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NUTRIENT DISCHARGE FROM WALKER BRANCH WATERSHED[1,2]

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ABSTRACT--Streamflow discharge of nutrient elements (N, P, K, Ca, Mg, Na and S) has been studied on Walker Branch Watershed for up to six years. Annual discharges of N, P and S are less than atmospheric inputs whereas Ca, Mg, K and Na discharges exceed atmospheric inputs. Seasonal nutrient discharges are dependent on water yield. Concentration behavior of nutrients during storms has been used to identify processes within the watershed influencing nutrient release from the catchment. During storms, three patterns of concentration behavior are observed: dilution of concentration during stormflow (Ca and Mg); concentration increases during storms (N and S); and little change in concentration (dissolved K, P, Na) except for some concentration increase during autumn storms. These different patterns are caused by processes such as bedrock weathering, canopy and litter leaching, and expansion of the stream channel into variable source areas. Stormflow discharge is especially important in the transport of nitrogen and other elements primarily incorporated in organic matter.

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DISCLAIMER

INTRODUCTION

The Hubbard Brook study of the effects of forest denudation (Bormann and Likens 1967; Likens et al. 1970) on nutrient cycling first alerted many ecosystem scientists to the utility of using experimental watersheds for nutrient distribution and transport studies. Since that time a number of watershed facilities have been used to quantify nutrient cycles in a variety of undisturbed ecosystems (Fredrikson 1972; Henderson and Harris 1975; Johnson and Swank 1973). In addition, some experimental catchments have been manipulated to investigate the effects of different harvesting techniques, fertilization and vegetation conversion on water quality (Aubertin and Patric 1974; Aubertin et al. 1973; Johnson and Swank 1973). On Walker Branch Watershed the objectives of our nutrient cycling research have been to:

1. Increase the understanding of the basic factors controlling nutrient cycling processes within a landscape.
2. Quantify nutrient cycles for our watershed ecosystem in order to establish baseline data with which to compare patterns of nutrient cycling among different ecosystem types under differing climatic, vegetation and soil regimes.
3. Compare nutrient cycling in different forest types within a given landscape and establish the relative importance of the various cycling processes within these types.

The transfers (cycling) of nutrients between components are mediated by two carrier systems — water and biomass. A third carrier system, namely atmospheric transport, influences the import of nutrients to a landscape. By conducting nutrient cycling studies on experimental watersheds, the export of nutrients from the landscape in streamflow can be measured in conjunction with deposition from the atmosphere. These data enable the analysis of nutrient cycling processes within a watershed in relation to the integrated landscape behavior. And, in a larger scope, data on nutrient export in streamflow allow the interfacing of terrestrial and aquatic ecosystems. In this paper we present the behavior of Walker Branch Watershed with regard to net accumulation or loss of nitrogen, phosphorus, calcium, magnesium, potassium, sodium and sulfur, and discuss the physical, chemical and biological processes which control the concentrations of these nutrients in stream water and, therefore, their discharge from the watershed.

EXPERIMENTAL METHODS

Nutrient balances for Walker Branch Watershed are calculated from estimates of atmospheric deposition and discharge in streamflow. Samples of precipitation (wetfall) and dry particulate fallout (dryfall) were collected weekly at each of five sites on the watershed using modified Wong samplers. A detailed description of sample collection and processing techniques is given by Swank and Henderson (1976). Samples of streamflow are composited proportional to discharge and collected weekly for each subcatchment under baseflow conditions. During storm events when flow rate increases, separate samples are collected at 15 or 30 minute intervals. These samples are analyzed individually or combined over short time intervals in order to assess concentration changes associated with rapidly increasing and decreasing flow rates.

Calcium, Mg, K and Na concentrations are measured by standard atomic absorption spectrophotometry techniques with Lanthanum added to Ca determinations to eliminate interferences. Phosphate was determined by the molybdate blue method; ammonium by indophenol blue; nitrate by reduction to nitrite and reaction with sulfamilamide; and sulfate by methyl-thymol blue (Technicon Industrial Systems 1971; McSwain and Watrous 1974). These analyses ($PO_4^=$, NO_3^-, NH_4^+, $SO_4^=$) are automated spectrophotometric methods (Technicon Autoanalyzer). Total nitrogen (NH_4^+ and organic forms) was determined by Kjeldahl digestion and distillation and analysis of the distillate for ammonium as above.

RESULTS AND DISCUSSION

Nutrient Input-Output Balances

Elements can be classed on the basis of their behavior with respect to net retention by the landscape. For Walker Branch, three classes of behavior occur: 1) net loss (i.e., inputs < outputs) — Ca and Mg; 2) net accumulation (i.e., inputs > outputs) — N, P, and S; and 3) little net change (i.e., inputs $\cong$ outputs) — K and Na. The annual balances which show these relationships are presented in Tables 1–4 for Ca and Mg; N; P and S; and K and Na, respectively.

Calcium and Magnesium

The net annual loss of Ca averaged 133 kg/ha from 1970–74 (Table 1). Inputs to the watershed from the atmosphere averaged 14.3 kg/ha annually and varied little from year to year. About two-thirds of the deposition occurred as wetfall, but little correlation exists between the total amount of weekly precipitation and Ca concentration (Swank and Henderson 1976). Conversely, Ca outflow from the watershed was closely associated with hydrologic yield. Annual losses ranged from 120 kg/ha in 1970–71 to 183.6 kg/ha in 1972–73. Annual Mg outputs exceeded inputs by 75.0 kg/ha during the 1970–74 period (Table 1). Total Mg outputs were about 50% of those for Ca and showed the same year to year variation with lower discharges in 1970–71 and 1971–72, and highest losses in 1972–73. Magnesium inputs from the atmosphere averaged 2.1 kg/ha/year with very little annual variation. Input occurred about equally as wetfall and dryfall.

The large losses of Ca and Mg in stream water relative to atmospheric inputs are due to weathering of the dolomitic bedrock. The ratio of Ca:Mg in streamflow is about 2:1, the same ratio as occurs in the dolomite (Auerbach 1971). The amount of Ca and Mg discharge during a given year is a function of the amount of streamflow (i.e., the amount of water contacting the bedrock) and the distribution of streamflow (precipitation) within any year. For similar amounts of annual streamflow, years with a greater proportion of summer discharge will have greater amounts of Ca and Mg loss due to higher streamflow concentrations of these elements during this season.

Nitrogen, Phosphorus and Sulfur

Nitrogen, P, and S are accumulating in Walker Branch Watershed. Of the 8.7 kg/ha annual N input in precipitation, only 1.8 kg/ha is discharged in streamflow resulting in an annual net input to the watershed of 6.9 kg/ha (Table 2). Inputs were measured in the nitrate, organic and ammonium forms and these account for 45, 32 and 23% of the total input, respectively. The proportions of the different forms of input remained essentially the same even though there was nearly a 50% difference in the total input between the two years. While nitrate and ammonium are important forms of nitrogen input, they account for only about 20% of the N loss in streamflow; the bulk of the discharge occurs in the organic form.

Phosphorus inputs to Walker Branch Watershed averaged 0.54 kg/ha over the 1970–74 period and about 90% occurred as dryfall (Table 3). Over 95% of these inputs were retained within the watershed. In contrast to P, over 80% of the annual 18.1 kg/ha SO_4–S input occurs as wetfall (Table 3). While S is accumulating within the watershed, a greater proportion of the annual S input (65%) is being discharged in streamflow. The amount of annual S loss in streamflow is directly related to the amount of annual streamflow (Henderson et al. 1977).

Nitrogen accumulation is occurring within the vegetation on the watershed (Henderson and Harris 1975). Incorporation of phosphorus and sulfur in the annual wood growth (net production) can also account for the net annual accumulations of these elements on the watershed. However, the pathways of nutrient movement through the soil-microorganism-plant system are complex. Transient accumulation and subsequent release from each of these ecosystem components occurs and is important in overall element retention by the watershed.

Potassium and Sodium

Potassium and Na discharge from the watershed were greater than inputs from the atmosphere for the period from 1970–74 (Table 4); however, the net loss was much less than for Ca and Mg. Annual K and Na discharge were greatest during years with larger amounts of streamflow. Dryfall accounted for nearly 70% of the total K input and both dryfall and wetfall accounted for nearly 75%

of the annual Na input. While dryfall inputs of Na varied little from year to year, wetfall inputs were greatest during years with higher precipitation.

Using Ca discharge to approixmate bedrock weathering rates and concentrations of K and Na in the dolomite (Auerbach 1971) the calculated annual discharge of K and Na due to bedrock weathering amounts to 1.4 and 0.2 kg/ha, respectively. These amounts correspond to 20 and 5% of the total annual loss of K and Na. Sodium is not found in appreciable quantities in watershed vegetation and soils and mobility within the watershed is great, resulting in outputs which closely correspond to inputs. Potassium, on the other hand, is found in large amounts in the soil (32,000 kg/ha in the surface 60 cm) and the weathering of secondary soil minerals contribute to streamflow losses, thereby resulting in a slight net annual loss of this nutrient.

Streamflow Nutrient Concentration Patterns

Changes in nutrient concentrations in streamflow during storms reveal processes controlling discharge from a watershed. These processes may be physically and chemically based such as due to geology, soils and meteorology, or they may be biological such as those related to vegetation and land use. Concentration changes during periods of changing streamflow discharge fall into three classes: 1) dilution – lower concentrations during high discharge; 2) little or only seasonal changes in concentration; and 3) concentration – higher concentrations during high discharge. For Walker Branch, Ca and Mg concentrations are diluted, N and S concentrations are concentrated, K concentrations are seasonally concentrated, while Na and P show little change in concentration during storms. These patterns will be illustrated in Figs. 1–3 for Ca, K, and Na, respectively. These streamflow concentration data were collected during two storms: one is typical of summer precipitation (August 9, 3.3 cm of rain in 1.5 hours) and the other is representative of winter precipitation (November 7, 2.5 cm of rain in 4 hours).

Calcium concentrations are predominantly influenced by the residence time of water with the dolomite bedrock underlying the catchment (Fig. 1). During periods of increasing flow, Ca concentration decreases and when flow decreases Ca concentration increases. During high flow regimes baseflow, which has a long residence time with the bedrock, comprises a smaller proportion of the streamflow and is diluted by water arriving at the channel by other routes such as direct channel input. The amount of concentration decrease depends on the amount of stormflow relative to baseflow. This relationship holds during all seasons, although during winter storms which produce exceptionally high streamflow, Ca concentration reaches a minimum value and does not decrease further even though streamflow continues to increase. This minimum concentration is 10–20% of normal baseflow concentration and is similar to values in soil water at a depth of 75 cm in the soil profile. Thus, during these relatively short periods, soil solution chemistry is more important than bedrock dissolution in controlling streamflow Ca concentrations.

Potassium concentration patterns in streamflow are influenced by season of the year (Fig. 2). During late winter, spring and summer (e.g., August 9 storm), K concentrations remain nearly constant during periods of changing streamflow. In contrast, during early winter and especially autumn (e.g., November 7 storm), K concentration increases markedly during the initial period of storm and then returns to the baseflow concentration relatively quickly. Streamflow K concentration is primarily controlled by leaching through the soil profile for most of the year. However, in autumn and early winter, vegetation is responsible for the higher concentrations associated with initial streamflow increases. Potassium is leached from senescent leaves directly over the stream or from freshly fallen litter in the streambed giving use to higher streamflow concentrations.

Nitrogen concentrations in streamflow from Walker Branch Watershed are closely associated with the hydrologic response of the catchment (Fig. 3). Concentration changes during storms are due to transport of particulate organic and inorganic material. The pattern observed for individual storms most commonly consists of an initial decrease in concentration followed by an increase and then another decrease to levels below those prior to storm initiation. The initial concentration decrease is caused by dilution from direct channel input. The subsequent concentration increase is due to increased transport of organic and inorganic particulates dislodged by high flow rates (NO_3^-–N and NH_4^+–N concentrations are less than 5 ppb). Lower concentrations at the end of the storm are the result of reduced amounts of particulates available for transport because of the earlier flushing of materials. The highest concentration recorded for the two storms in Fig. 3 was approximately 0.7 ppm N; however, peak concentrations of 2.0 ppm N have been measured for larger storms. Our work further indicates that 80–90% of the annual particulate nitrogen loss occurs during a 5–10 hour period during each of the three of four largest storms of the year. During these periods streams expand into hydrologic source areas and transport material from intermittent drainages. Thus, hydrologic source areas are also important sources of elements which are primarily transported from watersheds in particulate form.

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Table 1. Annual calcium and magnesium balances on Walker Branch Watershed.

Water Year[a]	Inputs[b] Dryfall	Wetfall	Total	Output[c]	Net Retention or Loss[d]
		CALCIUM			
			kg/ha		
1970–71	5.6	9.0	14.6	120.0	–105.4
1971–72	6.4	8.1	14.5	128.9	–114.4
1972–73	4.8	9.6	14.4	183.6	–169.2
1973–74	4.3	9.5	13.8	157.5	–143.7
Four-Year Average	5.3	9.1	14.3	147.5	–133.2
		MAGNESIUM			
			kg/ha		
1970–71	1.4	1.1	2.5	68.7	–66.2
1971–72	1.1	1.0	2.1	66.1	–64.0
1972–73	1.1	1.0	2.1	94.4	–92.3
1973–74	0.8	0.9	1.7	79.3	–77.6
Four-Year Average	1.1	1.0	2.1	77.1	–75.0

[a]A water year extends from September 1 to August 31 of the following year.

[b]Inputs are: Wetfall = rain-scavenged; dryfall = dry particulate sedimentation; total = wetfall plus dryfall.

[c]Lost from the watershed dissolved in streamflow.

[d]Total input minus output ("+" = retention; "–" = loss).

Table 2. Annual nitrogen balance on Walker Branch Watershed.

Water Year[a]	Inputs[b] NO_3–N	Inputs[b] NH_4–N	Inputs[b] Total N[d]	Outputs[c] NO_3–N	Outputs[c] NH_4–N	Outputs[c] Total N[d]	Net Retention or Loss[e]
	kg/ha						
1972–73	4.7	2.4	10.6	0.1	0.3	2.1	+8.5
1973–74	3.1	1.5	6.8	0.2	0.2	1.5	+5.3
Two-year average	3.9	2.0	8.7	0.2	0.3	1.8	+6.9

[a] A water year extends from September 1 to August 31 of the following year.

[b] Carried into the watershed in precipitation (wetfall).

[c] Lost from the watershed in streamflow.

[d] Total nitrogen is the sum of NO_3–N and Kjeldahl-N (NH_4–N and Organic N).

[e] Total N input minus total N output ("+" = retention; "–" = loss).

Table 3. Annual balances for phosphorus and sulfur on Walker Branch Watershed.

Water Year[a]	Inputs[b] Dryfall	Inputs[b] Wetfall	Inputs[b] Total	Output[c]	Net Retention or Loss[d]
		PHOSPHORUS			
			kg/ha		
1970–71	0.43	0.06	0.49	0.01	+0.48
1971–72	0.49	0.05	0.54	0.02	+0.52
1972–73	0.55	0.08	0.63	0.03	+0.60
1973–74	0.46	0.05	0.51	0.03	+0.48
Four-year Average	0.48	0.06	0.54	0.02	+0.52
		SULFUR (SO_4–S)			
			kg/ha		
1973–74	4.0	16.5	20.5	16.6	+3.9
1974–75	2.8	14.3	17.1	10.7	+6.4
1975–76	2.9	13.8	16.7	7.1	+9.6
Three-year Average	3.2	14.9	18.1	11.5	+6.6

[a]A water year extends from September 1 to August 31 of the following year.

[b]Inputs are: Wetfall = rain-scavenged; dryfall = dry particulate sedimentation; total = wetfall plus dryfall.

[c]Lost from the watershed dissolved in streamflow.

[d]Total input minus output ("+" = retention; "–" = loss).

Table 4. Annual balances for potassium and sodium on Walker Branch Watershed.

Water Year[a]	Inputs[b] Dryfall	Inputs[b] Wetfall	Inputs[b] Total	Output[c]	Net Retention or Loss[d]
			POTASSIUM		
			kg/ha		
1970–71	1.7	0.8	2.5	5.5	–3.0
1971–72	2.0	0.9	2.9	5.3	–2.4
1972–73	2.2	1.2	3.4	8.4	–5.0
1973–74	2.7	0.9	3.6	8.1	–4.5
Four-year Average	2.2	1.0	3.1	6.8	–3.7
			SODIUM		
			kg/ha		
1970–71	0.9	2.0	2.9	4.1	–1.2
1971–72	1.2	2.2	3.4	3.3	+0.1
1972–73	1.0	4.1	5.1	5.5	–0.4
1973–74	1.1	3.2	4.3	4.9	–0.6
Four-year Average	1.1	2.9	3.9	4.4	–0.5

[a] A water year extends from September 1 to August 31 of the following year.

[b] Inputs are: Wetfall = rain-scavenged; dryfall = dry particulate sedimentation; total = wetfall plus dryfall.

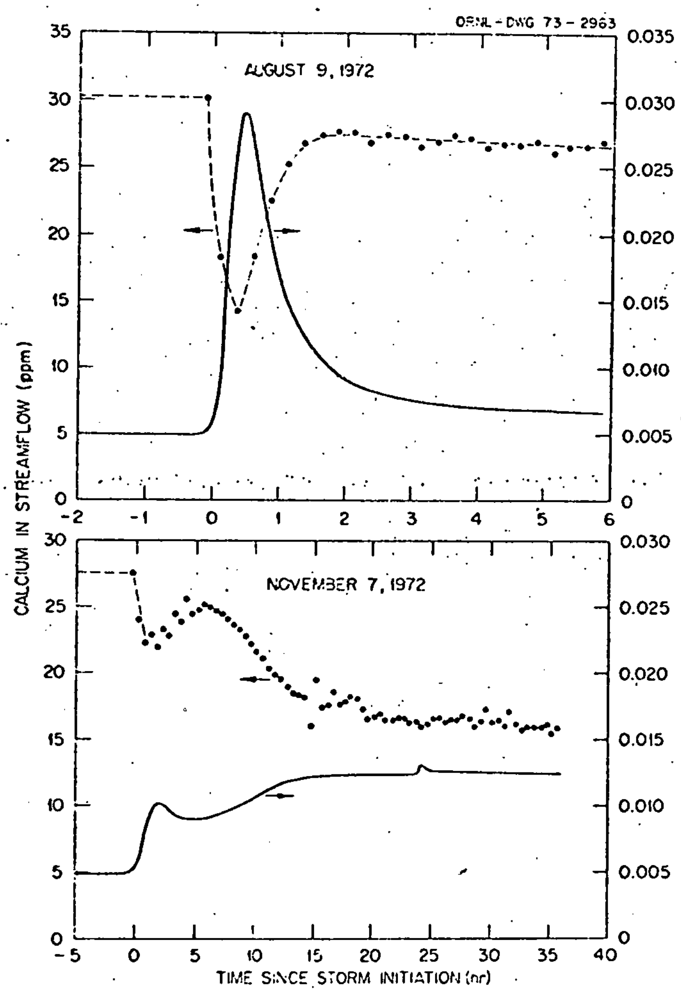
[c] Lost from the watershed dissolved in streamflow.

[d] Total input minus output ("+" = retention; "–" = loss).

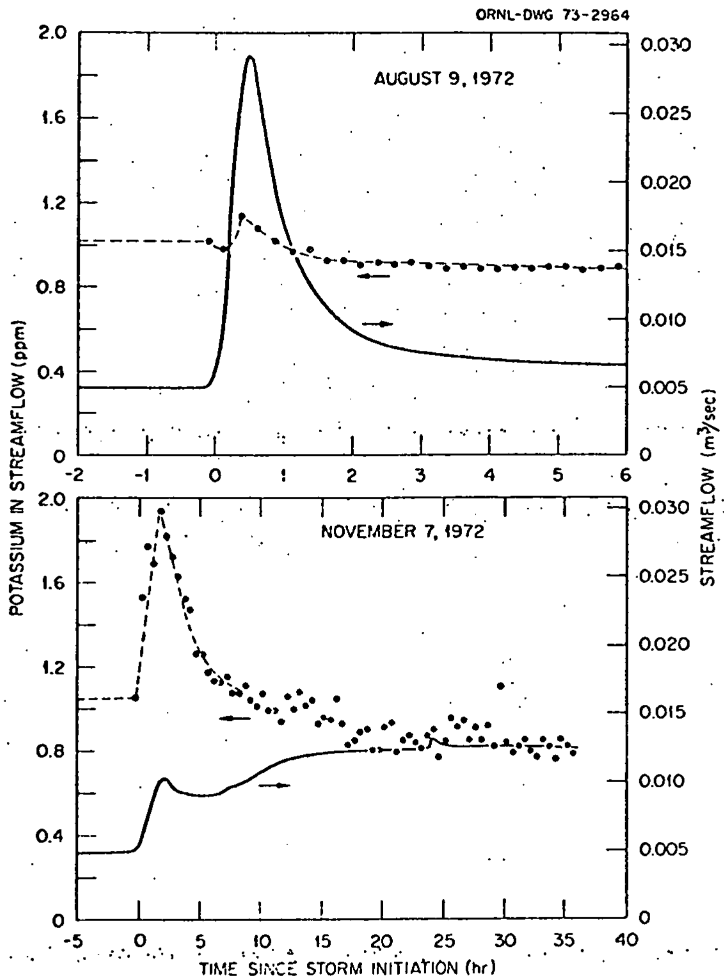
Fig. 1. Relationships between calcium concentration in streamflow and discharge rate for two storms on Walker Branch Watershed. Solid lines are stream discharge rates while points connected by dashed lines are calcium concentrations and the dashed lines to time 0 are the pre-storm concentrations.

Fig. 2. Relationships between potassium concentration in streamflow and discharge rate for two storms on Walker Branch Watershed. Solid lines are stream discharge rates while points connected by dashed lines are potassium concentrations and the dashed lines to time 0 are the pre-storm concentrations.

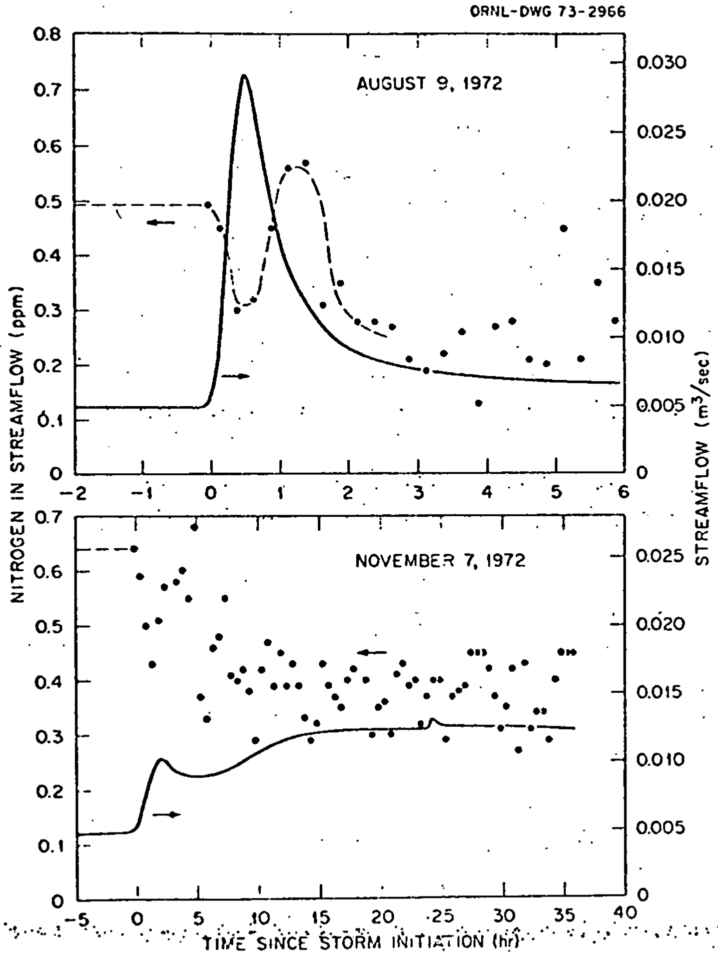
Fig. 3. Relationships between nitrogen concentration in streamflow and discharge rate for two storms on Walker Branch Watershed. Solid lines are stream discharge rates while points connected by dashed lines are nitrogen concentrations and the dashed lines to time 0 are the pre-storm concentrations.



ORNL-DWG 73-2963
AUGUST 9, 1972
NOVEMBER 7, 1972
CALCIUM IN STREAMFLOW (ppm)
STREAMFLOW (m³/sec)
TIME SINCE STORM INITIATION (hr)



ORNL-DWG 73-2964
AUGUST 9, 1972
NOVEMBER 7, 1972
POTASSIUM IN STREAMFLOW (ppm)
STREAMFLOW (m³/sec)
TIME SINCE STORM INITIATION (hr)
2.0
1.6
1.2
0.8
0.4
0
0.030
0.025
0.020
0.015
0.010
0.005
-2 -1 0 1 2 3 4 5 6
-5 0 5 10 15 20 25 30 35 40


ORNL-DWG 73-2966
AUGUST 9, 1972
NOVEMBER 7, 1972
NITROGEN IN STREAMFLOW (ppm)
STREAMFLOW (m³/sec)
TIME SINCE STORM INITIATION (hr)