Requisite Sampling Frequency for Measuring Nutrient and Pesticide Movement with Runoff Waters

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This paper presents an analysis of the time and number of samples needed to measure the movement of nutrients and pesticides carried in waters running off agricultural lands. Nutrient and pesticide concentrations in runoff waters from experimental watersheds were subjected to statistical analyses to evaluate the degree of concentration variation in sampling during given storms and between different storms. The concentration of a given constituent was found to vary as much as 100-fold from one storm event to another, and even twofold from one high water flow to another during the same major storm. The concentration during each high water flow remained constant within the sampling variation, with the exception of the orthophosphate concentration, which tended to increase. The mean concentration of representative samples at each high water flow × the volume of water transported during that flow is an adequate estimate of the amount of the constituent transported.

The loss of nutrients and pesticides from agricultural land has been receiving increased attention in recent years because of its possible contribution to the pollution of streams and lakes. Since 1966, two organizations of the U. S. Department of Agriculture, the North Appalachian Experimental Watershed, Coshocton, Ohio, and the U.S. Soils Laboratory, Beltsville, Md., have cooperated in a detailed study of the movement of nutrients and pesticides from agricultural land during rain storms. The objective of this communication is to report a statistical analysis of the variation in the data collected on the concentration of nutrients and pesticides in runoff water. These results are important because they provide information for estimating the time and number of samples required in the design of future research programs on this problem.

It has often been assumed that the concentration of a constituent does not change during the period of interest. With this assumption, the flux of the constituent is obviously a constant function of the water flow and the quantity transported is the product of the concentration and the total volume of water. If the concentration does change with time, then the quantity transported must be calculated by integrating the flux of the constituent which is the product of the constituent concentration and the water flow. Usually the concentration is not measured continually during the runoff period, but is determined on samples of the runoff water taken at different times during the storm. The number of concentration and water measurements needed for an adequate estimate of the amount transported can be greatly different in these two cases.

EXPERIMENTAL

Samples of runoff water were taken from 36 different storm events on five watersheds at the North Appalachian Experimental Watershed, Coshocton, Ohio. These watersheds had different fertilizer and dieldrin applications, ranged in size from 0.5 to 3.1 ha, and had slopes from 7.5 to 15.8%. The watersheds were instrumented for continuous measurement of the water flux and intermittent sampling of the runoff water (Harrold *et al.*, 1967). The samples were obtained under the supervision of L. L. Harold and W. M. Edwards at the watershed and analyzed by members of the staff of the U.S. Soils Laboratory, Beltsville, Md. The chemical procedures used for the analysis of potassium, chloride, nitrate nitrogen, ammonium nitrogen, orthophosphate-P, and dieldrin will be described in a more detailed report of the entire study at a later date. The use of their unpublished data for this evaluation is gratefully acknowledged.

The measured and calculated data shown in Figure 1 for the July 24, 1968, storm on watershed 128 are an example of the data used in this analysis. The upper part of the figure shows the measured water flow (hydrograph) and the phosphate-P concentrations measured in the seven samples taken during the storm event. The lower part of Figure 1 shows the resulting phosphate flux calculated from the water flow and phosphate concentrations.

OVERALL SAMPLING VARIATION

In addition to the samples taken automatically, a number of samples were taken manually during some of the events. Occasionally, samples were taken manually and automatically at the same time. Those pairs of samples were used as duplicates to estimate the overall variation, which included the relatively small analytical variation. As a result of fertilization and seasonal changes, the measured concentrations varied 100-fold during the time of the whole sampling program. In order to obtain a reliable estimate of the sampling variation for each constituent and to test the variation in the different storm events, all concentration variations were normalized to percentages of the arithmetic mean concentration of its group.

The statistical estimate of the sampling variation was the variance, $S_p^2 = (\Sigma D^2)/2n$. D is the difference of each pair as a percent of the mean of that pair and n is the number of pairs. Table IA contains the average D, the standard deviation, S_p, and the number of pairs.

Since less than 5% of the variation can be attributed to the chemical measurement, the large difference between duplicate samples indicates the heterogeneity of the runoff water. The water at the sampling point is a mixture of waters from different parts of the watershed and it appears that the mixing processes preceeding the sampling point are incomplete. Although this large degree of variation is not too unusual in biological systems, it does mean that only major concentration differences can be considered statistically significant.

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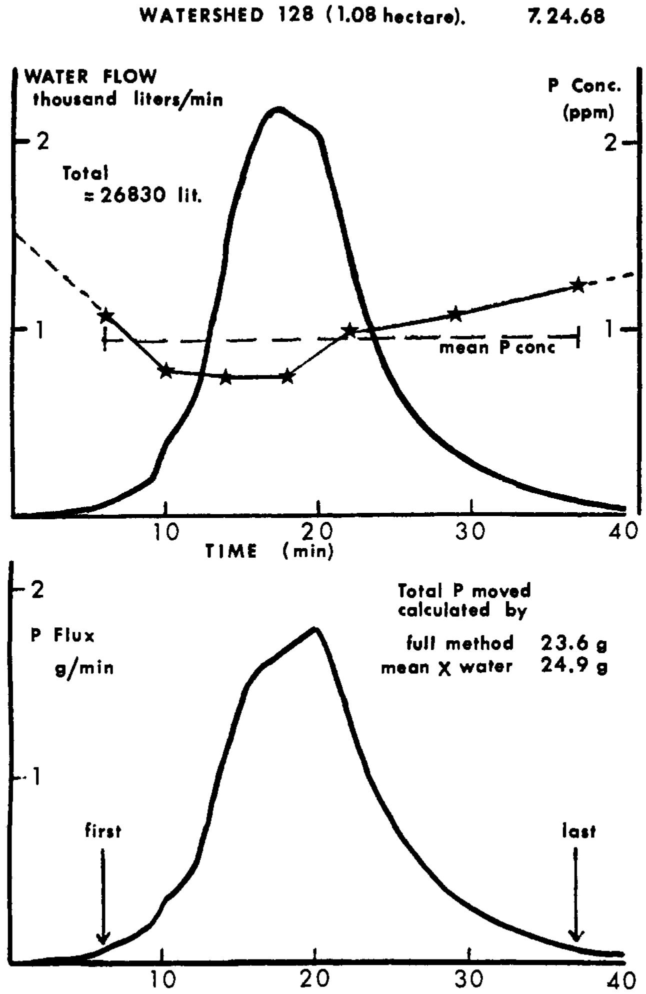

Figure 1. An example of the measured water flow and phosphate-P concentrations during a storm event and the resulting calculated phosphate-P flux

VARIATION DURING STORM EVENTS

The arithmetic mean concentration was calculated for each storm event as the sum of the concentrations divided by the number of samples. For each event with four or more samples, the statistical estimate of the variation during the event was the variance.

$$S_e^2 = \frac{\Sigma(x)^2 - (\Sigma x)^2/n}{n - 1}$$

The symbol x is the concentration as a percent of the arithmetic mean and n is the number of samples, usually four to ten.

The magnitude of the variation during the events is summarized in Table IB where the number of events with a significantly greater variation than that of sampling is reported. These events were determined by computing the ratio of variances, S_e^2/S_p^2, and selecting those larger than the 5% probability levels in the F or variance ratio test table (Snedecor, 1956). Thus, it is obvious that in most cases the variation during an event is not any greater than that expected from the sampling variation where two similar samples are taken at the same time.

The concentration and water flow data of those events with significant variation were examined for possible nonrandom patterns or trends in the variation. Some of the events were composed of several water flow peaks. Where possible, the concentration data were separated into subsets corresponding to the individual water flow peaks. The ratio of variances was calculated for these subsets which were, in most cases, nonsignificant at the 5% level. The arithmetic mean concentration of these subsets differed by as much as twofold and thus was the major source of variation during the complete storm event.

When the potassium, chloride, nitrate, and ammonium concentration data were considered on an individual water peak basis, a trend was found in only one or two events. The phosphate concentration showed a trend in four events, always increasing with time. The number and distribution of samples were not sufficient for further analysis of this trend except to note that three of the events occurred in March on a watershed that had been fertilized the previous year. The dieldrin concentration in three of the four significant events showed trends, but not the same trend each time. This inconsistent behavior of dieldrin is probably the result of its being applied as an organic compound in minute oil droplets which are immiscible in water.

CALCULATION OF THE TOTAL AMOUNT TRANSPORTED

The hydrographs were converted to a series of points that could be connected by straight-line segments. The concentrations of the constituents corresponding in time to these points on the hydrograph were calculated by linear interpolation between the measured concentrations. The flux of the constituent was calculated for each point in time by multiplying the water flow by the interpolated concentra-

Table I. The Statistics of Variation of Concentration in Runoff Water

	Potassium	Chloride	Nitrate nitrogen	Ammonium nitrogen	Ortho-phosphate	Dieldrin
A	Overall variations in paired samples taken simultaneously					
Average difference	9.0%	33.3%	18.7%	23.9%	11.0%	16.4%
Standard deviation	11.0%	38.6%	20.7%	23.5%	10.7%	16.6%
Number of pairs	10	11	17	12	10	8
B	Variation during storm events					
Total storm events	21	23	24	20	16	14
Events with significant variation	3	4	6	2	8	4
Significant events with a trend	1	2	1	1	4	3
C	Differences between arithmetic and integrated mean concentrations					
Average difference	2.4%	1.0%	6.1%	8.1%	4.7%	8.1%
Standard deviation	3.0%	13.2%	1.8%	7.5%	5.6%	10.8%
Number of events	37	45	47	30	28	27

tion and is illustrated by the phosphate-P flux in the lower part of Figure 1.

The integral of the constituent flux between the first sample and the last sample is calculated using the trapezoidal rule, the sum of the areas under the straight-line segments. The value of this integral for the phosphate-P flux is listed in the lower part of Figure 1 as the full method and, for comparison, the arithmetic mean concentration × the similar integral of the water flow is also given.

The validity of assuming a constant concentration in calculating the amount of transport was tested by comparing arithmetic mean concentrations with integrated mean concentrations. The integrated mean is the ratio of the integral of the constituent flux to the integral of the water flow and is therefore weighted by the water flow that actually occurred during the sampling. The comparison of the two means is given in Table IC as a relative difference. For computational convenience the percentages in this case are relative to the integrated mean.

It is obvious that there is little difference in the means even for phosphate, which showed a trend of increasing concentration. As seen in Figure 1, the flux of water changes more than any concentration during a storm event, and as a result the water behavior dominates any calculation of the amount of material transported. The higher concentrations of phosphate occur at low water fluxes and thus contribute very little to the total amount transported.

SUMMARY AND CONCLUSIONS

The concentration of nutrients and pesticides in runoff waters from small agricultural watersheds was found to vary as much as 100-fold during the year. When a major storm event was composed of more than one peak of water flow, the average concentrations were found to vary as much as two-fold between the different water flow peaks, but during each peak the concentrations were constant within the limits expected from the sampling variation. Orthophosphate-P was a possible exception since its concentration sometimes increased during the storm.

There were no differences between the arithmetic mean concentrations and the integrated mean concentrations, indicating that the amount of the constituent transported in the runoff can be calculated for each peak of water flow by multiplying the arithmetic mean concentration by the total water runoff. Samples of each water flow peak must be taken because the concentrations can be different and the samples should be taken at the time of maximum water flux because the water flux is the dominant factor in the amount of transport.

The number of samples required for the estimation of each arithmetic mean concentration depends upon the objective of the research program and the level of significance desired. For example, the standard deviation in Table IA can be used with the "t" distribution (Snedecor, 1956) to predict that 95% of the time the average nitrate concentration of five samples will be within ±24% of the true mean. If ten samples are taken then the interval will be ±15%.

LITERATURE CITED

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