# STREAMFLOW AND NUTRIENT FLUX RELATIONSHIPS IN THE MISSOURI OZARKS

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- - - - - - - - - - - - - - - - ABSTRACT - - - - - - - - - - - - - - - - -

A nutrient budget approach has been used to investigate the flux of nitrogen, phosphorous, calcium, magnesium, potassium, sodium and silica from four small forested watersheds in the southeast Missouri Ozarks. The quality of the precipitation input and the nutrient loss to streamflow from the experimental drainages have been monitored for two years. Concentrations of exported ions have varied with season and stream discharge rate. Nutrient flushes have been noted during the growing season at the initiation of storm runoff as the hydrograph begins to rise. Considering the annual flux balance the research watersheds tend to have a net loss of calcium, magnesium, potassium, sodium and silica, and a small net gain in total phosphorous and ammonium, and nitrate nitrogen.

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## INTRODUCTION

Although there is considerable published information from the far west and northeast on the effect of certain cutting practices and associated harvesting techniques on erosion and stream sediment yield (Cole et al. 1967; Hart and DeByle 1975; Verry 1972; Likens et al. 1970; Aubertin and Patric 1972; Williams and Mace 1975), very little data is available for the central hardwood region. More recently, forest hydrology researchers have been looking at nutrient yield as well as other water quality criteria. So far, research results have been variable. High nitrate nitrogen concentrations of 90 mg/l were found in streamflow at Hubbard Brook in New Hampshire following clearcutting and herbiciding (Likens et al. 1970). Concentrations of other ions, such as calcium, magnesium, and potassium, varied from 5 to 30 times normal during the

first three years of devegetation. These results tend to be somewhat misleading, since the trees were not removed from the watershed and revegetation was inhibited for a number of years. In addition, shallow bedrock underlying the Hubbard Brook watershed prevented downward percolation of nutrient-bearing waters and diverted a high proportion directly to streamflow. The objective of the study was to maximize watershed nutrient yields. This drastic response has not been noted elsewhere (Douglass and Swank 1972; Aubertin and Patric 1972; Verry 1972; Hart and DeByle 1975).

## NUTRIENT CYCLING VERSUS NUTRIENT FLUX

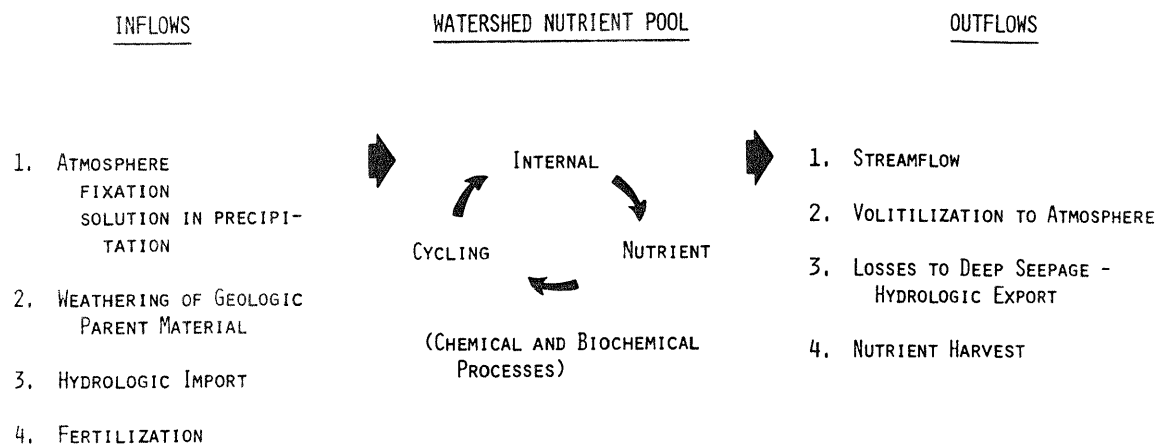
Nutrient cycling studies have been carried out in various parts of the country in an attempt to identify the pertinent processes leading to these treatment responses. Nutrient cycling studies on undisturbed watersheds have also provided baseline data for post treatment comparisons.

Many nutrient cycling studies (particularly those conducted by hydrologists) might better be called nutrient flux research. An examination of the generalized model of watershed nutrient cycling in table 1 reveals some of the complexities involved. There are a number of ways in which a watershed may gain and lose a particular nutrient. With some nutrients, the processes are relatively simple; with others, such as nitrogen in its many forms, things become complicated. Most nutrient flux studies, including the present one being conducted in the Missouri Ozarks, merely consider the precipitation inputs and the runoff losses. More comprehensive works may delve into nutrient pathways at some of the in-between steps by examining streamflow, litter leachate and soil water. It is well established that the cycling of nutrients within the ecosystem is generally much larger than the flux into and out of the watershed (Cole et al. 1967; Woodwell and Whittaker 1967; Gosz et al. 1972; Gosz et al. 1973; Williams and Mace 1975). Patric and Smith (1975) present an excellent review of the nutrient cycling literature as it pertains to the eastern hardwoods. In addition to covering both internal cycling and flux aspects, they discuss some of the effects of forest management including fertilization and timber harvest and suggest that disruption of the internal cycle by devegetation is probably responsible for the increase in certain nutrients in streamflow.

## RESEARCH IN THE OZARKS

Early in 1973, the School of Forestry, Fisheries and Wildlife began a water quality study on the water yields from four experimental watersheds at its University Forest facility in the southeast Missouri Ozarks. The long range study objective is to determine the impact of certain Ozark land use practices on water quality. Two practices being considered for examination at this time are timber harvest (including clearcutting) and forest land conversion to pasture. Both are growing in importance in the region in terms of total area involved and potential impact on water quality.

Table 1. Inflows nutrient pools and outflows of the nutrient cycle.




In the initial period prior to treatment efforts have been directed toward investigating some of the more basic processes and relationships. Net nutrient movement into and out of the watershed systems is being monitored in a flux study. Other studies are being conducted concurrently to look at some of the internal mechanisms.

## Study Objectives

During the initial phase of the flux study being reported here the following objectives were established:

1. Compare the flux of specific nutrients between the several experimental watersheds.
2. Examine the relationships between the nutrient inflow from precipitation and outflow from runoff as a function of total streamflow and discharge rate.

## Study Area and Methods

The watersheds range in size from approximately 9 to 18 acres (Fig. 1). A small spring maintains perennial flow from watershed 4 while the others yield runoff intermittently for varying durations depending on storm parameters and antecedent conditions. All catchments have an even-aged, predominantly oak and hickory forest cover that has been undisturbed since establishment 50 to 70 years ago.

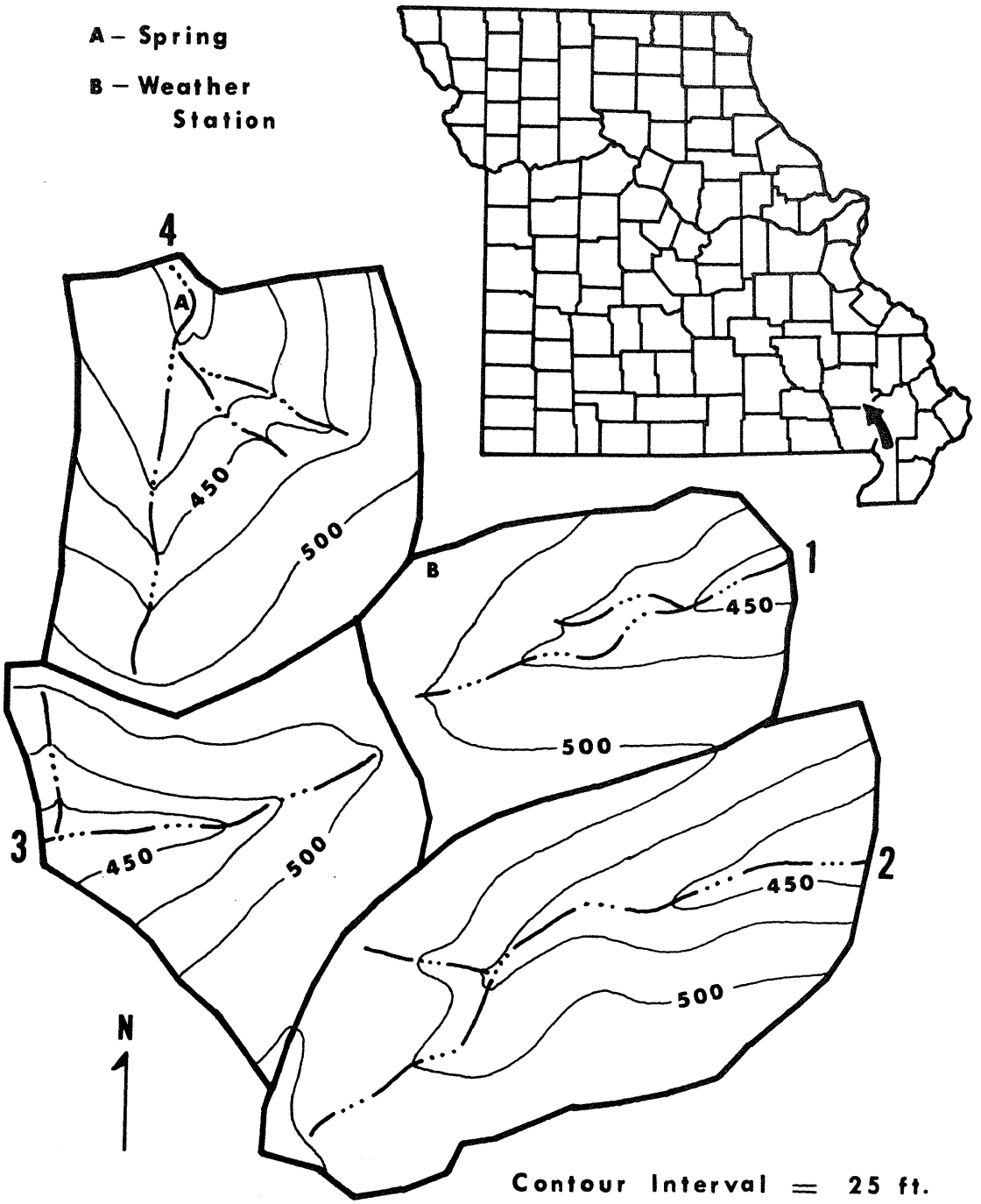



Figure 1. Location of the University Forest Watersheds.

The watersheds overlie carbonate bedrock and the potential for periodic losses to deep seepage has already been demonstrated (Settergren and Boehm 1972). During the 1968-1969 water year, 8.14 inches of deep seepage out of a total annual precipitation of 47.49 inches were calculated for watershed 4 using a modified water balance approach. The potential nutrient flux inflows from springs and outflows through deep seepage will be discussed briefly in a later section.

The soils on the research watersheds are derived from the weathered residuum of the underlying dolomitic limestone and sandstone geology, primarily of the Roubidoux formation series. Locally this mantle of residuum varies from 50 feet thick on the interbasin divide to somewhat less on the slopes and lower portions of the drainages. The soils are classified as Clarksville stony loam. The Clarksville series is a member of the loamy-skeletal, siliceons, mesic family of Typic Paleudults. These soils typically are cherty silt loam and strongly acid at the surface. They tend to increase in density, percent clay and chert with depth. In spite of the high density, subsoil drainage is relatively good (at least in comparison with most other Ozark soils) and these soils are frequently droughty during the late summer. Some soils of local alluvial origin can be found to a very limited extent in the extreme lower portion of these drainages.

Stream discharge has been gauged since 1967. Water quality samples are obtained automatically for each storm event using a gang of single-stage collectors similar to those designed by Sartz and Curtis (1967). This system samples only on the hydrograph rise. Numerous grab samples taken at various discharge rates supplement these data. Precipitation was measured and sampled at the centrally-located weather station. No dry fallout was included in the precipitation collected. Average concentrations were obtained using standard analytical methods described below and the total nutrient yield was calculated for each precipitation and runoff event. Although some streamflow nutrient concentrations were found to be related to flow rate, the absolute differences measured over a range in stages were small. In light of this, it was felt that the averaging technique and a weighing by total storm discharge would provide close approximations of actual long-term yield. This discharge dependency and other similar relationships will be discussed in greater detail.

## Sample Preparation and Nutrient Analysis

Following collection, the samples were frozen and stored at University Forest until they could be transported to the laboratory at the University in Columbia for analysis, usually on a monthly basis. Upon arrival at the laboratory each batch was thawed and prepared for analysis. The samples were initially filtered through 0.45 $\mu$ membrane filters which had previously been leached for 24 hours in two changes of

deionized distilled water. After filtration, each sample was divided into three parts. Twenty-five mililiters were preserved for Ca and Mg determination with 0.075 mililiters of 1:1 $HNO_3$ and 2.5 mililiters of a 50 grams per liter lanthanum solution. A second 25 mililiter aliquot, to be used for the determination of K and Na, was preserved with 0.075 mililiters of 1:1 $HNO_3$. The remaining portion, to be used in the $NH_4^+$-N, $NO_3^-$-N, $SiO_2$, and total phosphorous analyses, was refrigerated at 4°C until the determinations could be made.

Colorimetric procedures using Hach Chemical Company techniques were used to determine the concentrations for all constituents except the major cations. A Bausch and Lomb Spectronic 70 spectrophotometer with a 19 mm light path was used for all colorimetric analyses. Calcium and magnesium concentrations were determined by atomic absorption spectroscopy using a Perkin-Elmer 290-B unit. Sodium and potassium, due to their shorter emission wavelength, were determined by flame emission. A breakdown of the analyses employed can be seen in table 2.

Table 2. Methods Used in Water Quality Analysis

| Water Quality Parameter | Method |
|---|---|
| Ca | Atomic absorption |
| Mg | Atomic absorption |
| K | Flame emission |
| Na | Flame emission |
| $NH_3$-N | *Direct Nesslerization |
| $NO_3$-N | *Cadmium reduction - diazotization |
| Total Phosphorous | *Persulfate digestion - ascorbic acid |
| $SiO_2$ | *Molybdosilicate |

* Hach Co. chemicals and procedures.

Not all the major nutrients are included in the flux data presented. Because of inadequate laboratory facilities and sampling capabilities we were unable to obtain total Kjeldahl nitrogen.

Over the two year study period there were a number of storms for which water quality data, for one reason or another, were not obtained. In order to present the nutrient flux on an annual basis it was necessary to generate this information. An adequate number of storms were available with complete nutrient data to develop predictive models. Data were separated by watershed for each season of the year and equations were generated for the specific nutrients based on a total storm discharge function.

## Nutrient Flux

Annual nutrient inflows from precipitation and outflows to runoff for two of the four watersheds are presented in table 3 for the 1973-74 and 1974-75 water years (April through March). The flux, the difference between inflow and outflow, is presented for each nutrient as a net gain (+) to or loss (-) from the watershed. Although there were some differences noted in the concentrations of certain nutrients in individual runoff events as a function of discharge and season of the year, the absolute range was small. Again, some of the relationships will be discussed later. With a few notable exceptions, the nutrient flux variations displayed between years and between watersheds is due more to total volumetric loading than to actual differences in average concentrations. The 1973-74 water year was one with extremely high precipitation and runoff while 1974-75 was more near normal.

In terms of the flux balance, these watersheds annually lose calcium, magnesium and silica. During years of above normal precipitation, such as 1973-74, there may also be a small net loss of potassium and sodium. Ammonium, nitrate and total phosphate are accumulated.

## Discussion

The annual nutrient yields to streamflow and the nutrient flux from the University Forest watersheds are in general agreement with levels found by other researchers in the oak-hickory (Johnson and Swank 1973). The flux for most undisturbed forested watersheds has been reported as very low quantitatively and the total annual runoff may determine whether there is a small gain or loss during any particular year.

Close examination of the storm by storm nutrient flux or, more specifically, the nutrient yield to streamflow, reveals some interesting phenomena. Further, greater insight is provided into some controlling internal watershed cycling and hydrologic processes. Certain nutrients appear to be flushed from the watershed during the rise of the storm hydrograph. High yields of ammonium, phosphorous, potassium and calcium occur most frequently in the summer and early fall as these nutrients are picked up by rainfall from the tree foliage and decomposing leaf litter. The relative concentrations also appear to be related to the storm magnitude and the time since the previous flushing event. Phosphorous and potassium yields were closely correlated with stream turbidity, an indication that these nutrients probably are removed with flushes of organic and inorganic particulate matter.

It is interesting to compare the flux balance for potassium and sodium for the two study years, 1973-74, a wet year, and 1974-75, a year with more near normal precipitation. Under the higher moisture regime these soluable ions are flushed from the watershed to the extent that the flux becomes negative. Furthermore, since deep seepage occurs on all

Table 3. Nutrient flux for University Forest Watersheds for 1973 and 1974.

| 1973-74 Water Year | | | | | |
|---|---|---|---|---|---|
| | Precipitation (Total 79.52 inches) | Watershed 1 (Total Runoff 24.20 inches) | | Watershed 4 (Total Runoff 30.50 inches) | |
| Nutrient ion | Nutrient Inflow kg/ha | Nutrient Outflow kg/ha | Flux kg/ha | Nutrient Outflow kg/ha | Flux kg/ha |
| Ca | 7.86 | 10.21 | -2.35 | 107.48 | -99.62 |
| Mg | 1.07 | 5.78 | -4.71 | 73.91 | -72.84 |
| K | 5.17 | 5.51 | -0.34 | 6.41 | -1.24 |
| Na | 4.44 | 5.04 | -0.60 | 6.25 | -1.81 |
| $NH_3$-N | 9.89 | 3.15 | 6.74 | 1.70 | 8.28 |
| $NO_3$-N | 2.71 | 0.39 | 2.32 | 0.38 | 2.33 |
| T-Phosphorous | 0.68 | 0.25 | 0.43 | 0.06 | 0.62 |
| $SiO_2$ | 0.68 | 5.21 | -4.53 | 44.47 | -43.79 |

| 1974-75 Water Year | | | | | |
|---|---|---|---|---|---|
| | Precipitation (Total 52.84 inches) | Watershed 1 (Total Runoff 9.47 inches) | | Watershed 4 (Total Runoff 13.45 inches) | |
| Nutrient ion | Nutrient Inflow kg/ha | Nutrient Outflow kg/ha | Flux kg/ha | Nutrient Outflow kg/ha | Flux kg/ha |
| Ca | 4.79 | 4.00 | -0.79 | 44.91 | -40.12 |
| Mg | 0.64 | 2.29 | -1.65 | 29.25 | -28.61 |
| K | 3.09 | 2.22 | 0.87 | 2.90 | 0.19 |
| Na | 2.81 | 2.28 | 0.53 | 2.73 | 0.08 |
| $NH_3$-N | 5.90 | 1.01 | 4.89 | 0.79 | 5.11 |
| $NO_3$-N | 1.75 | 0.14 | 1.61 | 0.18 | 1.57 |
| T-Phosphorous | 0.38 | 0.05 | 0.33 | 0.05 | 0.33 |
| $SiO_2$ | 0.53 | 2.01 | -1.48 | 18.34 | -17.81 |

these watersheds to some degree and since there was no way to sample this component, the measured concentrations for some of the more soluable and mobile ions may be somewhat lower than the actual watershed outflows. Samples of outflow from watershed 4, with permanent flow sustained by a local groundwater source, may yield a more accurate measure of the flux loss. A previous water balance study indicates that the continuous discharge can be accounted for from water reserves within the watershed. The positive fluxes for many of the ions are so small that, taking the deep seepage component into consideration, they may actually be negative for most hydrologic years.

High yields of silica, calcium and magnesium are associated with the winter and spring seasons when increased soil moisture levels probably facilitate the geologic weathering, solution and movement of these minerals. In terms of the flux balance, these high yields must not be interpreted to indicate a depletion of these nutrients from the watershed. Rather they are evidence of other continuing internal processes.

The high outflows and negative flux from watershed 4 for calcium, magnesium and silicon probably indicate local solution of the dolomitic geology and weathered residuum. As such they are measures of a process occurring at considerable depth and the legitimacy of their use in a flux study may be questioned.

## CONCLUSIONS

The nutrient flux of undisturbed forested watersheds in the central hardwoods region, considering only the precipitation inflows and streamflow outflows, is, for the most part, small. Variations in yields of specific ions can be associated with internal watershed processes such as annual plant-soil nutrient cycling and geochemical weathering.

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