmetic mean" method, in which all of the samples were used in the calculation. The quantity of nutrient discharged was computed as the product of the arithmetic mean nutrient concentration and the volume of water or sediment discharged for the event. The all-sample arithmetic method of calculation will be referred to in this report as method no. 2.

The second calculation is the product of the "major-runoff mean" concentration and the water or sediment discharged for that event.

TABLE 2. DISCHARGES OF WATER AND SEDIMENT FOR MAJOR STORMS.

| Event date | Watershed 1 | | | | Watershed 2 | | | |
|-------------|-------------|---------|----------------|----------------|-------------|---------|----------------|----------------|
| | Runoff | | Sediment | | Runoff | | Sediment | |
| | Total | Sampled | Total | Sampled | Total | Sampled | Total | Sampled |
| | cm. | cm. | ton(metric)/ha | ton(metric)/ha | cm. | cm. | ton(metric)/ha | ton(metric)/ha |
| 7/17/69 | 0.43 | 0.33 | 1.08 | 0.43 | 0.41 | 0.36 | 0.87 | 0.87 |
| 8/20/69 | 0.51 | 0.18 | 1.66 | 0.36 | 0.46 | 0.36 | 0.81 | 0.43 |
| 5/12/70 | 1.09 | 0.71 | 14.04 | 8.13 | 0.99 | 0.71 | 10.44 | 6.61 |
| 5/12/70* | 0.18 | 0.18 | 1.41 | 1.41 | 0.20 | 0.20 | 1.14 | 1.41 |
| 8/2/70* | 2.29 | 2.29 | 9.59 | 9.59 | 1.78 | 1.75 | 4.68 | 4.59 |
| 5/6/71 | 0.28 | 0.25 | 1.25 | 1.08 | 0.08 | 0.08 | 0.29 | 0.29 |
| 5/6/71 | 0.18 | 0.18 | 0.60 | 0.60 | 0.05 | 0.05 | 0.18 | 0.18 |
| 5/6/71 | 0.36 | 0.36 | 1.50 | 1.50 | 0.18 | 0.18 | 0.69 | 0.69 |
| 5/10/71 | 0.36 | 0.36 | 0.81 | 0.81 | 0.18 | 0.10 | 0.40 | 0.22 |
| 5/10/71* | 1.14 | 1.14 | 6.56 | 6.56 | 0.76 | 0.74 | 4.26 | 4.19 |
| 5/10/71* | 1.47 | 1.47 | 4.55 | 4.55 | 1.19 | 1.17 | 4.26 | 4.23 |
| 5/17/71* | 0.91 | 0.91 | 5.98 | 5.98 | 0.36 | 0.36 | 2.22 | 2.22 |
| 5/18/71* | 0.46 | 0.46 | 1.77 | 1.77 | 0.20 | 0.20 | 0.76 | 0.76 |
| 5/18/71* | 2.11 | 2.11 | 15.28 | 15.28 | 1.42 | 1.42 | 13.10 | 13.10 |
| 5/18/71 | 0.51 | 0.51 | 0.83 | 0.83 | 0.43 | 0.41 | 1.10 | 1.10 |
| 5/5/72* | 1.55 | 1.45 | 23.03 | 14.43 | 1.07 | 1.04 | 17.54 | 14.90 |
| 9/25&26/73* | 1.14 | 0.94 | 1.75 | 0.87 | 1.70 | 0.97 | 1.61 | 0.29 |

*Name of product is listed for the benefit of the reader only and does not imply endorsement of preferential treatment by the U.S. Department of Agriculture or cooperating agencies.

*Events common to both watersheds where at least three samples were collected during major runoff ($>0.28 \text{ m}^3/\text{sec}$).

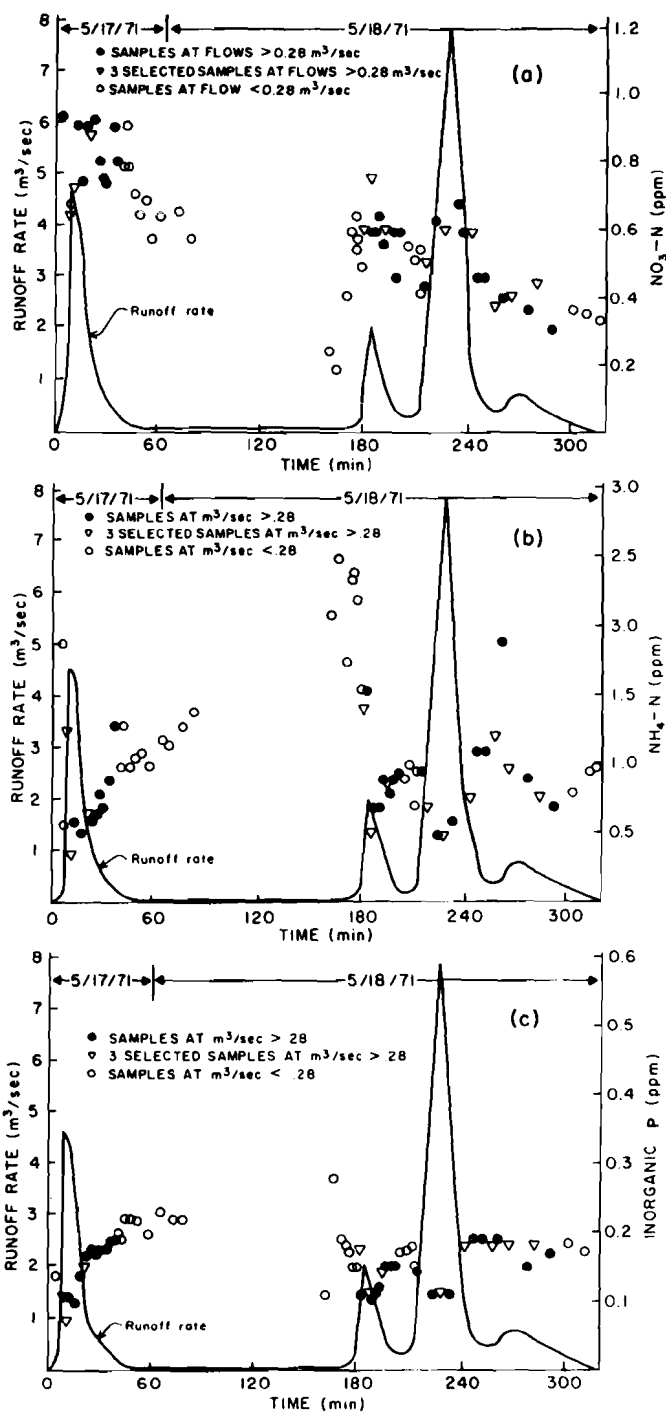


FIG. 1 Concentration of [a] $\text{NO}_3\text{-N}$, [b] $\text{NH}_4\text{-N}$, and [c] inorganic P as related to runoff, Watershed 1, May 17-18, 1971, surface runoff events.

The major-runoff mean method is the arithmetic mean concentration of the nutrient for samples collected at flow rates equal to or greater than $0.28 \text{ m}^3/\text{sec}$ (about 60 percent of all samples collected). The major-runoff mean method of calculation will be referred to in this report as method no. 3.

The third method is referred to as the "three-sample mean" method, which considered only three samples collected (about 24 percent of all samples) during the major portion

(flow rates equal to or greater than $0.28 \text{ m}^3/\text{sec}$) of a runoff event. The quantity of nutrient discharged is the product of the arithmetic mean concentration for three samples collected during major runoff and the water or sediment discharged for that event. The three-sample mean method of calculation will be referred to in this report as method no. 4. Frere (1971) reported that water flux was the dominant factor determining the amount of nutrient transported and suggested that concentration samples

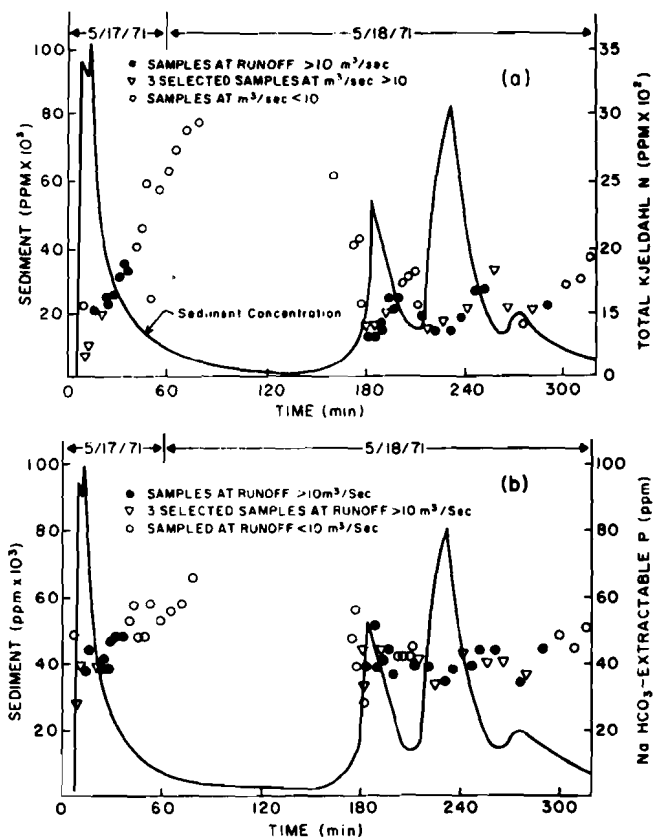


FIG. 2 Concentration of [a] total Kjeldahl N and [b] NaHCO_3 -extractable P, as related to sediment concentration, Watershed 1, May 17-18, 1971, surface runoff events.

be obtained near the peak of water flow. To test Frere's observation for the study reported herein, a sample was selected nearest the water flow peak, and second and third samples were arbitrarily selected during the water flow rise and recession for each storm event at flow rates equal to or greater than $0.28 \text{ m}^3/\text{sec}$.

RESULTS AND DISCUSSION

Seventeen surface runoff events produced appreciable discharges of water, sediment, and nutrients during the 1969-1973 cropping seasons (Table 2). However, only nine of these events had sufficient nutrient sample coverage to permit a statistical evaluation of the calculation methods described. These nine events for which comparable nutrient samples were obtained for the two watersheds are designated in Table 2. Nutrient sample coverage for these events for both watersheds represented 94 percent of the total runoff and 90 percent of the total sediment discharges; only a small fraction of the runoff and sediment discharges was inadequately sampled for these events. The runoff and sediment discharge data (Table 2) and historical records (1964-1973) revealed that runoff and erosion

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characteristics differ slightly for the two watersheds. Watershed 1 has consistently had more annual runoff and erosion than watershed 2, probably because of differing land-slopes, even though the two watersheds were managed similarly. Sample coverage for characterizing nutrient discharges from these watersheds was considered good as evaluated by comparison of total storm discharges of runoff and sediment with sampled storm discharges shown in Table 2.

Nutrient concentration varied considerably within surface runoff events. The extent to which the variation influenced discharge of each nutrient needed to be ascertained for various sampling methods.

The variation in concentration for $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and inorganic P is

illustrated in Figs. 1a, 1b, and 1c, respectively, for a series of four storm events occurring on May 17 and 18, 1971 at watershed 1. Variation of sediment-associated nutrient (total Kjeldahl N and NaHCO_3 -extractable P) concentrations is illustrated in Figs. 2a and 2b, respectively. The figures also illustrate the sampling frequency and nutrient concentration as related to water or sediment fluxes within storm events. Nitrate-N concentration decreased progressively with time among the four events shown in Fig. 1a. Schuman et al. (1973) reported progressive seasonal decreases and suggested progressive removal of $\text{NO}_3\text{-N}$ by crop use and N immobilization as factors related to this phenomenon. The leaching of $\text{NO}_3\text{-N}$ from the soil surface during runoff

could account, in part, for this decrease. Therefore, to determine the discharge of $\text{NO}_3\text{-N}$ for the cropping season, sampling of each storm event is required, or an accounting must be made of the storm-to-storm decreases. Ammonium-N, inorganic P, total Kjeldahl, and NaHCO_3 -extractable P concentrations revealed little or no storm-to-storm effect as illustrated in Figs. 1b, 1c, 2a, and 2b, respectively.

The discharges for sediment-associated nutrients (total Kjeldahl N and NaHCO_3 -extractable P) are shown in Table 4. Data were selected from storm events common to both watersheds and for which at least three nutrient samples were collected during major runoff. Nine storm events were common to the two watersheds for water-soluble nutri-

TABLE 3. STORM DISCHARGES OF $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, AND INORGANIC P, COMPUTED BY FOUR SAMPLING METHODS.

| Event date* | Watershed 1 Computation method no. | | | | Watershed 2 Computation method no. | | | |
|---|---------------------------------------|-----------------------------|-------------------------------|-------------------------------|---------------------------------------|-----------------------------|-------------------------------|-------------------------------|
| | 1 Integration | 2 All- sample mean | 3 Major- runoff mean | 4 Three- sample mean | 1 Integration | 2 All- sample mean | 3 Major- runoff mean | 4 Three- sample mean |
| ----- kg/ha ----- NO ₃ -N | | | | | | | | |
| 5/12/70 | 0.06(8)† | 0.07 | 0.06(5) | 0.07 | 0.01(7) | 0.02 | 0.01(3) | 0.01 |
| 8/2/70 | 0.16(18) | 0.21 | 0.19(12) | 0.15 | 0.10(16) | 0.09 | 0.09(13) | 0.07 |
| 5/10/71 | 0.12(8) | 0.12 | 0.12(8) | 0.12 | 0.07(14) | 0.06 | 0.06(9) | 0.06 |
| 5/10/71 | 0.12(6) | 0.12 | 0.12(4) | 0.12 | 0.08(8) | 0.08 | 0.08(7) | 0.08 |
| 5/17/71 | 0.07(24) | 0.07 | 0.07(12) | 0.07 | 0.01(8) | 0.01 | 0.02(4) | 0.02 |
| 5/18/71 | 0.02(19) | 0.02 | 0.02(10) | 0.03 | 0.10(10) | 0.01 | 0.01(4) | 0.01 |
| 5/18/71 | 0.12(11) | 0.11 | 0.11(9) | 0.11 | 0.07(8) | 0.06 | 0.06(8) | 0.06 |
| 5/5/72 | 0.37(5) | 0.45 | 0.36(4) | 0.30 | 0.19(16) | 0.18 | 0.19(7) | 0.19 |
| 9/25/25&26/73 | 0.07(10) | 0.07 | 0.07(7) | 0.08 | 0.04(26) | 0.04 | 0.03(9) | 0.03 |
| TOTALS | 1.11(109) | 1.24 | 1.12(71) | 1.05(27) | 0.58(113) | 0.55 | 0.55(64) | 0.53(27) |
| ----- NH ₄ -N ----- | | | | | | | | |
| 5/12/70 | 0.03 | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 | 0.02 | 0.02 |
| 8/2/70 | 0.09 | 0.10 | 0.09 | 0.10 | 0.11 | 0.11 | 0.11 | 0.13 |
| 5/10/71 | 0.09 | 0.10 | 0.10 | 0.10 | 0.06 | 0.04 | 0.06 | 0.04 |
| 5/10/71 | 0.09 | 0.12 | 0.09 | 0.10 | 0.06 | 0.07 | 0.06 | 0.06 |
| 5/17/71 | 0.07 | 0.09 | 0.07 | 0.07 | 0.03 | 0.04 | 0.02 | 0.02 |
| 5/18/71 | 0.03 | 0.06 | 0.04 | 0.04 | 0.02 | 0.02 | 0.01 | 0.01 |
| 5/18/71 | 0.13 | 0.17 | 0.16 | 0.13 | 0.09 | 0.11 | 0.11 | 0.10 |
| 5/5/72 | 0.13 | 0.15 | 0.16 | 0.15 | 0.04 | 0.04 | 0.03 | 0.04 |
| 9/25&26/73 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.02 | 0.02 | 0.04 |
| TOTALS | 0.68 | 0.83 | 0.75 | 0.73 | 0.45 | 0.47 | 0.44 | 0.46 |
| ----- Inorganic P ----- | | | | | | | | |
| 5/12/70 | 0.003 | 0.003 | 0.002 | 0.002 | 0.003 | 0.003 | 0.002 | 0.002 |
| 8/2/70 | 0.039 | 0.046 | 0.043 | 0.056 | 0.018 | 0.024 | 0.021 | 0.019 |
| 5/10/71 | 0.020 | 0.020 | 0.020 | 0.020 | 0.004 | 0.006 | 0.006 | 0.004 |
| 5/10/71 | 0.029 | 0.025 | 0.022 | 0.021 | 0.018 | 0.018 | 0.017 | 0.016 |
| 5/17/71 | 0.012 | 0.017 | 0.013 | 0.010 | 0.004 | 0.004 | 0.002 | 0.002 |
| 5/18/71 | 0.006 | 0.007 | 0.006 | 0.007 | 0.002 | 0.001 | 0.001 | 0.001 |
| 5/18/71 | 0.027 | 0.031 | 0.030 | 0.030 | 0.016 | 0.015 | 0.015 | 0.011 |
| 5/5/72 | 0.010 | 0.011 | 0.011 | 0.010 | 0.012 | 0.016 | 0.009 | 0.007 |
| 9/25&26/73 | 0.013 | 0.012 | 0.012 | 0.011 | 0.020 | 0.020 | 0.013 | 0.013 |
| TOTALS | 0.159 | 0.172 | 0.159 | 0.167 | 0.097 | 0.107 | 0.086 | 0.075 |

*Events common to both watersheds where at least three samples were collected during major runoff (>0.28 m³/sec).

†Value in parentheses indicates number of samples included in computation; the number of samples for "all-sample mean" computation is the same as for the number used in integration; the number of samples for $\text{NH}_4\text{-N}$, inorganic P computations is the same as for $\text{NO}_3\text{-N}$ computations.

ents, and eight events were common for sediment-associated nutrients. The integrated method of calculation was the standard for comparison. Data for the two watersheds were combined for

the analysis. Separate analyses for each of the two watersheds revealed results similar to those reported in Table 5.

Differences between nutrient dis-

charges calculated by the integrated method (considered the true or actual discharge) and the other methods were examined to determine which of the nonintegrated methods

TABLE 4. STORM DISCHARGES OF TOTAL KJELDAHL N AND NaHCO₃-EXTRACTABLE P COMPUTED BY FOUR SAMPLING METHODS.

| Event date* | Watershed 1 Computation method no. | | | | Watershed 2 Computation method no. | | | |
|---|---------------------------------------|-----------------------------|-------------------------------|-------------------------------|---------------------------------------|-----------------------------|-------------------------------|-------------------------------|
| | 1 Integration | 2 All- sample mean | 3 Major- runoff mean | 4 Three- sample mean | 1 Integration | 2 All- sample mean | 3 Major- runoff mean | 4 Three- sample mean |
| ----- kg/ha ----- Total Kjeldahl N | | | | | | | | |
| 5/12/70 | 1.90(7)† | 1.94 | 1.79(5) | 1.87 | 1.83(7) | 2.60 | 1.61(3) | 1.61 |
| 8/2/70 | 11.96(17) | 14.08 | 12.54(12) | 12.35 | 6.20(15) | 6.37 | 6.09(13) | 6.33 |
| 5/10/71 | 9.76(5) | 9.89 | 9.89(5) | 9.20 | 5.97(14) | 6.59 | 6.32(9) | 6.48 |
| 5/17/71 | 8.27(22) | 11.23 | 9.08(12) | 7.69 | 2.77(7) | 3.44 | 2.56(4) | 2.58 |
| 5/18/71 | 2.44(16) | 2.83 | 2.51(10) | 2.43 | 1.09(10) | 1.12 | 0.93(4) | 0.92 |
| 5/18/71 | 19.88(11) | 22.11 | 21.52(9) | 20.66 | 17.43(8) | 16.97 | 16.97(8) | 16.12 |
| 5/5/72 | 18.82(5) | 20.61 | 18.84(4) | 19.24 | 22.70(16) | 26.60 | 19.98(7) | 19.04 |
| 9/25&26/73 | 1.13(9) | 1.14 | 1.13(7) | 0.97 | 0.58(16) | 0.62 | 0.56(6) | 0.58 |
| TOTALS | 74.16(92) | 83.83 | 77.30(64) | 74.31(27) | 58.57(93) | 64.31 | 55.02(54) | 53.66(27) |
| ----- NaHCO ₃ -Extractable P ----- | | | | | | | | |
| 5/12/70 | 0.03 | 0.04 | 0.03 | 0.03 | 0.04 | 0.06 | 0.03 | 0.03 |
| 8/2/70 | 0.38(18) | 0.50 | 0.45(12) | 0.45 | 0.15(16) | 0.18 | 0.16 | 0.13 |
| 5/10/71 | 0.25 | 0.26 | 0.26 | 0.22 | 0.15 | 0.16 | 0.15 | 0.13 |
| 5/17/71 | 0.24 | 0.28 | 0.25 | 0.21 | 0.08(8) | 0.10 | 0.08 | 0.08 |
| 5/18/71 | 0.07 | 0.08 | 0.07 | 0.07 | 0.02 | 0.03 | 0.03 | 0.03 |
| 5/18/71 | 0.56 | 0.60 | 0.59 | 0.59 | 0.43 | 0.49 | 0.49 | 0.48 |
| 5/5/72 | 0.48 | 0.45 | 0.46 | 0.34 | 0.30 | 0.48 | 0.32 | 0.40 |
| 9/25&26/73 | 0.02(8) | 0.02 | 0.02(6) | 0.02 | 0.01(15) | 0.01 | 0.01 | 0.01 |
| TOTALS | 2.03(92) | 2.23 | 2.13(63) | 1.93(27) | 1.18(94) | 1.51 | 1.27(54) | 1.29(27) |

*Events common to both watersheds where at least three samples were collected during the major portion of runoff (>0.28 m³/sec).

†Value in parentheses indicates number of samples included in computation; the number of samples for "all-sample mean" computation is the same as for the integration method; the number of samples of NaHCO₃-extractable P computation is the same as for TKN computation unless otherwise indicated.

TABLE 5. MEANS AND COMPARISONS OF FOUR METHODS FOR DETERMINING STORM DISCHARGES OF NO₃-N, NH₄-N, INORGANIC P, TOTAL KJELDAHL N, AND NaHCO₃-EXTRACTABLE P (WATERSHEDS 1 AND 2 COMBINED).

| Characteristic | NO ₃ -N | NH ₄ -N | Inorg. P | Total Kjeldahl N | NaHCO ₃ Ext. P |
|-------------------------------------|--------------------|--------------------|-------------------|------------------|---------------------------|
| ----- kg/ha ----- | | | | | |
| Means: | | | | | |
| Integrated method, no. 1 | 0.094 | 0.063 | 0.0142 | 8.30 | 0.2006 |
| All-sample method, no. 2 | 0.099 | 0.072 | 0.0155 | 9.26 | 0.2338 |
| Major-runoff sample method, no. 3 | 0.093 | 0.066 | 0.0136 | 8.27 | 0.2125 |
| Three-sample method, no. 4 | 0.088 | 0.066 | 0.0134 | 8.00 | 0.2013 |
| Differences* from integrated method | | | | | |
| All-sample method, no. 2 | | | | | |
| Mean difference | -0.006 | -0.009† | -0.0013 | -0.96† | 0.0331† |
| 95 percent confidence interval | -0.017 to 0.006 | -0.017 to -0.002 | -0.0027 to 0.0001 | -1.59 to -0.33 | -0.0588 to -0.0075 |
| No. of observations | 18 | 18 | 18 | 16 | 16 |
| Major-runoff sample method, no. 3 | | | | | |
| Mean difference | 0.001 | -0.003 | 0.0006 | -0.03 | -0.0119 |
| 95 percent confidence interval | -0.004 to 0.006 | -0.009 to 0.003 | -0.0009 to 0.0021 | -0.42 to 0.47 | -0.0237 to 0.00004 |
| No. of observations | 18 | 18 | 18 | 16 | 16 |
| Three-sample method, no. 4 | | | | | |
| Mean difference | 0.006 | -0.003 | 0.0008 | 0.29 | -0.0006 |
| 95 percent confidence interval | -0.003 to 0.015 | -0.008 to 0.002 | -0.0019 to 0.0034 | -0.22 to 0.81 | -0.0267 to 0.0255 |
| No. of observations | 18 | 18 | 18 | 16 | 16 |

*Small differences are due to rounding.

†Significantly different from zero (p < 0.05).

would give results that were acceptably accurate. For this analysis, data were selected and combined from storm events common to both watersheds and for which at least three nutrient samples were collected during major runoff. The results are summarized in Table 5.

Methods with (a) small mean differences and (b) narrow confidence intervals were considered superior. By this criteria, both method no. 3 and method no. 4 were superior to method no. 2 for the five nutrient constituents measured. Method no. 3 appeared to be slightly better than method no. 4; however, neither method was significantly different ($p < 0.05$) from the integrated method for the characteristics measured. Method no. 2 differed significantly for $\text{NH}_4\text{-N}$, total Kjeldahl N, and $\text{NaHCO}_3\text{-extractable P}$. It appears that relatively high concentration values were obtained at low water flow rates ($< 0.28 \text{ m}^3/\text{sec}$) which introduced a sampling bias if concentrations were indiscriminately averaged. Thus, method no. 2 overestimated the storm discharges of some nutrients.

These results show that the use of elementary discretion in averaging nutrient concentration values will provide acceptable accuracy in determining runoff discharges of these nutrients. A comparison was made of the number of samples used for each sampling method (Tables 3 and 4). Sixty percent of the total number of samples collected was used to determine nutrient discharges by method no. 3. Only 24 percent of the total number of samples collected was used to determine nutrient discharges by method no. 4. Therefore, the number of samples required to accurately determine the discharges of nutrients considered can be reduced by as much as 75 percent of the samples collected

for this study.

SUMMARY

Surface runoff data collected from two corn-cropped watersheds in southwestern Iowa during a 5-yr period were analyzed to evaluate sampling methods needed to determine storm discharges of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, inorganic P, sediment N (total Kjeldahl N) and sediment P ($\text{NaHCO}_3\text{-extractable P}$). Three methods of averaging sample nutrient concentrations were described for calculating storm nutrient discharges, and these were compared with a standard integrated method.

The arithmetic mean of nutrient concentrations for samples collected during major runoff ($> 0.28 \text{ m}^3/\text{sec}$) multiplied by the quantity of water or sediment was superior to the all-sample mean and the three-sample mean methods for determining $\text{NO}_3\text{-N}$ and $\text{NaHCO}_3\text{-extractable P}$ discharges. Sixty percent of the total number of samples collected was used for the major-runoff mean method of calculation. The arithmetic mean of all samples collected consistently overestimated nutrients discharged. Relatively high concentration of nutrient at water flow rates of less than $0.28 \text{ m}^3/\text{sec}$ caused a sampling bias when the all-sample mean method was used. The three-sample mean method of calculation which involved only three samples collected at runoff rates greater than $0.28 \text{ m}^3/\text{sec}$ (24 percent of total samples collected) was more favorable than the all-sample mean method for determining storm discharges of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and sediment N. The three-sample mean method would probably give satisfactory accuracy for most surveys, with savings in field work and laboratory time.

A storm-to-storm decrease of $\text{NO}_3\text{-N}$ concentration was observed, indicating that each storm should be sampled or an accounting made for this decrease to quantify cropping season discharges of $\text{NO}_3\text{-N}$. This storm-to-storm effect was not evident for $\text{NH}_4\text{-N}$, inorganic P, sediment N, and sediment P, suggesting that sampling of each event was not required, but unsampled events could be estimated.

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