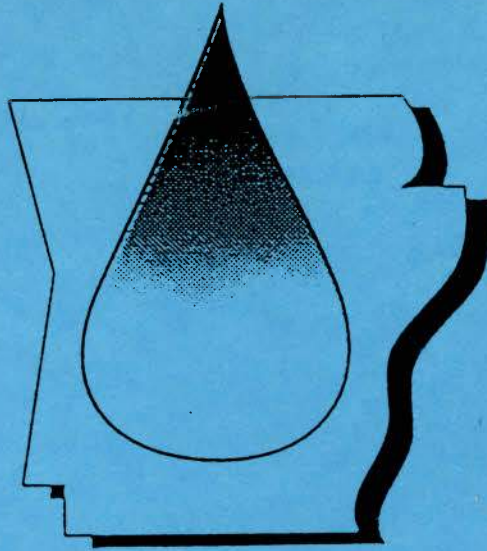


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**STORM AND BASE FLOW WATER QUALITY FOR  
BEAR, CALF, AND TOMAHAWK CREEKS**

**SUBMITTED TO THE BUFFALO NATIONAL RIVER**

**BY**

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AND  
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## EXECUTIVE SUMMARY

Because of the conversion of 92,780 acres of forest to pasture land in the Buffalo River watershed over a 27 year period, there is concern about the affect of agricultural activities on the water quality of the river. Three tributaries (Bear, Calf and Tomahawk creeks) located about mid-length of the Buffalo River were chosen to investigate the affect of agricultural activity on water quality because these streams provide the greatest amounts of fecal bacteria, nitrate+nitrite and phosphorus to the river, despite comprising only 13% of the watershed.

The specific objectives of this study were to:

1. investigate the impact of land use on the water quality.
2. compare water quality during base flow and storm flow conditions.
3. determine the effect of season on water quality.

The primary method used to quantify the effect of land use on the water quality of the agricultural tributaries was comparison of these water quality data with those for a pristine watershed in the headwaters of the Buffalo River 45 miles to the west. The pristine watershed is similar in size and physical characteristics to the tributary watersheds.

All three tributaries consistently had nutrient and bacteria concentrations and loads two to three orders of magnitude greater than the pristine site. Fecal coliform bacteria and nutrient *concentrations* at peak discharge for the tributaries were as much as 125 times and 44 times greater, respectively compared to the pristine site. Bacteria storm *loads* for the tributaries compared to the pristine site were even greater than comparisons of peak storm concentrations. The ratios of tributary to pristine bacteria and nutrient loads were as great as 416 and 138, respectively. These large increases in concentrations and loads for the tributaries in comparison to the pristine stream are examples of the degrading effect of agricultural and other non-point pollution sources on the water quality of the tributaries.

The impacts of agricultural activity on water quality were greatest during storms. Nutrient and bacteria peak discharge concentrations were two to five orders of magnitude greater than for base flow with the exception of nitrate. The total load of a storm can have the equivalent load of hundreds or even thousands of base flow days. For example, during three days of storm flow in November, Bear Creek contributed a fecal coliform load to the Buffalo River that was equivalent to 1,752,000 days of base flow at the pristine site.

Seasonal affects on water quality are primarily related to the amount and vigor of vegetation, temperature and discharge. Nitrate was often higher in base flow samples, especially, during the winter and fall when there was little nutrient uptake by the vegetation. Bacteria concentrations were lowest during the winter which is consistent with colder temperatures reducing bacteria viability. Total phosphorus, and perhaps ammonia and phosphate, concentrations appear to have

been lower during the winter and fall which may be the result of dilution by increased base flow discharge in the winter and fall.

During storms bacteria and nutrients (with the exception of nitrate) generally increased in concentration as total suspended solids increased. This is a result of nitrogen- and phosphorus-containing organic material comprising part of the sediment and also adsorption of phosphorus and bacteria to the sediments. It is possible that the results of storms may continue to affect water quality for weeks or months following a storm. This study has shown total Kjeldahl nitrogen and total phosphorus are transported and deposited with sediments during storms. These elements stored in the stream sediments then may become a source of nutrients as base flow stream and hyporheic waters leach nutrients from the sediment. Increased nutrients alter natural aquatic communities of organisms, especially in clear, "warm" streams such as the Buffalo River and its tributaries.

Although it was originally hypothesized that the rank of the tributaries based on agricultural activity (e.g., acres of pasture) would be consistent with the rank based on measures of water quality (concentrations or loads), this was *not* always the case. Variations in physical factors, (e.g., rain intensity, duration and distribution; soil saturation; season, spatial and temporal variations in land management) sometimes elevated and sometimes attenuated the relative effect of agricultural impacts on water quality. Nonetheless, it was observed that Bear Creek generally was the largest contributor of storm derived pollutants, followed by Calf Creek and then Tomahawk Creek which is the order predicted by the indicators of agricultural activity.

Because of the increase in the number of animals and pasture land in the tributary watersheds during the past 15 years (length of monitoring records), trends in water quality through time were also examined. Analysis of base flow data produced few statistically significant trends. This is probably the result of uneven sampling among the seasons, relatively low concentrations, change in detection limits and other site specific factors.

Base flow concentrations sometimes exceeded state standards for these streams. The most common standards exceeded were for fecal coliform, sulfate and total phosphorus. During storms, almost 100 percent of the samples exceeded the standards for fecal coliform bacteria and turbidity. Large increases in fecal coliform bacteria (over 40,000 colonies/100 mL) far exceed the 200 and 400 colonies/100 mL standards set for primary contact waters and the maximum concentration at the pristine site (520 col/100 mL). The total phosphorus guideline of 0.1 mg/L was often exceeded as well.

Because water quality standards are routinely exceeded in these agricultural tributary watersheds, it is imperative to determine how to respond to this situation. Implementation of appropriate best management practices (BMPs) can mitigate the impacts of land use activities on the water quality. Water quality information should be disseminated to the public so that all stakeholders can assist decision

makers in determining the proper methods for maintaining adequate water quality for the Buffalo River.

## INTRODUCTION

The Buffalo River is a major natural resource of Arkansas and the nation. In 1972 the federal government established the Buffalo National River as part of the National Park Service in order to preserve it as a free-flowing stream and to preserve its unique scenic and scientific features. The State also has recognized the tourism and environmental value of the river and in order to preserve it has named the Buffalo River an "Extraordinary Natural Resource" (ADPC&E, 1995). This designation requires that the Buffalo River meet standards that exceed that for most streams in Arkansas, along with pursuing land management protection of the watershed.

Only a narrow corridor consisting of 11% of the Buffalo River drainage basin lies within the Buffalo National River (Scott and Smith, 1994). Agricultural land use in this external portion of the watershed is growing and is affecting the river water quality (Mott, 1997). The vast majority of these agricultural lands are pasture and hay lands which will be simply referred to as "pasture" throughout this document. Animal (cattle, dairy and swine) production has increased in parts of the watershed and reflects increases in pasture land. During storm events, bacteria, suspended sediments and nutrients are carried by the runoff from the watersheds into streams. The bacteria potentially pose a health threat to the animals and humans that come in contact with the contaminated waters. Excessive nutrient levels may lead to the eutrophication of the stream. This condition is unfavorable for aesthetics and it threatens the aquatic health of the stream.

Three tributaries near mid-length of the Buffalo River, Bear, Calf and Tomahawk creeks, were selected to investigate the impact of agriculture on the river. Samples were collected from these tributaries during four rain events over a two year period from April of 1994 to December of 1995 for this study. Bear and Calf creeks are adjacent and Tomahawk Creek is across the river north of the other creeks (Figure 1). The town of Marshall, AR (pop. 1,318) lies partially within the Bear Creek drainage basin. Effluent from the municipal sewage treatment plant and half of the storm effluent from the town which includes a 1,000-head sale barn, drains into the upper reaches of Bear Creek. There are also 3,269 beef cattle and 932 dairy cows within the watershed. The adjacent Calf Creek basin has 2,382 beef cattle and 244 dairy cows and the Tomahawk Creek watershed has 1,724 beef cattle, 313 dairy cows, and an unconfined swine operation with 400 pigs [sic] (NRCS, 1995). The total pounds of animal waste per acre per year for Bear, Calf and Tomahawk creeks is 3,655; 2,119 and 1,833, respectively. Almost 100 percent of these watersheds are under private ownership (Table A1).

Bear, Calf and Tomahawk tributaries are the largest contributors of fecal coliform bacteria, nitrate+nitrite, and phosphorus to the Buffalo River. For example, Bear, Calf and Tomahawk creeks contribute approximately 50% of the



fecal coliform bacteria that pass down the river, despite composing only 13% of the total drainage basin (NRCS, 1995; Scott and Smith, 1994).

#### **OBJECTIVES**

Three Buffalo River tributaries, Bear, Calf, and Tomahawk creeks with significant animal production in the tributary watersheds were selected to determine the impact of agricultural land use (pastures) on stream water quality. Specifically the objectives were to:

1. investigate the impact of land use on the water quality.
2. compare water quality during base flow and storm flow conditions.
3. determine the effect of season on water quality.

### **STUDY AREA DESCRIPTION**

#### **LOCATION**

Figure 2 shows the location of the Buffalo River within the state of Arkansas. The Buffalo River flows from the west to the east and is a western tributary to the White River. The Buffalo River watershed contains over 857,000 acres and includes nine north-central Arkansas counties (Scott and Smith, 1994). Figure 1 shows the narrow Buffalo National River park corridor and study tributaries.

#### **SAMPLING SITES**

The sample collection site locations for Calf Creek (T-10) and Tomahawk Creek (T-14) are located near the confluence of each tributary with the Buffalo River. The Bear Creek *storm* sampling site is about 2 miles upstream from the tributary junction with the Buffalo River which is the site for base flow sample collection (T-12). During storm events it is not possible to reach the usual monitoring site because of road flooding; therefore, a storm monitoring site was established at the bridge on Arkansas Highway 65. In addition to storm monitoring, this site has been monitored during base flow as part of the Arkansas Water Education Team (WET) Program. Analyses for this program were conducted at the Buffalo National River Water Laboratory. Only data from the portion of the watershed upstream of the storm collection site is directly pertinent for the evaluation of storm water quality. Occasionally, this portion of the Bear Creek watershed will be referred to as "Upper Bear Creek" to emphasize that this is the critical portion of the watershed for storms.

Mott (1997) has shown that the storm sampling site (Highway 65) has higher base flow nitrate-N (0.634 mg/L), orthophosphate-P (0.083 mg/L) and

ammonia-N (0.074 mg/L) concentrations than the base flow sampling site further down stream. Nitrate concentrations are about 6 times higher, phosphate about 12 times higher and ammonia about 3 times higher at the Highway 65 site than the usual monitoring site (T-12). Base flow at Highway 65 is provided by resurgence of stream water from a losing stream section several miles upstream. This resurgence occurs at Bear Spring which is located about 0.5 miles upstream of this site. Because of the karstic environment of the area, the higher base flow nutrient concentrations at Highway 65 (Bear Spring) may reflect the impact of the town of Marshall (e.g., sewage effluent) and other point sources of contamination. Because there are no other sources of water entering the creek downstream, the decreases in nutrient concentrations at the downstream site (T-12) must be the result of chemical factors and/or biological assimilation. These factors make selection of a truly representative base flow site (either T-12 or Highway 65) difficult. Because the T-12 site is more consistent with the other tributary base flow sites, it will be used throughout this report to represent base flow conditions for Bear Creek. This means that *all* of Bear Creek is represented by the base flow site (T-12) but *only* Upper Bear Creek represents the drainage basin for the storm collection site (Highway 65).

R1 is a pristine site located in the extreme upper reaches of the Buffalo River headwaters at the downstream edge of the Wilderness Area (Figure 1). Prior to April, 1989, the R1 collection site was located at the Boxley bridge (or if this site was dry, samples were collected at the edge of the Wilderness Area). The change in the R1 sampling location could cause apparent changes in water quality. All of the sites are part of the National Park Service monitoring network for the Buffalo River. The station designation for the creeks in parentheses are those assigned for the Buffalo National River monitoring network (Mott, 1997). For this report only base flow data were used—samples associated with rising or falling stream water levels were removed from the monitoring data set for this study.

## GEOLOGY

Bear and Calf creeks and the upper Buffalo River (R1) have headwaters located in the Boston Mountains and the lower portions of the watersheds are located in the Springfield Plateau Region. Most of the Tomahawk Creek watershed is located on the Springfield Plateau but a small portion of its drainage area is on the Salem Plateau (Scott and Smith, 1994). There are a number of stratigraphic units and rock types in each of the three sub-basins (Figure 3 and 4). For example, the surficial geology of the Tomahawk Creek basin is dominated by chert and limestone (Boone Formation) and sandstone (St. Peter and Everton formations). Small amounts of shale are also present in the Bloyd Formation (Figure 3 and (Table 1).

In the Bear and Calf creeks sub-basins the Bloyd, Cane Hill, and the Upper Mississippian formations that crop out are composed of shale, sandstone, and minor amounts of limestone as shown in the stratigraphic column in Figure 3. The Osagean Boone Formation is also dominant in the sub-basins of Bear and Calf creeks (Hofer et al., 1995). The Everton, St. Peter, Cason, and Plattin formations crop out near the mouth of Bear Creek, over a very limited area.

In summary, there are approximately equivalent amounts of Osagean (Boone), Chesterian and Morrowan formations exposed in the Bear and Calf creek watersheds. Some Silurian and Ordovician rocks are exposed in Calf Creek. In comparison, the Tomahawk Creek watershed has a larger percentage of the Boone Formation exposed and very small amounts of Morrowan rocks. Sixty-five percent of the Tomahawk Creek sub-basin is underlain by the Boone Formation compared to 19 and 40% for Bear and Calf Creek sub-basins. In addition, the Tomahawk Creek basin has significantly more Ordovician rocks than Bear Creek and has minor amounts of Silurian rocks. The portion of the Boone Formation exposed in the study area is subject to significant karstification. The solution-enlarged fractures in the limestone allows rapid infiltration of contaminated runoff into the ground water system with little if any natural filtration. Because of the this increased permeability of the Boone Formation streams flowing over this formation typically are losing streams which flow only during, and for a short time following, storms. Where the stream valleys intersect less permeable Ordovician rocks ground water returns to the stream channels.

There are several mapped faults in the watersheds. The Tomahawk Creek basin has the most faults with seven. The Bear Creek basin has only one fault and the Calf Creek basin has no mapped faults (Figure 4).

## SOILS

The geology in the three sub-basins is variable and as a result soil types also are diverse. The soil series map (Figure 5) illustrates soil variability between the sub-basins. There are two basic differences among the soils in these watersheds. Firstly, the Bloyd, Cane Hill, and Upper Mississippian formations are widely exposed in the Bear (57%) and Calf Creek (64%) sub-basins, but have restricted exposure (1%) in the Tomahawk Creek sub-basin. The soils resulting from these formations are the Nella, Newnata, and Enders soil types. These soils are characterized as "deep, well-drained, slow-moderate permeability that form from residuum and colluvium of interbedded sandstones and shales" and represent the majority of the Bear and Calf creeks drainage basin (Fowlkes et al., 1988). Secondly, the St. Peter and Everton formations are the dominant surficial geology in the Tomahawk basin but represent only a small area of the Bear and Calf creeks drainage basins. The soil type formed from these interbedded sandstones and limestones is the Estate soil type (Fowlkes et al., 1988). All three sub-basins are

similar in that they all contain a large percentage of Nixa and Noark soil types. These soils are present where the underlying geology is the Boone Formation and are described as "a very cherty, silty loam" (Fowlkes et al., 1988). Table 2 provides the areal distribution of the soils in the watersheds.

#### LAND USE

Although Bear Creek watershed has the largest amount of pasture land (17,121 acres), it has the lowest percentage of pasture (33) because of its large size (51,300 acres). The watersheds of Calf and Tomahawk creeks have about the same number of pasture acres (11,800 acres) but as a result of the differences in total watershed area there are differences in percentage of pasture (38 and 50%, respectively) (Scott and Hofer, 1995) (Table 3 and Tables A2 and A3). Table 4 provides the number of animals in each watershed in 1994 (NRCS, 1995). With an increase in percent pasture land and animals, there is a potential for a corresponding increase in runoff (i.e., discharge), as well as higher bacteria, nutrient and TSS concentrations (NRCS, 1995).

Quality of the pastures are another important aspect concerning the impact of pasture land on water quality. The NRCS (1995) has identified "problem" areas and characterized them with regard to cover conditions, soil texture, geology, distance to streams and percent slope (Tables B1-B7).

Combined the three study watersheds compose about 13.3% of the total Buffalo River watershed (Upper Bear 6.8%, Calf 3.7%, Tomahawk 2.8%) (Scott and Smith, 1994). In the past, these three sub-basins have been, and continue to be, subject to agricultural development. Figures 6 and 7 show the land use distribution for the watersheds in 1992 and 1965, respectively. Table 5 and Figure 8 show the pasture land lost and gained between 1965 and 1992. The three watersheds had higher percentage of pasture than the Buffalo River watershed as a whole in 1965 (26 versus 14%, respectively). From 1965 to 1992 pasture acreage in the entire basin increased 75% (i.e., increased from 14 to 25%); whereas, the combined pasture acreage in the three tributary watersheds increased by 52% (i.e., increased from 26 to 38%) (Table 3 and Tables A2 and A3). These data show the importance and growth of agriculture in the Buffalo River watershed, especially in the three sub-basins.

In comparing land use and/or land cover maps developed by different methods and data bases, one must be cautious in making comparisons because of the differences in resolution and the methods used to identify land use and land cover. For example, it is sometimes difficult to distinguish pastures from transition zones (pastures reverting to forest) and cedar glades. The land use data for the upper Buffalo River (R1) provides such an example. The land use in this area has remained relatively unchanged for the past 23 years but the land use for 1965 (1,641 acres) and 1992 (4,885 acres) indicate a significant increase in pasture

land. Because the 1965 data were based on land use maps manually interpreted and not developed from satellite imagery using computer interpretation, the 1965 data is considered to best represent the upper Buffalo River watershed even for 1992.

#### **TOPOGRAPHY AND SLOPE**

The maximum relief for the Bear and Calf creek sub-basins is 1,475 feet and 1,480 feet, respectively; whereas, the maximum relief in the Tomahawk Creek sub-basin is only 870 feet. Tables 6 and C1 and Figure 9 show that the distribution of percent slope among the three sub-basins. Pastures with slopes >15% are of most concern because of the potential for increased erosion and the inability to effectively manage steep slopes leading to increased runoff and increased concentrations of nutrients, bacteria and sediments in runoff. The watersheds of Calf and Upper Bear creeks have 20% and 25% of pasture with slopes greater than 15%, respectively. Despite the low maximum relief in the Tomahawk Creek watershed, this watershed has 34% of pasture with slopes greater than 15%. These data demonstrate that about 25% of the pasture in these three watersheds is on relatively steep slopes which could lead to increased transport of bacteria, TSS and nutrients. Tables 7 and C2 gives the percent of pasture on slopes with greater than 15% slope in 1965. The number of acres used as pasture with slopes greater than 15% has increased about 2-3x from 1965 to 1992 (Tables 6 and 7).

Because of a recommendation to not clear slopes greater than 15 degrees, the land use of the tributary sub-basins was characterized with regard to degrees slope (Tables 8, C3 and C4). There are small percentages of the sub-basins with pastures developed on slopes of 15 degrees (33%) or greater. Tomahawk Creek has the greatest percentage (7%) of pasture land on slopes of 15 degrees or greater. The percentage of pastures on slopes of 15 degrees or greater increased the most for the Tomahawk Creek watershed where the percentage increased from 2 to 7% from 1965 to 1992. Tomahawk Creek watershed also has the greatest percentage of pasture in the next category (slopes of 7-14 degrees or 15-32%) with 14% of its pasture in this slope category. The percentage of pastures with 7-14 degrees slopes increased by 6 percentage points from 1965 to 1992 for all of the tributaries (Table 8).

#### **PREVIOUS WORK**

There have been a number of investigations of the Buffalo River and its tributaries, especially those dealing with water quality, beginning with a reconnaissance study by Nix (1973) and a study of non-flood stage loads of the river in 1974 (Steele and Wagner, 1977). Other projects coordinated with these water quality investigations studied stream sediment chemistry, fish, algae and

microinvertebrates (Bowen, and Steele, 1976; Babcock, 1976; Steele and Wagner, 1975; Babcock and MacDonald, 1975; Steele et al., 1975 and Wauer, 1974). Until the National Park Service began its monitoring network in 1985 there was no focused, on-going research of the river.

Mott (1990), Mott and Steele (1991) and Weeks (1992) described the impact of the cattle and hay fields on the water quality of the Buffalo River in Boxley Valley in the headwaters of the river. In 1991 Mott prepared a report for the National Park Service in which he summarized degradation of the Buffalo River from 1985 to 1990. Recently this report has been updated (Mott, 1997) as a 10-year report on the water quality of the Buffalo River in which he includes discussions of base flow, storm flow, and the need for water quality standards for the river.

Two studies by Mathis (1992 and 1991) used biological indicators of water quality. Mathis used macroinvertebrate surveys and community structure as a measure of the water quality. He is currently investigating sites in the middle portion of the river which include the three tributaries in this study.

The above studies determined significant changes in water quality of the river due to the nutrient and bacteria inputs from the pasture land. This impact is magnified during storm events. In 1995 the USDA Natural Resources Conservation Service published "Watershed Plan-Environmental Assessment for Buffalo River Tributaries Watershed." This report provides several scenarios of the impact of agricultural growth and best management practices on the water quality of the river.

The U.S. Geological Survey has included several sites in the Buffalo River watershed as part of the National Water-Quality Assessment Program, Ozark Plateaus region (Petersen et al., 1998, Adamski, 1997, Davis et al., 1995). The number of chemicals analyzed in this project not only include the typical water quality parameters but also include a comprehensive list of trace elements and pesticides (Bell et al., 1997 and Bell and Joseph, 1996). The background data from this program will provide data for comparison of the river water quality to other streams within the region and also on changes in water quality over time.

There have been several projects to prepare geographical information systems (GIS) data layers for the river watershed and to use these data for modeling. An early study of this type was conducted in 1982 by Nyquist who analyzed land cover from land use maps. Hofer et al. (1992) compiled information on the spatial distribution of the surficial geology and 1992 land use in the Buffalo River watershed. Scott and Smith (1994) developed soils, elevation, land use and other attributes for the Buffalo River watershed. Scott and Hofer (1995) using GIS technology, studied the spatial and temporal (1965 to 1992) morphology and land use characteristics of the Buffalo River watershed. More recently a report by

Culpepper and Bayard (1998) compared the Arkansas Gap vegetation map to the 1995 land use/land cover map of the Buffalo National River watershed.

## **METHODOLOGY AND PARAMETER DESCRIPTION**

Stream water samples were manually collected from Bear, Calf and Tomahawk creeks for four rain storms during 1994 and 1995 by National Park Service and Arkansas Water Resources Center (AWRC) personnel. The repeat sampling allows for comparison of storms and the evaluation of seasonal effects on water chemistry. All water samples were collected and analyzed following U.S. EPA (Keith, 1992) and/or standard methods protocol (APHA, 1992). Base flow samples were collected and analyzed in a similar fashion as part of the National Park Service monitoring program for the Buffalo National River.

There were a number of field and laboratory parameters measured during this project. The most complete sets of storm data were for:

1. rainfall
2. discharge
3. conductance
4. temperature
5. dissolved oxygen
6. pH
7. nitrate
8. total Kjeldahl nitrogen (TKN)
9. total phosphate
10. total suspended sediments
11. turbidity
12. fecal coliform

The first six parameters were determined in the field. Bacteria analyses were conducted at the Buffalo River Water Quality Laboratory. All of the other parameters were analyzed by the Arkansas Department of Pollution Control and Ecology Laboratory. A brief description of these parameters and the analytical methods used are discussed below.

Additional parameters were either not routinely analyzed, had few analyses above detection limits, or little change in concentration and therefore will not receive as much emphasis in this report. The analytical results for these parameters are included in Appendices D and E with the other parameter data for this project.

12. ammonia
13. orthophosphate
14. total organic carbon
15. chloride
16. sulfate

Water samples were collected in new plastic containers (milk jugs) for the analysis of all laboratory parameters except bacteria. The samples for bacteria analyses were collected in sterile whirlpak bags. Once the bag was in position for sample collection underwater, the air tight seal on the bag was broken and the bag filled with a sample. Then the bag was closed and brought to the surface and sealed.

Samples were collected as close to the center of the stream as possible (mid width and 0.6 of total depth). The streams were turbulent; thus, inputs to the streams were rapidly mixed. Care was taken to avoid contaminating the sample by touching inner portions of collection container and by collecting water upstream of the collector. Sample containers were labeled with collection time, location and the initials of the collector with water insoluble ink prior to collection of a sample. Water to be analyzed for nitrate, ammonia, chloride, orthophosphate, sulfate and total organic carbon were filtered through a 0.45 micron pore-sized membrane using a syringe at the Buffalo River Water Quality Laboratory prior to placement in new polyethylene bottles for shipment to the Arkansas Department of Pollution and Ecology laboratory in Little Rock. At maximum discharge the amount of suspended sediment present often required the membrane to be changed several times in order to obtain the required volume of water. All samples were analyzed within U.S. EPA specified holding times (Keith, 1992) except for one set of samples for Calf Creek collected during the December storm. Because the delay (3 days) for these TKN analyses was short and the values reported for this storm seem reasonable, these data will be utilized in water quality interpretations for this report. Appendix F contains the quality assurance for the analyses performed by the Arkansas Department of Pollution and Ecology.

## **FIELD PARAMETERS**

### **Rainfall**

Rainfall was measured by an automated tipping bucket rain gauge that records the amount of precipitation to the nearest 0.04 inches. Rainfall measurements were taken continuously throughout each precipitation event. Each of the sub-basins had one rain gauge in its basin. The rain gauge sites were at Marshall, Point Peter and St. Joe for Bear, Calf and Tomahawk creeks, respectively.



### **Discharge**

Discharge was calculated from stream stage readings using a rating curve. Staff gauge readings were made from permanently mounted laser light and staff rod holders to insure consistent leveling for readings made at the sample collection sites for Calf and Tomahawk creeks. Bear Creek has a staff gauge on the bridge abutment at Arkansas Highway 65. Each time a sample was collected a staff gauge measurement was made.

### **Dissolved Oxygen**

The dissolved oxygen (DO) measurements were made with an Orion 840 DO meter by placing the probe of the hand held unit into the top 6-12 in of the stream. The measurements were taken and values were recorded when the device displayed a constant reading for several seconds. The meter was standardized using an air calibration chamber prior to each collection event.

Dissolved oxygen is a measure of the concentration of oxygen in solution in a liquid. In natural waters, it is dependent on biochemical oxygen demand, chemical oxygen demand, rate of atmospheric reaeration, photosynthesis, respiration and water temperature (Mott, 1990). The DO minimum for streams with watersheds 10-100 mi<sup>2</sup> in the Ozark Highlands is 6 mg/L for the primary season (temperature less than 22<sup>o</sup> C) and 5 mg/L for the critical season (temperature equal to or greater than 22<sup>o</sup> C) (ADPC&E, 1995).

### **pH**

pH is the negative logarithm to the base 10 of the hydrogen-ion concentration of a solution. An Orion 290A pH meter was used to measure this parameter at the time of sample collection. The pH meter was standardized with two pH buffer solutions (7 and 10) prior to each collection event and then checked regularly against a standard to ensure proper calibration.

Most natural waters are buffered solutions which resist changes in pH (Chow, 1964). All three tributaries have a large amount of limestone exposed which keeps the run-off well buffered. Arkansas Water quality standards for pH state that pH levels must not fluctuate more than 1.0 in a 24 hour period and may not be above 9.0 or below 6.0 (ADPC&E, 1995).

### **Specific Conductance and Temperature**

The meter for conductance and temperature measurements was an Orion 122 conductivity meter. The probe was placed directly in the upper 6-12 in of the stream for measurements. Conductance is a measure of the electrical conductance of the water. Conductance is not only dependent on the concentration of ions present but is also dependent upon ionic charge and water temperature. Because conductance is temperature dependent, it is reported at a standard temperature of

25 degrees Celsius, i.e., specific conductance. The conductivity meter was standardized with appropriate solutions prior to each collection event.

## LABORATORY ANALYSES

### Nitrate

The analytical method used for nitrate was the Hydrogen Reduction Method (4500-NO<sub>3</sub>) (APHA, 1992) which also measured NO<sub>2</sub>. The holding time for nitrate analyses is 48 hours. For the purposes of this study NO<sub>3</sub> and NO<sub>2</sub> are reported as NO<sub>3</sub>-N because nitrite converts very rapidly to nitrate and, thus, nitrite concentration is negligible in natural waters.

Nitrate (NO<sub>3</sub>) is a soluble form of the nitrogen. The primary source of nitrate in water is the end product of the aerobic stabilization of substances containing organic nitrogen (Tchobanoglous and Schroeder, 1987). Stream ecosystems may benefit from limited amounts of nitrogen; however, excessive amounts can lead to prolific growth of aquatic plants. In streams, nitrate is quickly returned to the organic nitrogen state by photosynthetic processes of plants. Agricultural watersheds are especially susceptible to excessive nitrogen input due to land use. Pasture lands may receive nitrate from inorganic fertilizers and/or animal wastes.

### Total Kjeldahl Nitrogen

Samples for total Kjeldahl nitrogen (TKN) analyses were digested in sulfuric acid, potassium sulfate, and copper sulfate and then analyzed by the Specific Ion Method (4500-N<sub>org</sub> without removal of ammonia) (APHA, 1992). TKN is the sum of organic nitrogen and ammonia. Seven days is the maximum storage time for analysis of TKN.

### Total Phosphorus (TP)

Phosphorus samples have a 48 hour storage limit. Samples were collected in polyethylene bottles and later digested in persulfate which frees phosphates from any sediments; i.e., total phosphorus in the water sample. The 4500-P Ascorbic Acid analysis method was used as specified in Standard Methods (APHA, 1992).

Total phosphorus is the measure of both organic and inorganic forms of phosphate (Reddy, 1980) in unfiltered water samples. Agricultural fertilizers and biological wastes and residues are relatively high in phosphorus--all of which are common in drainage basins with significant agricultural activity. Typically animal manure is applied to pasture land based on nitrogen requirements. Because the N:P ratio is such that when N is used to determine the manure application rate, P exceeds that required by the grass.

The ADPC&E (1995) states that total phosphorus concentration limits may not exist at levels that promote excessive algal growth. As a general guideline 0.1 mg/L is cited as the total phosphorus limit for streams.

#### **Orthophosphate**

Orthophosphate ( $\text{PO}_4\text{-P}$ ) is a readily soluble phosphate that is common in natural waters. This parameter requires filtration prior to analyses. These samples have a 48 hour holding time. They were analyzed using 4500-P Ascorbic Acid Method (APHA, 1992). Orthophosphate is the form of phosphate that can be used directly by algae (Bowen, 1978).

#### **Total Suspended Solids**

Total Suspended Solids (TSS) are defined (APHA, 1992) as all materials too large to pass through a 2.0 micron pore-sized filter. A water sample was filtered and then the dry weight of the material on the filter was reported TSS (APHA, 1992). TSS is important in terms of the effect of the sediments on aquatic organisms, especially when the suspended sediments are deposited on fish eggs or change the environment for benthic organisms.

#### **Turbidity**

Turbidity detracts from the aesthetic qualities of a stream and is defined as the ability of suspended and colloidal materials to diminish the penetration of light (Chow, 1964). Turbidity samples have a 72 hour holding time and were analyzed with a HACH 2100A turbidimeter at the Buffalo River Water Quality Field Laboratory for grab samples but the storm samples were analyzed by the Arkansas Department of Pollution Control and Ecology Laboratory. Turbidity is a measure of the colloids and suspended sediments present in a water sample. The regulations for turbidity are that "there shall be not distinctly visible increase in the turbidity of receiving waters attributable to industrial, agricultural, other waste discharges or in-stream activities. Specifically, in no case shall any such...activity cause the turbidity values to exceed" 10 NTU for the Ozark Highlands (ADPC&E, 1995).

#### **Fecal Coliform**

The Arkansas Department of Pollution Control and Ecology designates Bear, Calf and Tomahawk Creek as "primary and secondary contact by recreation use" (NRCS, 1995). The "Regulation Establishing Water Quality Standards for Surface Waters of the State of Arkansas" states that for "Primary Contact Waters - Between April 1 and September 30, the fecal coliform content shall not exceed a geometric mean of 200/100 mL nor shall more than 10 percent of the total samples during any 30-day period exceed 400/100 mL. During the remainder of the

calendar year, these criteria may be exceeded, but at no time shall the fecal coliform content exceed the level necessary to support secondary contact recreation” (ADPC&E, 1995). The Secondary Contact regulation states that “...fecal coliform content shall not exceed a geometric mean of 1000/100 mL, nor equal or exceed 2000/100 mL in more than 10 percent of the samples taken in any 30-day period” (ADPC&E, 1995).

Standard methods allow 6 hours maximum holding time between collection and incubation (APHA, 1992). Due to the relatively short holding time it was necessary to perform fecal coliform analyses (Membrane Filtration Method—9222.D, APHA, 1992) at the Buffalo River Water Quality Field Laboratory.

## **STORM EVENTS**

Water quality data were collected for four storms during this study. The dates of the storms were:

1. April 29-30, 1994
2. November 2-5, 1994
3. January 13-14, 1995
4. December 17-18, 1995

Because of distance between sampling points and field analysis logistics, it was not possible to collect samples from all sites with a collection interval less than two hours if more than one tributary was monitored.

### **APRIL STORM**

All three tributaries were sampled for approximately 24 hours during the storm on April 29-30, 1994. There were two periods of intense rainfall which caused two discharge peaks during the storm at each tributary collection site (Figure 10 and Table D1). Although discharge did not completely return to pre-storm levels, there was sufficient decrease in discharge to produce a distinct second discharge peak. In effect, this storm can be treated as two storms to investigate the effect of a recent preceding storm on the water quality of a second storm (Figure 11). The rainfall among the tributaries was 2.12, 2.80, and 2.33 inches for Bear, Calf and Tomahawk creeks, respectively (Table 9) (average of 2.4 inches).

### **NOVEMBER STORM**

The second rain event occurred on November 3-5, 1994. This was an extremely large rain event produced by a stationary front which averaged 7.91

inches for all three watersheds. One would expect significant variation in rainfall areally during summer thunder storms and more uniform rain distribution during a stationary storm, at least over relatively short distances. Uniform rainfall distribution did *not* occur for the November rain. The range in rainfall was 6.57, 9.13, and 8.03 inches for Bear, Calf and Tomahawk creeks, respectively (Table 9). All three tributaries were monitored during this event. Although the runoff generated by this storm was large, it would have been even greater if the soil had not been very dry. This unusually large rainfall storm did not produce typical discharge hydrographs. The third discharge peak for Tomahawk Creek (Figure 12) is not a true discharge peak but rather the result of the large rise in the Buffalo River (about 23 feet at the time and eventually cresting at about 35 feet on November 5, 1994) that blocked the flow of water from Tomahawk Creek from entering the river. Based on field observations, rainfall data and the behavior of the other streams and the Buffalo River, the discharge data from the last two data points were not used in calculations of total discharge or loads. The data for Bear Creek in this storm and data for Tomahawk Creek during the January storm, made possible the extrapolation of data for Tomahawk Creek (Tables D2 and D3). Bear and Tomahawk creeks recorded rising portions of the hydrograph but because of the rapid rise in water level (dry to about 1000 cfs in three hours or less) for Calf Creek site the initial rising portion of the hydrograph for this creek was not measured (Figure 12). A second rise (about 3200 cfs) in water level 17 hours later was measured but because the access road to the monitoring site was soon flooded, peak discharge and the falling portion of this portion of the hydrograph was not measured. Lack of most of the rising limb of the hydrograph for the first peak in discharge and uncertainty about the second discharge peak and lack of the falling limb for this portion of the hydrograph made meaningful load calculations for Calf Creek for this storm impossible.

#### JANUARY STORM

Tomahawk Creek was the only stream sampled during the January 13-14, 1995 storm which allowed samples to be collected with very short time intervals; thus, providing a very detailed hydrograph (Figure 13 and Table D3). The total rainfall for this storm was 2.28 inches. Twenty-three samples were collected over a period of 19 hours which provided an average sampling interval of about 50 minutes compared to sampling intervals over 3 times greater for other storms. This detailed hydrograph provided critical data for the exploration of hydrographs for other storms. Almost identical rainfall amounts were recorded for this storm (2.28 inches) and the previously monitored April storm (2.33 inches) (Table 9). If the differences in rainfall are accurate then the differences in discharge and water quality must be related to seasonal factors such as vegetation cover or soil saturation and/or rainfall intensity.

## DECEMBER STORM

The final storm sampled occurred on December 17-18, 1995. Bear and Calf creeks were the two streams sampled. The rain totals were 2.17 in for Bear Creek and 1.93 in for Calf Creek (Table 9). The rising limb of the hydrograph was sampled and a significant portion of the falling limb was also sampled for both tributaries (Figure 14) (Table D4).

## R1 JANUARY, 1989 STORM

Data for the January 25-26, 1989 storm for the pristine headwaters area of the Buffalo River (R1) was chosen for comparison with results for the tributaries. This storm was chosen from the four available because:

1. this storm had the greatest discharge and greatest loads.
2. it is about the same size as three of the storms in this study. During 20 hours, 2.08 inches of rain fell (Mott, 1990).
3. it had the most samples which was important in determining a complete hydrograph.

Because this storm had the greatest discharge and loads, comparisons using these data are *conservative*, i.e., differences between R1 and the tributaries would be greater using data for the other R1 storms (Table D5).

## DISCUSSION

### General

Storm data can not only provide information on the quantity of nutrients, bacteria and sediment being transported by a stream but can also provide information on the factors affecting transport of these materials. This type of information is essential for planning management strategies for the protection of the water quality of streams. Storm hydrographs are very helpful in interpreting storm water quality and transport mechanisms. A single sustained rainfall event results in increased runoff which produces a well-developed hydrograph. Typical hydrographs (discharge versus time) are asymmetrical, displaying a relatively rapid rise to a peak and a slower decline back to pre-storm conditions. The January, 1995 and December, 1995 storms of this study provide good examples of discharge hydrographs (Figures 13 and 14). Long rains provide more opportunity for fluctuation in rain intensity resulting in multiple peaks in the hydrographs. The multiple peaks for Tomahawk Creek during the April and November storms are examples of this type of storm (Figures 10 and 12). Other hydrographs (plots of other parameters, e.g., nitrate or bacteria versus time) also provide important information.

Factors that may affect hydrograph shape are:

- season
- temperature
- duration of rain
- total rainfall amount
- rain intensity
- rainfall homogeneity over the basin
- length of time since a previous rain (i.e., soil saturation)
- vegetation quantity
- vegetation type
- vegetation distribution
- vegetation vigor
- land use
- geology
- soil type
- size, shape and slope of the drainage basin.

Although factors such as rain quantity, intensity, homogeneity, soil saturation and season may vary from one rain event, to another; factors such as soils, size, shape, geologic conditions and slope are constant for a basin, and over short time periods land use/ land cover also may be considered constant.

Because of the general similarity of watershed size, slope, soils, land-use and rainfall, hydrograph responses among the three tributaries are generally similar. Figure 15 illustrates all three tributary hydrographs during the April rain event along with the cumulative rainfall amounts. The rainfall amounts and intensities are broadly similar (32% variation) for all three basins and all three show double discharge peaks (Figure 15). The tributaries are generally similar in regards to slope, geology, soil type and vegetation. These observations suggest that one or several aspects of rainfall (intensity, distribution, duration, time since previous rain) must be controlling the hydrograph.

#### **Comparison Of Storms Of Similar Size**

Seasonal changes bring differences in soil saturation levels and vegetation quantity and vigor. Comparison of the *same* tributary during *different* storm events of approximately the same amount of rain would help determine the effects of season on discharge and water quality. The April storm recorded a cumulative rainfall of 2.33 inches and the January event recorded a rainfall value of 2.28 inches, a difference of only 0.05 inches which provided an ideal situation for determination of the effects of season on discharge and water quality. Despite similar rainfall amounts, the January discharge values ( $3.4 \times 10^9$  L) for Tomahawk

Creek were about three times greater than those for the April event ( $1.1 \times 10^9$  L). The geology and soils, and the size, shape and slope of the drainage basin were constant for the two events. Because the cumulative rainfall totals were approximately the same (Table 9), rainfall intensity, vegetation cover and vigor, and soil saturation condition must have played an important role in determining runoff quantities. Another possible explanation is that the rain gauge readings are not representative of the rainfall for the entire watersheds.

If rain factors are considered similar for the two, then the increased overland flow for the January storm may be attributed to greater soil saturation and less vegetation. There were 4 days of dry weather prior to the January storm and 3 days of dry weather prior to the April storm. Preceding the dry days there was 0.6 in of rain in 17 days during January and 1.0 in of rain in 16 days during April (NPS, 1998). In April transpiration (and evaporation) would have removed much of the moisture from the soil and retarded the rate of runoff; whereas, in January there would be less vegetation to retard runoff rates and the largely dormant vegetation would not have removed much of the soil moisture. Less soil saturation would have increased rain infiltration resulting in less runoff in April. The ultimate result of increased vegetation and lack of soil moisture is a decrease in total discharge, and a broader hydrograph due to slower draining velocities over the watershed.

#### **Effect Of Prior Storm (Soil Saturation)**

The length of time prior to a subsequent rain event can be a dominant factor in controlling soil saturation. Overland flow begins when rainfall intensity exceeds infiltration capacity (Fetter, 1994). Lag time and hydrograph shape both are affected by the relationship between the time rainfall started and the onset of overland flow. The two pulses of discharge for the April storm indicate the importance of soil saturation (Figures 15). Although less than half of the rain fell after the first hydrograph peak, the second discharge peak was higher for all three tributaries. The discharge peaks for Bear and Calf creek discharges were over double that of the first peak; whereas, the differences between the first and second peaks for Tomahawk Creek were much less. Another possible explanation is that the rain gauge amounts are not representative of the rain received for the entire basin.

#### **Potential Errors In Rainfall**

Rainfall distribution among the tributary drainage basins is important when comparing hydrographs. Even among these closely spaced watersheds rainfall can be rather variable (Table 9). Although the readings among the rain gauges were similar for some of the rains in this study, there were some potentially significant variations for the November and April storms. The range of variation for the



November storm was 2.56 inches (39%) and 0.68 inches (32%) for the April storm. Apparently, Bear, Calf and Tomahawk creeks are large enough (78, 49, and 37 square miles, respectively) to allow for significant variation in rain distribution within basins.

Differences in rainfall intensity are indicated by the data for the November storm which demonstrates wide variability of storm discharge possible even for two adjacent watersheds. Tomahawk Creek had two distinct discharge peaks as a result of periods of intense rain. The third discharge peak is the result of “damming or backing up” of Tomahawk Creek by the large rise (about 23 feet) in the level of the Buffalo River during this collection period. Bear Creek had a single discharge peak. Although Calf Creek had about 3 inches more rain than Tomahawk Creek, it did not reach peak discharge before the road to the monitoring site was flooded but its hydrograph probably parallels that of Bear Creek (Figure 12). These observations illustrate the problems of obtaining accurate rainfall data for even relatively small watersheds in close proximity to one another. These observations indicate that single rain gauges in each watershed do not always represent accurate rain distribution within the entire watershed.

### PARAMETER BEHAVIOR DURING STORMS

Nutrient, TSS and fecal coliform response to storm events is a primary focus of this study. An understanding of how these parameters react and interact during rain episodes is the first step toward controlling their damaging impacts to waterways. For these tributaries, changes in most parameter concentrations are positively associated with discharge (e.g., Figure 16). Nitrate is a notable exception to this statement (e.g., Figures 17).

Although collection sites were selected for collection of samples representative of the *entire* watershed, the storm sampling site for Bear Creek (approximately 2 miles upstream of the confluence with the river) represents only the upper portion of the watershed. Despite careful selection of the collection sites, there is a potential problem of local runoff and/or turbulence upstream of the collection site. This situation would be most noticeable near the beginning of the storm when the stream discharge is still low but the parameter level (e.g., TSS) could be relatively high because of the concentrated nature of the runoff and relatively high ratio of runoff to stream discharge. This type of situation is suggested by some of the data. For example, the fecal coliform concentration of 16,000 col/100mL early in the January storm indicates a much higher concentration than would be expected for the relatively low associated discharge (175 cfs) (Figure 18).

Although plots of nutrient concentration versus time provide a qualitative graphical analysis of response to rain events, statistical methods provide quantitative evaluation. The statistical tool used to assess relationships among storm event parameters was the Pearson correlation coefficient (R) (Downie and Heath, 1970 and Spooner, 1996). R is a measure of relationship between two variables which ranges from 1 to -1. A perfect positive correlation between two variables would have a coefficient of 1, a "perfect negative correction is -1, and no correlation is represented by 0. The likelihood of the correlation occurring by chance is give by the probability value. A probability of 0.05 (or smaller) was chosen to be an acceptable chance of random correlation for this project.

The square of R explains the amount of variability of x that can be explained by variability of y. Correlation coefficients of 0.7 or greater are considered to be meaningful for this study, i.e., 49% of the variability of x is attributable to variability of y. For example, during the December storm Calf Creek recorded an R value of 0.872 for TSS versus TKN.  $R^2$  for this example indicates that 76%  $[(0.872)^2 = 0.7603 \times 100]$  of the variability of TKN is explained by TSS concentrations. Appendix G provides the correlation coefficients and probability values for each parameter versus each of the others for the tributaries and R1 for each storm .

#### PARAMETERS ASSOCIATED WITH SUSPENDED SOLIDS

Despite the general parallel of changes in discharge and many parameters (e.g., Figure 16), there are not many statistically significant correlations for discharge and other parameters. The lack of correlation is because the two parameter values are sometimes "offset," i.e., the discharge and the parameter do not reach peak concentration at the same time and the difference in the behavior of the storm on the rising and recessional limbs of the hydrographs. This offset is about 2.5 hours for Bear Creek during the December storm (Figure 19). The reason for this offset may be that peak *surface* water discharge occurs before the peak in *total* stream discharge which includes the peak contribution of water from soil piping and the vadose zone. The first "flush" of overland flow has the highest concentrations of TSS and associated parameters (especially TKN, total phosphorus and bacteria); therefore, these parameters may reach a maximum concentration with the peak in surface water discharge and *not* with the peak in total discharge which includes significantly more vadose and soil derived water. Vadose and soil derived water do not contain as much TSS and associated parameters as surface water; thus, the concentrations of these parameters decreases as a result of dilution at maximum stream discharge. The vadose water contribution for these streams may be relatively large compared to streams in other areas because of the karstic character of the limestone in these tributary

watersheds. The lack of measurable “off-set” for every situation is probably the lack of sufficient sampling frequency. Furthermore, the parameter concentration for a given discharge on the rising portion of the hydrograph is usually not the same on the falling portion of the hydrograph (e.g., Figure 19). This is probably the result of more sediment being removed on the rising portion of the hydrograph as a result of less cohesion of surface sediment and/or more turbulence on the rising limb of the hydrograph causing more erosion.

Generally, the parameters can be divided into two groups—those that correlate with suspended sediment and those that do not correlate with suspended sediment. The first group represents those parameters that are attached to the sediments or incorporated into organic material in the sediments. The second group is comprised of those parameters that are very soluble and present as dissolved ions or ionic complexes. Because of these relationships, the behavior of parameters during storms will be discussed in terms of these two groups.

#### **TSS and Turbidity**

Total suspended solids (TSS) and turbidity are important in interpreting storm-event data because many nutrients and bacteria are transported attached to suspended particles. Turbidity and TSS responses to storm events are consistent among the tributaries and for all storm events sampled. Correlation coefficients between TSS and turbidity normally ranged from 0.91 to 0.99 with acceptable probability values ( $<0.05$ ) (Tables G1-G5). Figure 20 graphically illustrates the correlation between TSS and turbidity ( $R = 0.97$ ). This figure indicates that turbidity values greater than about 40 FTU can be used to predict TSS concentrations.

During storm events TSS and turbidity concentrations make an abrupt rise to a peak at or before the peak in discharge and then decline quickly (relative to discharge) back to near pre-storm concentrations (Figure 19). This rapid rise and decline in turbidity and TSS values relative to discharge demonstrates that these values do not correlate with discharge despite paralleling trends. The amount of suspended solids in stream water is dominantly controlled by overland flow and stream velocity and turbulence. Another major controlling factor is the availability of sediment to be transported. When overland flow begins, available sediments are quickly transported to the stream. Another possible explanation is that a large portion of total flow was contributed by ground water or vadose water which can have low TSS concentrations. This situation is illustrated in Figure 21 for Calf Creek during the April event of 1994. During the first peak of the hydrograph, discharge values rise to 660 cfs and TSS concentrations peak at 419 mg/L. Even though the second discharge peak value is three times greater than the first peak (2,100 cfs); the corresponding TSS concentration is only 296 mg/L. Although the second pulse of discharge was large enough to transport significant

quantities of TSS, TSS concentrations were lower than for the first smaller pulse of discharge because the sediments readily available for transport had already been removed. Other factors possibly contributing to the contrasts for these two storms include differences in rain intensity and in ground water contribution (i.e., flow paths and delivery mechanisms of ground were different).

#### **Total Kjeldahl Nitrogen**

Total Kjeldahl nitrogen correlates very strongly with TSS (Tables G1-G5). This correlation indicates that TKN transported during the storm events is being carried on suspended particles. Heng and Nikolaidis (1998) showed that a significant amount of nitrogen was transported as organic nitrogen (21%) and particulate nitrogen (23%) during storms in the Muddy Brook watershed in northeastern Connecticut. Berner and Berner classify 85% of river nitrogen as organic nitrogen and state that most of the inorganic nitrogen is derived from organic matter decomposition. Correlation coefficients for TSS versus TKN show that at least 80% of the TKN variation is explained by variation in TSS. The R value for all storms and all tributaries was above 0.87 with a significance level of 0.05 or less. During the November rain event an especially high TKN and TSS correlation coefficient of 0.99 with an extremely low probability value of 0.0001 was determined for Calf Creek. This exceptional correlation may reflect the fact that the majority of the 10 samples for this storm were on the rising limb of the hydrograph. This strong correlation of TSS and TKN is illustrated in Figure 22, where TKN rises quickly with TSS and then rapidly declines to near base-level concentrations. A similar relationship was identified for the upper headwaters section of the Buffalo River by Mott (1990).

#### **Total Phosphorus**

Total phosphorus (TP) is also associated closely with TSS and turbidity. Suspended particles in the Buffalo River contain phosphorus in both organic and inorganic forms (Mott, 1990). Figure 23 shows the close association between TSS and TP. Correlation coefficients for TP versus turbidity and TSS range from 0.71 to 0.99, with an average about 0.93 for all storms (Table G1-G5).

#### **Fecal Coliform Bacteria**

A comparison of TSS and fecal coliform concentrations for the December storm indicates a strong correlation between the two parameters (Figures 24 and 25). Indeed most of the storms produce relatively large correlation coefficients (as high as 0.99 and with an average of 0.76) for TSS versus fecal coliform for all storm events and tributaries (Tables G1-G5). Based on these results it appears that it might be possible to estimate fecal coliform concentrations based on TSS concentrations (or turbidity values); however, there are occasional divergent

results as discussed below. Attempts to develop a method to estimate bacteria concentrations based on turbidity values was not successful for two other northwestern Arkansas streams (Marshall, 1996).

Despite the correlations between TSS and fecal coliform concentrations, there were three notable exceptions. Two low R values, 0.47 and -0.25, occurred for Bear (Figure G1) and Calf Creeks (Figures G2 and G3), respectively during the unusually large November storm. These poor correlations are probably the result of the large magnitude of discharge which did not represent local turbulent conditions during the storm. The other low value was correlation of TSS and fecal coliform was 0.53 for Tomahawk Creek during the January storm. A large flux of fecal coliform, with concentrations over 16,000 col/100mL, occurred early in the January storm for Tomahawk Creek despite only a small increase in discharge (175 cfs). After the initial large fecal bacteria pulse, the fecal bacteria concentration parallels discharge, especially in the falling portions of the hydrograph (Figure 18). TSS exhibits a pattern similar to that for bacteria (Figure 26). An example of poor correlation of fecal coliform with discharge and with TSS is shown in Figure 27. One would expect greater discharge to cause an increase in TSS and bacteria concentration due to the increased stream velocity and turbulence. The anomalous peaks may be related to local conditions around the collection site, i.e., the entry of fecal coliform-rich runoff immediately upstream of the sampling site. Animal waste in or near the stream upstream of the collection site could cause this response.

It is interesting to note that fecal coliform bacteria can live for days in dry soil. Teague (1996) has shown that fecal coliform in soil amended with broiler litter change from about  $\ln 10^{18}$  to  $10^{11}$  colonies per gram of dry soil after 77 days at 20° and 30° C. Fecal coliform concentrations in a small northwestern Arkansas stream have been reported to be about 28,000 MPN (most probable number of colonies) per kilogram of dried sediment eight days after a storm (Marshall, 1996). These data demonstrate that fecal coliform can survive for some time in the environment.

Mott (1990) observed that "fecal coliform concentrations demonstrated better correlation with turbidity, TKN, and TP than with the dissolved constituents in the upper Buffalo River." The bacteria may be associated with TSS from stream bed sediments and/or flushed into the stream from upland areas during the initial rise in the hydrograph. Discharge in later stages of the hydrograph (peak and immediately following the peak) have less affect on the bacteria, TSS, TKN, and total phosphorus concentrations (e.g., Figure 28). This behavior during the later stages of the hydrograph is the result of most of the sediments available for transport having already been flushed into the stream and/or re-suspended. As noted earlier, a higher ratio of ground or vadose water (with low suspended solid concentrations) to stream flow can also explain this situation. Even for situations

where there is a strong correlation between TSS and fecal coliform concentration with discharge, the concentrations often increase more rapidly and decrease more rapidly than discharge. One explanation for this situation is that bacteria are preferentially associated with a relatively large-size fraction of sediments (probably organic). As turbulence and velocity decrease this relatively small volume of sediments are deposited removing a relatively large portion of the bacteria.

The correlation coefficients indicate that fecal coliform bacteria are more likely to be attached to sediment particles than to exist as water extractable organisms; nonetheless, only about 58% of the bacteria variability is explained by TSS variation. Variability of the sediment, size, type (organic versus inorganic) and possible influence of local runoff explain most of this variability.

#### **PARAMETERS NOT ASSOCIATED WITH SUSPENDED SOLIDS**

##### **Dissolved Oxygen**

Dissolved oxygen (DO) in streams is depleted by bacteria oxidation of organic matter, both suspended and dissolved, and also benthic deposits. Re-oxygenation occurs from absorption of O<sub>2</sub> from the atmosphere (reaeration) and photosynthesis associated with aquatic plants and algae (Tchobanoglous and Schroeder, 1987). In rapidly moving streams, such as the three tributaries in this study, aeration is the most important process of replenishing dissolved oxygen (Hitchman, 1978). Occasionally, there is a relationship between dissolved oxygen and discharge (Figure 29). This relationship occurs for Bear Creek during the April and December events where the correlation coefficients were 0.75 and 0.90, respectively (probability less than 0.05) for DO versus discharge. Dissolved oxygen does not consistently associate with discharge (Table G1-G5) as is illustrated in the January storm (Figure 30). Because of meter malfunctions in the wet sampling conditions for the November storm there is essentially no DO data available for this storm. Tomahawk Creek illustrated a brief rising trend followed by a very steady, constant decline in DO levels until the end of sample collection for the January storm. A possible explanation for this situation is that organic material (e.g., decaying leaves) and some inorganic material (e.g., Fe<sup>++</sup>) in runoff or re-suspended bottom sediments consumed a significant amount of oxygen. Although the temperature of the rain could change the stream temperature and thus DO concentration, a statistically significant trend was rarely observed which indicates that other factors were affecting DO.

##### **pH**

There is essentially no pH data available for the November storm because of instrument malfunction. pH values for the storms generally do not correlate

with discharge (Tables G1-G5) and fluctuate little (Appendix D) because of the buffered water. The stream water is buffered by bicarbonate ions and clay particles. For example, during the April storm discharge exhibited two peaks in discharge; whereas, pH decreased slightly from 7.9 to 7.8 near the beginning of the storm and then remained constant at 8.1 for the remainder of the sampling period (Figure 31). Although pH values are generally erratic, during the January storm Tomahawk Creek exhibits a decreasing trend in pH relative to discharge but R is only 0.66 for this trend (Figure 32). Near the start of the storm pH values were about 8.1 and decreased to about 7.9 at peak discharge and was beginning to increase again on the falling portion of the discharge hydrograph. The hydrogen ions necessary to cause decreases in stream pH were most likely from the oxidation of sulfide minerals in the rocks, decaying organic matter or low pH rain water. Lack of a significant correlation of pH and sulfate (Table G1-G5) argues against sulfide minerals as a source. The annual average pH of the rain in this area is about 4.8 in 1994 and 1995 (NADP, 1998). Although this is a relatively low pH, these buffered stream waters should be able to neutralize this relatively small absolute amount of acid easily. It appears that organic matter had a role in determining the pH levels of the tributaries. Decaying organic matter produced CO<sub>2</sub> resulting in an increase in carbonic acid causing the pH to decrease.

#### Nitrate

Nitrate compounds are very soluble in water and thus are subject to transport as dissolved, i.e., without attachment to suspended solids. For the storm events monitored, the trend of nitrate concentrations typically was erratic, i.e., there was no definite relationship of nitrate with discharge or other parameters (Tables G1-G5); however, occasionally, nitrate concentrations correlated with some parameters. For example, nitrate correlates with TSS,  $R = -0.76$  and  $-0.94$ , respectively at Bear and Calf creeks and with conductance ( $R=0.91$ ) at Calf Creek during the November storm. These correlations are consistent with dilution of stream water by runoff with lower nitrate concentrations, i.e., the ground water (base flow) has higher nitrate concentrations. The dynamic and complex nature of nitrate behavior is indicated by the lack of these trends for other storms.

Seasonal changes should play a role in the behavior of nitrate during storm events. In winter storms, nitrate-N concentrations were erratic with a range from 0.2 to 0.9 mg/L. For example, during the December storm, Bear Creek exhibited a peak in nitrate concentration just prior to the peak in discharge but exhibited a second peak in nitrate concentration near the end of the monitoring period for this storm (Figure 33). In winter, nitrate is not extracted from soil water by the largely dormant vegetation and thus the soil, ground and stream water become enriched in nitrate compared to spring storms (April storm) when the vegetation is utilizing nitrate. Only Tomahawk Creek during the January storm exhibited a nitrate

concentration trend suggestive of dilution by runoff. During this storm nitrate decreased in concentration before exhibiting a consistent increasing trend (Figure 34).

The range in nitrate-N concentrations for the April storm is 0.2 to 0.6 mg/L. Both Bear and Calf creeks exhibit a single peak in concentration despite the

double peak in discharge (Figures 35 and 36) which suggests that most of the soluble nitrate in the watersheds was removed during the first peak in discharge. In contrast Tomahawk Creek exhibited a consistent decrease in nitrate concentration (about 0.4 to 0.2 mg/L) (Figure 37). The decrease in nitrate concentrations is consistent with the 1994 and 1995 annual nitrate concentration of rain (about 0.2 mg/L) collected at a nearby study site (NADP, 1998) which allows for dilution of the stream concentrations at minimum flow conditions. It is interesting that at end of the falling limb of the hydrograph that Bear and Calf creeks return to concentrations that are about the same as that for rain water (Figures 35 and 36).

## **STREAM LOAD**

The stream load for a storm is the entire amount of nutrients, TSS or number of bacterium (or other materials) that have been transported during a rain event. The units for storm load are milligrams for nutrients and TSS and the number of colonies for fecal coliform. During a storm the amount of nutrients, TSS and bacteria transported by a stream is a direct reflection of the environmental conditions of the watershed. If natural environmental factors are similar, the controlling factor is land use.

### **STORM LOAD CALCULATIONS**

Storm load is the total amount of a parameter transported by a stream during a storm, i.e., concentration multiplied by discharge (volume) for a time period (the length of the storm). In order to obtain an accurate "true" value, one must have a flow-weighted sample for the entire storm or calculate the load from data for discrete samples. Because some researchers have only a few data points for storm data, load is sometimes calculated from the total discharge for the storm (usually from an automated device) and the average concentration. Unfortunately, often this is not an accurate method for determining load. Other researchers utilize a few discrete sample concentrations and the average discharge for each collection time interval. Although this method may provide improvement in load accuracy, it is still not the most accurate method, because concentration and discharge can change at different rates which affects the product of the two values. The method used to calculate load for this study is based on the previous method but uses an



average of about 40 small time increments based extrapolation and interpolation of discharge and concentrations. The accuracy of this method improves with more actual data, but can also be improved with more interpolated data points.

#### **INCREMENTAL AND TOTAL DISCHARGE**

The first step in calculation of storm load was to plot a “discharge versus time,” graph (a hydrograph) with grid lines from the available storm data. Many of the hydrographs for this study did not have complete data for the falling portion of the hydrograph. This incomplete record required extrapolation of the data back to base flow, i.e., discharge level prior to rainfall. In theory, this point is a function of drainage basin size and can be approximated by the following formula (Linsley et al., 1975).

$$D = A^{0.2}$$

D = Number of days from peak until the end of overland flow

A = Area of drainage basin in square miles

For this study the results of the D values were used only as general guideline for return to base flow rather than to determine a precise cut-off time (Table 10). These tributaries are small and this equation was developed for larger streams. The hydrograph for Tomahawk Creek during the January storm was used as the major guide for the extrapolation of discharge and other parameter values. Figure 38 illustrates the extrapolation of discharge nearly to base flow values for Tomahawk Creek during the January storm.

The next step was to determine discharge values at the mid-point of each time increment along the X-axis (Figure 39). Depending on the storm and tributary, there were 31 to 50 (average 41) discharge values for each storm event. Each discharge value represents the average discharge for that time period; thus, each discharge value multiplied by the time interval for each grid produced the volume of water that was transported during that time interval. The total discharge for the storm is obtained by summing all of the discharge values for each time interval.

#### **PARAMETER LOAD**

Load is the mass of a parameter or the number of bacterium transported during a time period (e.g., storm). Because runoff may cause a dilution of

concentration, but actually transport more material, concentration is not always the best criteria for comparison of streams. Load takes into account the volume of water and thus potentially provides a better mechanism of comparison.

The method for obtaining the concentration for a time interval is similar to that described above for discharge. A graph of "parameter concentration versus. time" was created with grid lines. This chemograph was created with the same time increments between the grid lines as the corresponding discharge hydrograph (described above).

The concentration data (Figure 40) were also extrapolated on the falling limb of the hydrograph using more complete data from other storms (primarily the January storm for Tomahawk Creek). The storm event parameter extrapolation was terminated at exactly the same time as the discharge hydrograph. For example, the graphs in Figures 39 and 40 both begin at exactly 1/13/95 at 0:00 and continued until 1/14/95 at 9:36.

Concentrations of parameters were determined for each time increment. Loads (i.e., the amount of material transported per time interval) were obtained by multiplying the parameter concentration by the corresponding discharge value for this time interval. Summation of these values provided total amount of parameter transported during the storm.

#### **POTENTIAL LOAD ERRORS**

The storm event data are incomplete, thus requiring extrapolation and interpolation of data. For incomplete hydrographs, the continuation of discharge and concentration curves without the input of actual measured data points may introduce some of error into the total load calculation. The storm data are complete enough (full rising half and partial falling limb) to allow for a confident extrapolation of the discharge and concentration curves.

One must realize that a calculated load is only an approximation of the true load. Only an analysis of a sample from the entire water volume for a storm would provide a "true" load. As the number of increments (actual or interpolated) increases, the difference between the calculated load and true load decreases. When 25 increments were used to calculate the load for fecal coliform for Tomahawk Creek during the January storm versus 35 increments, there was a difference of about 5%. Additional increments would lower the difference. It was concluded that an "error" of 5% or less was acceptable; therefore, all storm load calculations were based on graphs with at least 30 time increments.

For storm load calculation, the rising limb, the peak, and a small portion of the falling limb is by far the most critical portions of the storm. This is especially true for parameters associated with TSS and discharge. Even without a large portion of the falling limb of the hydrograph, 97% of the Bear Creek fecal coliform load was included in the sampling period (Figure 41). Although the

storm was not sampled to completion (end of overland flow), the majority of the bacteria load had already passed when the sampling was concluded. These results indicate that the extrapolation of data introduces little error (maximum about a 3%) for these storms.

## **INDIVIDUAL STORM LOADS**

### **APRIL STORM**

The April rain storm represents the most complete water-quality data set in terms of number of tributaries monitored and the sample distribution over the hydrograph (Table D1). The April storm event allows for a comparison of the streams during a spring storm. Bear and Calf creeks consistently have the greatest load values in comparison to Tomahawk Creek. Bear and Calf creeks recorded very similar total loads for the storm, with the exception of nitrate ( $\text{NO}_3\text{-N}$ ) (Table 11) which is consistent with the fact that the two watersheds have approximately equal pasture area (Table 3).

Calf Creek had about 2.5 times as much discharge as the slightly smaller Tomahawk Creek watershed. Calf Creek had approximately 45x as much fecal coliform, 2.3x more nitrate, 17x more TKN, 5.8x more total phosphorus, and 4.7x more TSS than Tomahawk Creek (Table 11). These results indicate that the runoff from the Calf Creek watershed was more concentrated relative to that of Tomahawk Creek.

### **NOVEMBER STORM**

For the November storm event, only data from Bear and Tomahawk creeks could be used for load calculations (Table 11). As noted previously, blockage of Tomahawk Creek by the large rise in the Buffalo River required removal of the spurious discharge and associated load values. It is estimated that the *flow* of Tomahawk Creek backed up temporarily about 1:15 am on November 15, 1994. It also is estimated that not more than an 8% error has been introduced based on these adjustments (Figure 18). Because Calf Creek was missing critical portions of the hydrograph, load calculations were not possible for this storm.

Despite having less than half the area of Bear Creek, Tomahawk Creek had only 18% less discharge and higher TSS and TKN loads. Bear Creek, however, had larger fecal coliform, nitrate and total phosphorus loads. There was no significant difference in fecal coliform values between the two tributaries.

### **JANUARY STORM**

Only Tomahawk Creek was monitored for the January storm event (Table 11). These data were very useful because the samples were collected using a short

time interval; thus, providing very detailed discharge and concentration hydrographs.

Another benefit of this January storm event is that Tomahawk Creek recorded a very similar rainfall total (2.28 inches) as the April storm event (2.33 inches). This allows for the comparison of Tomahawk Creek load during similar rain events in two different seasons. In comparison with the April storm, there was a three-fold increase in discharge for the January storm but fecal coliform concentrations increased 50x, TKN increased 40x, and nitrate increased by almost 4x. As discussed previously, this is interpreted to be a result of the inter-relationship of the degree of soil saturation, and vegetation cover and vigor.

#### **DECEMBER STORM**

For the December event, Bear and Calf creeks were the two streams monitored. Table 11 shows that Bear Creek consistently had the highest loads for all parameters during this storm. These results are consistent with Bear Creek having more pasture land (17,121 and 11,888 acres, respectively) and greater discharge ( $1.6 \times 10^9$  and  $2.4 \times 10^8$  L, respectively).

#### **DISCUSSION**

Quantifying the nutrient and bacteria load contribution of each tributary is one of the main foci of this study. Stream load is a primary method for quantifying pollution impact. Management decisions can be made based on stream loads to determine which watersheds are in need of more or different land-use management practices.

All other factors being equal, the size of a watershed is the principal controlling component that effects discharge and which in turn affects load. A larger drainage basin produces more discharge for a homogeneous rain storm. Although this relationship is typical, it did not occur for these watersheds during all storm events (Table 11). During the December storm, as anticipated, Bear Creek (51,300 acres) had a total discharge nearly 7x that of Calf Creek (31,500 acres) ( $1.6 \times 10^9$  versus  $2.4 \times 10^8$  L) as a result of 2.17 and 1.93 inches of rain, respectively. During the April rain event the difference in total discharge between the two tributaries was negligible ( $2.9 \times 10^9$  vs.  $2.8 \times 10^9$  L for Bear Creek and Calf Creek, respectively). Despite the close proximity of these relatively small watersheds, it appears that a single rain gauge does not always provide data representative of the entire watersheds. The large difference in discharge for Bear and Calf creeks during December suggests that more rain fell in the Bear Creek basin than was recorded.

During the November event, Tomahawk Creek (23,800 acres) produced a slightly smaller total discharge ( $1.1 \times 10^{10}$  versus  $1.3 \times 10^{10}$  L, respectively) relative to the considerably larger Bear Creek watershed (51,300 acres). As these

examples have shown, watershed size is not the only factor that controls total discharge for a storm event.

Bear Creek had the greatest loads for all parameters during the December storm which is consistent with greater discharge. During the November storm, the smaller Tomahawk Creek watershed recorded larger TSS and TKN loads (Table 11). The loads for the April event show that Calf and Bear creeks had comparable loads for every parameter except TSS.

When comparing the tributaries during the three storm events for bacteria, TSS and nutrient loads, there are few consist patterns. One important observation is that Bear Creek is contributing the most fecal coliform bacteria to the Buffalo River. Typically Bear Creek is also contributing the largest amounts of the other parameters. Calf Creek is the second leading contributor of parameters into the Buffalo River.

## **METHODS OF TRIBUTARY COMPARISON**

### **MEASURES OF WATER QUALITY**

It is desirable to compare or rank the tributaries using storm data in terms of the impact of agricultural impact on water quality because of the importance of storms in transporting materials. Higher discharge invariably leads to greater amounts of materials transported and this may be true even if concentration decreases. There are several potential methods that can be used as measures of water quality. These methods are peak concentration and peak load during a storm, stream load for the entire storm (i.e., storm load) and flow-weighted concentration. Each of these is described and discussed below.

#### **Storm Peak Concentration**

Using maximum storm concentrations as a measure of water quality is attractive because of its simplicity and low cost, but it is limited to only one point in time and thus may not be truly representative of the entire storm. Shapes of the hydrographs are important in determining peak concentration and can vary from storm to storm, and even from tributary to tributary during the same storm depending on hydrological and environmental factors. Determining when to collect a stream sample that will represent maximum concentration is not possible unless one collects a number of samples over the hydrograph which is expensive and time consuming. Because peak concentration values generally coincide with peak discharge, peak discharge can be used to define the collection time for a sample to approximate peak concentration.

The major weakness with peak concentration as a measurement of water quality is that it is dependent upon the amount of discharge. For example, two

watersheds may have the same amount of TKN transported in runoff but have different amounts of runoff (discharge). Even though there is no difference in the amount of TKN transported, the basin with less discharge will have the greater concentration. Increases in discharge can dilute the initial concentration of TKN for the storm. Despite these weaknesses and limitations, peak concentrations data will be presented because concentration is commonly used for comparisons.

#### **Storm Peak Load**

Pathways for storm flow in forests produce lower runoff velocities than those in pastures. As a result infiltration rates are increased in forests relative to pastures; thus, reducing the amount of overland flow. Because of these factors removal of trees from a watershed increases the peak flow during storms. The effects of land use can be evaluated, to some extent, by studying peak flow and peak load (Ward and Elliot, 1995).

Because of the time and cost involved in obtaining storm loads, the use of loads at peak discharge as a surrogate for storm load was also investigated. If there were a reliable relationship between the two, a stream could be sampled only at peak discharge, eliminating excess sampling and still providing a load value that could be useful in predicting storm loads. Although not as accurate as stream load, this value might provide sufficient, inexpensive information for prioritization of watersheds for focused education and management programs.

Peak loads were calculated by multiplying maximum discharge and by the corresponding concentration of a parameter at the same point in time. Usually the peak discharge coincided with the maximum load peak (e.g., Figure 42). In a few instances, however, concentrations of a particular nutrient were high enough that even though stream discharge was not at a peak value, the load was at a maximum. In these rare instances the discharge was nearly at a maximum. An example of this latter situation occurred during the December storm event on Bear Creek (Figure 43).

#### **Storm Load**

As described previously storm load is the summation of the products of discharge and concentrations over short time intervals during a storm. Load can be a very useful measure of water quality because this method takes into account the influence of water volume (discharge) on the amount of material transported. The amount of a parameter transported during a storm (load) is directly related to potential impact on the stream and other water bodies into which it flows.

#### **Storm Flow-Weighted Concentration**

Although load is a good measure of water quality and the impact of individual streams, it does not take into account the differences in discharge

among the streams. Flow-weighted concentrations (storm load divided by total storm discharge) allow comparison among streams that have different total discharge volumes for a storm. In effect, flow-weighted concentration is the concentration that would be obtained by collecting and analyzing all of the water discharged during the storm. Even in similar, spatially close watersheds such as in this study, there are differences in discharge which result in differences in load. For example, two watersheds may have the same concentrations of a parameter but have different amounts of runoff (discharge) which produces differences in load that are related to amount of discharge and not land use. Because flow-weighted concentration takes into account the absolute amount of a parameter transported, as well as the effect of discharge on load, it is considered the best measure of the impact of land use on water quality.

## **MEASURES OF AGRICULTURAL ACTIVITY**

### **Pasture Area**

Ideally, watersheds should be of equal size for comparison of discharge and loads. Because this is rarely the case, it is difficult to compare watersheds of different sizes directly. For example, it is difficult to compare the storm load for Tomahawk Creek (11,800 acres) to that of Bear Creek (17,100 acres) when the number of pasture acres in the Bear Creek drainage basin is nearly 50% greater than that in the Tomahawk Creek basin. Because one would expect more runoff, TSS, nutrients and bacteria from pastures than from forested lands, differences in amount of pasture land can be minimized by normalizing concentration to pasture area (*pollutant source area*). With this approach the tributaries are evaluated only by the land area that is producing the concentrated nutrient, TSS and bacteria runoff.

This normalization approach assumes that the amount of pasture acreage reflects the amount of fertilizer applied regardless of whether the fertilizer is in the form of animal waste or commercial inorganic fertilizers. In addition, there is also the implicit assumption that geology, soils, topography (slope), discharge, pasture distribution, pasture quality and Best Management Practices (BMPs) are similar among the basins.

### **Percentage Of Pasture In The Watershed**

Because percentage of pasture does not relate directly to the amount of a parameter in a watershed, it cannot accurately reflect the impact of agricultural activities on water quality. It is also possible that a very large watershed might have a relatively small portion of pasture that is much larger than the pasture area in other watersheds. The fact that the watershed has a small percentage of pasture

is not compatible with the large loads and flow-weighted concentrations that will be produced by the large number of pasture acres.

#### **Animal Waste**

There are cattle, dairy cows and unconfined swine in the pastures in the study area (Tables 4 and 12). The amount of animal waste in a watershed would be expected to directly impact the amount of fecal coliform bacteria in the watershed. The animal waste may also impact the amount of nutrients and perhaps TSS available to runoff. Because commercial fertilizers are used in these watersheds and farmers seek to have optimum nutrients for their pastures, there should be little over application of fertilizer (Sid Lowrance, personal communication, 1998). Theoretically, the amount of nutrients per acre should be about the same for all watersheds. Because the amount of nutrients are based on the amount of nitrogen needed, it is possible that the animal waste may have added more phosphorus than necessary for agronomic needs. The animals might increase TSS because their waste may add organic sediments to runoff or because of erosion caused by their movement through the pastures and streams.

In order to compare the potential effect of animal waste on water quality in these watersheds, it was necessary to calculate the amount of waste generated by each type of animal, as well as the amount of N and P in the waste (Table 12). This was accomplished using published data for the amount of waste generated by these types of animals (Barth et al., 1992). It was necessary to supplement these data with other information which was supplied by Casey Dunigan (Water Quality Specialist, Washington County Conservation District), Charles Maxwell (Professor of Animal Sciences, University of Arkansas), and Sid Lowrance (District Conservationist, NRCS, Marshall Field Office) in 1998. The data utilized for these calculations are presented in Appendix H. The annual amount of total animal waste per sub-basin was 31,290; 18, 138 and 15,689 tons, respectively for Bear, Calf and Tomahawk creeks. This sequence of amount of waste is generally consistent with the number of acres of pasture for these sub-basins. The amounts of nitrogen and phosphorus in the animal waste (Table 12) follow the pattern for total wastes among the sub-basins.

#### **Animal Waste Per Acre Of Pasture**

If two watersheds have the same amount of a parameter (e.g., nitrogen) applied, the smaller one would have the greater application rate and should produce higher nitrogen concentrations in runoff for equal rainfall (and other factors being equal) within the basins. Total phosphorus could be an exception to this statement. If there was a high rate of application of animal waste with phosphorus concentrations above agronomic needs, it is possible that the soil might become saturated with phosphorus resulting in increased phosphorus



concentrations in runoff from these soils. Differences in the length of time of pasture use could also result in differences in phosphorus soil saturation. Loads are not dependent on the rate of application but only on the total mass of the nutrients and thus could be better measures of relative agricultural activity than simple concentrations.

The estimated annual rates of animal waste application per pasture acre for the sub-basins are 3,655; 2,119 and 1,833 lbs for Bear, Calf and Tomahawk creeks. The rates of nitrogen and phosphorus application in the animal waste mirror the total animal waste rates (Table 12 and Figure H1). The ranking of animal waste application rates for the tributary watersheds suggest that there should be more bacteria, nitrogen and phosphorus in runoff from Bear Creek, followed by Calf Creek and then Tomahawk Creek.

### **COMPARISON OF THE TRIBUTARIES**

As discussed above there are several measures of water quality that can be used for comparison of streams. The four listed below were used for comparing the impact of agricultural activities on the water quality of the three watersheds in this study.

1. Peak storm concentration.
2. Peak storm load.
3. Storm load.
4. Flow-weighted concentration for a storm.

Because the agricultural measures (with the exception of percent pasture) for the watersheds in this study each provide the same sequence for these watersheds, the discussion of these measures is simplified (Table 12). The percent pasture for Bear, Calf and Tomahawk creeks are 33, 38 and 50%, respectively which is the only indicator of agricultural activity that does not rank Bear Creek first, Calf Creek second and Tomahawk Creek last. All of these measures of agricultural activity indicate that the Bear Creek watershed has the most agricultural land use followed by Calf Creek watershed and lastly Tomahawk Creek watershed.

Comparison of the tributaries is made in tabular form with highlighting as the indicator of tributary rank for each water quality measure. This method not only provides comparison of the watersheds, it also allows evaluation of the relative effectiveness of each water quality measure based on the pattern of tributary rankings.

#### **STORM PEAK CONCENTRATION**

Although peak concentration is not considered the best method for comparing these streams, results are presented for this method because of the common practice of using concentration values for comparison. Peak concentration does not indicate a consistent relationship among the tributaries for the storms with regards to agricultural activities measures (Tables 12 and 13) (e.g., Figure 44). Despite this lack of complete consistency among all storms, it is interesting to note that during the April storm that Tomahawk Creek had the lowest peak concentrations for every parameter and Calf Creek had the highest peak concentrations. During the December storm, Bear Creek consistently had higher peak concentrations than Calf Creek. These observations, except for the frequent higher values for Calf Creek during the April storm, are generally consistent with Bear Creek having the highest ranking for all of the agricultural activity measurements. Peak concentrations for the November storm indicate that Tomahawk Creek had greater TKN and TSS values than either Bear or Calf creeks even though it has the lowest agricultural activity rank.

#### **STORM PEAK LOAD**

Although peak load is considered to be a better measure of water quality than peak concentration, the relationship for peak load and measure of agricultural activities is not quite as good as for peak concentration. In the December storm Bear Creek had higher peak loads for three parameters and Calf Creek had higher loads for two parameters. During the April storm Tomahawk Creek had the lowest and Calf Creek the highest values (i.e., similar to peak concentration). Results for the November storm show Tomahawk Creek with the greatest peak loads, although it had the lowest discharge primarily because of its greater discharge (about 28% greater than Bear Creek but almost 3x that of Calf Creek) (Table 14) (e.g., Figure 45).

#### **STORM LOAD**

As noted earlier, incomplete hydrograph data for the November storm decreased the reliability of the loads for this storm and in the case of Calf Creek made the calculation of meaningful values impossible. Although Tomahawk Creek had the lower agricultural activity measures, it had higher TKN and TSS storm loads. Bear Creek had higher values than Calf Creek for every parameter including total discharge for the December storm. During the April storm Tomahawk Creek had the lowest loads except for TSS. These TSS loads were about an order of magnitude higher than for Bear Creek and about an order of magnitude higher than for Calf Creek (Table 11) (e.g., Figure 46). These results do not correlate well with measures of agricultural activity.

### FLOW-WEIGHTED CONCENTRATION

Flow-weighted concentrations (Table 15) (e.g., Figure 47) do not correlate well with measures of agricultural activity. During the April storm Calf Creek is ranked first for all parameters. Despite being ranked first in agricultural activity, Bear Creek has the lowest values for all parameters except its second ranking for fecal coliform.

For the December storm Bear Creek was ranked first for the flow-weighted concentrations of each parameter except for fecal coliform. During the November storm Bear Creek had the higher values except for TKN and TSS (Table 15). The relationships of agricultural activity measures are worst using flow-weighted concentration rather than load. This is unexpected since flow-weighted concentrations take into account differences in discharge among streams which in turn influence load.

### COMPARISON OF PEAK AND STORM LOADS

A simple method of comparing the peak and storm loads is to determine how many times Bear Creek is ranked first in terms of the five parameters (Tables 11 and 14). Bear Creek was chosen for this comparison because it is the highest ranked tributary in terms of agricultural activity. Because of the unusual volume of rain for the November storm and the associated problems with calculating reliable storm loads, results will be provided with and without this storm. Using *peak* load Bear Creek was ranked first seven times out of 40 possibilities (six times out of 25 possibilities if the November storm is omitted). The random chance of being ranked first for all three storms is 38% (i.e., 15 times) and for two storms is 41% (i.e., 10 times) (Table 14). Both of these random chance numbers are higher than the actual numbers (i.e., 7 versus 15 and 6 versus 10).

Using *storm* load Bear Creek is ranked first 13 times out of 35 possibilities (10 out of 25 possibilities times if the November storm is omitted) (Table 11). The random chance of being ranked first in all three storms is 44% (i.e., 15 times) and is 41% for the two storms (i.e., 10 times). These statistically determined random numbers are about the same as the actual numbers (i.e., 13 versus 15 and 10 versus 10). These results indicate that there are complex factors of hydrology and/or land use affecting the loads of these streams which mask the simple agricultural activity factors in Table 12.

An example of the lack of relationship between peak load and storm load is demonstrated by the rankings for Bear Creek during the April and December storms based on TSS loads. Bear Creek was ranked #1 based on *peak load* ( $1.8 \times 10^7$  mg/sec) but ranked #3 based on *storm load* ( $2.9 \times 10^9$  mg). For the December storm Bear Creek was ranked #2 based on *peak load* ( $2.7 \times 10^6$  mg/sec) but ranked #1 based on *storm load* ( $9.0 \times 10^{10}$  mg) (Tables 11 and 14).

Not only were there inconsistency of rankings based on peak and storm loads between storms, there were also inconsistencies for parameters within a single storm. For example, during the April storm, as shown above, the TSS for load Bear Creek was ranked #1 based on *peak load* but #3 based on *storm load*. The rankings of the two loads were reversed for fecal coliform, i.e., *peak load* for fecal coliform ( $1.3 \times 10^{10}$  mg/sec) ranked Bear Creek #2 versus a #1 ranking based on *storm load* ( $3.6 \times 10^{14}$  mg) (Tables 11 and 15).

Because of differences in the shapes of the discharge and parameter hydrograph curves and the differences in the shapes (including multiple peaks) of these curves from storm to storm, it was not possible to determine a relationship for peak load and storm load. Peak loads provide an advantage over concentration because discharge is included, but storm load is superior to peak load because the total mass of parameter transported is considered.

#### POTENTIAL PROBLEMS WITH COMPARISON METHODS

The relationship of the various measures of water quality with the tributaries in terms of agricultural activity is not strong. If the November storm is excluded because of its unusual character, the association improves (Tables 11, and 13-15). Generally, Tomahawk Creek has the lowest values for the April storm with three exceptions—flow-weighted concentrations for TKN, TP and TSS (Table 15) and TSS storm load (Table 11); thus, Bear and Calf creeks are generally first or second ranked. For the December storm Bear Creek had the higher storm loads (Table 14), peak concentrations with the exception of TSS (Table 13), and higher peak loads with the exception of TP and TSS (Table 14)

There are several reasons for the less than perfect relationship of the measures of water quality with the agricultural activity within the tributary watershed. Differences in pasture and forest distribution, slope, pasture quality and BMPs may be affecting water quality more than agricultural activity alone. For example, proximity of pastures to streams, the slopes of these pastures and presence or absence of vegetation buffer zones among the watersheds could mask the impact the agricultural measures on water quality (Appendix I). Others (NRCS, 1995) have characterized the sub-basins based on “problem pasture areas” and factors within the problem areas (Tables B1-B7) but relative ranking of each tributary based on these factors is complex and not easily done. In addition, there is not enough detailed information on location of the problem areas within the watershed to allow maximum interpretation. Nonetheless, the concept of problem areas and the factors affecting them is an excellent attempt to better understand the environmental factors affecting water quality and with enough of information these factors also could be used as agricultural activity measures for comparison of the tributary watersheds. A summary of the characterization of the problem areas is presented in Table 16. In addition, the dynamic nature of the hydrological

parameters (e.g., variable rain intensity and stream turbulence) and the karstic nature of the Boone Formation contributes to a complex hydrological environment which makes interpretations more difficult. Also, there is the potential problem that local conditions near the collection site may bias sample water quality. Finally, it is interesting to note that the three tributary watersheds did not relate well with base flow nitrate concentrations [water quality measure] and percent pasture [measure of agricultural activity] (Mott, 1997) which is consistent with the patterns for the storm data.

### **DETERMINATION OF AGRICULTURAL INFLUENCE ON WATER QUALITY**

In order to assess the impact of animal production on water quality of the three watersheds in this study, one can compare concentrations of water quality parameters between the agriculturally influenced streams and a "pristine" stream. Such a "pristine" watershed exists about 45 miles to the east of this study area. This drainage basin is located in the extreme upper headwaters of the Buffalo River and contains 36,358 acres of almost totally pristine, undeveloped, forested wilderness area (Mott, 1990). This basin is similar in size to the three tributary streams that are the focus of this study. The watershed has been part of the National Park Service Buffalo River monitoring network (minimum flow data) and has been studied during several storms during 1989 (Mott, 1989). The collection site for this undeveloped portion of the Buffalo River is designated as R1 by the National Park Service. Because R1 is similar in size and other environmental factors (e.g. slope and geology) to the study tributaries and is located relatively close to them, it is an ideal watershed for determining land use impacts on stream water-quality in the Buffalo River area. Data available for this site is from January and May, 1989 (Mott, 1989). The data from January 25-26, 1989 was chosen for comparison with the results of this study because:

1. The rain storm on these dates was about the same size (2 inches) of the storms occurring on April, December and January for this study.
2. Three of the storms for this study occurred within two months of January.
3. This storm had the highest loads for R1 and thus provides a conservative estimate of increased concentrations of water quality parameters at the three stream site.

### **BASE AND PEAK FLOW CONCENTRATION RATIOS**

One approach of evaluating the effect of agricultural practices on the water quality of these streams is to compare the base flow water quality data for the pristine site (R1) and the tributaries. Another approach is to use peak flow concentration.

Base flow is similar to the type of data readily available for most monitoring studies which makes this type of comparison desirable. The ratio of water quality parameters for each of the three streams to corresponding data for R1 shows that generally there is a change in concentration by a factor of 0.3 to 130 times (Table J1). A ratio less than 1.0 indicates that there was a higher concentration for the pristine site rather than for the tributary. The low ratios are primarily associated with TKN and with ammonia and orthophosphate to some extent (Figure 48). The most likely reason for this situation is that the pristine site (R1) actually has more organic input than the pastures because of the large amount of litter associated with the forest (Richard Meyer, Botany Professor Emeritus, personal communication, 1998). Because of the large number of below detection values for nitrate, only general indication of the ratios for nitrate are possible.

It is important to consider storm data in comparing pristine and impacted streams because of the potential for overland flow to transport large amounts of nutrients, sediments and bacteria to streams (i.e., non-point source pollution) and the potential of re-suspension of stream sediments and associated materials. Note the much higher concentrations at maximum storm flow compared to base flow concentrations in Table J2 (e.g., Figure 49) which underscore the importance of storm data. Although often not as readily available, peak discharge concentrations provide another means of comparing the streams in this study with R1. Maximum storm flow concentrations range from 2 to several 1,000 times that of base flow but are generally in the hundreds. Nitrate concentrations often exhibit an opposite relationship compared to the other parameters which indicates that a significant amount of the nitrate must be reaching the streams via ground water. Nitrate concentrations are lowest during storm flow when base flow water (ground water) is diluted by runoff. The nitrate concentration in rain water in the vicinity of the study site is about 0.17 to 0.20 mg/L as nitrogen for 1994 and 1995 (NADP, 1998) which is slightly lower than that for the tributaries at base flow (0.18 to 0.30 mg/L). Because the other parameters are associated with particulate matter, the concentration of these parameters increase as the suspended sediment load peaks during the storm. These ratios produce a similar pattern as those determined at base flow.

### **BASE AND PEAK FLOW LOAD RATIOS**

Loads calculated at base flow and peak discharge take into account the stream discharge and should represent a better method of comparison than using

concentrations only. Loads produce the same general pattern as concentrations described above and underscore the significant increase in parameter transport during storms (Table J3) (e.g., Figure 50) compared to base flow, i.e., very large ratios, typically between 8 and 10,000 with the higher numbers associated with maximum discharge.

The ratios for base and peak flow loads provide a greater differential between the tributaries and the pristine site than the corresponding ratios based on concentration. The streams have base flow loads that may be greater than  $10^6$  times that of the pristine site (for example fecal coliform) (Table J3). Load ratios continue to indicate that more TKN is transported by the pristine stream. Because of the importance of storms in transport of materials, peak discharge load provides another means of comparing the two types of streams. Peak nutrient loads were determined by multiplying maximum discharge by the corresponding parameter concentration for that time. Usually the peak discharge coincided with the maximum concentration (e.g., Figure 42). Even in cases where parameter maximum concentration did not correspond to peak discharge, the load at peak discharge produces the greatest load because the volume of water is the dominant factor for loads for these streams.

The ratios of stream peak discharge load to R1 data are larger than for base flow in about two thirds of the situations (Table J4). This observation indicates that much of the pollutants from the land enter the streams during storms or are associated with stream sediments that are re-suspended during storms (however, ultimately the pollutants are from the land). Both base flow load and storm load ratios indicate significant increases in bacteria concentrations in the agricultural areas compared to the pristine site. Higher nitrate, ammonia and total phosphorus ratios occur for base flow than for storm flow (e.g., Figure 51) (Table J4) which indicates the very pristine nature of the R1 base flow concentrations.

#### **STORM LOAD RATIOS**

The amount of material transported by a stream during an entire storm (Table 11) should provide a better method of comparing agriculturally influenced streams with a pristine site rather than single peak load values. As described earlier the load of a stream is determined by summing the products of discharge and concentration collected during short time increments for the period of the storm. Missing portions of the November hydrograph for Calf Creek made it impossible to calculate a storm load for this storm. The results using storm loads produce lower ratios than for the peak discharge load ratios (tributary/R1) (Tables 17 and J3).

Ratios for tributary and R1 storm loads are 1.08 to 382 for bacteria and total phosphorus (Table 17). For example, during the April event Calf Creek had a storm load value nearly 13 times greater than R1 for total phosphorus. Although

the TKN ratios for November and January indicate higher TKN loads for the tributaries, R1 had the greater loads for the April and December storms. The TKN loads for the tributaries relative to R1 for the April and December storms are either nearly similar (i.e., ratio is near 1.0) or show TKN loads for R1 4 to 33 times those of the tributaries. The Bear Creek fecal coliform storm load for the April event is 92 times greater than that of the R1 value. The fecal coliform load of  $4.6 \times 10^{12}$  colonies for Tomahawk Creek is only slightly larger than the total load value for R1 at  $3.9 \times 10^{12}$  colonies (Table 11). Bear Creek sub-basin is larger and Tomahawk smaller than the R1 watershed. Calf Creek, however, is very similar in size to R1 (31,600 vs. 32,700 acres) and it recorded significantly higher fecal coliform values than R1 during the April and the December events. These results indicate that basin size is not a major factor in determination of these ratios.

The majority of nitrate concentrations for R1 were below the detection limit of 0.005 mg/L. Because of the low number of samples above the detection level, it is impossible to get an accurate calculation of load; however, for comparison purposes, a maximum estimate was made. In order to estimate load, all nitrate values <0.005 mg/L were given a value of half of the detection limit concentration, i.e., 0.0025 mg/L. The estimated load value determined was  $1.1 \times 10^7$  mg. This is 15 times less than the lowest nitrate value of  $1.7 \times 10^8$  mg (Calf Creek during the December rain event) recorded for this study (Tables 11 and 17).

#### **FLOW-WEIGHTED CONCENTRATION RATIO**

A final method of comparison is to determine a flow-weighted concentration (Table 14)(storm load divided by total storm discharge) and use this value in determining a ratio between the streams and R1. Because this concentration value takes into account the differences in discharge among the tributaries and the pristine site, it is considered the superior method of comparing the impact of land use on water quality. Generally, the ratios (tributary to R1) decrease using the flow-weighted concentrations compared to the ratios based on loads (Tables 17, 18 and J4). The occurrence of some ratios indicating higher TKN concentrations at R1 continue with this method also.

#### **COMPARISON OF METHODS**

All of the comparison methods indicate a significant impact of agricultural practices on the water quality of the streams compared to a pristine watershed. The storm load and storm load flow-weighted concentration data are the most costly. Of the remaining methods, the loads for base flow and peak flow provide the greatest magnitude ratio between the streams and R1. Despite the lower ratios with the storm load ratio method compared to the peak and storm loads, it appears to be the best method of comparison. It is considered to be best because despite the similarity in the amount of rain for three of the storms, there are significant



differences in the amount of discharge among the tributaries which are not accounted for by the other methods.

## **BASE FLOW**

Base flow is defined as stream flow which is derived entirely from ground water (Chebotarev, 1966 and Domenico and Schwartz, 1990). Base flow data for Bear, Calf and Tomahawk creeks were selected from the monitoring data base using this definition. Base flow water quality sample collection was conducted from 1985 through mid-1997. Data for some stations are more comprehensive than others. For example, temperature, conductance, pH and fecal coliform data are the most extensive for the ten year period. Other parameters such as NO<sub>3</sub>-N, TKN, TSS, and were analyzed less frequently. There only one or two years of data for total phosphorus and TKN. Table 19 gives a typical distribution of data for the other parameters for this monitoring period using ammonia as an example. Another characteristic of the data is unbalanced sampling among seasons, especially during the first six years when samples were collected primarily during the spring and summer seasons. After 1991, tributaries were monitored approximately every other month throughout the year (Mott, 1997). Mott has shown that the emphasis on summer sampling from 1985 through 1990 produced a negative trend in fecal coliform concentrations. The unbalanced seasonal sampling could effect other parameters. Another factor that may influence the data is the analyses of the samples by several laboratories. The Arkansas Department of Pollution Control and Ecology has been conducting laboratory analyses since 1990 (Mott, 1997).

Often ground water drainage basins are similar in shape and size to surface water drainage basins. Nutrients on the surface will be transported with the infiltrating water and become part of the ground water; therefore, storm and base flow data are both affected by the land use conditions within a drainage basin. Storm event parameter concentrations, as shown earlier, are typically much greater than for base flow conditions. Although base flow has lower concentrations, base flow comparison of watersheds removes the complications of rainfall intensity, duration, distribution and soil saturation. Another important reason for comparing base flow data is this type of data makes up the greatest amount of stream data and is relatively inexpensive to obtain.

### **ANNUAL TRENDS**

The base flow annual concentrations from 1985 to mid-1997 (Table K1) were statistically analyzed to determine if there were any significant trends over time for the sites. Linear regression was used to determine significant slopes

(trends). Trends were considered significant that had probability (p-YR in Table K1) less than 0.100. As with most trend analyses major differences in concentration near the beginning or ending of the trend period have a greater influence on the p value than those for the middle years (Ron McNew, Professor of Agricultural Statistics, University of Arkansas, personal communication, 1998). Annual values were computed by averaging the seasonal means for each tributary. The p value for season in Table K1 tests the similarity of the of the seasonal values, i.e., low p values indicate that there are differences among the seasonal concentrations. The p values for nutrients, fecal coliform and turbidity indicate that there are differences among the seasons. The variance was pooled across the four seasons to obtain the p value for the trend. The only statistically significant trends were for Tomahawk Creek and the upper Buffalo River site, R1.

Although trends for turbidity, fecal coliform and nutrients were the focus of annual trends, some other parameters were investigated (Table L1). Tomahawk Creek had significant trends for ammonia (decreasing), nitrate (increasing), orthophosphate (increasing) and dissolved oxygen (increasing). The trends for phosphate and dissolved oxygen were influenced by one or two higher concentration years near the end of the of the period of investigation, e.g., Figure 52. Note that the orthophosphate concentrations are near the detection limit in Figure 52. It is interesting that ammonia has a negative slope; whereas, nitrate has a positive slope (Figures 53 and 54). The ammonia and nitrate trends appear to be meaningful but it is difficult to evaluate the trend because unbalanced seasonal sampling can have significant effects on trends.

Because R1 is relatively undeveloped and little change in land use has occurred during the past 25 years, one would expect no trends for this site; however, R1 had significant trends for total phosphorus (increasing), pH decreasing), chloride (decreasing) and sulfate (increasing). The total phosphorus trend is the result of five years of low concentrations ( $< 0.10$  mg/L) near the beginning of the monitoring period (1985) followed by three years of higher ( $> 0.025$  mg/L) but decreasing concentrations (Figure 55). The other trends are probably due to the unbalanced distribution of samples across seasons during the early years of the base flow monitoring program which emphasized spring and summer sampling. Other possibilities are the re-location of the site to the Wilderness Boundary site from the Boxley bridge site in April, 1989 and changes in analytical laboratories.

In summary, statistical analyses indicate several significant trends for annual data at Tomahawk Creek and at R1. Inspection of graphical plots of the trends indicate that of the nutrient and fecal coliform trends, only the increasing trend of nitrate and decreasing trend for ammonia at Tomahawk Creek appear to be meaningful. It is possible that the amount of nitrate applied to the pasture land has increased and the ammonia decreased because of agricultural management

practice changes in the watershed. The trends at R1 are related to anomalous data for this site or to uneven sampling across seasons and/or re-location of the site in 1989.

Because variation in discharge could affect concentration, annual trends were investigated using loads. There were no statistically significant trends for loads for any of the tributaries or R1 (Tables L2 and M1).

### SEASONAL TRENDS

Because of difference in seasonal base flow values (Figure 56), the data were stratified by season (Table 20) to investigate trends on a seasonal basis. This approach has two important aspects. Firstly, the seasonal stratification takes into account the possible water quality differences among the seasons and secondly, it minimizes the unbalanced sample collection from 1985-1990. The factors that were used to define "seasons" were rainfall, temperature, growing season, and application of fertilizer.

The seasonal trends and associated p values are given in Table K2. The seasonal concentration averages by year are given in Table L3. The same statistical criteria were used for the seasonal trend analysis as for the annual trend analysis. The p value for the seasonal data gives the reliability of the trend; whereas, the "homogeneous p" value tests the hypothesis that the slopes for the four streams are equal. Low "homogeneous p" values indicate that the seasonal slopes are different. If the data were balanced among seasons, the average of the seasonal trends in Table K2 would be equal to the annual trends in Table K1.

For the winter season there were significant trends for Bear Creek for dissolved oxygen (increasing), Tomahawk Creek for dissolved oxygen (increasing), pH (decreasing) and nitrate (increasing) (Figure 57) and R1 for total phosphorus (increasing), dissolved oxygen (increasing) and pH (decreasing). There are only three data points for total phosphorus at R1 so more data are necessary before this trend can be validated.

During the spring season there were significant trends for Calf Creek for turbidity (decreasing), and R1 for total phosphorus (increasing), for chloride (decreasing) and nitrate (decreasing). One large turbidity value (9 FTU) in 1985 compared to FTU values less than 2 for the next seven years of record produced the turbidity trend at Calf Creek (Table K1). The nitrate trend for R1 is the result of one anomalous high concentration for 1987 (Figure 58). The other trends for R1 are probably related to re-location of the sampling site and/or changes in analytical laboratories because the data through 1988 are consistently low compared to the last two years (e.g., Figure 59).

There were significant trends during the summer for Bear Creek for total phosphorus (decreasing), for Calf Creek for fecal coliform (increasing), for Tomahawk Creek for ammonia (decreasing), and for R1 for dissolved oxygen

(decreasing) and pH (decreasing). Because there were only two data points for total phosphorus for Bear Creek a negative trend was developed. One anomalous concentration for 1995 (about 110 col/100 mL) produced the fecal coliform trend for Calf Creek (Table K1). The ammonia trend for Tomahawk Creek is the result of one anomalous sample collected during 1989 (Figure 60). R1 trends are probably related to site re-location and/or uneven sampling among the seasons.

During the fall there were significant trends for Bear Creek for nitrate (increasing) and pH (decreasing), for Calf Creek for nitrate (increasing) and pH (decreasing), for Tomahawk Creek for fecal coliform (decreasing) and sulfate (decreasing) and for R1 for total phosphorus (increasing) and sulfate (increasing). The decreasing trend in fecal coliform appears to be "real" (Figure 61). All of the other trends are based on four or five data points and it is difficult to conclusively attach any true significance to these trends.

There is no pattern of trends among the tributaries. The increasing trends for nitrate and fecal coliform at Tomahawk Creek appear to be the only significant water quality trends. It is interesting to note that Tomahawk Creek also produced the only significant trends from the annual data. The lack of trends for the other nutrients at Tomahawk Creek may be simply a reflection of low concentrations and/or low number of samples.

Because of the possible influence of discharge variation and other seasonal factors on concentration, seasonal trends were also investigated using loads (Table M2). Seasonal load averages are given in Table L4. There was only one significant correlation for loads for the tributaries and R1 which was for fecal coliform during the spring season at Calf Creek. Because this trend is based on only four years of data and six data points, additional data will be helpful in establishing the meaningfulness of this trend (Figure 62).

#### SEASONAL VARIATION

Figures 63-64 and N1-N 5 and Table L5 focus on comparison of the tributaries based on the average seasonal concentrations. In all four seasons Tomahawk Creek had the highest concentrations of fecal coliform compared to the other tributaries and during the spring also had the highest nitrate concentrations. During the winter Calf Creek appears to have had the second highest fecal coliform concentrations. The highest TKN and total phosphorus seasonal concentration occur at R1 during the winter and fall. R1 also has the highest seasonal ammonia concentration which occurs in the winter. Other than these observations, the concentrations by season and annual averages of seasonal concentrations indicate no major differences among the tributaries (Figures 63-64 and N1-N5). There was some annual variation of the relative ranking of the tributaries based on concentration. For example, Figure 65 illustrates that with the

exception of one year (1987) Tomahawk Creek had the highest fecal concentration among the three tributaries

The reason that Tomahawk Creek had the highest base flow concentrations for fecal coliform and nitrate is probably related to both geology and land use. About 65% of the surface area within the Tomahawk Creek basin is composed of the Boone Formation (Osagen Series) and it has 50% pasture land. Nineteen and 40% of Bear and Calf creek watersheds are underlain by the Boone Formation and have 33 and 38% pastures cover, respectively (Table 1 and Figure 4). The calcite portion of this cherty limestone formation is susceptible to dissolution (Stumm and Morgan, 1996) and in this portion of the formation becomes karstified. This karstification allows rapid infiltration of surface water through the highly permeable aquifer with little natural filtration, thus increasing nitrate and bacteria concentrations in base flow and reducing overland flow. The presence of the Boone Formation plus the extensive pasture land within the tributary watershed are two possible reasons for the elevated base flow concentrations for Tomahawk Creek. The high seasonal values at R1 during the winter and fall for TKN and total phosphorus are consistent with forest litter being a major source of these ions. Miller et al. (1997) have shown that streams underlain by carbonate bedrock were more likely to contain elevated concentrations of inorganic nitrogen than streams underlain by other rock types.

Although there are variations in the *concentrations* of the nutrients and fecal coliform among the tributaries, there are some generalizations that can be made about seasonal variation (Figures 63 and 64 and Table L5). The winter season has the lowest concentrations of bacteria which is consistent with colder temperatures reducing bacteria viability. There were lower concentrations of nitrate during the spring and summer when plants are utilizing nitrogen (Figure 63) which is consistent with other researchers interpretations, e.g., Wernick et al. (1998), Boyd (1996) and Dojlido and Best, 1993). Total phosphorus and perhaps ammonia and phosphate appear to have higher concentrations during the spring and summer which may reflect lack of dilution by increased base flow discharge in the winter and fall. Snyder et al. (1998) have also observed that phosphate and ammonia did not follow any specific trend but were generally higher during the summer for most stream sampling locations in Virginia. These patterns also may be influenced by the unbalanced seasonal sampling for these parameters.

Base flow *loads* for orthophosphate, total phosphorus and ammonia are generally higher for all of these streams in the winter and spring which suggest the release of them nutrients from decaying vegetation and possibly the application of fertilizers in the spring season (Figures 66 and 67). Generally the summer months have the lowest loads for fecal coliform with slightly higher loads for the winter and spring months; however, Tomahawk Creek has a very large load for nitrate during the Fall. Bakke and Pyles (1997) report peaks in nitrate load generally

occur in the winter and early spring and attribute this seasonally to precipitation and its pathway through the forest canopy, duff and soil where easily mobilized nitrate is acquired. These results from this study are influenced by differences in base flow discharge and may be affected the uneven seasonal sampling.

#### CORRELATIONS

The same criteria for statistical analyses of storm flow i.e.,  $R \geq 0.7$  and  $p \leq 0.05$ ) were used for base flow. The correlation coefficients of parameters at base flow produced far fewer correlations than for storm flow (Appendix O). This is primarily the result of the very low concentrations of suspended sediments to which phosphorus and bacteria bind and which contain organic matter that contributes to TKN and total phosphorus concentrations.

The correlations for R1 were discharge with conductance ( $R = -0.72$ ), temperature with conductance ( $R = 0.71$ ) and temperature with dissolved oxygen ( $R = -0.73$ ). The correlation of discharge with conductance probably is related to a large fraction of ground water that has high dissolved solids concentrations evapo-transpiration concentration of the slow moving stream water. Discharge affects temperature which explains the correlation of temperature and conductance. The negative correlation of dissolved oxygen and temperature is the typical relationship expected because DO decreases with increased temperature (APHA, 1992). There are only three total phosphorus concentrations for this site which makes this correlation suspect.

Bear Creek had TKN correlations with temperature ( $R = 0.97$ ) and conductance ( $R = 0.91$ ) and total phosphorus correlated with discharge ( $R = 0.82$ ) and conductance ( $R = -0.84$ ). All but the total phosphorus correlation with discharge may be the result of dilution caused by increased discharge. Both temperature and conductance have negative correlation coefficients with discharge ( $p$  less than 0.10) but with  $R$  less than 0.70. It is not obvious why total phosphorus would correlate with discharge and none of the other nutrients or bacteria also correlate with discharge.

Tomahawk Creek had correlations of TKN with turbidity ( $R = 0.81$ ) and with fecal coliform ( $R = 0.86$ ). There was also a correlation of nitrate with discharge ( $R = 0.81$ ). It is difficult to explain the turbidity correlation for TKN as meaningful because none of the other parameters associated with suspended sediments, such as total phosphorus and bacteria, exhibited this correlation. Note that there are only seven data points for TKN. One might explain the TKN and fecal coliform relationship as a consequence of both parameters being transported with organic sediment but there is no correlation of either with turbidity to substantiate this hypothesis. The lack of these expected correlations may be the result of poor accuracy for turbidity at the very low values for these samples (high value of 3.5 FTU). The nitrate correlation with discharge is consistent with higher

base flow discharge values occurring during the winter and fall when vegetation would not be utilizing nitrate, and thus resulting in increased nitrate concentrations in the ground water (base flow).

There were only two significant correlations for Calf Creek—conductance with temperature ( $R = 0.74$ ) and sulfate with chloride ( $R = 0.70$ ). As discussed above, the conductance and temperature relationship is most likely related to discharge. Both conductance and temperature have negative correlations with discharge ( $p$  less than 0.10) but with correlation coefficients less than 0.70. The sulfate and chloride relationships indicate a common source for these ions, perhaps shale.

The lack of consistent correlations for parameters among the tributaries suggest that many of these relationships may not actually be significant or that the low concentrations at base flow make it difficult for these relationships to be consistently shown statistically. For example, only Tomahawk Creek had a correlations of TKN with turbidity and fecal coliform and only Bear Creek had a correlation of total phosphorus and discharge. Others have noted that the mobility of phosphorus may be hindered by adsorption and geochemical reactions during base flow conditions (Miller et al., 1997). In one instance the criteria for statistical significant may have been too stringent. If a  $R$  value of 0.65 is used instead of 0.70, all of the tributaries have DO correlations with temperature.

#### **BASE FLOW SAMPLING VERSUS STORM EVENT SAMPLING**

When evaluating a watershed it is important to study storm event water quality, as well as base flow water quality. Random sampling of a stream (grab sampling), is not likely to produce a true representation of the conditions of the stream and watershed. If only “grab samples” are taken, which is often the case, the calculated load values will be grossly underestimated. The amount of nutrients and bacteria that are transported in one rain storm can equal several hundred equivalent days of base flow. Table 21 illustrates this point by comparing the storm loads of the tributaries to average base flow of R1 for one year (i.e., all 365 days are considered to be base flow). The lowest ratio is 0.09 for the fecal coliform load for Tomahawk Creek in the April storm which indicates that this storm transported the number of bacteria equivalent to 0.09 years, i.e., about 32 days, of base flow. The highest ratio (fecal coliform during the November storm at Bear Creek) indicates that the storm load was equivalent to 4,800 years of base flow loads! The inclusion of storm data is crucial in terms of mass of materials transported.

## COMPARISON WITH STANDARDS

It is of interest to compare the water quality of the tributaries with water quality standards. Arkansas does not have a complete list of maximum contaminant levels; therefore, the water quality of the study streams are compared to the average base flow concentrations plus two standard deviations (AVG+2) for all of the Buffalo River tributaries (Mott, 1997). Few of the parameters exceed the standards. Nine out of 72 base flow samples from Tomahawk Creek exceed the fecal coliform standards (based on geometric mean) and one of 81 samples from R1. A relatively high percent (40) of Calf Creek samples exceed TKN and orthophosphate standards and AVG+2 (Tables 22 and P1-P4). Many more of the storm samples exceeded the standards and AVG+2, especially for fecal coliform, turbidity, TKN and total phosphorus but the data vary from site to site for the same storm and also from storm to storm for a site, i.e., there are no consistent patterns for the water quality of the tributaries (Table 23). These data also point out the need for storm event sampling versus base flow sampling.

## CONCLUSIONS AND RECOMMENDATIONS

The water quality data for Bear, Calf and Tomahawk creeks illustrate the significant increases in concentrations and loads during storms. These observations demonstrate the importance of storm event sampling in determining the impact of land use on water quality, especially in these basins which are dominated by non-point sources of pollution. Seasonal affects on water quality, primarily related to the amount and vigor of vegetation, were also observed. During storms nutrients (with the exception of nitrate) and bacteria generally increased in concentration as TSS increased. The April storm demonstrated that "high" soil saturation can significantly increase discharge which can in turn affect water quality by transporting more contaminants such as bacteria or by diluting the concentration of others, such as nitrate.

All three tributaries consistently had higher nutrient and bacteria concentrations and loads compared to the pristine site. Bacteria and nutrient concentrations at peak discharge were as much as 125 times and 44 times higher, respectively for the tributaries compared to the pristine site. Bacteria storm loads for the tributaries were as much as 416 times higher than at the pristine site and the nutrient loads were as much as 138 times higher. These large increases in concentrations and loads show the degrading effect of agricultural and other non-point pollution sources on the water quality of the tributaries.



During storms, nutrient and bacteria concentrations increased one to six orders of magnitude, respectively, compared to base flow. A notable exception was nitrate which was often higher in base flow samples, especially during the winter and fall when there was little nutrient uptake by the vegetation. Another observation was that high intensity rains of small volume could cause bacteria concentrations to peak well ahead of the peak in discharge and without significantly increased turbidity or suspended sediments in the stream. For bacteria and nutrients, the total load for a storm event can have the equivalent load of hundreds or even thousands of base flow days. For example, during three days of storm flow in November, the total fecal coliform load delivered to the Buffalo River by Bear Creek was equivalent to 1,752,000 days of base flow at the pristine site.

At both the pristine site (R1) and the agricultural tributaries, the peak in total suspended solids sometimes preceded peak discharge. Increased sampling frequency are needed to determine if this occurs for most rain storms. A large portion of this suspended material was derived from water entering the streams via road ditches, gullies and other direct surface pathways. The time at which the proportion of direct surface runoff in the stream was highest coincides with the peak in suspended solids. At peak discharge, vadose and ground water inputs become significant contributors to the hydrograph resulting in dilution of direct runoff. As the storm proceeded, the relative proportion of vadose and ground water entering continuously increased, and concentration of suspended solids decreased on the falling limb of the hydrograph. Dissolved oxygen, pH, dissolved nutrients (nitrate, ammonia and orthophosphate) and conductance did not correlate with suspended solids and had variable relationships with the hydrograph.

Although it was originally hypothesized that ranking of the tributaries based on amount of pasture land and other agricultural variables would be supported by water quality results, there were no consistent relationships between measures of agricultural activities and water quality (concentrations or loads). Variations in physical factors, (e.g., rain intensity, duration and distribution; soil saturation; season, spatial and temporal variations in land management) caused larger loads or concentrations to emanate from the tributary most impacted by a given storm. Generally, it was observed that Bear Creek was the largest contributor of storm driven pollutants, followed by Calf Creek and then Tomahawk Creek which is the order predicted by the indicators of agricultural activity.

Because of the increase in the number of animals and pasture land in the tributary watersheds during the past 15 years, trends in water quality through time were also examined. Analysis of only base flow data produced few statistically significant trends. This is probably the result of uneven sampling among the seasons, relatively low concentrations, change in detection limits and other factors for specific sites.

The seasonal affects on water quality were primarily related to the amount and vigor of vegetation, temperature and discharge. Nitrate was often higher in base flow samples, especially, during the winter and fall when there was little nutrient uptake by the vegetation. The lowest bacteria concentrations occurred during the winter which is which is consistent with colder temperatures reducing bacteria viability. Total phosphorus, and perhaps ammonia and phosphate, concentrations appear to have been lower during the winter and fall which is probably the result of dilution by increased base flow discharge in the winter and fall.

Base flow concentrations sometimes exceeded state standards for these streams. The most common violations were for sulfate and fecal coliform (especially for Tomahawk Creek) and total phosphorus (especially for Calf Creek). During storms, almost 100 percent of the samples exceeded the standards for fecal coliform bacteria and turbidity. Large increases in bacteria (over 40,000 colonies/100 mL) far exceed the 200 colonies and 400 colonies/100 mL standards set for primary contact waters and the maximum concentrations at the pristine site (520 col/100 mL). The total phosphorus guideline was often exceeded as well. In the case of Calf Creek during the November storm, 100% of the samples exceeded the 0.1 mg/L criterium for total phosphorus.

Storms may have lasting affects on stream water quality. As shown by this study, nutrients associated with organic material, especially total phosphorus, are transported and deposited with the sediments during storms. These nutrients are then available to be leached by base flow stream and hyporheic waters and provide a source of nutrients to the system. Increased nutrients alter natural aquatic communities of organisms, especially in clear, "warm" streams such as the Buffalo River and its tributaries. Studies should be initiated which quantify the biological and physical changes occurring in these systems as a result of watershed disturbances which have impacted water quality of storm runoff.

If the amount of pasture land and agricultural intensity continues to increase as it has in the past 30 years, the health of the Buffalo River and its visitors will be in even greater jeopardy. Standards are routinely exceeded and it is imperative to determine how to respond to this fact. Implementation of the appropriate best management practices (BMPs) can mitigate impacts of land use activities on the water quality. The Natural Resources Conservation Service has implemented a watershed improvement/water quality enhancement project for these tributaries, and post-project storm and base flow monitoring should be conducted to determine the effectiveness of the BMPs. Efforts should be taken to disseminate water quality monitoring information, including this report, to the public so that an educated public can assist decision makers in determining the proper level of response.

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Table 1. Distribution of rock units within each of the tributary sub-basins.

Tributary	Pennsylvanian		Mississippian		Silurian		Ordovician		Total Basin			
	Acres	%	Acres	%	Acres	%	Acres	%	Acres	%		
Upper Bear Creek	25,347	49.35	16,060	31.27	9,945	19.36	11	0.02	0	0.00	51,363	100.00
Lower Bear Creek	0	0.00	282	3.91	5,890	81.64	149	2.06	894	12.39	7,215	100.00
Total of Bear Creek	25,347	43.27	16,342	27.90	15,835	27.03	160	0.27	894	1.53	58,578	100.00
Calf Creek	4,929	17.76	11,687	42.11	11,136	40.13	1	0.00	0	0.00	27,752	100.00
Tomahawk Creek	253	1.06	2,048	8.62	15,570	65.54	154	0.65	5,732	24.13	23,756	100.00

Table 2. Distribution of soil associations within each of the tributary sub-basins

Soil Series	Upper Bear		Lower Bear		Total Bear		Calf		Tomahawk	
	Acres	%	Acres	%	Acres	%	Acres	%	Acres	%
Arkana-Moko Complex	456	0.89	87	1.21	543	0.93	232	0.74	517	2.17
Caplina	30	0.06			30	0.05			154	0.65
Ceda							41	0.13		
Ceda-Kenn Complex	762	1.48			762	1.30			6,657	27.96
Clarksville	2,592	5.05	2,903	40.23	5,495	9.38	1,941	6.16	51	0.22
Elsah			56	0.78	56	0.10	43	0.14		
Enders	6,505	12.66	221	3.07	6,726	11.48	4,304	13.66	1,112	4.67
Enders-Mountainburg Assoc	24	0.05			24	0.04				
Enders-Nella	5,472	10.65	7	0.10	5,479	9.35	2,623	8.32		
Enders-Nella-Steprock Complex	17	0.03			17	0.03				
Ender-Steprock Complex	139	0.27			139	0.24				
Estate-Lily-Udothents Complex			32	0.45	32	0.06			2,205	9.26
Estate-Portia-Moko Assoc									3,772	15.84
Healing			66	0.91	66	0.11	97	0.31	5	0.02
Linker	1,371	2.67	56	0.78	1,427	2.44	547	1.73	792	3.33
Linker-Mountainburg Complex	1,418	2.76	8	0.12	1,427	2.44	1,024	3.25	142	0.59
Linker-Mountainburg Assoc	18	0.04			18	0.03				
Moko-Rock Outcrop Complex	399	0.78	271	3.76	670	1.14	628	1.99	368	1.55
Moko-Rock Outcrop-Eden Complex	496	0.97	2	0.03	498	0.85	1,564	4.96	14	0.06
Mountainburg	47	0.09			47	0.08	32	0.10		
Nauwoo	2,898	5.64			2,898	4.95	1,255	3.98		
Nella	160	0.31			160	0.27	295	0.94	133	0.56
Nella-Enders-Mountainburg Assoc	8	0.02			8	0.01				
Nella-Steprock Complex	4,556	8.87			4,556	7.78	231	0.73	72	0.30
Nella-Steprock Mountainburg Complex	7,389	14.38			7,389	12.61	2,649	8.41	99	0.42
Newnata-Eden-Moko Complex	5,637	10.98	26	0.37	5,664	9.67	3,903	12.38	135	0.57
Newnata-Summit	873	1.70			873	1.49	517	1.64		
Newnata-Summit Complex	782	1.52			782	1.33	616	1.95		
Nixa	6	0.01			6	0.01			1,334	5.60
Nixa-Noark Complex									1,059	4.45
Noark	4,133	8.05	2,519	34.92	6,652	11.36	6,096	19.34	4,364	18.33
Peridge	507	0.99			507	0.87	51	0.16		
Portia			18	0.24	18	0.03			369	1.55
Razor	931	1.81	642	8.90	1,573	2.69	1,086	3.45	323	1.36
Riverwash	114	0.22	44	0.61	158	0.27	63	0.20	55	0.23
Rock Outcrop	27	0.05	108	1.49	134	0.23	8	0.03	26	0.11
Samba	272	0.53			272	0.46	398	1.26		
Secesh	565	1.10	41	0.57	607	1.04	102	0.32		
Sidon	1,905	3.71			1,905	3.25	998	3.17		
Spadra	489	0.95			489	0.83	130	0.41		
Steprock-Mountainburg-Rock Outcrop Complex	68	0.13			68	0.12				
Steprock-Linker Complex	26	0.05			26	0.04				
Steprock-Mountainburg Complex	214	0.42			214	0.37			31	0.13
Widemann			62	0.86	62	0.11			18	0.07
Water	58	0.11	45	0.62	103	0.18	43	0.14		
<b>Total</b>	<b>51,363</b>	<b>100.00</b>	<b>7,215</b>	<b>100.00</b>	<b>58,578</b>	<b>100.00</b>	<b>31,517</b>	<b>100.00</b>	<b>23,808</b>	<b>100.00</b>

Table 3. Acres of pasture and percent pasture for the tributaries for 1965 and 1992.

<b>1965</b>			
Tributary	Land Cover		
	Acres of Pasture	% of Pasture	Total Acres
Bear Creek			
Upper	12,715	25	51,364
Lower	1,303	18	7,215
Total	14,019	24	58,579
Calf Creek	9,562	30	31,499
Tomahawk Creek	5,547	23	23,809
Total Tributaries	29,128	26	113,886
Buffalo River	122,175	14	883,977
<b>1992</b>			
Bear Creek			
Upper	17,121	33	51,364
Lower	2,300	32	7,215
Total	19,421	33	58,579
Calf Creek	11,888	38	31,499
Tomahawk Creek	11,794	50	23,809
Total Tributaries	43,103	38	113,886
Buffalo River	214,955	25	857,607

Table 4. Number of animals in the tributary sub-basins. After NRCS, 1995.

Tributary	Number of Animals		
	Cattle	Cows	Swine
<b>Bear</b>			
<b>Upper</b>	2,882	822	0
Lower	387	110	0
Total	3,269	932	0
<b>Calf</b>	2,382	244	0
<b>Tom</b>	1,724	313	454*

\* 400 pigs, 50 sows and 4 boar.

Data for sows and boars provided by Sid Lowrance, 1998.

Number of cattle in upper and lower Bear Creeks based on ratio of pasture acres for the two sub-basins.

Number of dairy cows in upper and lower Bear Creeks estimated from dairy cow density map (NRCS, 1995).

Table 5. Change of pasture land from 1965 to 1992 by sub-basin.

Stream	1965 Pasture lost	1992 Pasture gained	1965-1992 Pasture	Other Land Cover	% Net change in Pasture
Upper Bear Creek	2,695.63	7,101.29	10,019.64	31,547.57	34.65
Lower Bear Creek	443.90	1,440.40	859.35	4,471.01	76.46
Total of Bear Creek	3,139.53	8,541.69	10,878.99	36,018.58	38.54
Calf Creek	2,154.59	4,480.79	7,407.37	17,456.13	24.33
Tomahawk Creek	995.61	7,242.66	4,551.47	11,019.03	112.62
Buffalo River	122,175.00*	214,955.00**			75.94

\* Total pasture in 1965

\*\*Total pasture in 1992



Table 6. Acres of pastureland by percent slope categories for streams, by acres and percentage of pasture in each category for 1992.

Tributary	Total Area	Pasture	Slope %		
			0-7	8-14	>15
<b>Bear-Upper</b>					
Acres	51,364	17,121	7,262	5,554	4,305
%			42.42	32.44	25.14
<b>Bear-Lower</b>					
Acres	7,215	2,300	598	631	1,071
%			25.99	27.43	46.58
<b>Bear-Total</b>					
Acres	58,579	19,421	7,860	6,185	5,376
%			40.47	31.85	27.68
<b>Calf</b>					
Acres	31,499	11,888	5,981	3,532	2,376
%			50.31	29.71	19.99
<b>Tomahawk</b>					
Acres	23,809	11,794	3,297	4,491	4,006
%			27.95	38.08	33.97
<b>Buffalo-Upper</b>					
Acres	36,958	4,885	800	1,241	2,844
%			16.38	25.41	58.21

Table 7. Acres of pastureland by percent slope categories for streams, by acres and percentage of pasture in each category for 1965.

Tributary	Total Area	Pasture	Slope %		
			0-7	8-14	>15
<b>Bear-Upper</b>					
Acres	51,364	12,715	6,270	4,084	2,361
%			49.31	32.12	18.57
<b>Bear-Lower</b>					
Acres	7,215	1,303	489	392	423
%			37.49	30.07	32.44
<b>Bear-Total</b>					
Acres	58,579	14,019	6,758	4,476	2,784
%			48.21	31.93	19.86
<b>Calf</b>					
Acres	31,499	9,562	5,702	2,700	1,161
%			59.63	28.24	12.14
<b>Tomahawk</b>					
Acres	23,809	5,547	2,035	2,241	1,270
%			36.69	40.40	22.90
<b>Buffalo-Upper</b>					
Acres	36,358	1,635	478	600	558
%			29.21	36.69	34.10

Table 8. Acres of pasture and percentage of pasture by degrees slope in 1965 and 1992.

Tributary	1992 >15 degrees		1965 >15 degrees		1992 7-14 degrees		1965 7-14 degrees	
	Acres	%	Acres	%	Acres	%	Acres	%
Bear Creek								
Upper	1,026	6	473	4	5,263	31	3,266	26
Bear	419	18	148	11	890	39	410	31
Total	1,445	7	621	4	6,153	32	3,676	26
Calf	605	5	185	2	2,919	26	1,785	19
Tomahawk	786	7	111	2	4,996	42	1,979	36

Table 9. Discharge and rain for tributaries by storm. Total watershed acres given for each tributary.

Watershed Acres	Bear		Calf		Tomahawk		R1	
	Discharge Liters	Rain Inches	Discharge Liters	Rain Inches	Discharge Liters	Rain Inches	Discharge Liters	Rain Inches
	51,364		31,499		23,809		36,358	
<b>April</b>	2.920E+09	2.12	2.883E+09	2.80	1.130E+09	2.33	---	---
<b>November</b>	1.310E+10	6.57	---	---	1.684E+10	8.03	---	---
<b>January</b>	---	---	---	---	3.414E+09	2.28	---	---
<b>December</b>	1.574E+09	2.17	2.358E+08	1.93	---	---	3.02E+09	2.08

Table 10. Calculated number of hours from peak flow until overland flow ceases.

Tributary	Square miles	Hours from Peak (D*24)
Bear Creek	78.3	57
Calf Creek	49.4	52
Tomahawk Creek	36.9	49

Table 11. Storm loads for the tributaries and R1.

Tributary	April	November	January	December
<b>Storm discharge (L)</b>				
Bear	2.918E+10	1.310E+10		1.574E+09
Calf	2.825E+09			2.358E+08
Tom	1.130E+09	1.061E+10	3.414E+09	
R1			3.015E+09	
<b>Coliform storm loads (col/100 mL)</b>				
Bear	3.605E+14	1.496E+15		1.327E+14
Calf	2.094E+14			3.137E+13
Tom	4.612E+12	1.134E+15	2.323E+14	
R1			3.907E+12	
<b>NO3-N storm loads (mg)</b>				
Bear	7.565E+08	1.719E+10		1.019E+09
Calf	7.508E+08			1.662E+08
Tom	3.300E+08	4.407E+09	1.220E+09	
R1			1.100E+07	
<b>TKN storm loads (mg)</b>				
Bear	3.018E+09	1.722E+10		8.182E+08
Calf	2.825E+09			8.376E+07
Tom	1.613E+08	3.039E+10	6.431E+09	
R1			3.092E+09	
<b>TP storm loads (mg)</b>				
Bear	9.400E+08	1.626E+10		7.547E+08
Calf	1.072E+09			9.177E+07
Tom	1.849E+08	5.081E+09		
R1			8.494E+07	
<b>TSS storm loads (mg)</b>				
Bear	2.918E+09	3.649E+12		8.998E+10
Calf	3.149E+11			9.703E+09
Tom	6.674E+10	6.970E+12	1.387E+12	
R1			---	

Shaded values are the maximum values for each storm. Outlined values are the mid values where all three tributaries were monitored. Unmarked values are the lower or lowest values. Numbers not more than 10% different are rated the same. R1 is shown only for comparison and is not ranked with the tributaries.

Table 12. Comparison of measures of agricultural activities by tributary

	TRIBUTARY		
	Bear	Calf	Tomahawk
<b>Total Wastes lbs</b>	62,580,916	36,276,922	31,378,169
<b>Total N lbs</b>	321,104	188,161	162,579
<b>Total P</b>	83,801	57,821	46,075
<b>Pasture acres</b>	17,120	11,888	11,794
<b>Pasture %</b>	33	38	50
<b>Total Wastes lbs/pasture acre</b>	3,655	2,119	1,833
<b>Total N lbs/pasture acre</b>	18.8	11.0	9.5
<b>Total P lbs/pasture acre</b>	4.9	3.4	2.7
<b>*Rank</b>	1	2	3

\* Rank except for % pasture which is reversed.

Table 13. Comparison of stream discharge and peak concentration by storm.

Tributary	April	November	January	December
	<b>Storm discharge (L)</b>			
Bear	60,888	184,080		24,214
Calf	59,472	90,624		4,248
Tomahawk	15,151	254,880	133,104	
R1			33,984	
	<b>Coliform peak concentration (col/100 mL)</b>			
Bear	20,800	8,100		17,200
Calf	45,000	32,000		2,400
Tomahawk	8,200	20,000	1,400	
R1			360	
	<b>ak concentration (mg/L)</b>			
Bear	0.25	0.32		0.70
Calf	0.26	0.60		0.55
Tomahawk	0.22	0.30	0.24	
R1			0.02	
	<b>ak concentration (mg/L)</b>			
Bear	1.65	2.60		0.77
Calf	2.40	4.18		0.62
Tomahawk	1.30	4.64	3.40	
R1			1.28	
	<b>k concentration (mg/L)</b>			
Bear	0.54	1.03		0.39
Calf	0.67	0.60		0.24
Tomahawk	0.21	0.74	—	
R1			0.07	
	<b>TSS peak concentration (mg/L)</b>			
Bear	296	662		113
Calf	426	216		219
Tomahawk	128	1,190	1,036	
R1				

Shaded values are the maximum values for each storm. Outlined values are the mid values where all three tributaries were monitored. Unmarked values are the lowest values. Numbers not more than 10% different are rated the same. R1 is shown only for comparison and is not ranked with the tributaries.



Table 14. Comparison of stream discharge and peak load by storm.

Tributary	April	Tomahawk November	January	December
<b>Storm discharge (L/sec)</b>				
Bear	60,888	184,080		24,214
Calf	59,472	90,624		4,248
Tomahawk	15,151	254,880	133,104	
R1			33,984	
<b>Coliform peak load (flux) (col/sec)</b>				
Bear	1.27E+10	1.49E+10		4.16E+09
Calf	2.68E+10	2.90E+10		1.02E+09
Tomahawk	1.24E+09	5.10E+10	1.86E+09	
R1			1.22E+08	
<b>NO3-N peak load (mg/sec)</b>				
Bear	1.52E+04	5.946E+04		1.705E+04
Calf	1.55E+04	5.456E+04		2.319E+03
Tomahawk	3.35E+03	7.519E+04	3.221E+04	
R1			5.437E+02	
<b>TKN peak load (mg/sec)</b>				
Bear	100,465	478,608		18,644
Calf	142,733	378,808		2,634
Tomahawk	19,697	1,182,643	452,554	
R1			43,500	
<b>TP peak load (mg/sec)</b>				
Bear	3.31E+04	1.90E+05		1.02E+03
Calf	3.97E+04	5.42E+04		9.44E+03
Tomahawk	3.17E+03	1.89E+05	—	
R1			2.45E+03	
<b>TSS peak load (mg/sec)</b>				
Bear	1.802E+07	1.219E+08		2.736E+06
Calf	2.534E+07	1.957E+07		9.303E+05
Tomahawk	1.939E+06	3.033E+08	1.379E+08	
R1				

Shaded values are the maximum values for each storm. Outlined values are the mid values where all three tributaries were monitored. Unmarked values are the lowest values. Numbers not more than 10% different are rated the same. R1 is shown only for comparison and is not ranked with the tributaries.

Table 15. Storm flow-weighted concentrations for the tributaries and R1.

Tributary	April	November	January	December
<b>Storm discharge (L)</b>				
Bear	2.918E+10	1.310E+10		1.574E+09
Calf	2.825E+09			2.358E+08
Tom	1.130E+09	1.061E+10	3.414E+09	
R1			3.015E+09	
<b>Coliform flow-weighted concentrations (col/100 mL)</b>				
Bear	1.235E+03	1.142E+04		8.431E+03
Calf	7.412E+03			1.330E+04
Tom	4.081E+02	1.069E+04	6.804E+03	
R1			1.296E+02	
<b>NO3-N flow-weighted concentrations (mg)</b>				
Bear	2.593E-02	1.312E+00		6.474E-01
Calf	2.658E-01			7.048E-01
Tom	2.920E-01	4.148E+00	3.574E-01	
R1			3.648E-03	
<b>TKN flow-weighted concentrations (mg)</b>				
Bear	1.034E-01	1.315E+00		5.198E-01
Calf	1.000E+00			3.552E-01
Tom	1.427E-01	2.864E+00	1.884E+00	
R1			1.026E+00	
<b>TP flow-weighted concentrations (mg)</b>				
Bear	3.221E-02	1.241E+00		4.795E-01
Calf	3.795E-01			3.892E-01
Tom	1.636E-01	4.789E-01		
R1			2.817E+02	
<b>TSS flow-weighted concentrations (mg)</b>				
Bear	1.000E-01	2.785E+02		5.717E+01
Calf	1.115E+02			6.165E+00
Tom	5.906E+01	6.569E+02	4.063E+02	
R1			---	

Shaded values are the maximum values for each storm. Outlined values are the mid values where all three tributaries were monitored. Unmarked values are the lower or lowest values. Numbers not more than 10% different are rated the same. R1 is shown only for comparison and is not ranked with the tributaries.

Table 16. Conditions within each watershed after (NRCS, 1995). Percent is of problem ares unless noted otherwise.

Watershed Condition	Tributary		
	Bear	Calf	Tomahawk
Pasture Acres	24,117	12,475	11,295
% of watershed	40.92	39.46	47.83
Problem Acres	17,409	11,060	9,191
% of pasture	72.19	88.66	81.37
Poor Cover	3,007	2,150	5,155
%	17.27	19.44	56.09
Slope > 9%	6,726	5,817	7,154
%	38.64	52.59	77.84
< 0.5 mile to Nearest Stream	16,803	11,060	6,854
%	96.52	100.00	74.57
Proximity to River or Main Tributary	2,223	1,122	590
%	12.77	10.14	6.42
Silt Soil Texture	17,409	11,060	9,112
%	100.00	100.00	99.14
Underlain by Limestone	9,936	8,427	2,946
%	57.07	76.19	32.05

Table 17. Ratio of tributary storm loads to the January 25-26, 1989 storm loads at R1.

<b>Tributary</b>	<b>April</b>	<b>November</b>	<b>January</b>	<b>December</b>
<b>Fecal Coliform</b>				
Bear Creek	92.27	382.90		33.96
Calf Creek	53.60			8.03
Tomahawk Creek	1.18	366.16	59.46	
<b>NO3-N</b>				
Bear Creek	68.77	1562.73		92.64
Calf Creek	68.25			15.11
Tomahawk Creek	30.00	400.64	110.91	
<b>TKN</b>				
Bear Creek	0.98	5.57		0.26
Calf Creek	0.91			0.03
Tomahawk Creek	0.05	9.83	2.08	
<b>TP</b>				
Bear Creek	11.07	191.43		8.89
Calf Creek	12.62			1.08
Tomahawk Creek	2.18	59.82		

Table 18. Ratio of tributary storm flow-weighted concentrations to the storm flow-weighted concentration for R1 during the January 28-29, 1989 storm

<b>Tributary</b>	<b>April</b>	<b>November</b>	<b>January</b>	<b>December</b>
<b>Fecal Coliform</b>				
Bear Creek	9.5	88.1		65.1
Calf Creek	57.2			102.7
Tomahawk Creek	3.1	82.5	52.5	
<b>NO3-N</b>				
Bear Creek	7.1	359.7		177.5
Calf Creek	0.3			193.2
Tomahawk Creek	80.1	113.9	98.0	
<b>TKN</b>				
Bear Creek	0.1	1.3		0.5
Calf Creek	1.0			0.3
Tomahawk Creek	0.1	2.8	1.8	
<b>TP</b>				
Bear Creek	1.1	44.1		17.0
Calf Creek	13.5			13.8
Tomahawk Creek	5.8	17.0		

Table 19. Example (ammonia) of the number of data points per year for Calf Creek during base flow conditions.

	1985	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997
WINTER				1			1	1	2	1	1	1
SPRING				4			2	1	1	1	1	
SUMMER							2	1	2	2	1	
FALL							1	1		1	1	

Table 20. Season designation for base flow data.

<b>Season</b>	<b>Months</b>
Winter (1)	January, February, March
Spring (2)	April, May, June
Summer (3)	July, August, September
Fall (4)	October, November, December

Table 21. Ratio of storm discharge and loads for the tributaries to the annual base flow discharge and load for R1. Ratio gives the number of years of base flow equal to each storm loads.

Tributary	April	November	January	December
<b>Storm discharge (L)</b>				
<b>Bear</b>	19.08	8.57		1.03
<b>Calf</b>	1.85			0.15
<b>Tomahawk</b>	0.74	6.94	2.23	
<b>R1</b>			1.97	
<b>Coliform storm loads (col/100 mL)</b>				
<b>Bear</b>	1,160.3	4,814.9		427.10
<b>Calf</b>	673.96			100.97
<b>Tomahawk</b>	14.84	3,649.8	747.67	
<b>R1</b>			12.57	
<b>NO3-N storm loads (mg)</b>				
<b>Bear</b>	2.34	53.24		3.16
<b>Calf</b>	2.33			0.51
<b>Tomahawk</b>	1.02	13.65	3.78	
<b>R1</b>			0.03	
<b>TP storm loads (mg)</b>				
<b>Bear</b>	0.88	15.21		0.71
<b>Calf</b>	1.00			0.09
<b>Tomahawk</b>	0.17	4.75		
<b>R1</b>			0.08	



Table 22. Number of base flow samples out of total samples exceeding standards and "average base flow plus two standard deviations" for all Buffalo River tributaries for the three study tributaries and R1.

PARAMETER	Standard	BASE FLOW CONDITIONS									
		Number of Samples Exceeding Standard			Average plus two std. dev	Number of Samples Exceeding Average two std. dev.					
		Bear	Calf	Tomahawk		R1	Bear	Calf	Tomahawk	R1	
Fecal Coliform col/100 mL	200-400	1/67	0/69	9/72 - 2/72	1/81	122	2/67	3/69	13/72	1/81	
Turbidity NTU	10	0/55	1/56	0/58	1/56	7.1	0/55	1/56	0/58	5/56	
NO3-N mg/L	None					0.492	1/27	3/26	5/39	0/56	
TKN mg/L	None					0.545	0/14	0/5	0/7	5/27	
Orthophosphate-P mg/L	None					0.059	0/22	4/21	1/36	6/44	
Total Phosphorus mg/L	0.1	0/10	4/10	0/14	0/35	0.04	0/10	4/10	1/14	6/35	
Ammonia-N mg/L	None					0.128	0/28	0/21	1/41	3/44	
Chloride mg/L	10	0/23	0/21	0/24	1/31	5.858	4/23	1/22	1/24	2/31	
Sulfate mg/L	10	8/19	11/18	3/35	1/40	17.284	0/19	0/18	1/35	0/40	

\* Standards from ADPC&E, 1995.

\*\* Base flow average of all Buffalo River tributaries (Mott, 1997).

Table 23. Number of storm samples out of total samples exceeding standards and "average base flow plus two standard deviations for all Buffalo River tributaries for the three study tributaries and R1 for each storm.

STORM FLOW CONDITIONS												
PARAMETER	Standard*	Number of Samples Exceeding the Standard Out of Total Samples										
		April			November			January			December	
		Bear	Calf	Tom	Bear	Calf	Tom	Tom	R1	Bear	Calf	
Fecal Coliform col/100 mL	200-400	10/10 - 9/10	10/10	10/10	6/9	9/9	12/12	27/27	3/10 - 1/10	15/15	15/15	15/15
Turbidity NTU	10	2/8	10/10	1/10	6/9	9/9	12/12	26/27	10/10	12/15	13/15	13/15
NO3-N mg/L	None	0/10	0/10	0/10	1/9	9/9	2/12	.	0/10	10/15	12/15	12/15
TKN mg/L	None	0/10	0/10	0/10	0/9	0/9	0/12	0.27	0/10	0/15	0/15	0/15
Orthophosphate-P mg/L	None	0/10	0/10	0/10	2/9	0/9	0/12	15/27	.	6/15	8/15	8/15
Total Phosphorus mg/L	0.1	0/10	10/10	1/10	0/9	0/9	0/12	0.27	0/10	0/15	0/15	0/15
Ammonia-N mg/L	None	0/10	1/10	0/10	0/9	0/9	0/12	15/27	.	6/15	8/15	8/15
Chloride mg/L	10	0/10	1/10	0/10	0/9	0/9	0/12	15/27	.	6/15	8/15	8/15
Sulfate mg/L	10	0/10	1/10	0/10	0/9	0/9	0/12	15/27	.	6/15	8/15	8/15
Number of Samples Exceeding the Average Plus Two Standard Deviations Out of Total Samples												
PARAMETER	Average* plus two std. dev.	April			November			January			December	
		Bear	Calf	Tom	Bear	Calf	Tom	Tom	R1	Bear	Calf	
		10/10	0/10	0/10	6/9	9/9	12/12	27/27	3/10	15/15	15/15	
Fecal Coliform col/100 mL	122	0/10	0/10	6/9	9/9	12/12	27/27	3/10	15/15	15/15	15/15	
Turbidity NTU	7.1	9/10	0/10	0/10	6/9	6/9	12/12	26/27	10/10	12/15	13/15	13/15
NO3-N mg/L	0.492	0/10	0/10	0/10	7/9	7/9	6/12	1/27	0/10	14/15	14/15	14/15
TKN mg/L	0.545	9/10	9/10	9/10	6/9	9/9	12/12	27/27	0/10	9/15	9/15	9/15
Orthophosphate-P mg/L	0.059	2/10	2/10	2/10	6/9	9/9	9/12	0/27	.	8/15	10/15	10/15
Total Phosphorus mg/L	0.04	0/10	0/10	0/10	1/9	9/9	2/12	.	0/10	10/15	12/15	12/15
Ammonia-N mg/L	0.128	1/10	1/10	0/10	0/9	0/9	0/12	0/27	0/10	0/15	0/15	0/15
Chloride mg/L	5.858	0/10	0/10	0/10	3/9	0/9	0/12	0/27	0/10	1/15	2/15	2/15
Sulfate mg/L	17.284	0/10	0/10	0/10	0/9	0/9	0/12	0/27	.	0/15	0/15	0/15

\* Standards from ADPC&E, 1995.

\*\* Base flow average of all Buffalo River tributaries (Mott, 1997).

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Figure 65. Annual fecal coliform concentrations for the three tributaries.

Figure 66. Average seasonal loads for the tributaries and R1.

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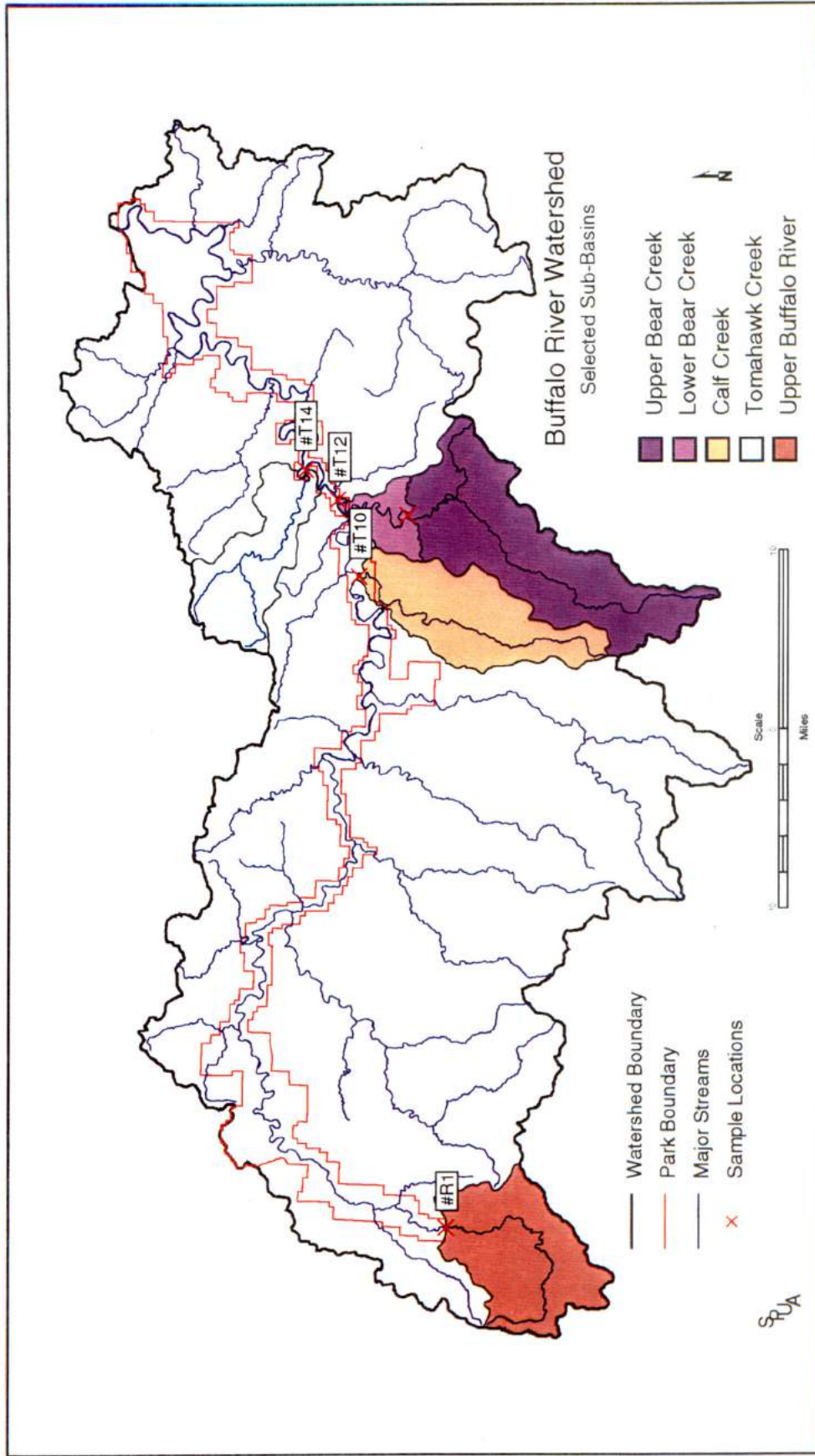


Figure 1. Location of the study tributaries and upper Buffalo pristine sub-basins and sample collection sites.

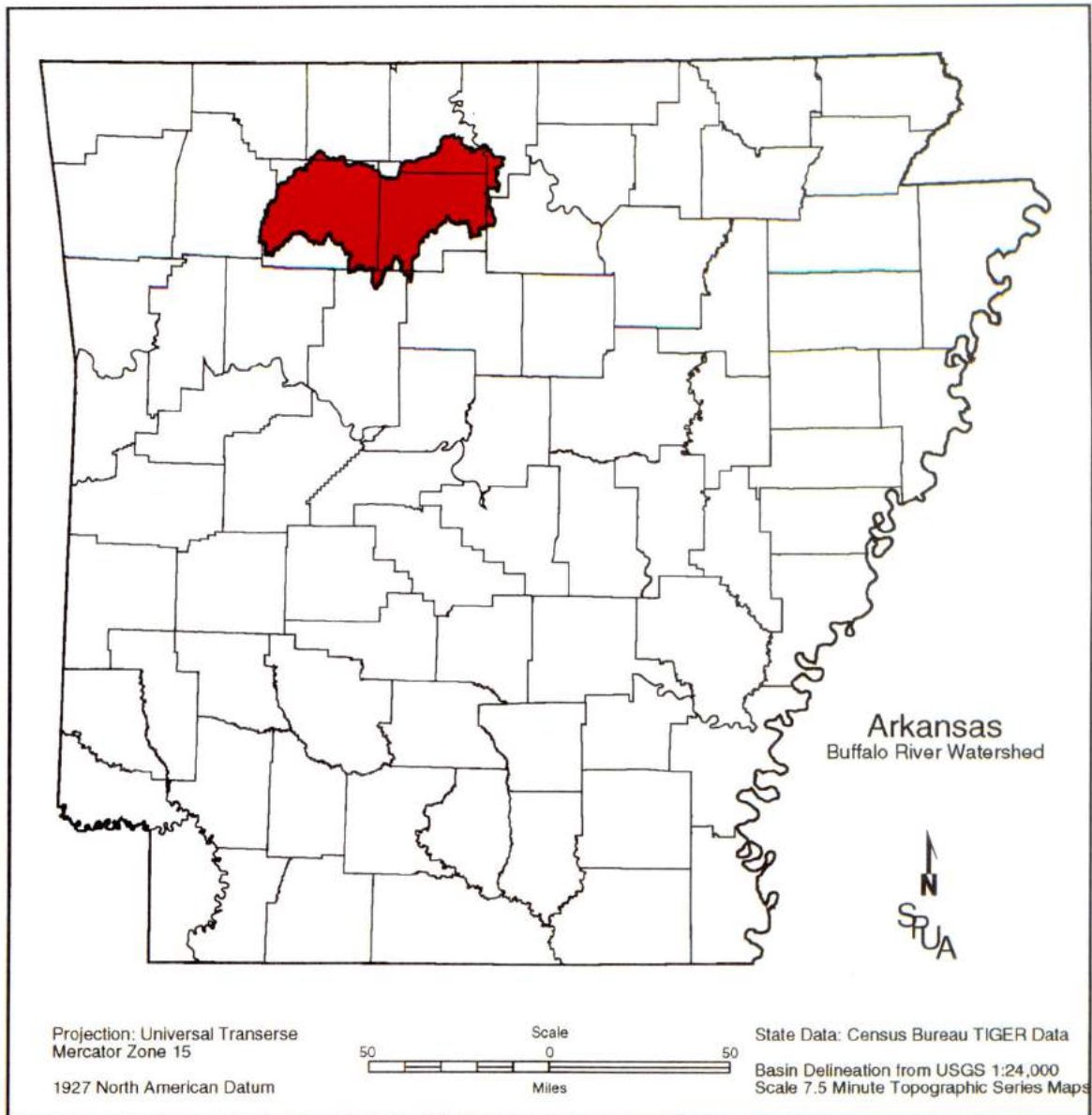


Figure 2. Location of the Buffalo River watershed with respect to the state of Arkansas.



SYSTEM	SERIES	FORMATION	MEMBER	PREDOMINANT ROCK TYPE
PENNSYLVANIAN	MORROWAN	YATOKA		SHALE, SANDSTONE AND MINOR AMOUNTS OF LIMESTONE
		BLOYD	TRACE CREEK KRESLER DYE MIDDLE BLOYD SANDSTONE BRENTWOOD	
		HALE	PRAIRIE GROVE CANE HILL	
MISSISSIPPIAN	CHESTERIAN	PITKIN		LIMESTONE AND CHERT
		FAYETTEVILLE	WEDINGTON	
		BATESVILLE		
	OSAGEAN	BOONE		
ST. JOE				
SILURIAN		LAFFERTY		LIMESTONE, SANDSTONE, AND SHALE
		ST. CLAIR		
		BRASSFIELD		
ORDOVICIAN	UPPER	CASON		SHALE
		FERNDALE		LIMESTONE
		PLATTIN		LIMESTONE
	MIDDLE	ST. PETER		SANDSTONE
		EVERTON		LIMESTONE AND DOLOSTONE

Figure 3. Stratigraphic column for the tributary study area. After Dillard, 1977 and CoE, 1945.

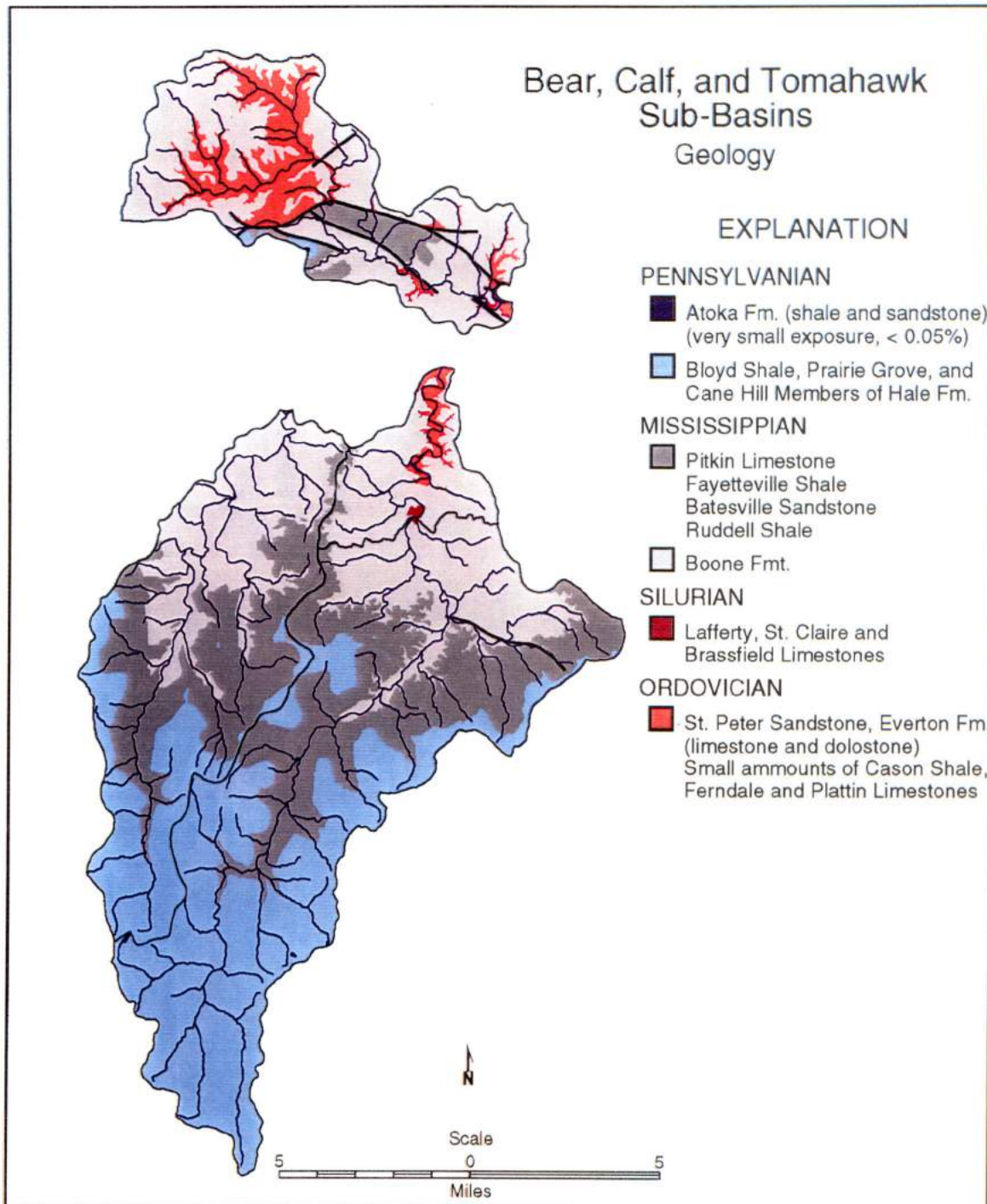


Figure 4. Geologic map of the tributary sub-basins.

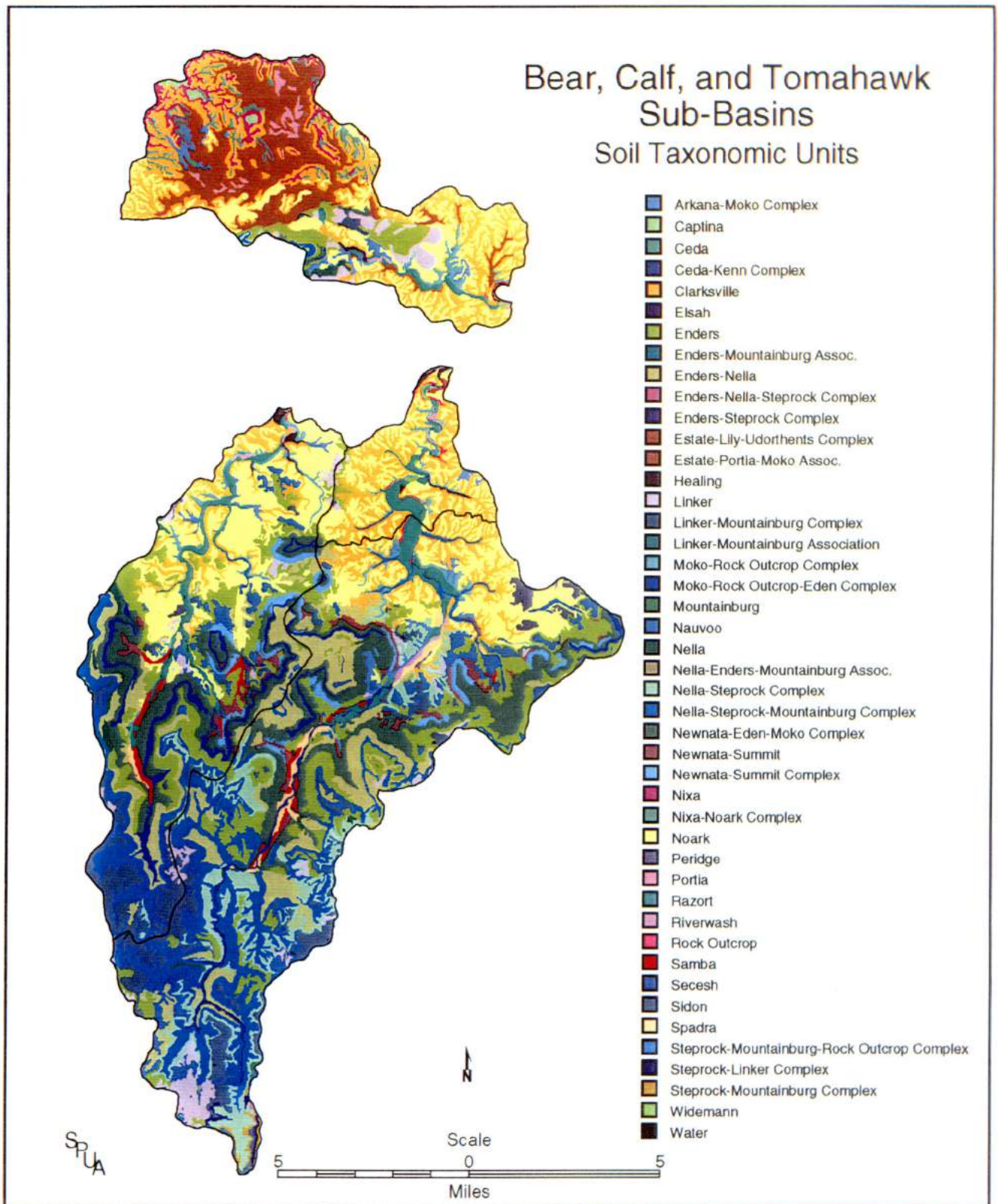


Figure 5. Soil series map for the tributary sub-basins.

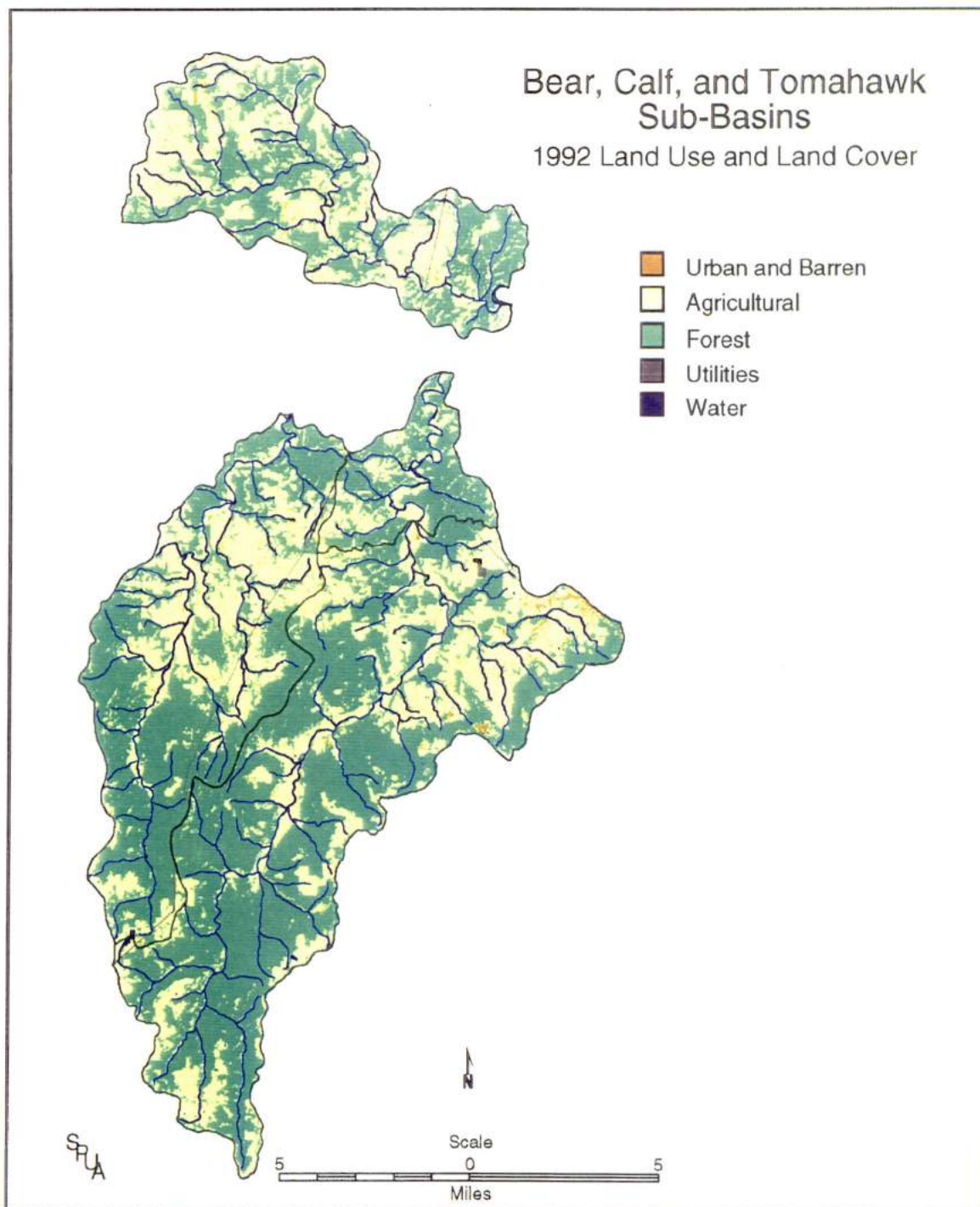


Figure 6. Land use and land cover of the tributary sub-basins in 1992.

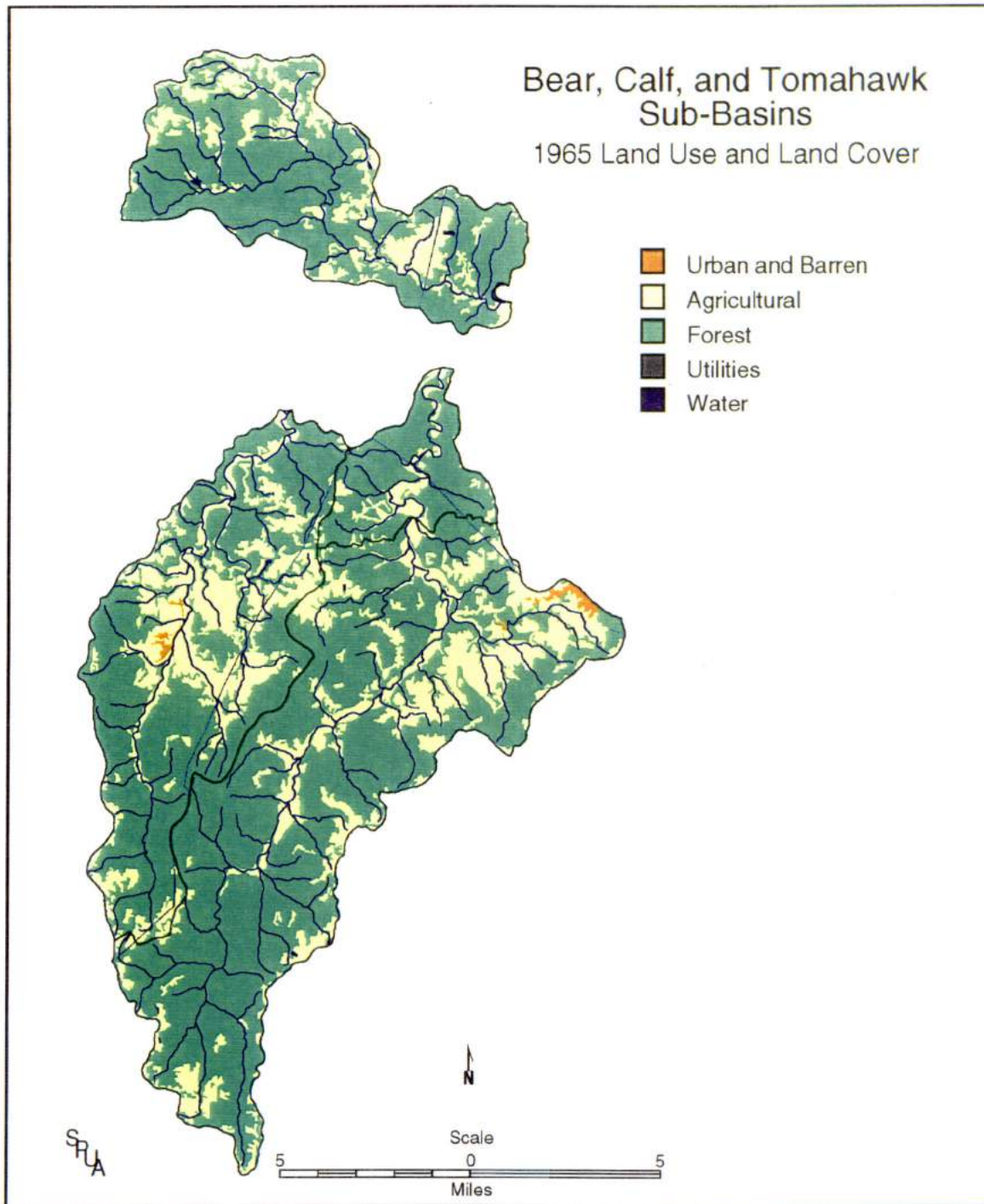


Figure 7. Land use and land cover of the tributary sub-basins in 1965.

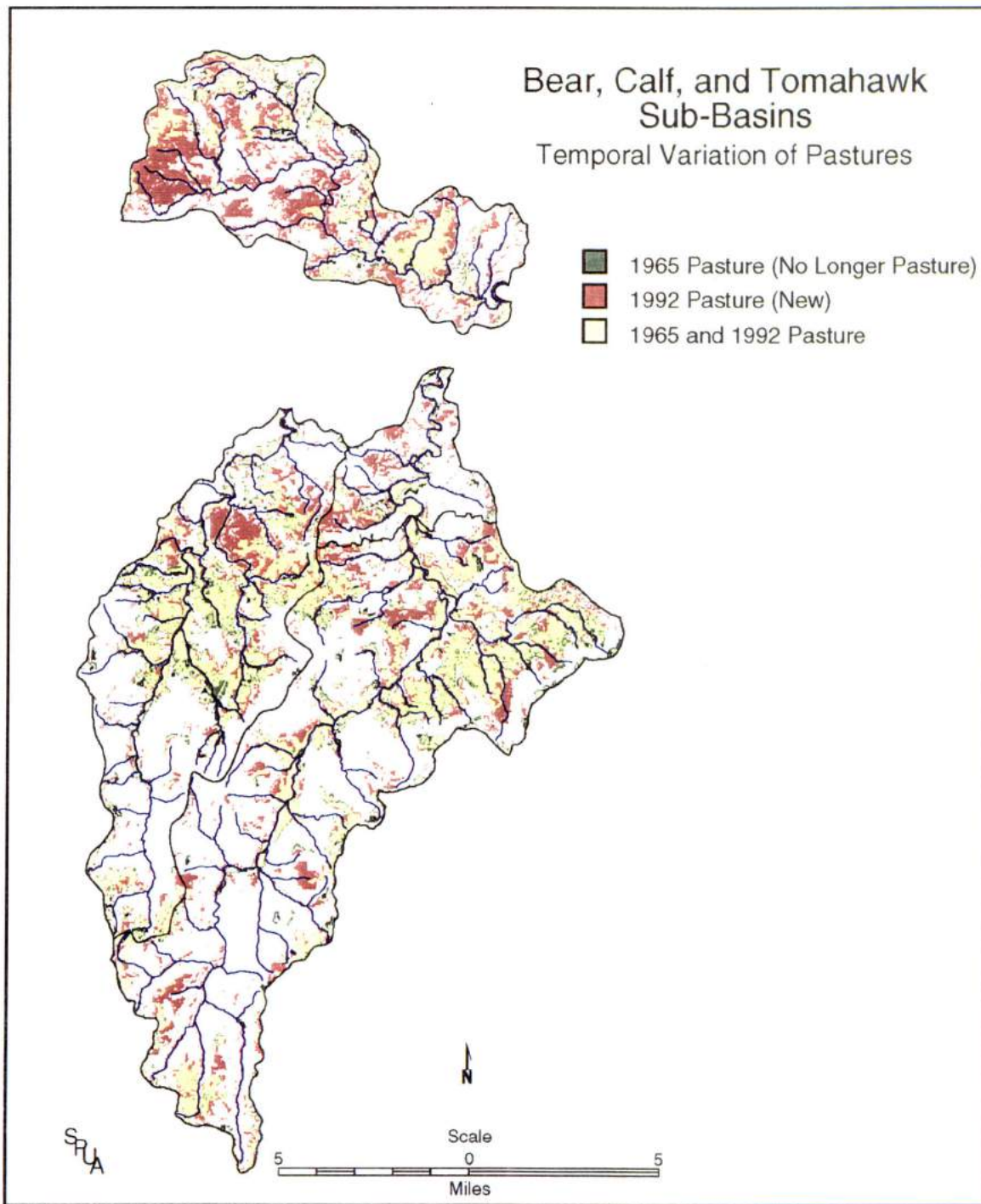


Figure 8. Pasture acres gained and lost from 1965 to 1992 and acres used as pastures in 1965 and 1992.

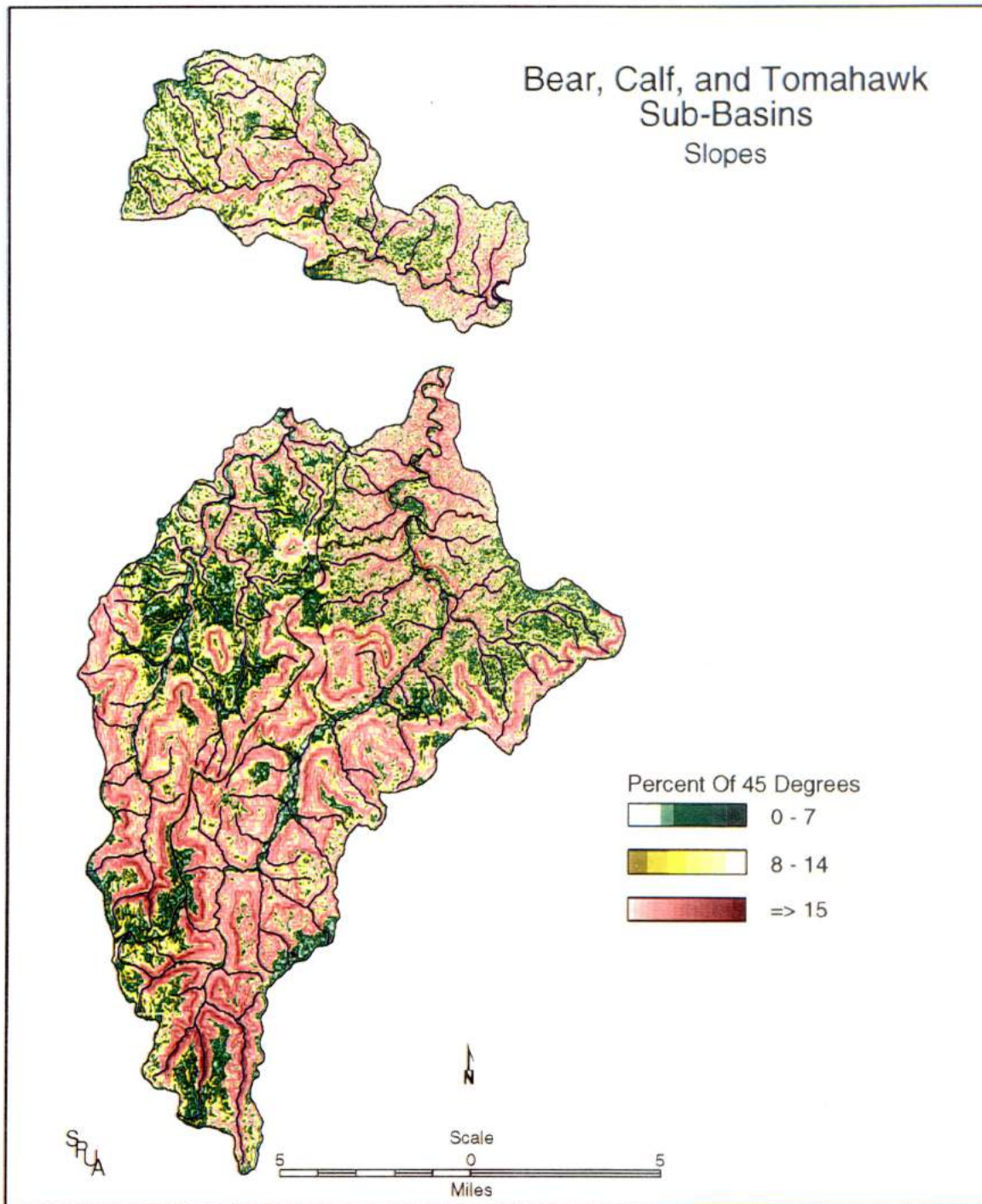


Figure 9. Percent slope of land surface of the tributary sub-basins.

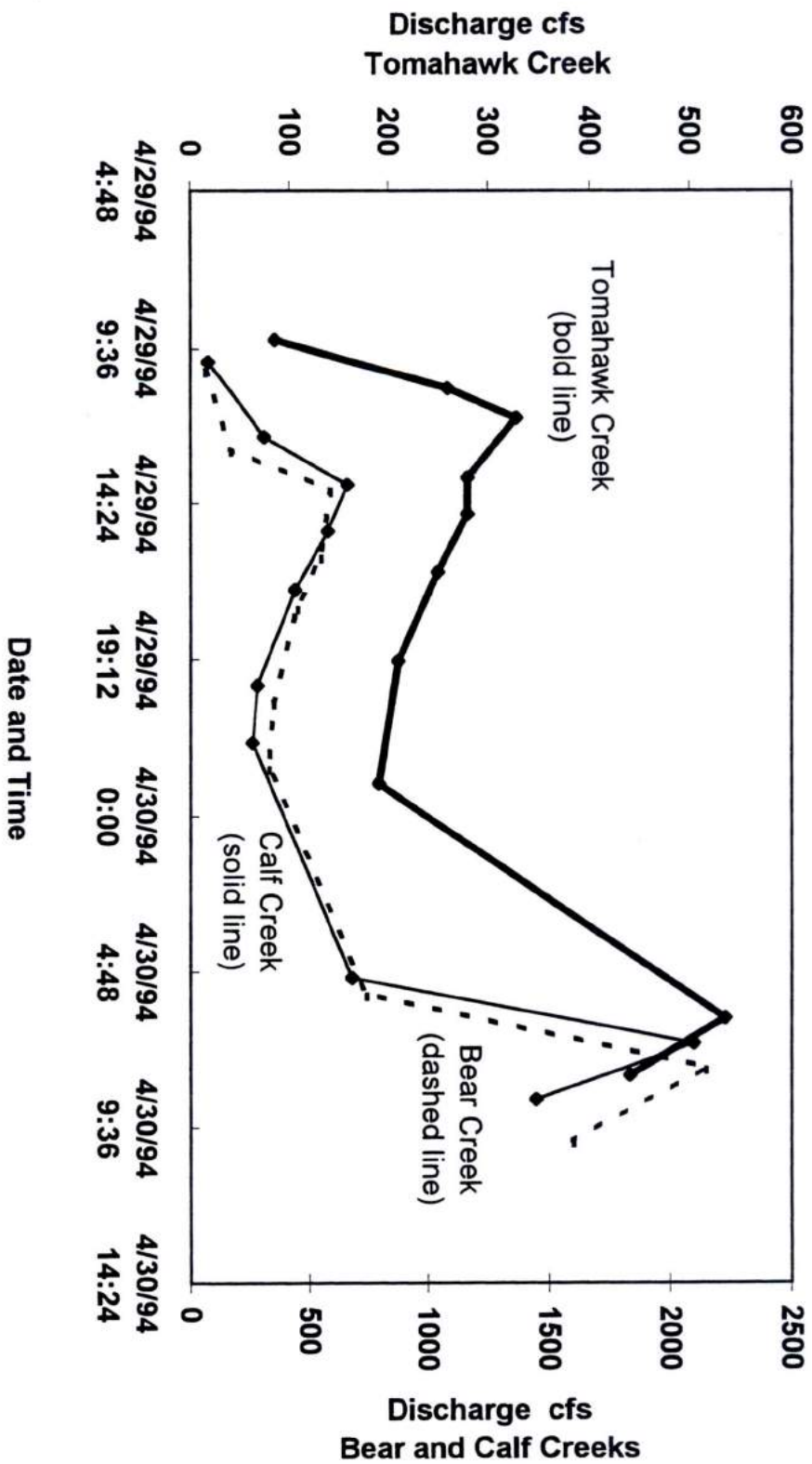


Figure 10. Discharge versus time for the tributaries during the April storm.



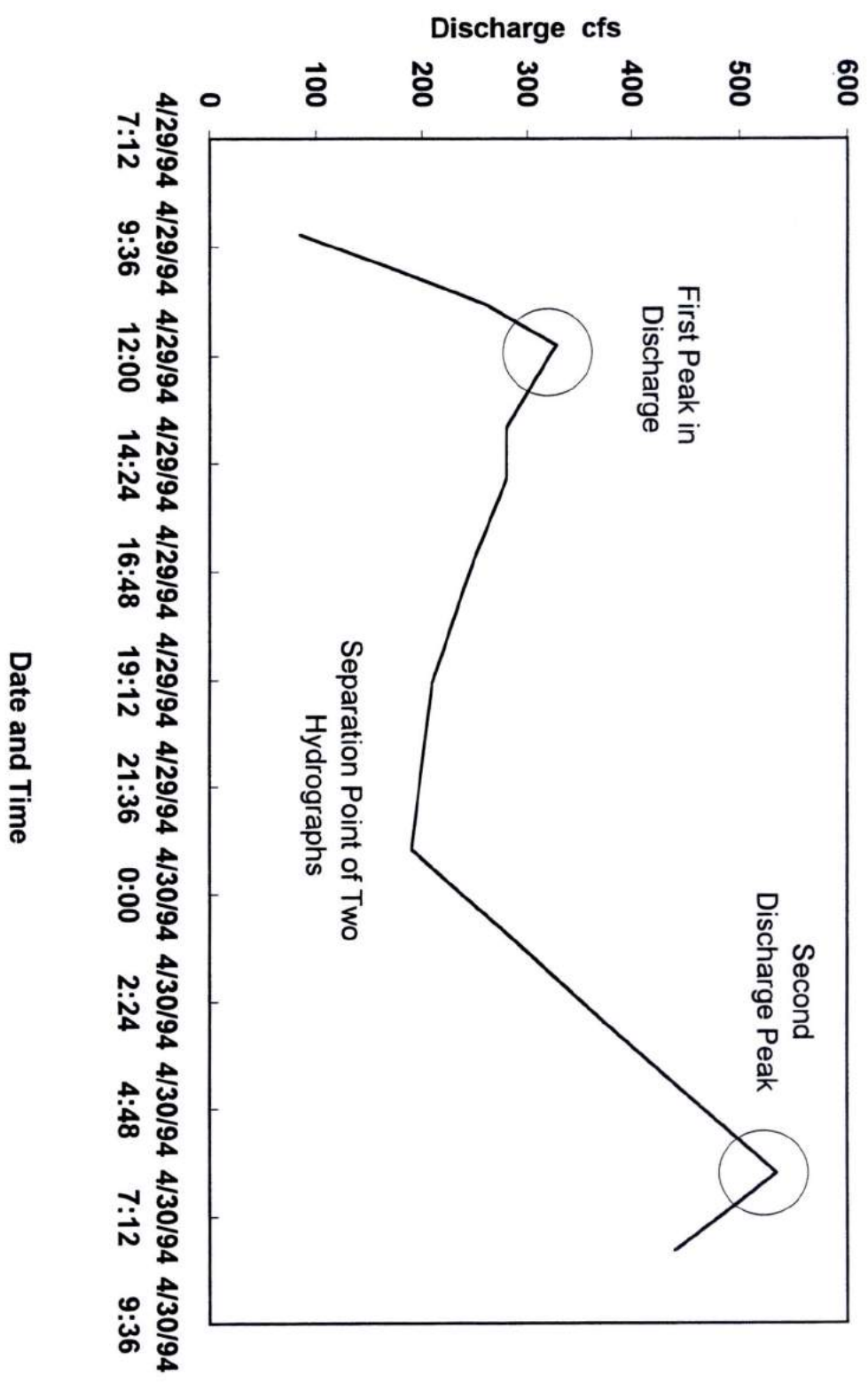


Figure 11. Discharge versus time for Tomahawk Creek during the April storm.

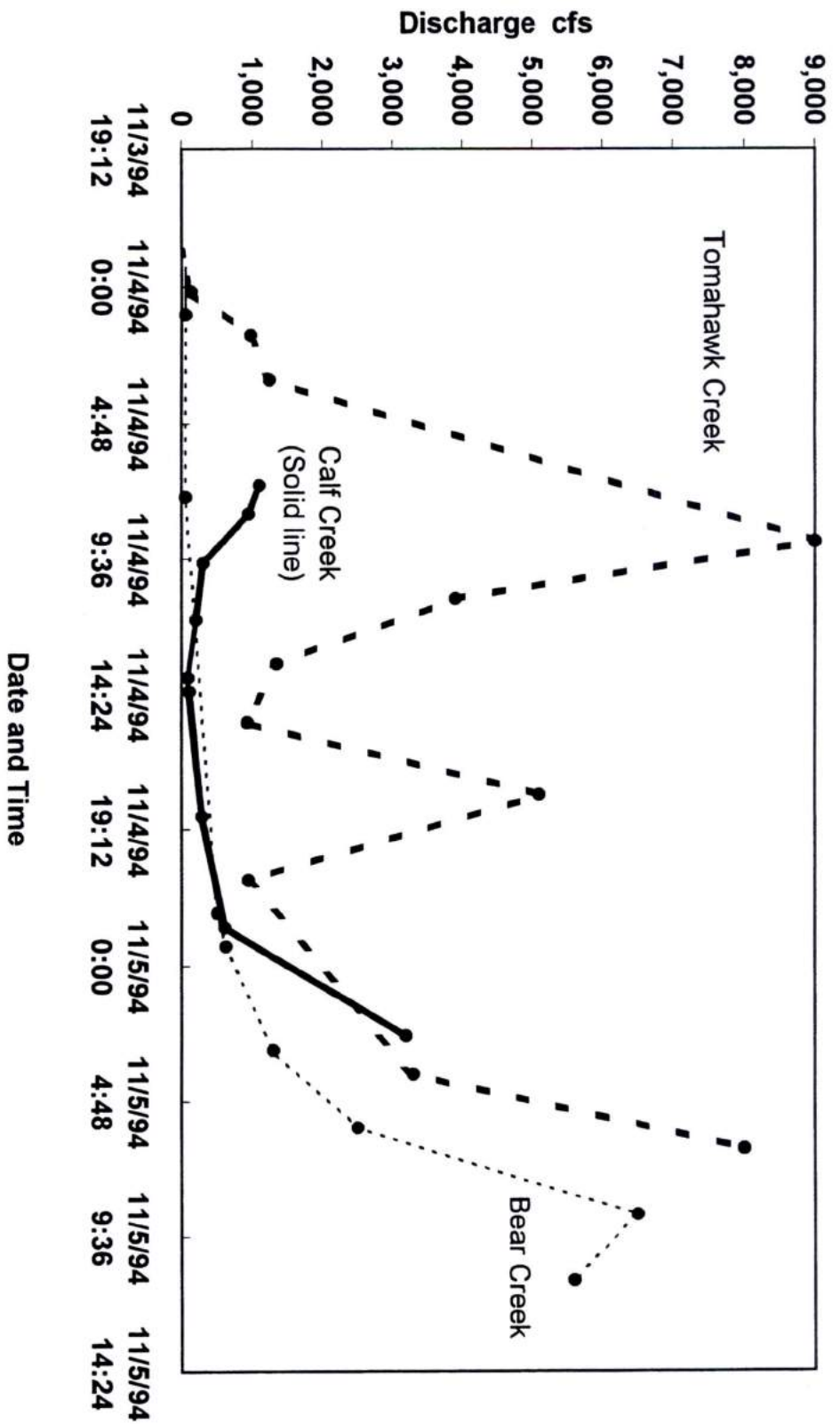


Figure 12. Discharge versus time for the tributaries during the November storm.

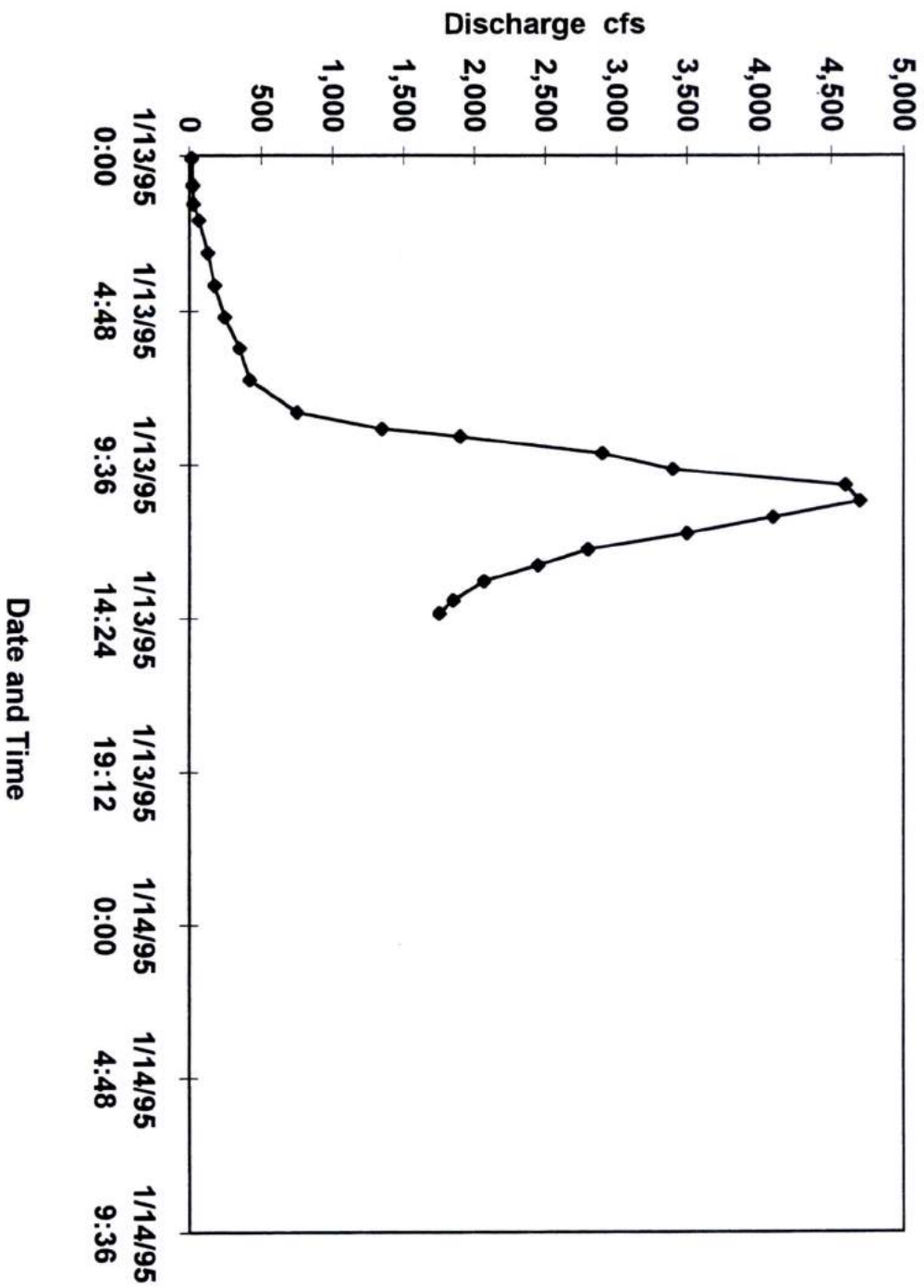


Figure 13. Discharge versus time for Tomahawk during the January storm.

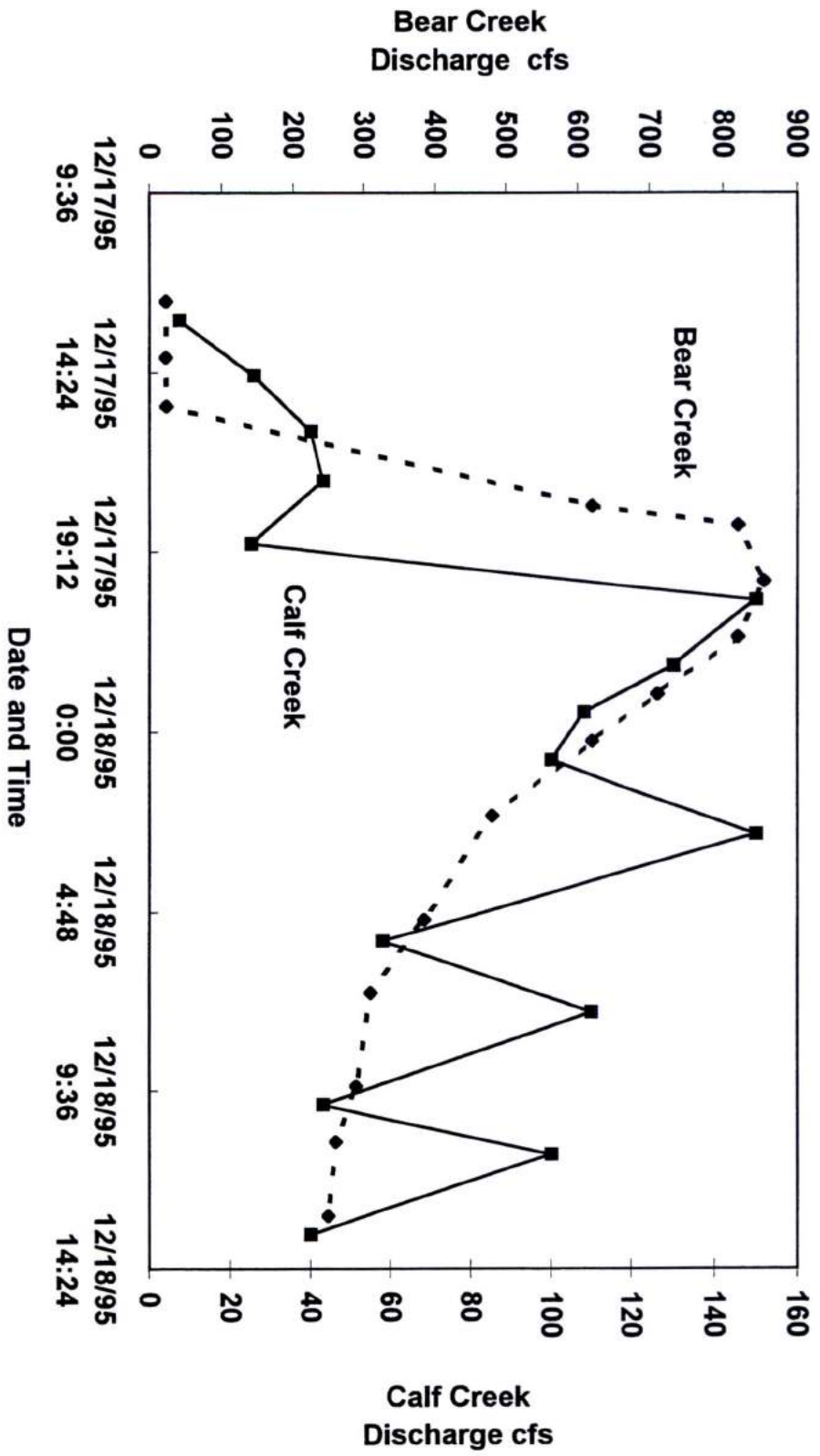


Figure 14. Discharge versus time for Bear and Calf creeks during the December storm.

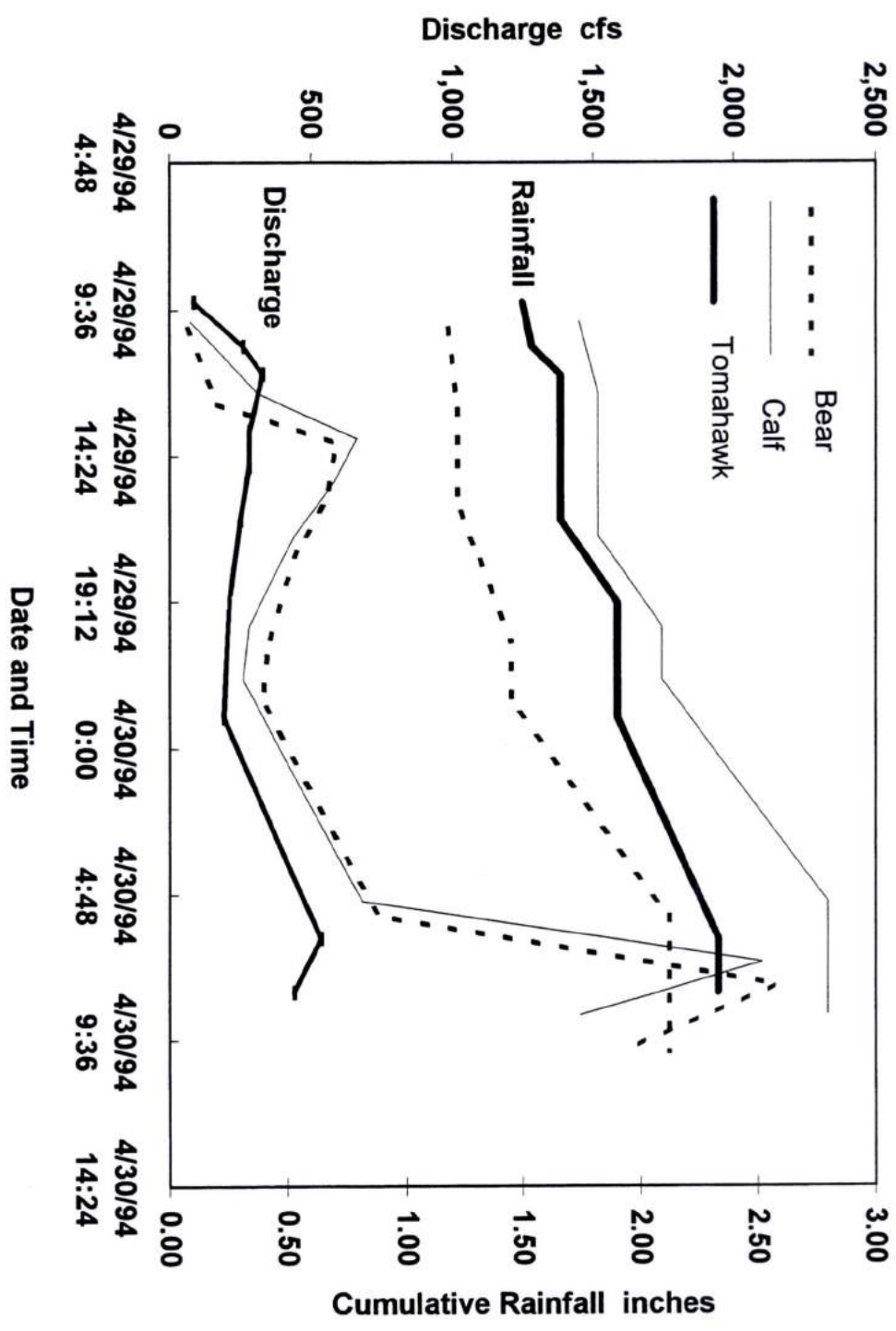


Figure 15. Discharge and cumulative rainfall versus time for the tributaries during the April storm.

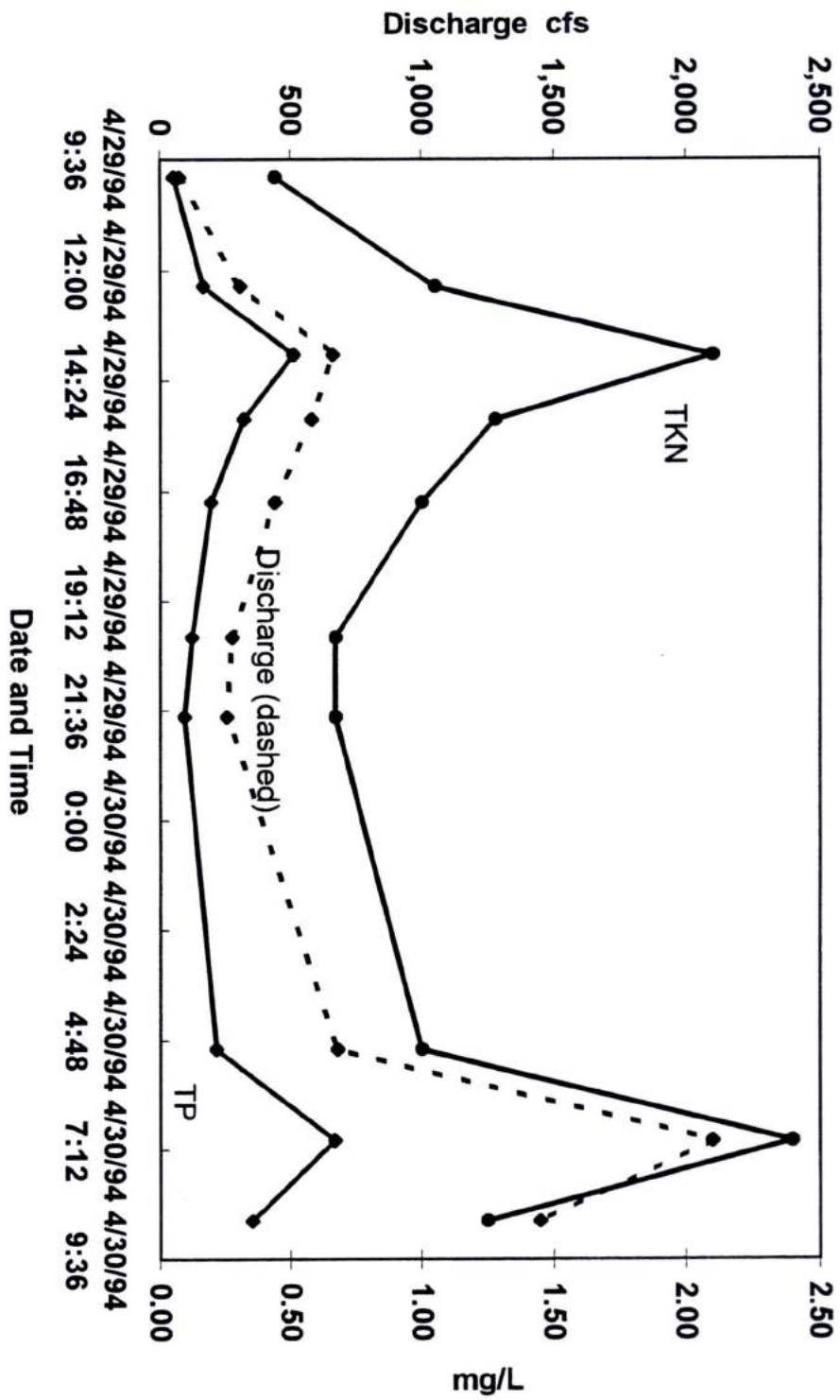


Figure 16. Discharge, TKN and total phosphorus versus time for Calf Creek during the April storm.

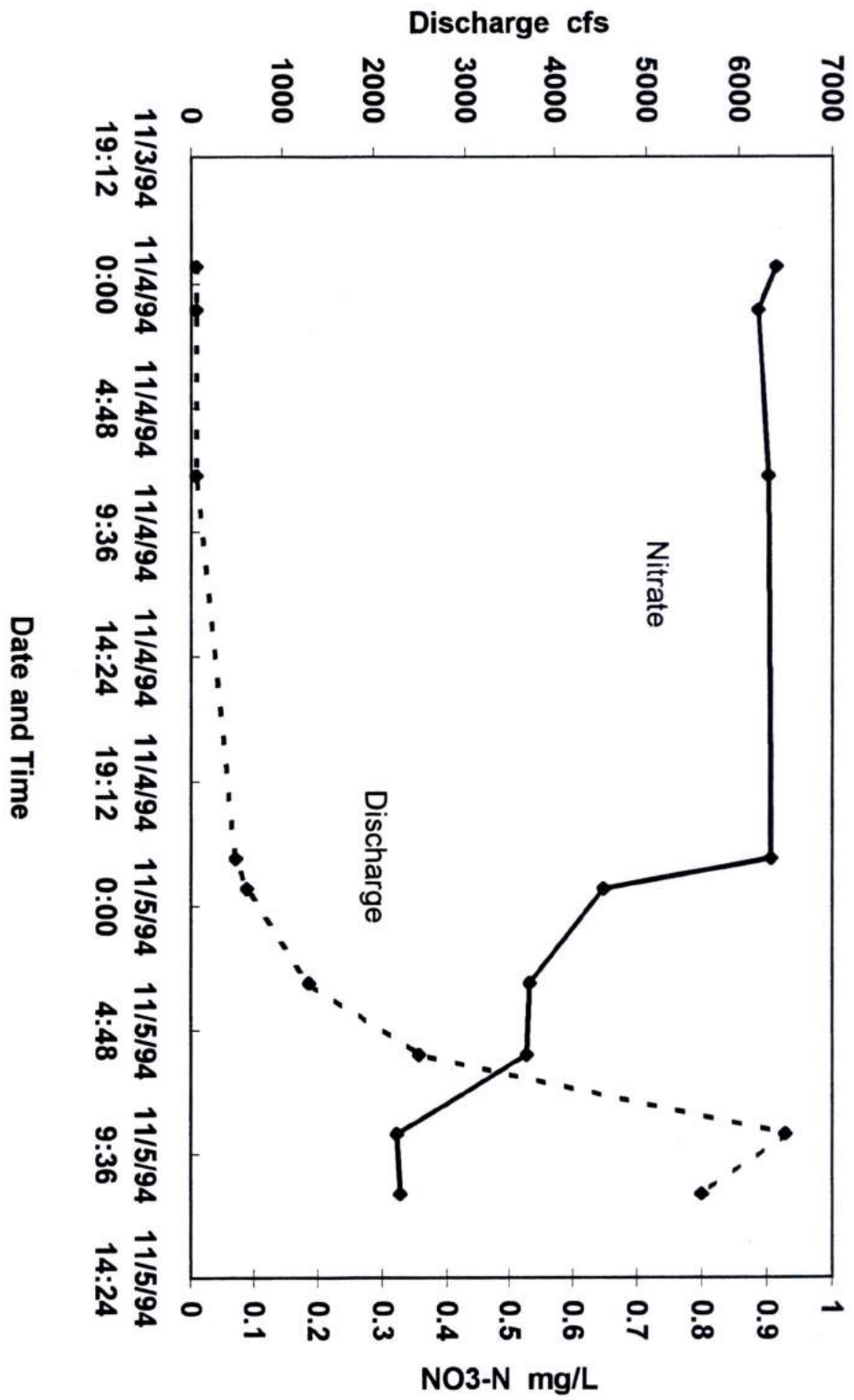


Figure 17. Discharge and nitrate versus time for Bear Creek during the November storm.

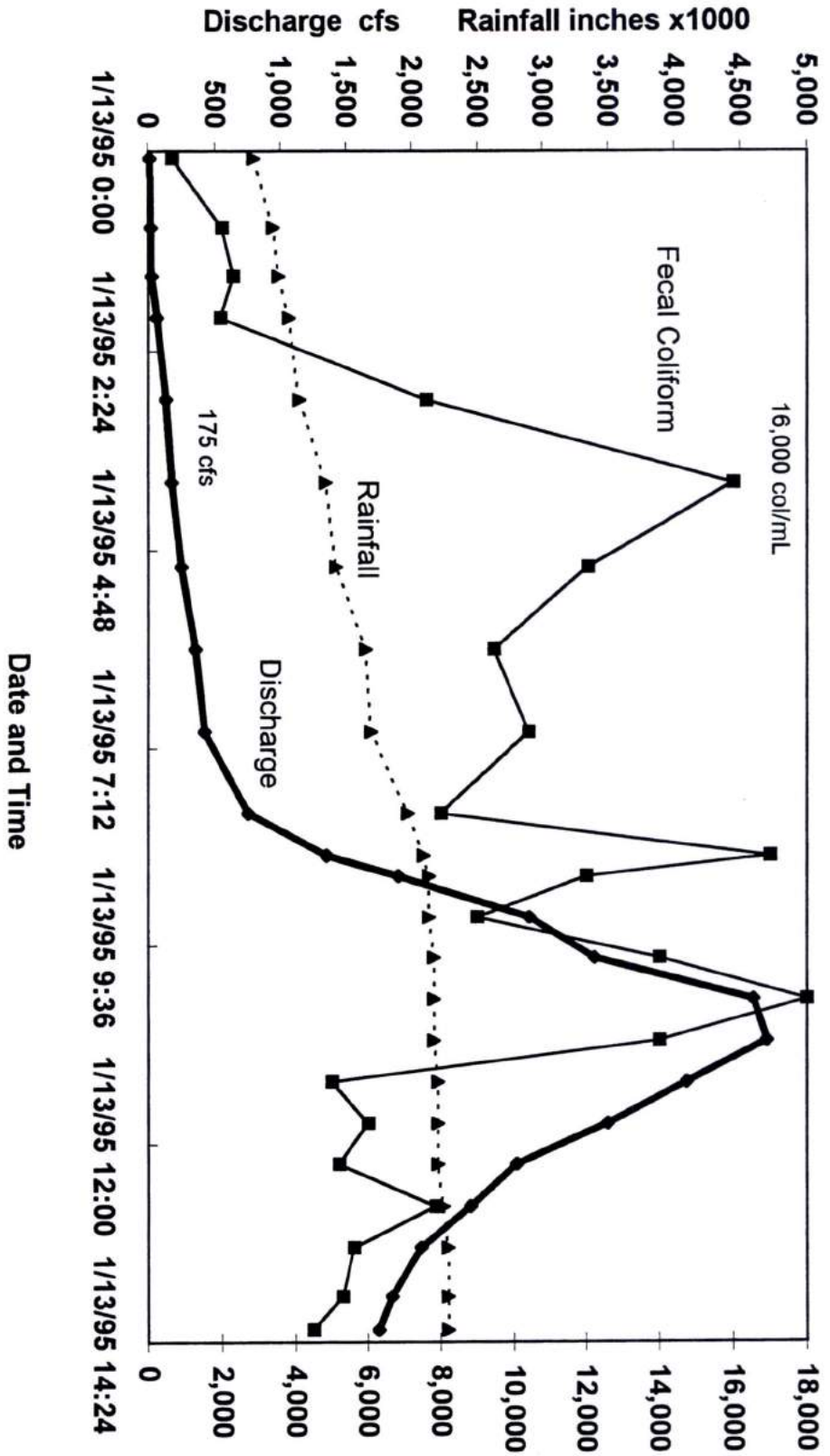


Figure 18. Discharge, fecal coliform and cumulative rainfall versus time for Tomahawk Creek during the January storm.



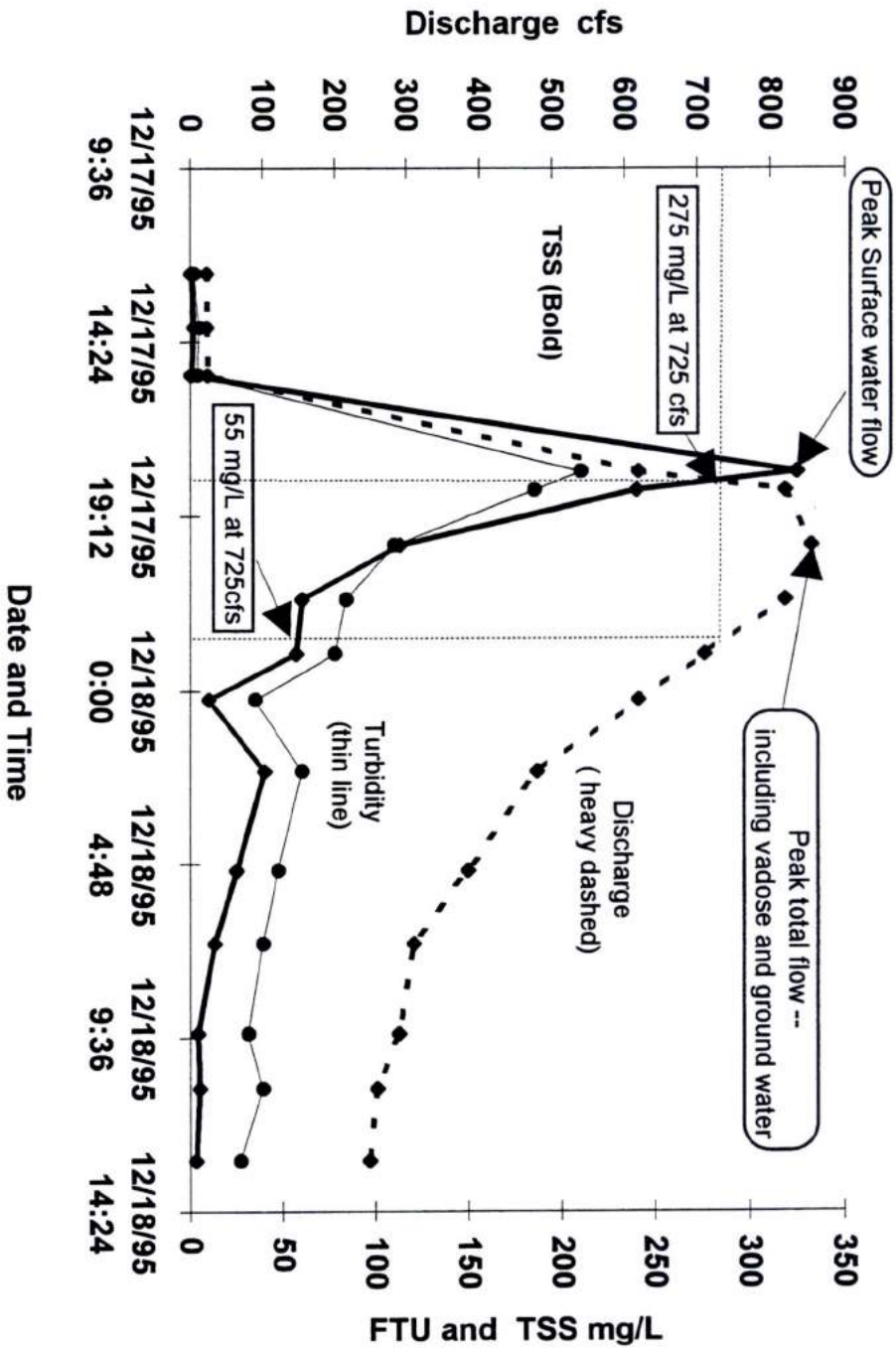


Figure 19. Discharge, TSS and turbidity versus time for Bear Creek during the December storm.

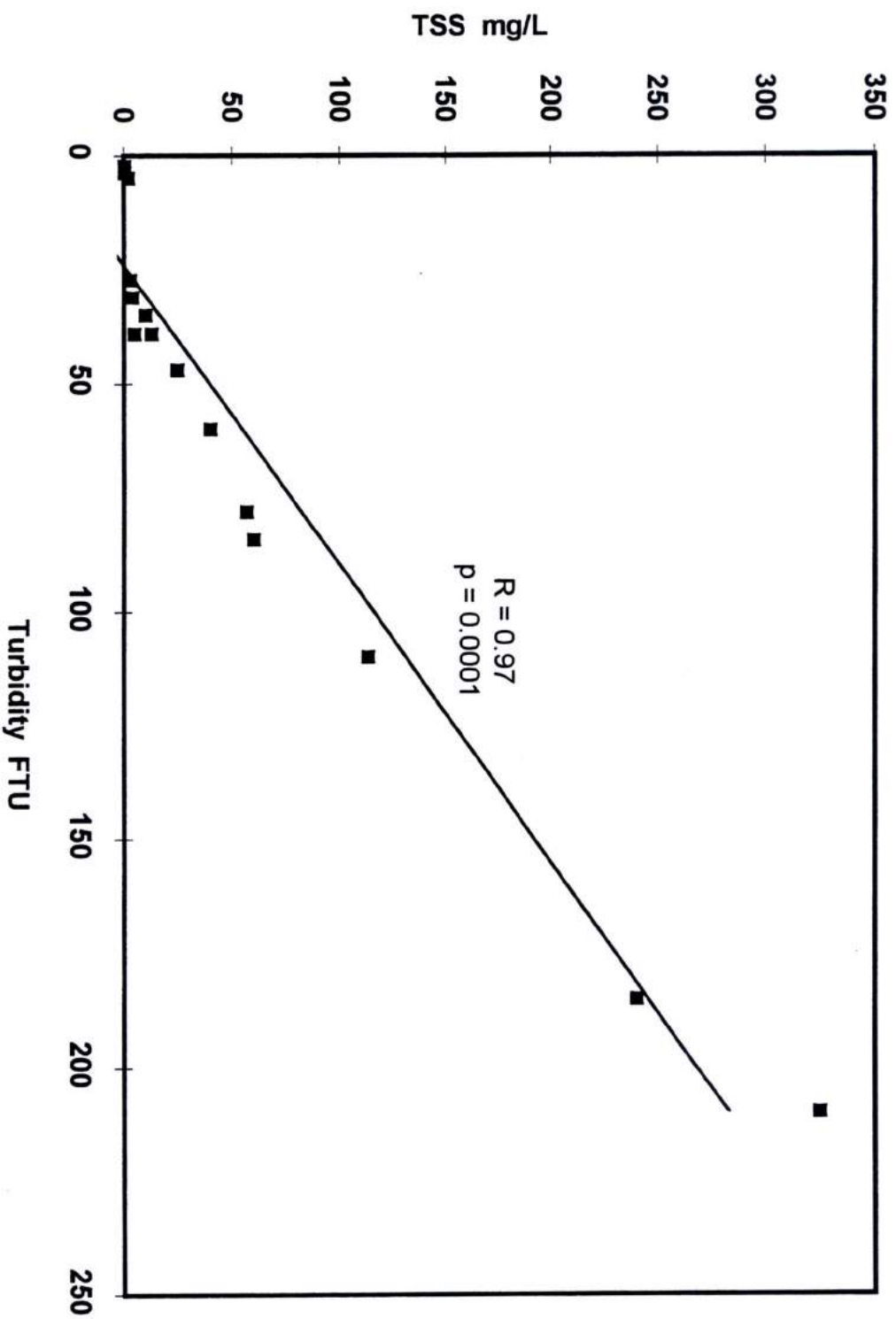


Figure 20. TSS versus turbidity for Bear Creek during the December storm.

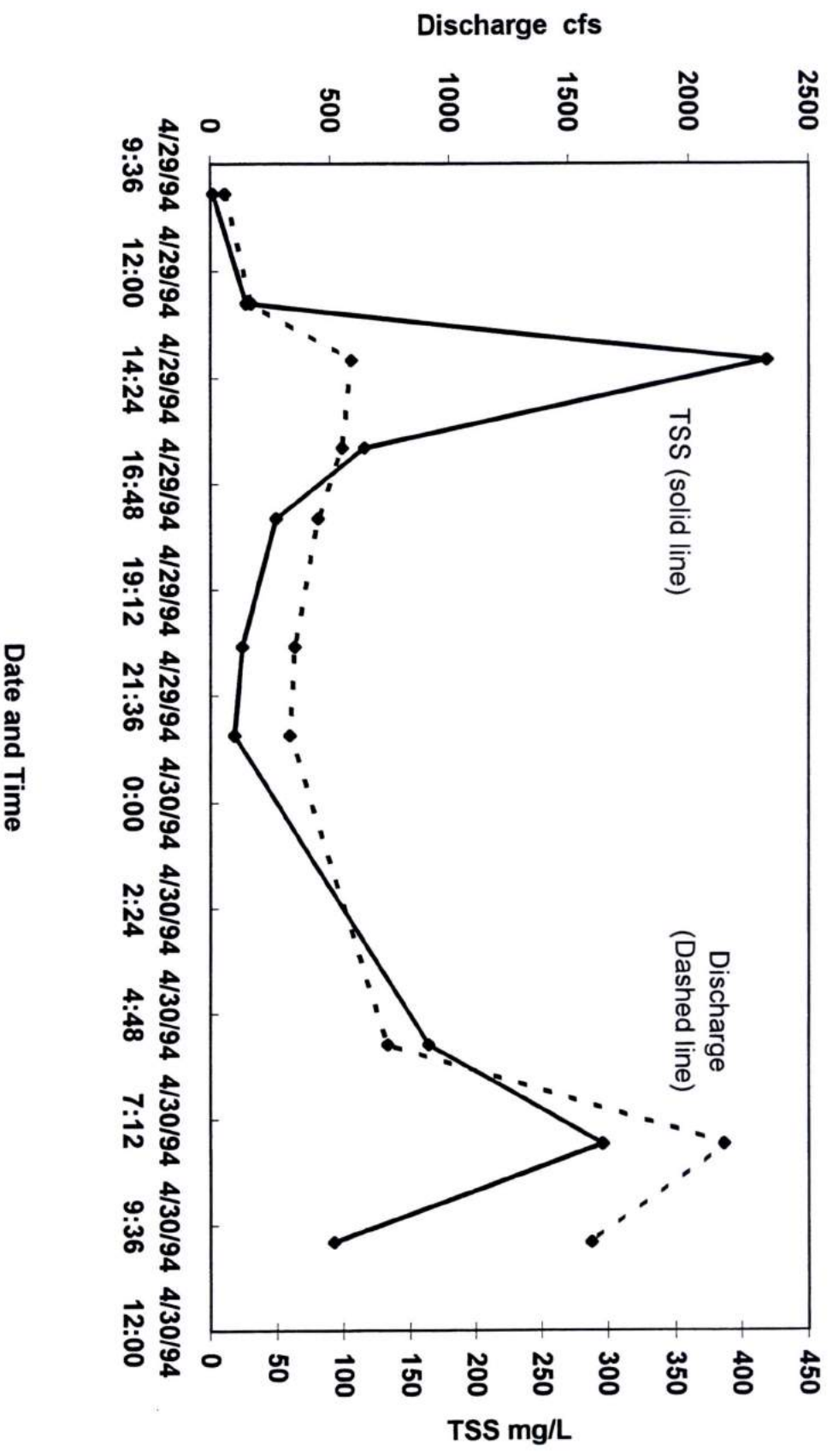


Figure 21. Discharge and TSS versus time for Bear Creek during the April storm.

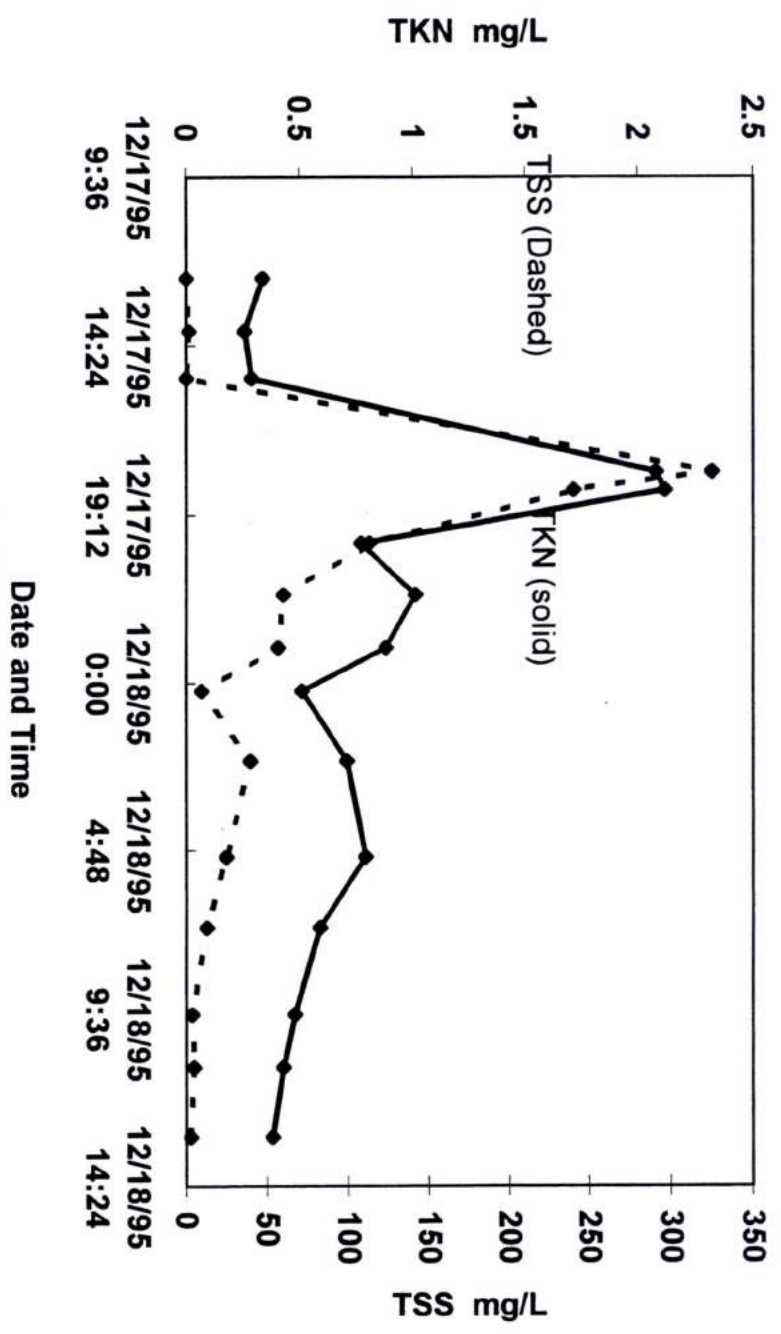


Figure 22. TKN and TSS versus time for Bear Creek during the December storm.

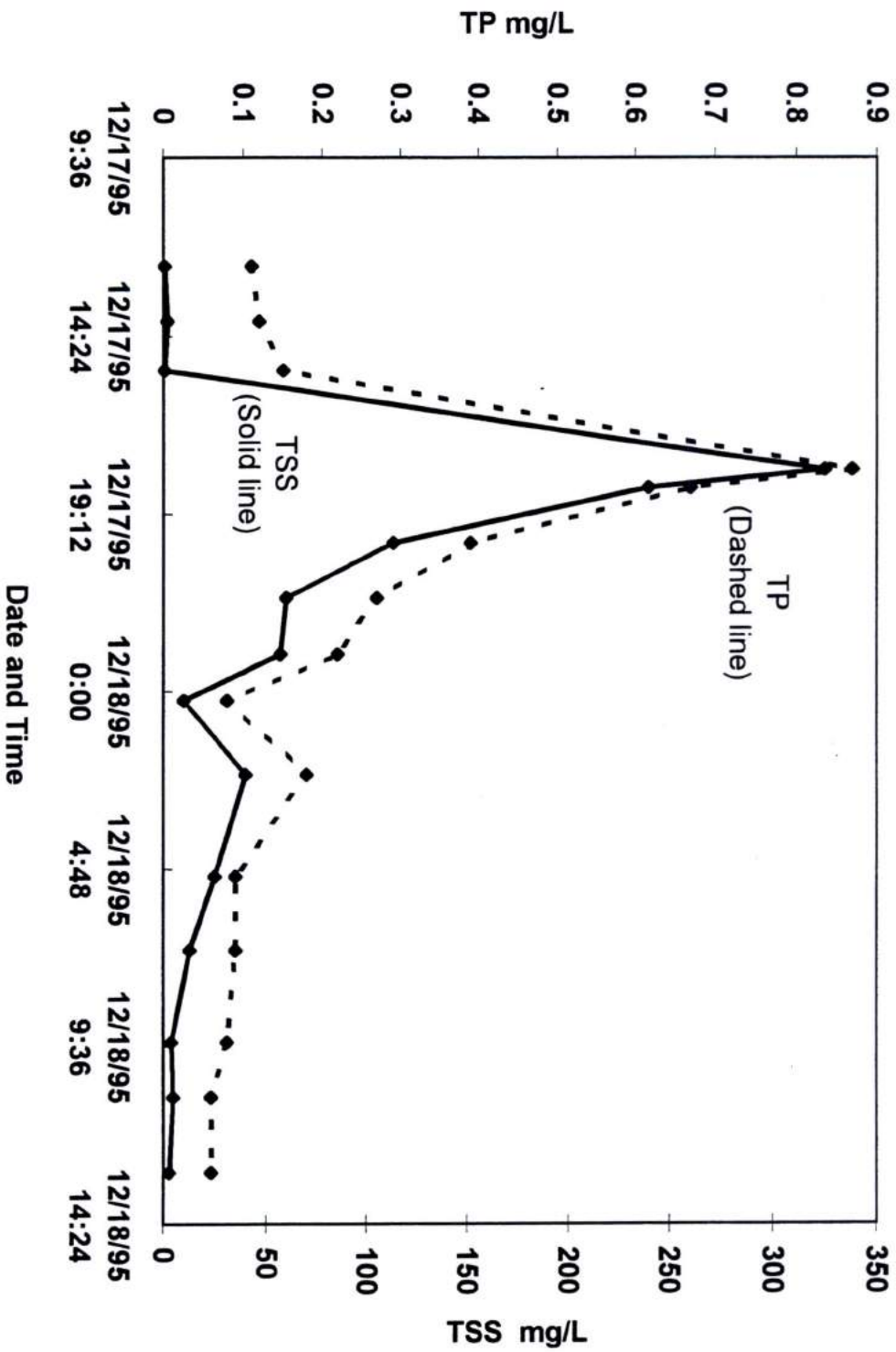


Figure 23. TSS and TP versus time for Bear Creek during the December storm.

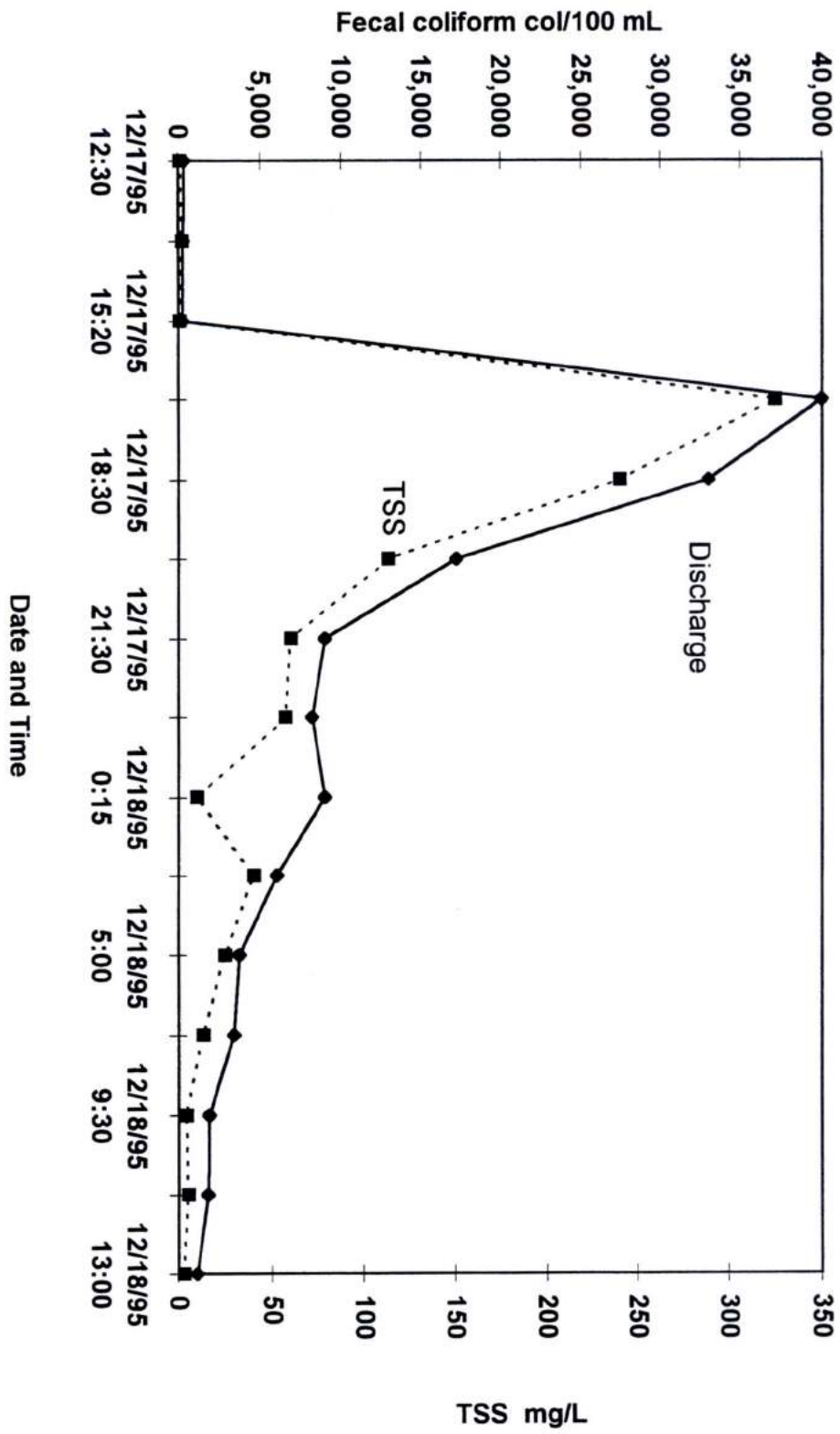


Figure 24. Fecal coliform and TSS versus time for Bear Creek during the December storm.

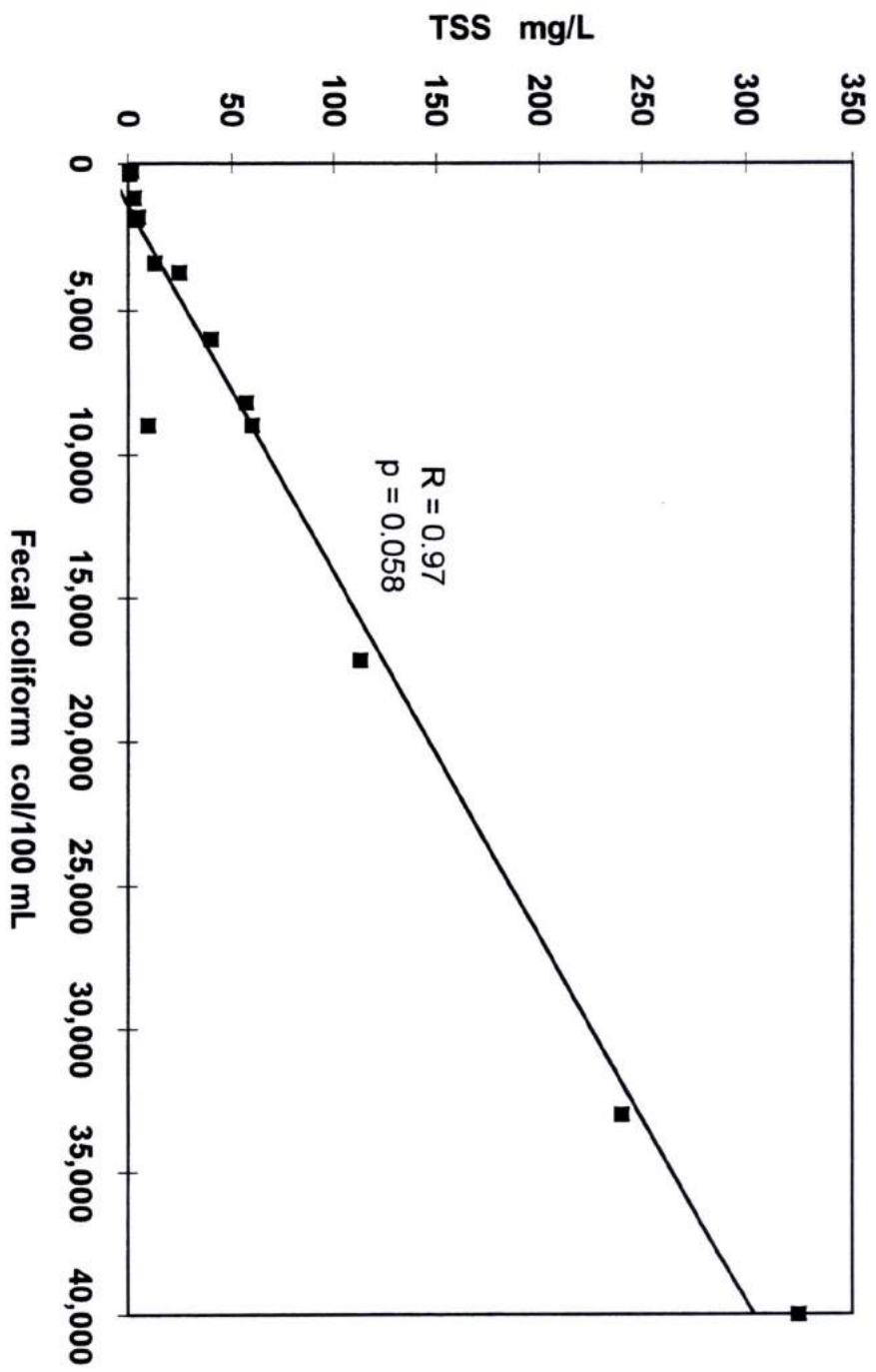


Figure 25. Fecal coliform versus TSS for Bear Creek during the December storm.

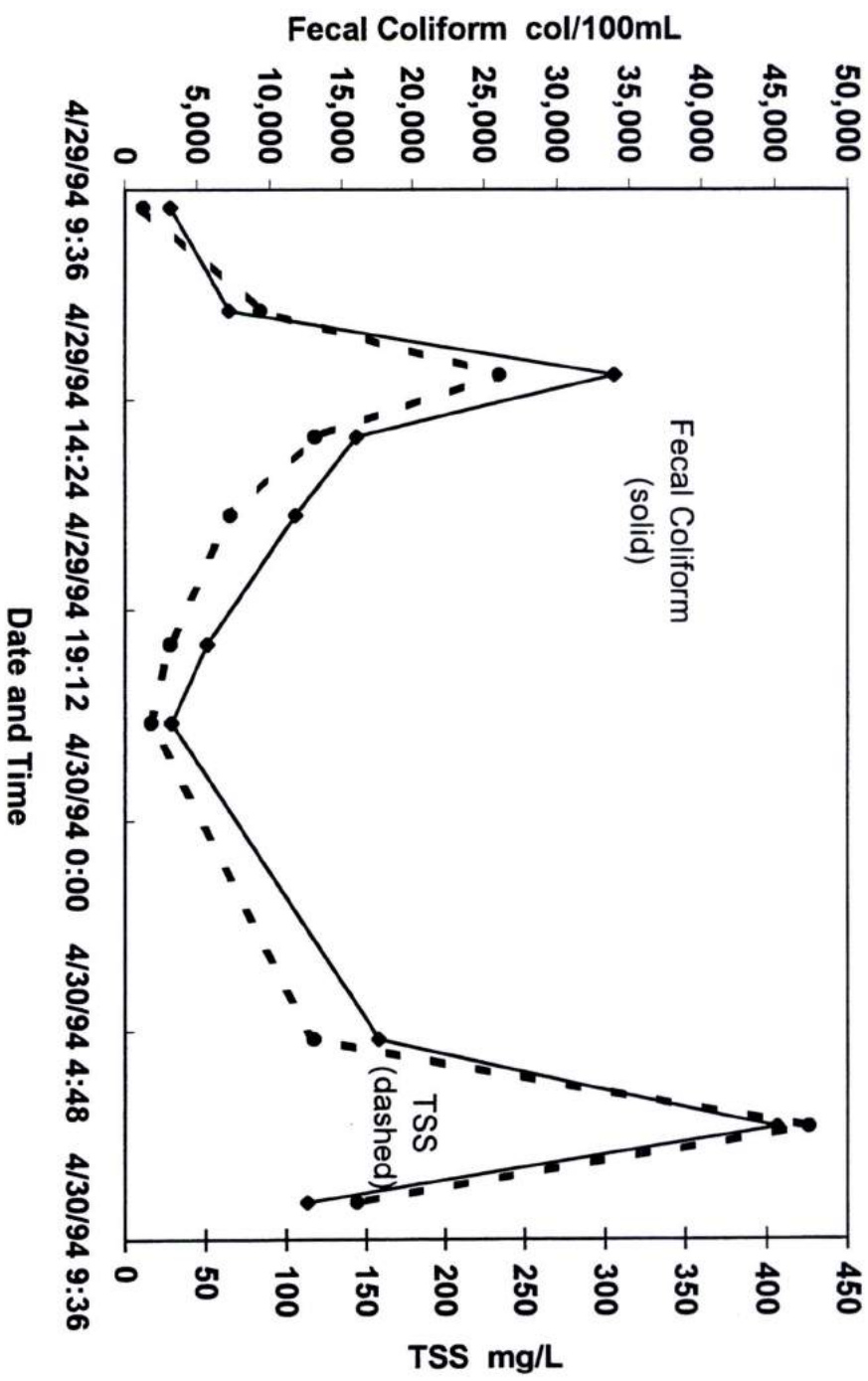


Figure 26. Fecal coliform and TSS versus time for Galf Creek during the April storm.



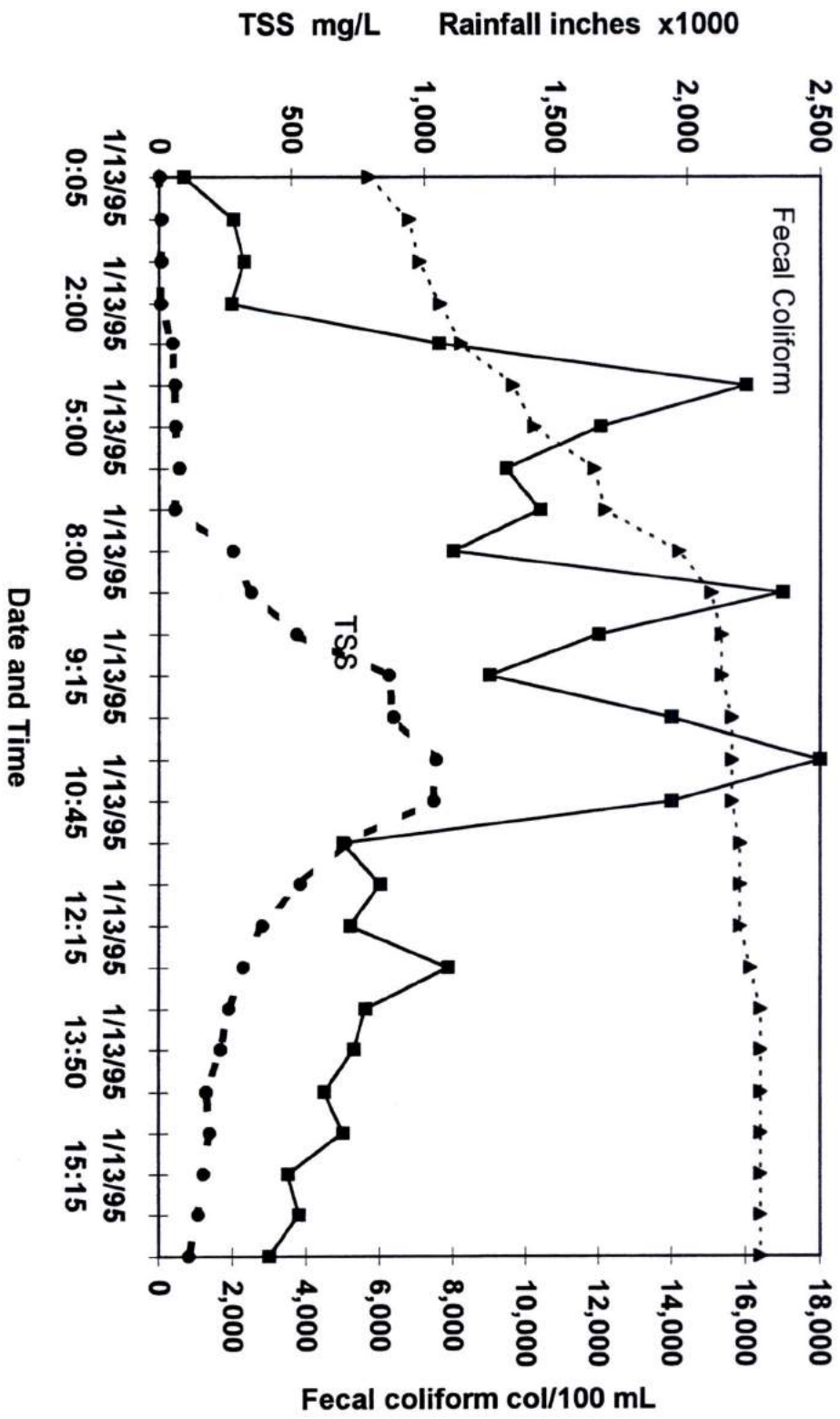


Figure 27. Fecal coliform, TSS and cumulative rainfall versus time for Tomahawk Creek during the January storm.

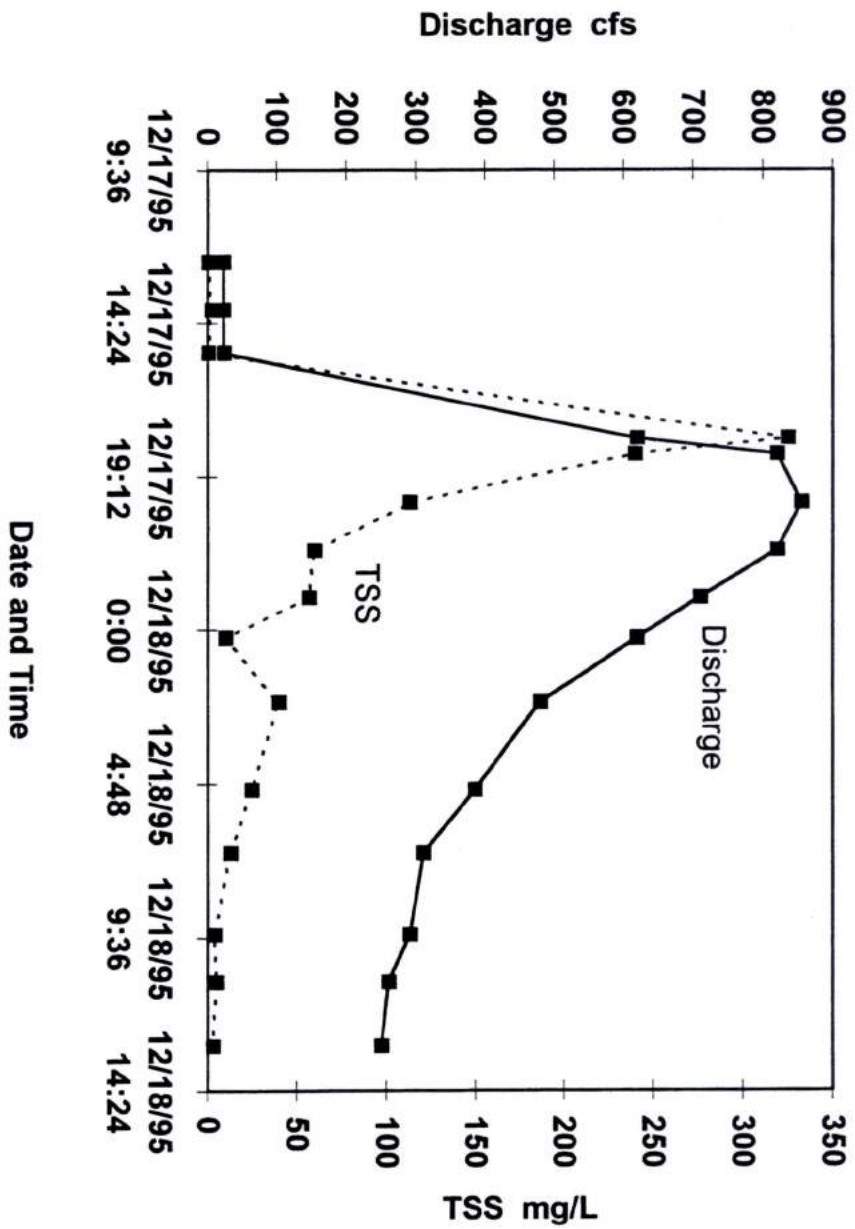


Figure 28. Discharge and TSS versus time for Bear Creek during the December storm.

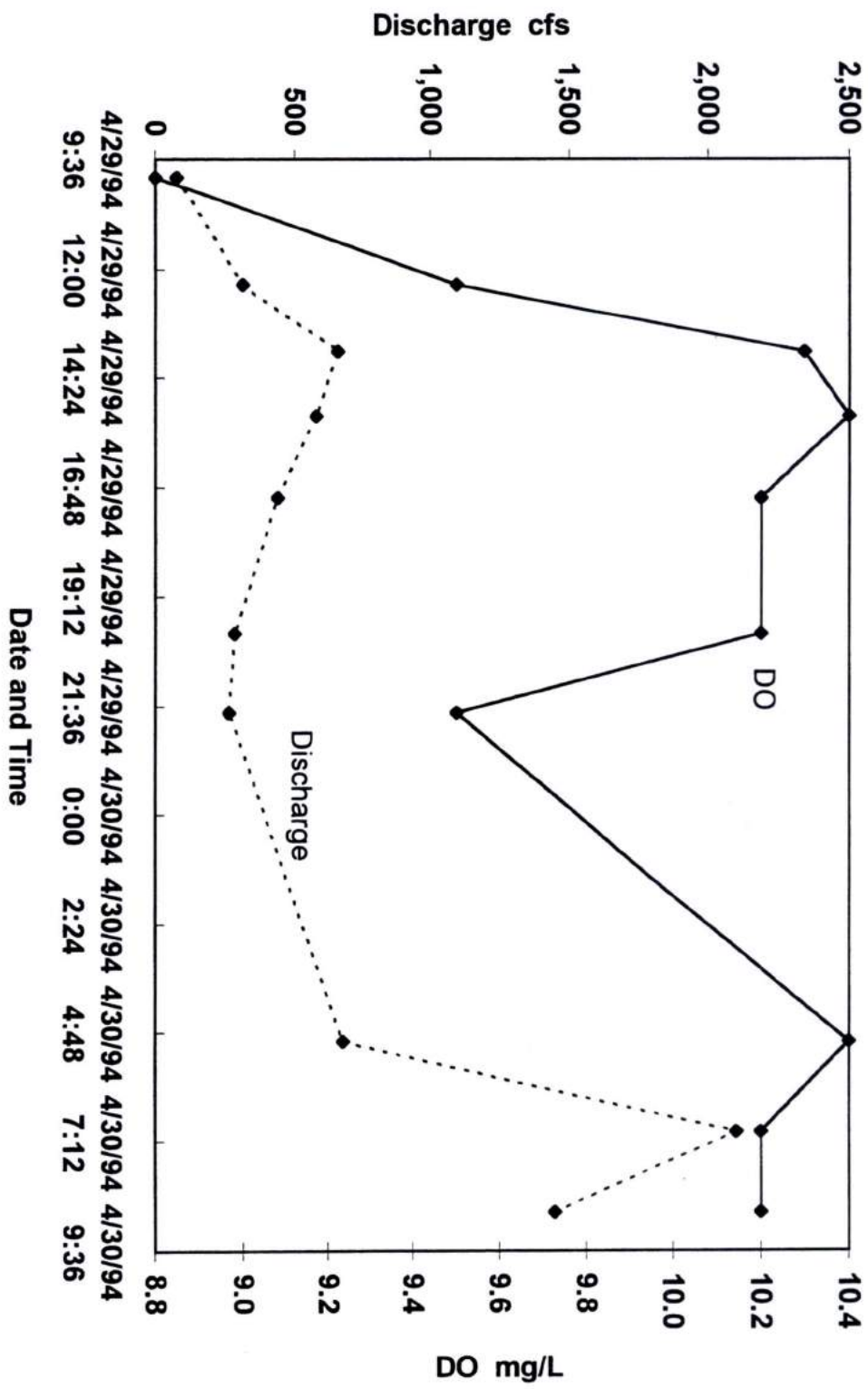


Figure 29. Discharge and dissolved oxygen versus time for Calf Creek during the April storm.

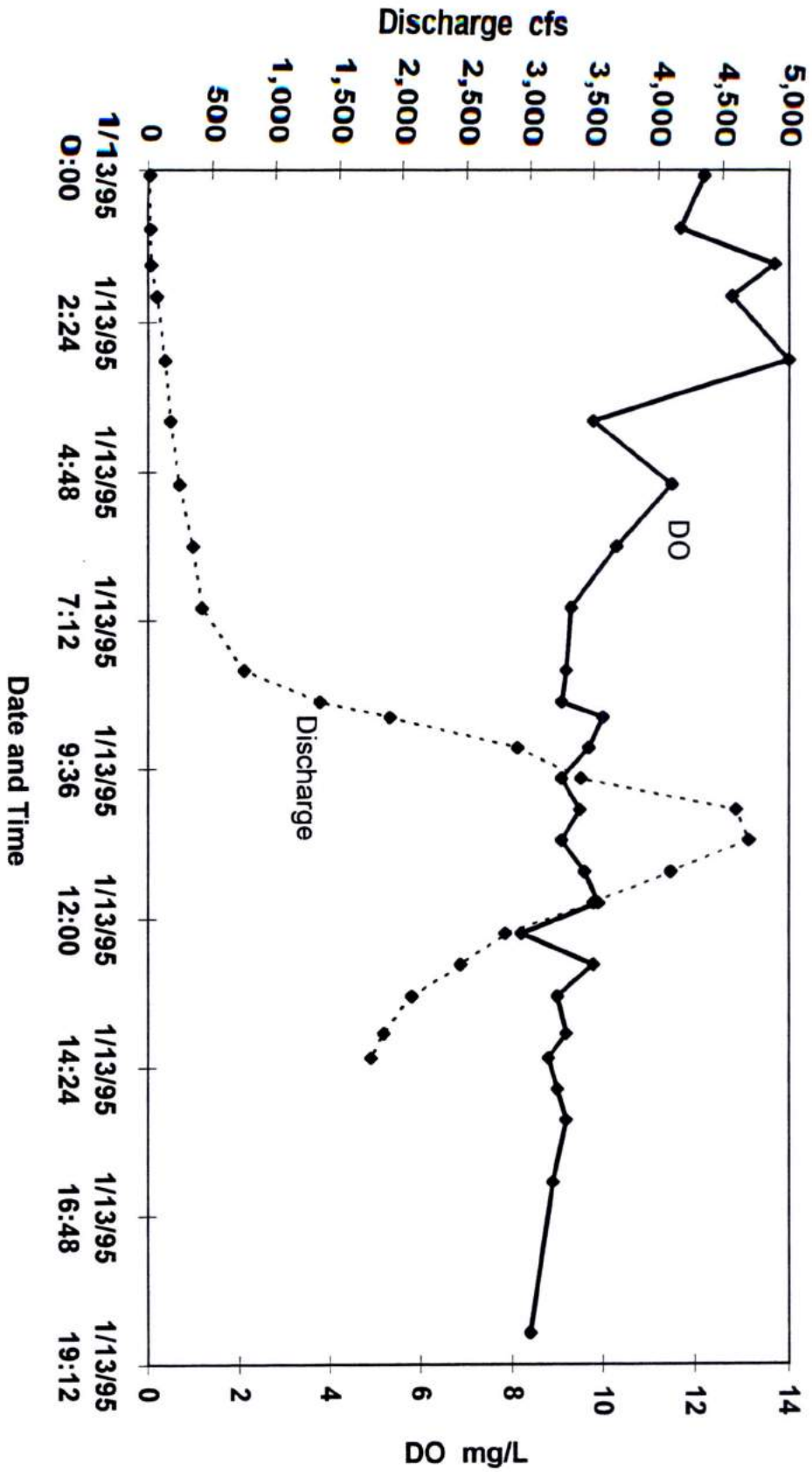


Figure 30. Discharge and dissolved oxygen versus time for Tomahawk Creek during the January storm.

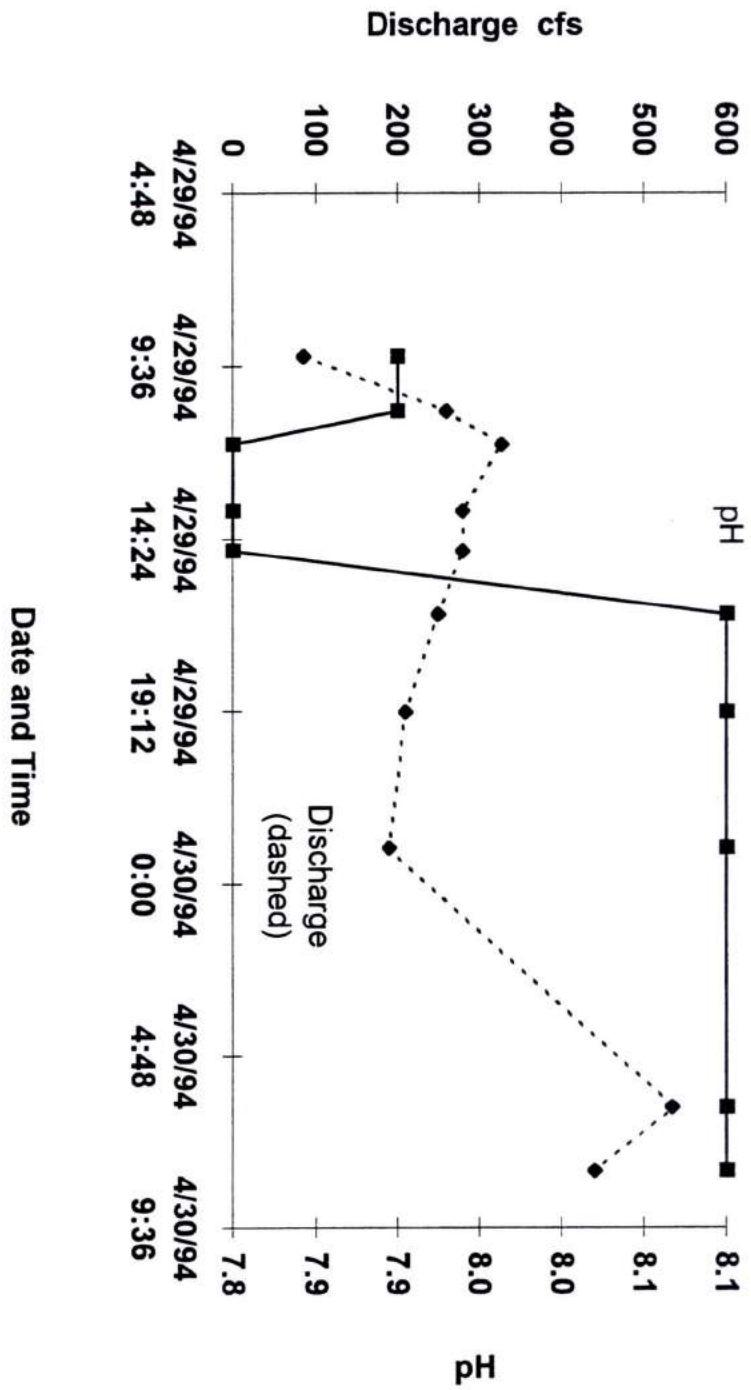


Figure 31. Discharge and pH versus time for Tomahawk Creek during the April storm.

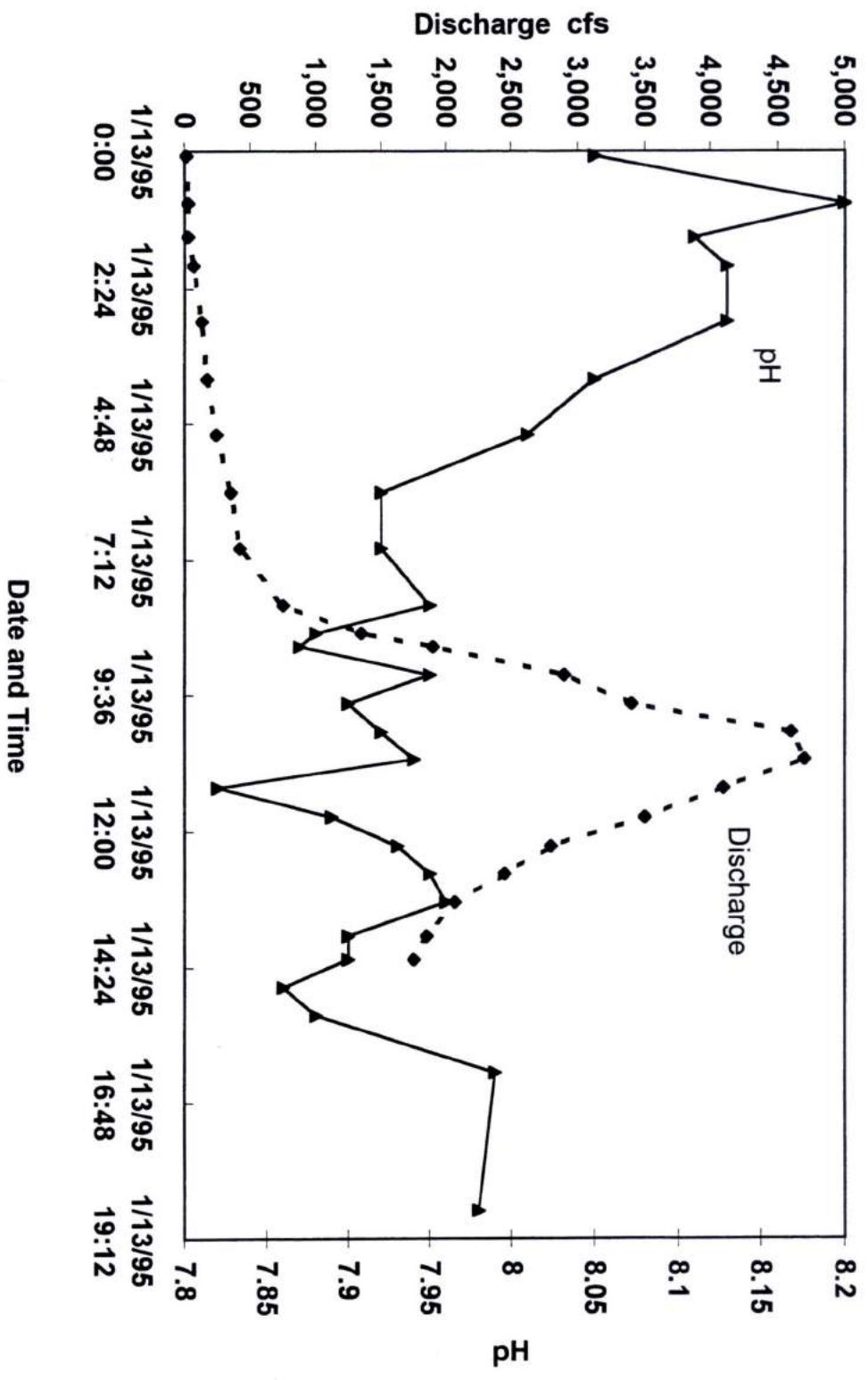


Figure 32. Discharge and pH versus time for Tomahawk Creek during the January storm.

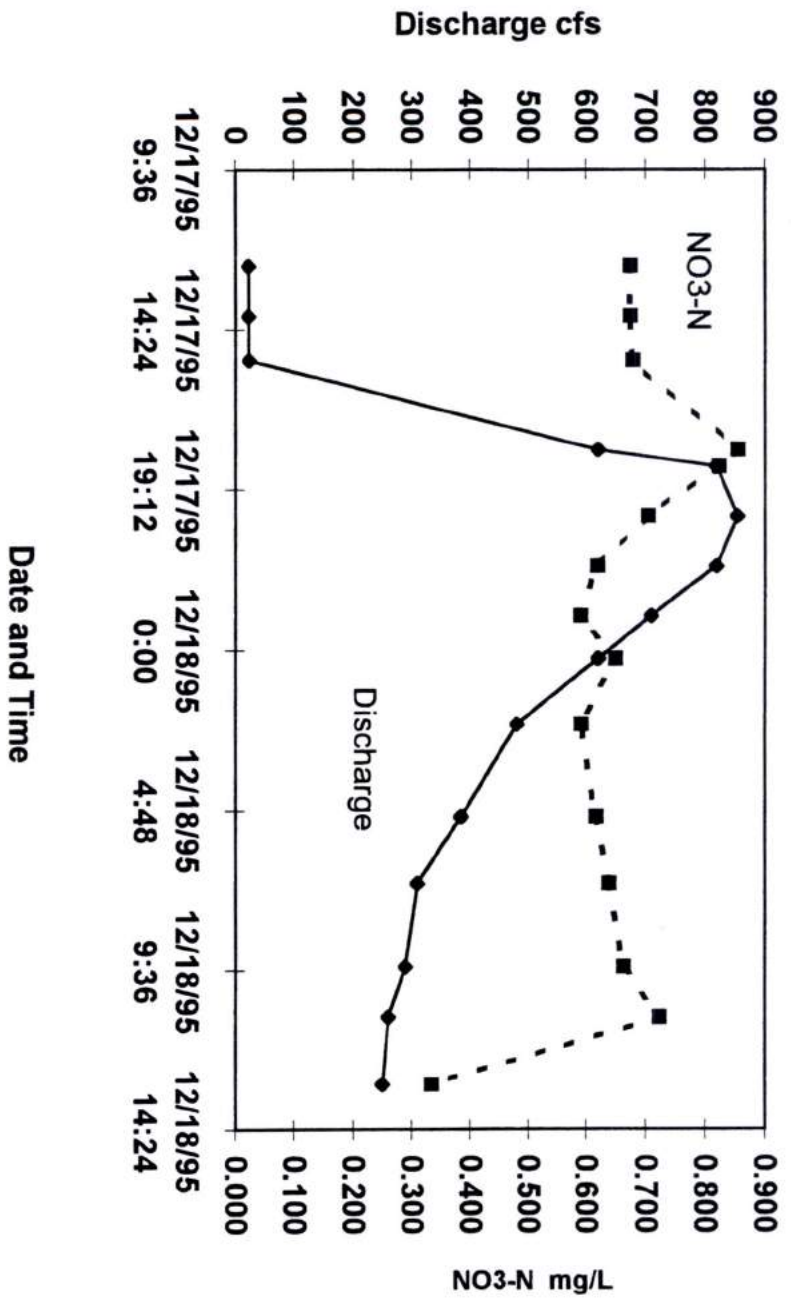


Figure 33. Discharge and nitrate versus time for Bear Creek during the December storm.

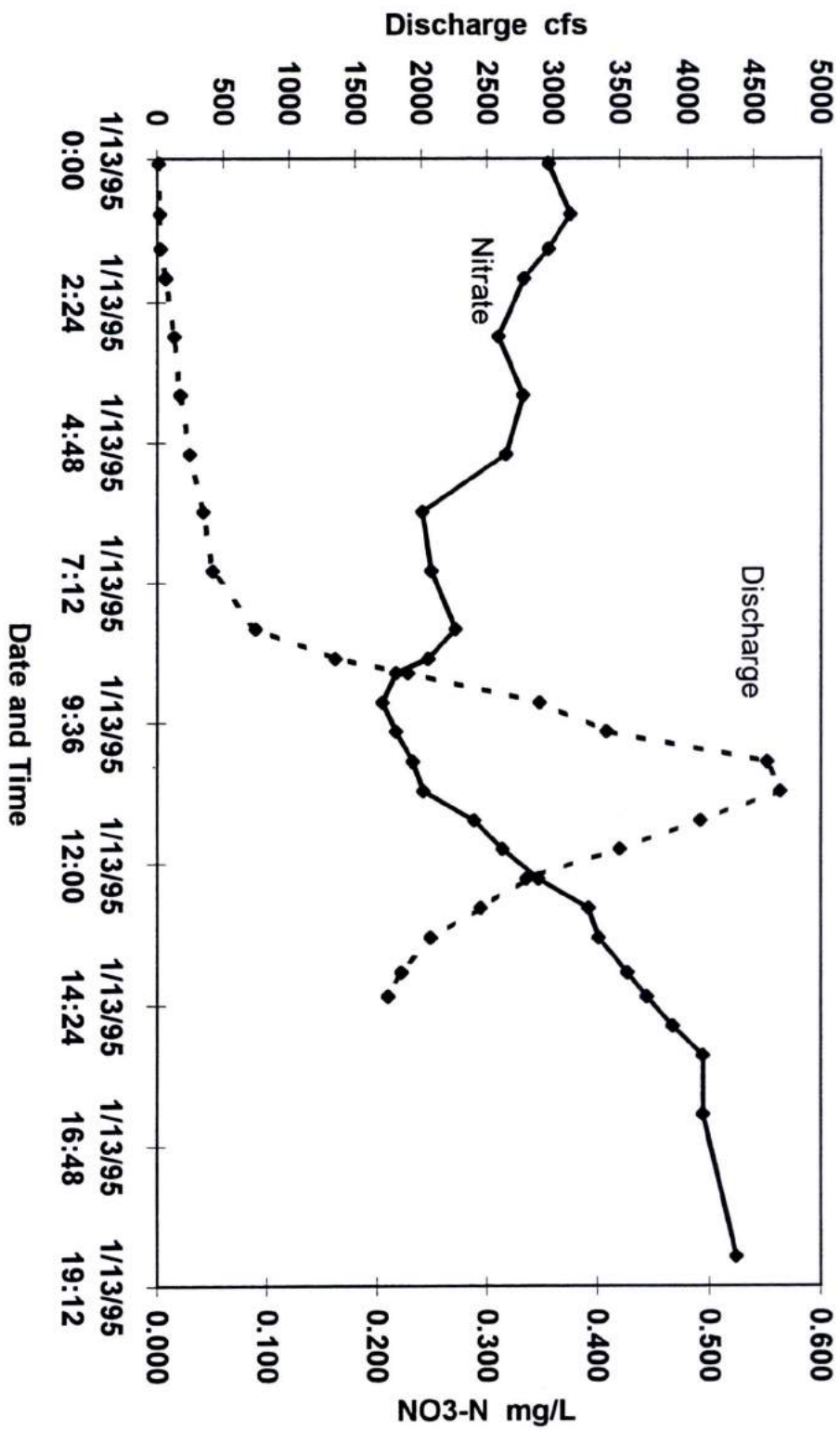


Figure 34. Discharge and nitrate versus time for Tomahawk Creek during the January storm.



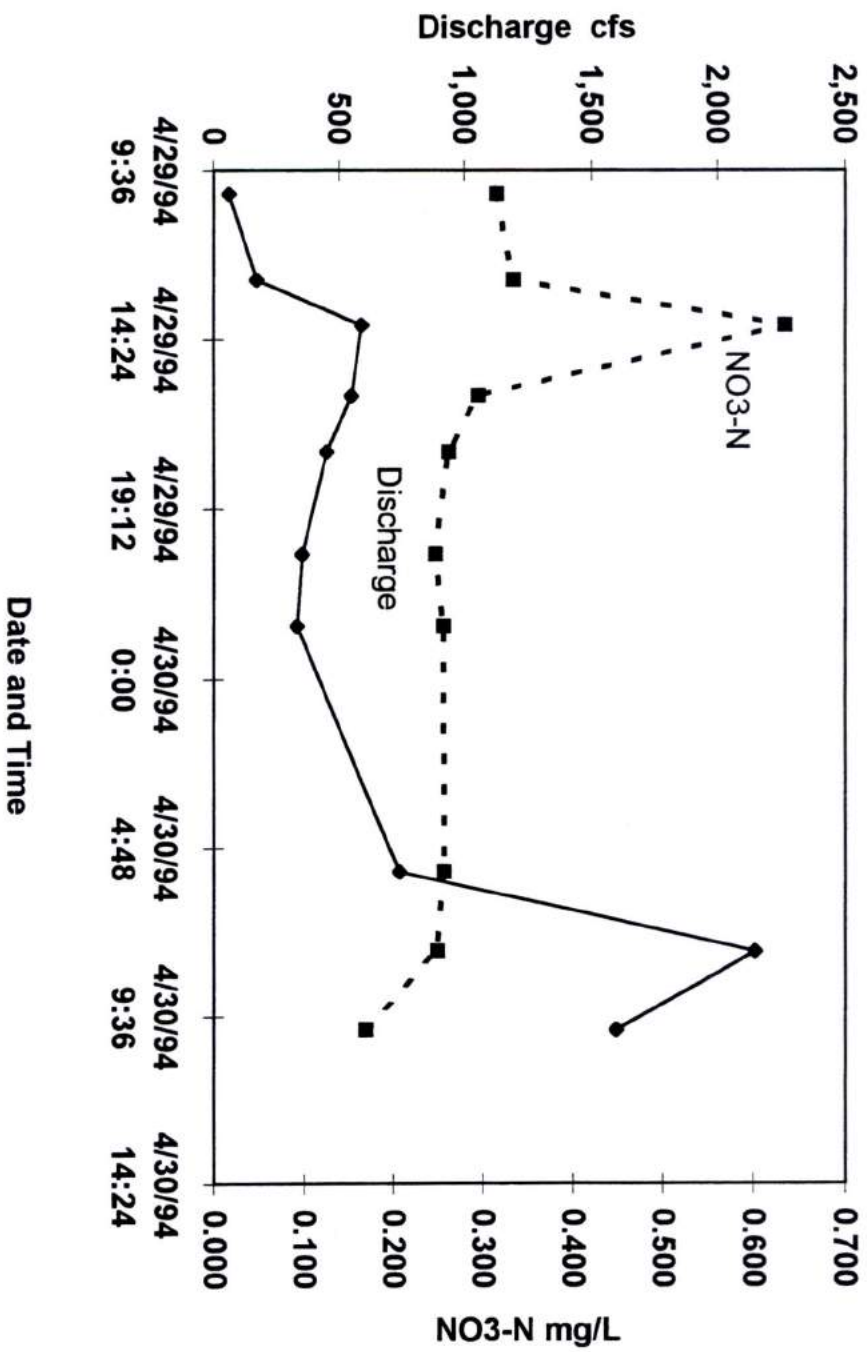


Figure 35. Discharge and nitrate versus time for Bear Creek during the April storm.

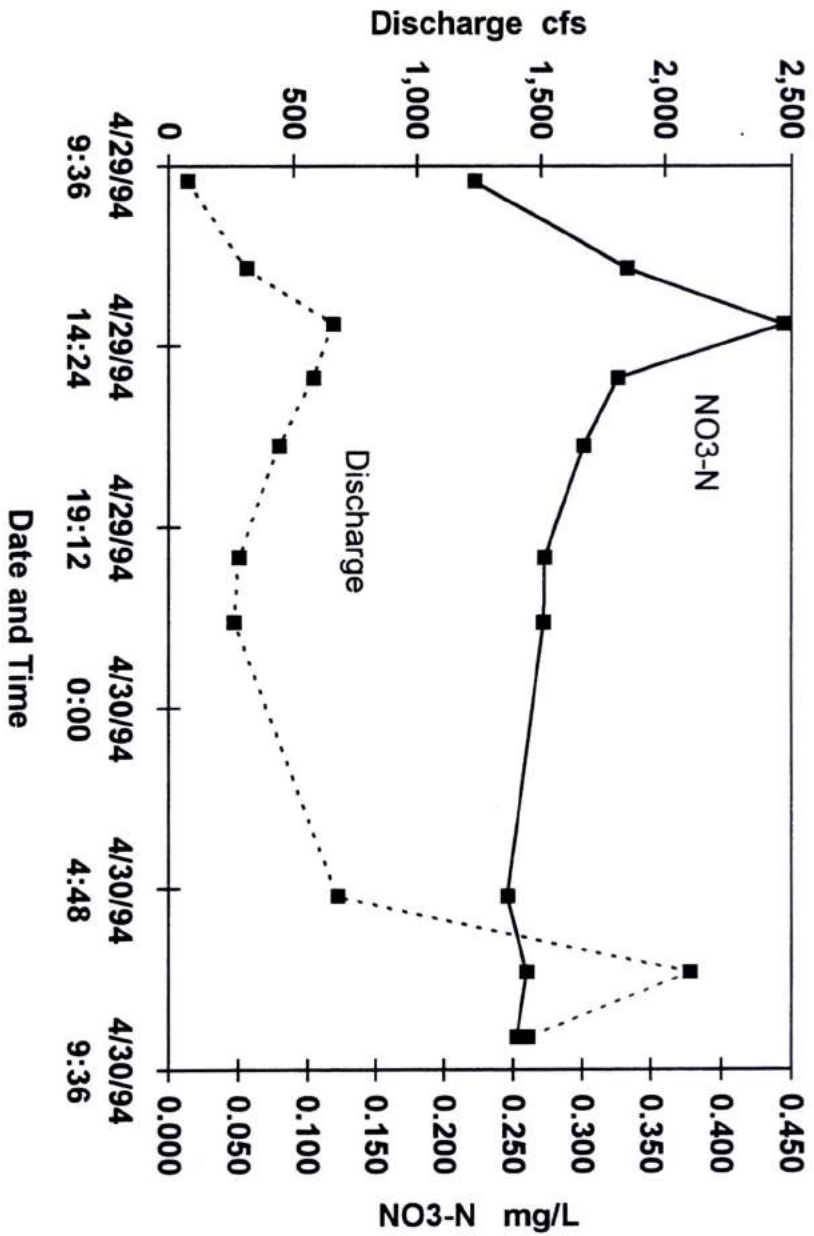


Figure 36. Discharge and nitrate versus time for Calf Creek during the April storm.

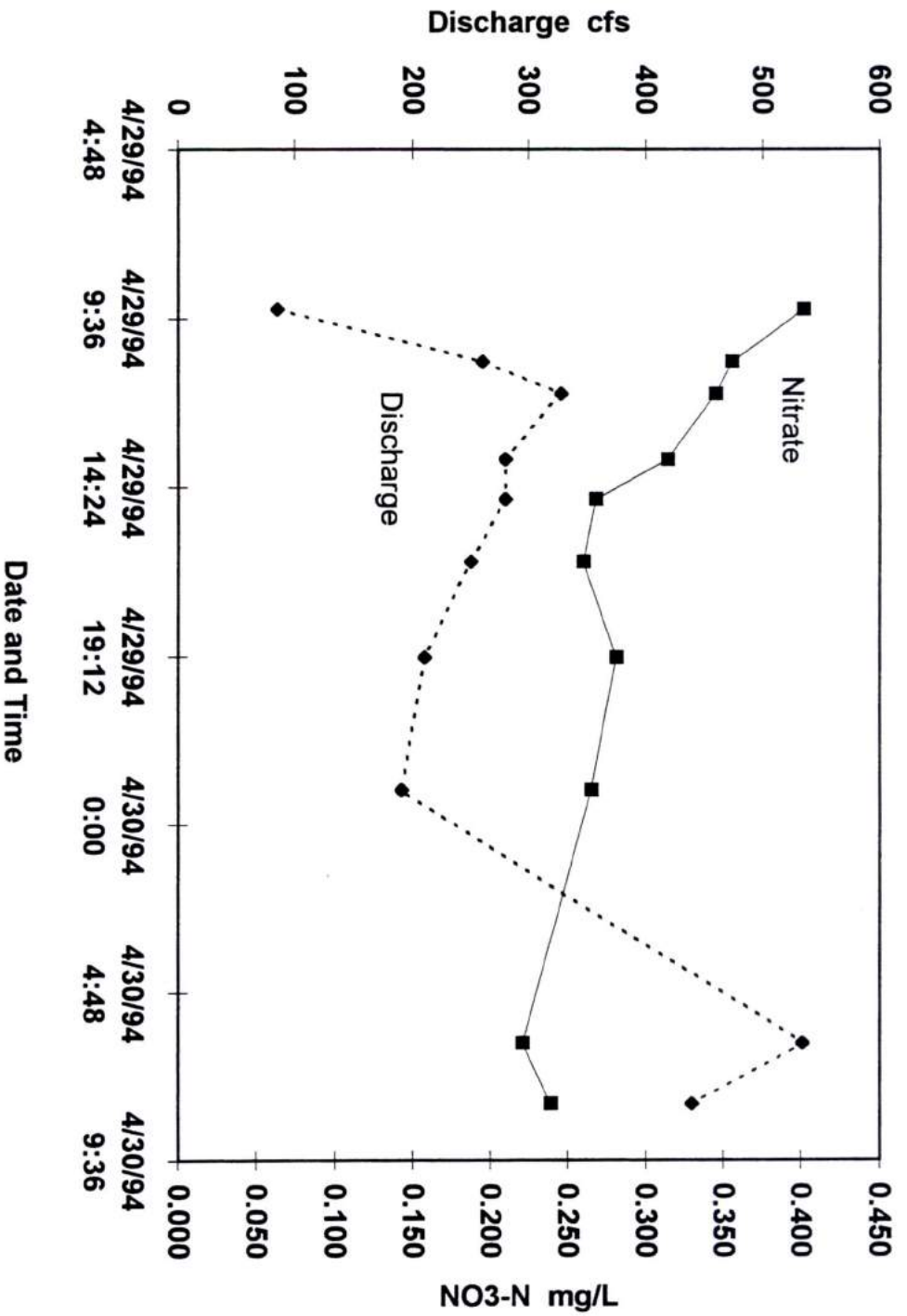


Figure 37. Discharge and nitrate versus time for Tomahawk Creek during the April storm.

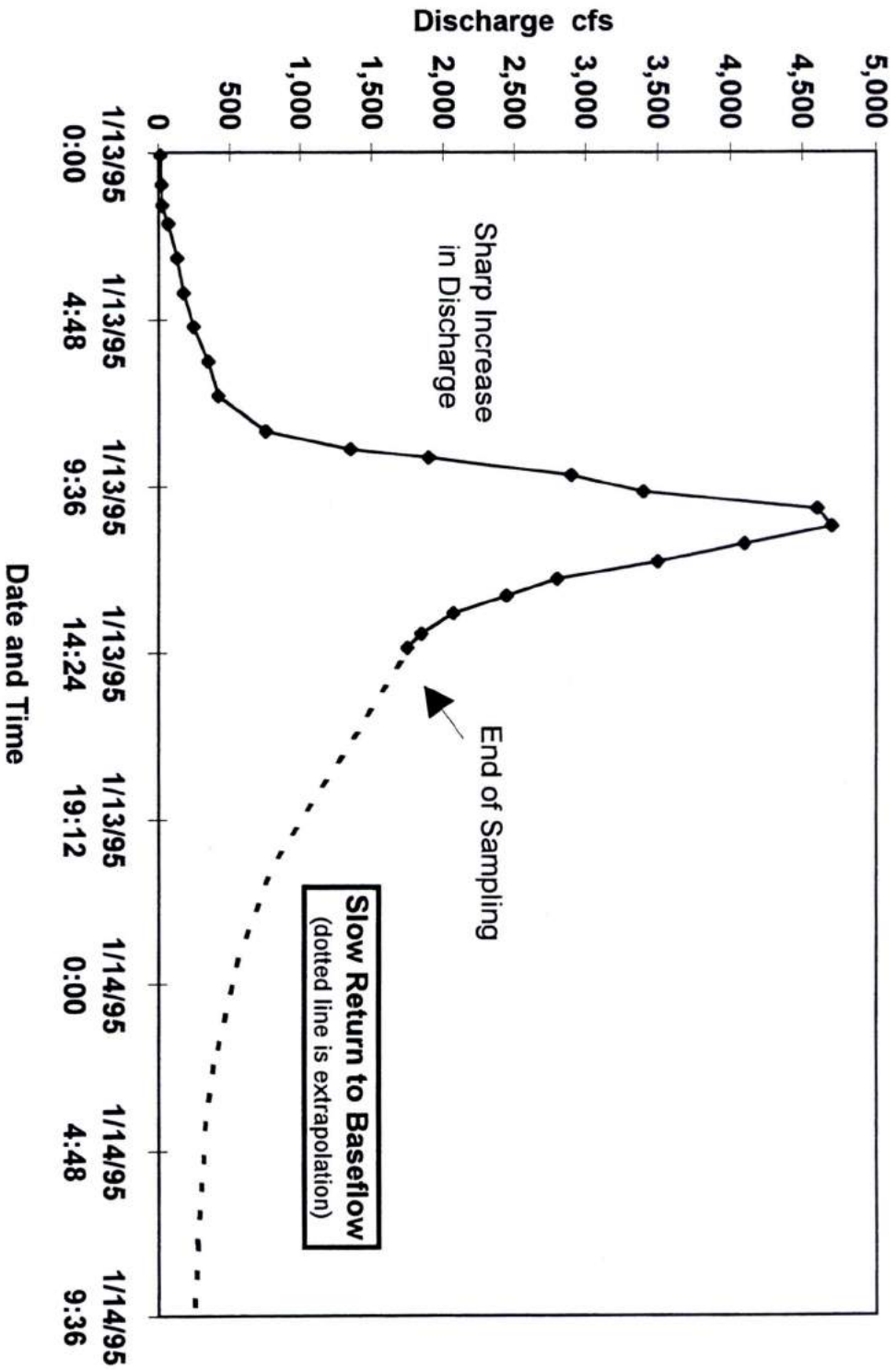


Figure 38. Discharge versus time for Tomahawk Creek during the January storm.

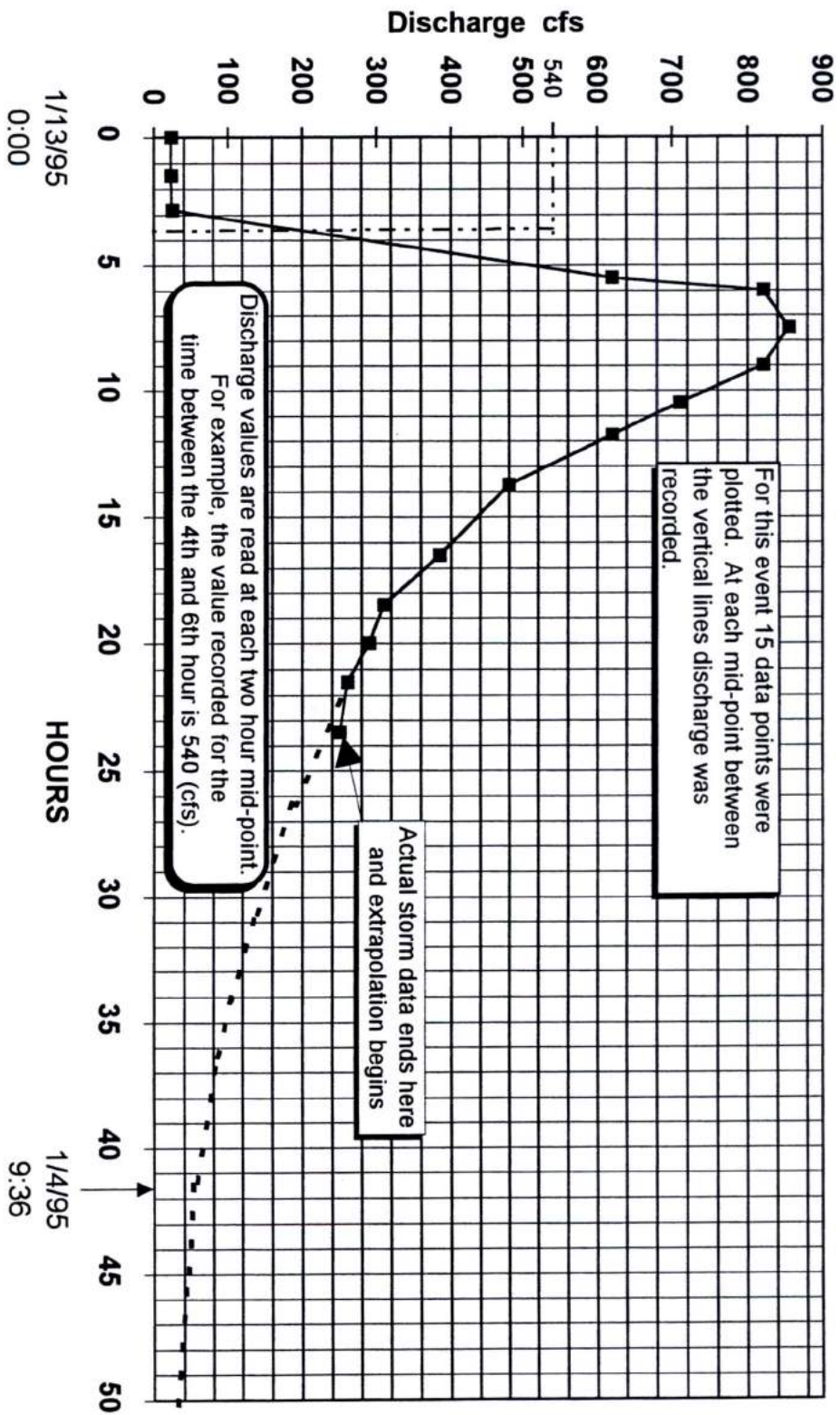


Figure 39. Example of extrapolation and interpolation of discharge data for Bear Creek during the December storm.

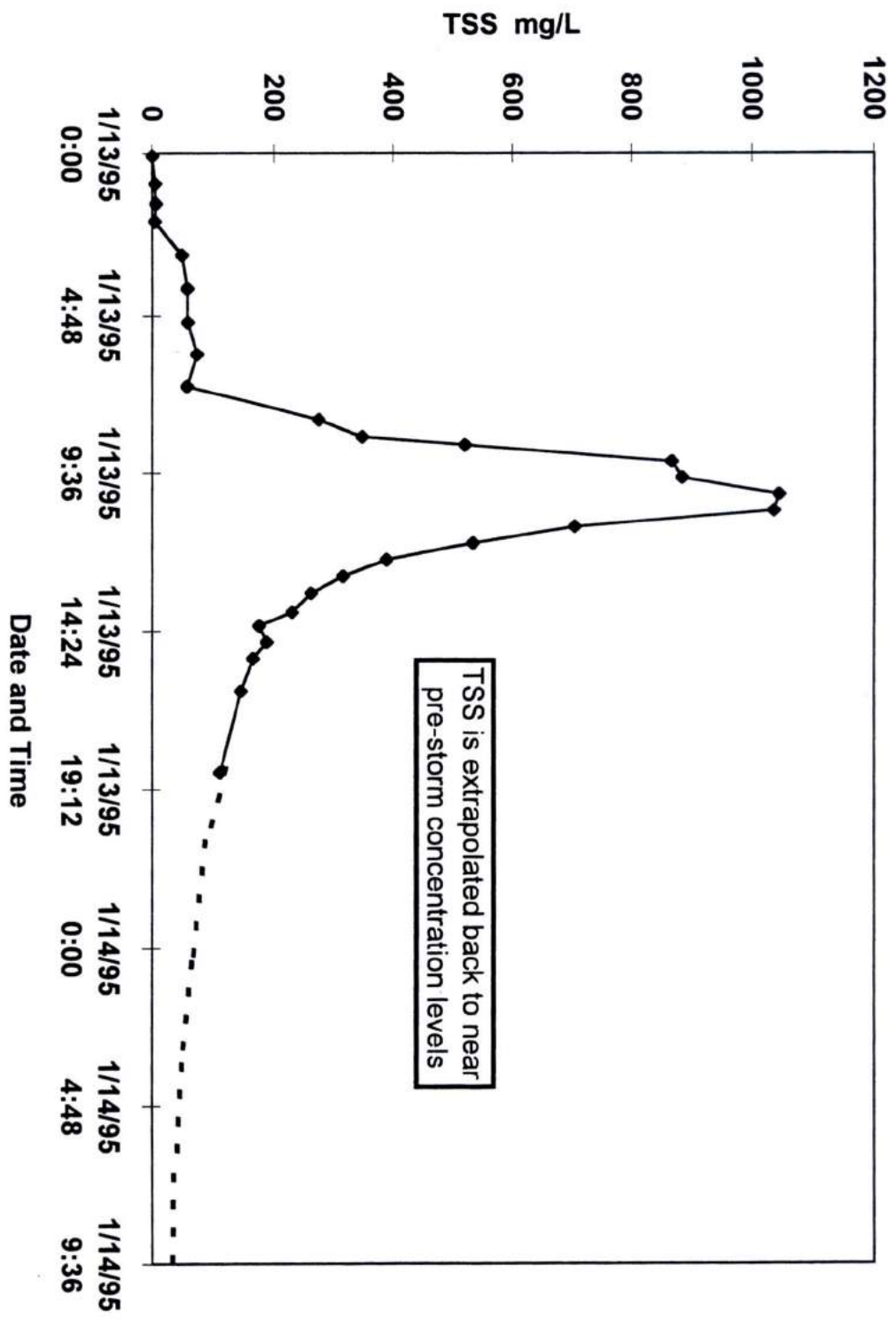


Figure 40. Extrapolation of TSS concentrations for Tomahawk Creek for the January storm.

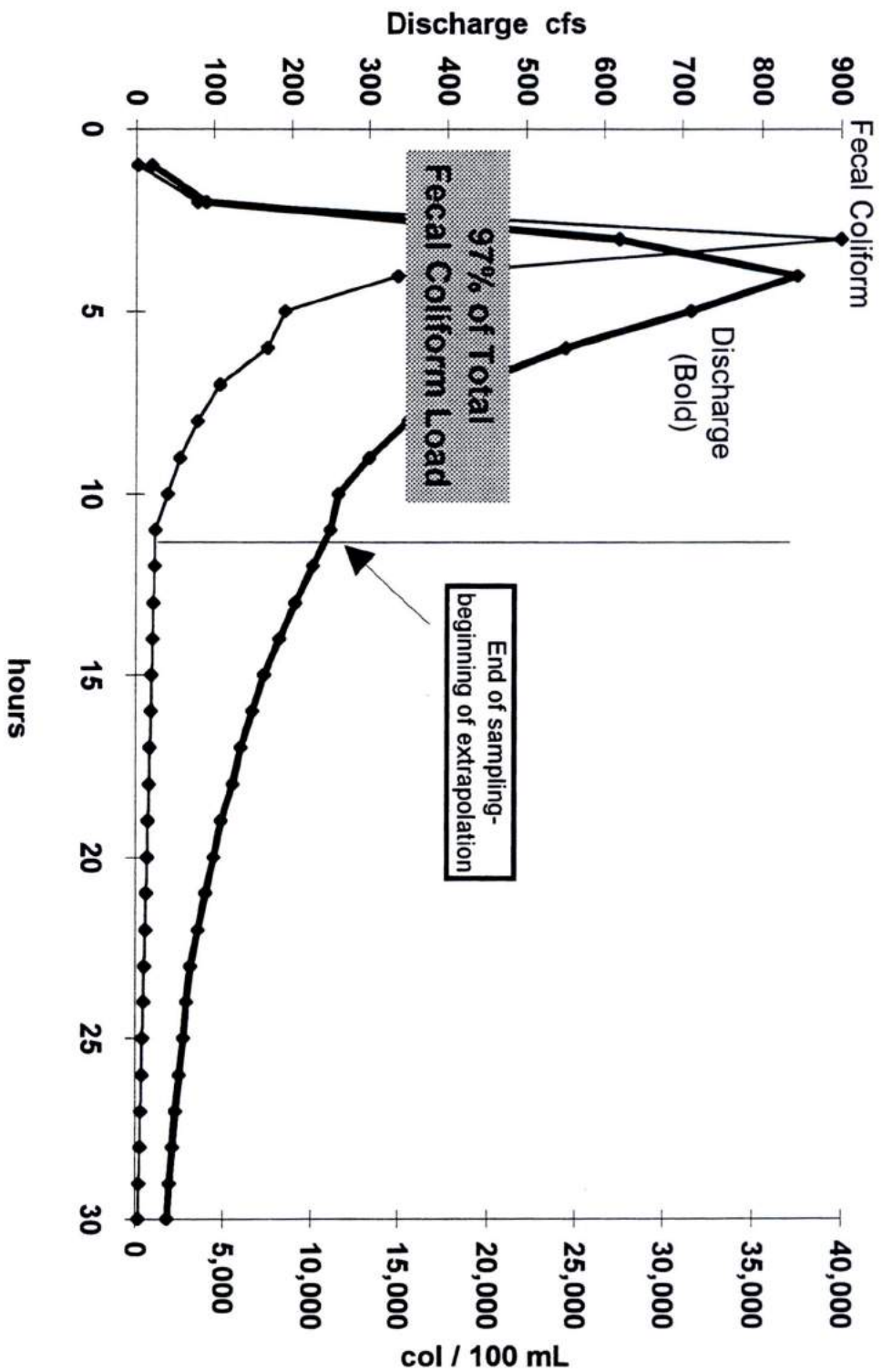


Figure 41. Example of extrapolation procedure for discharge and fecal coliform for Bear Creek during the December storm.

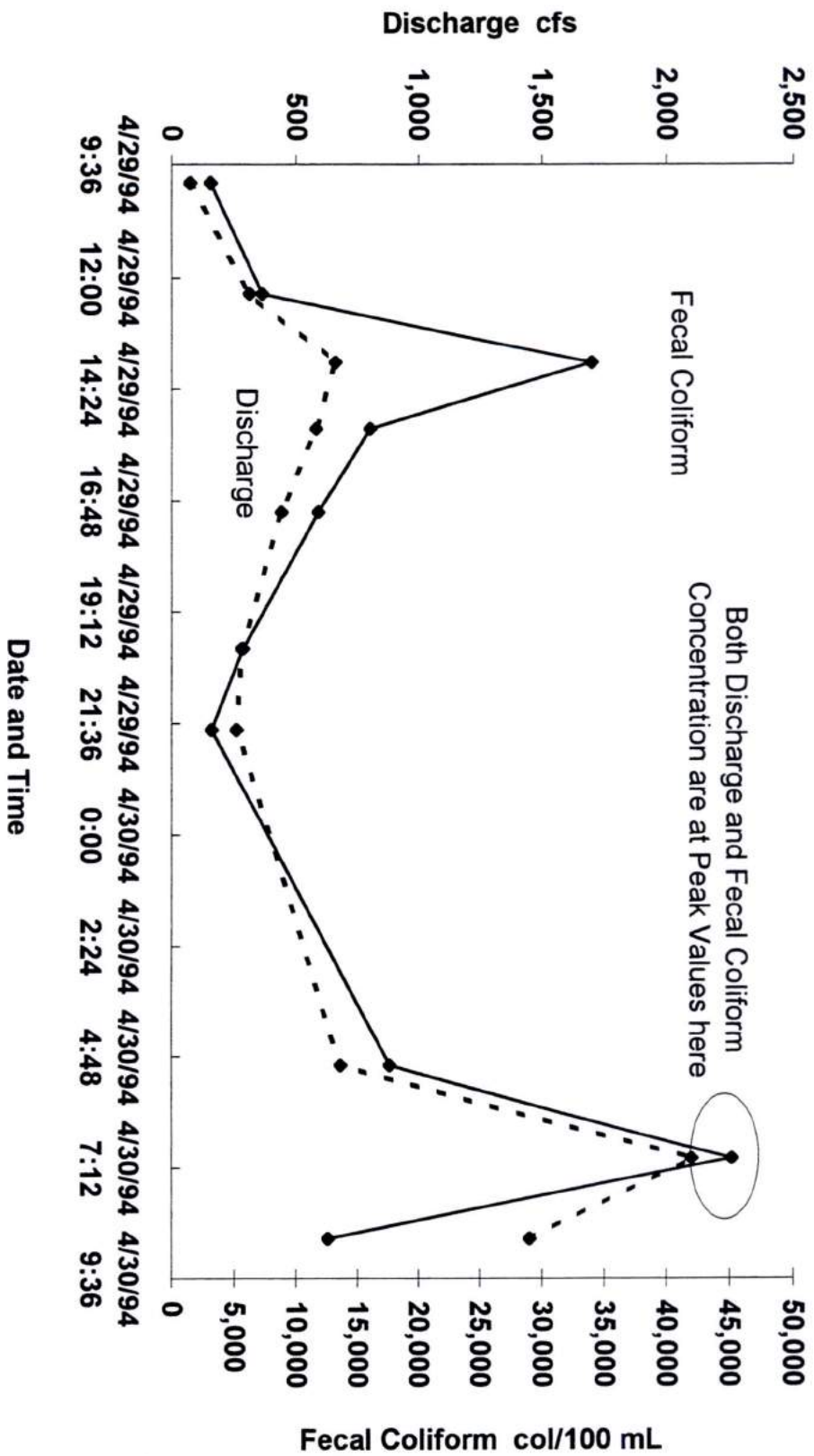


Figure 42. Discharge and fecal coliform versus time for Calf Creek during the April storm.



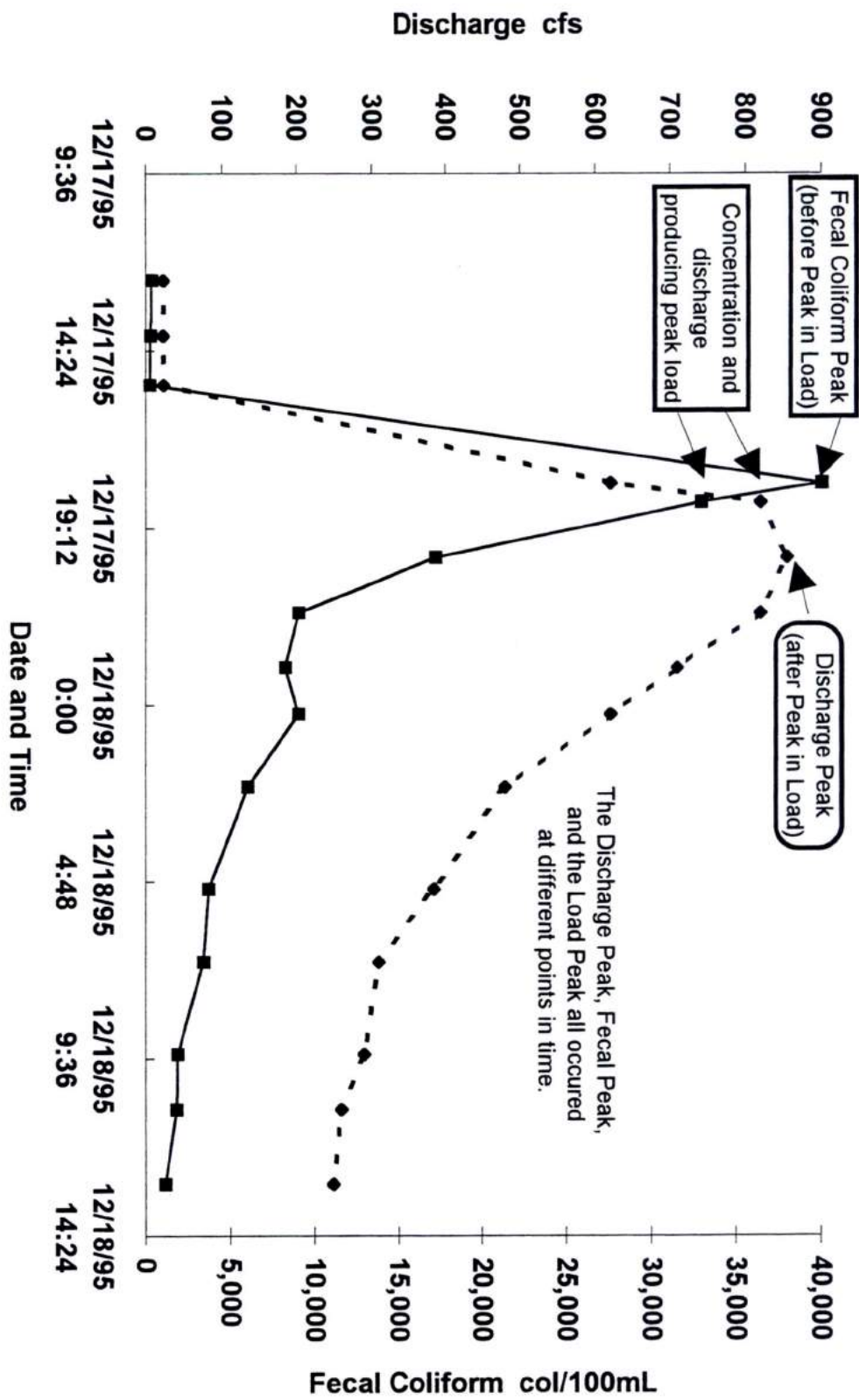


Figure 43. Discharge and fecal coliform versus time for Bear Creek during the December storm.

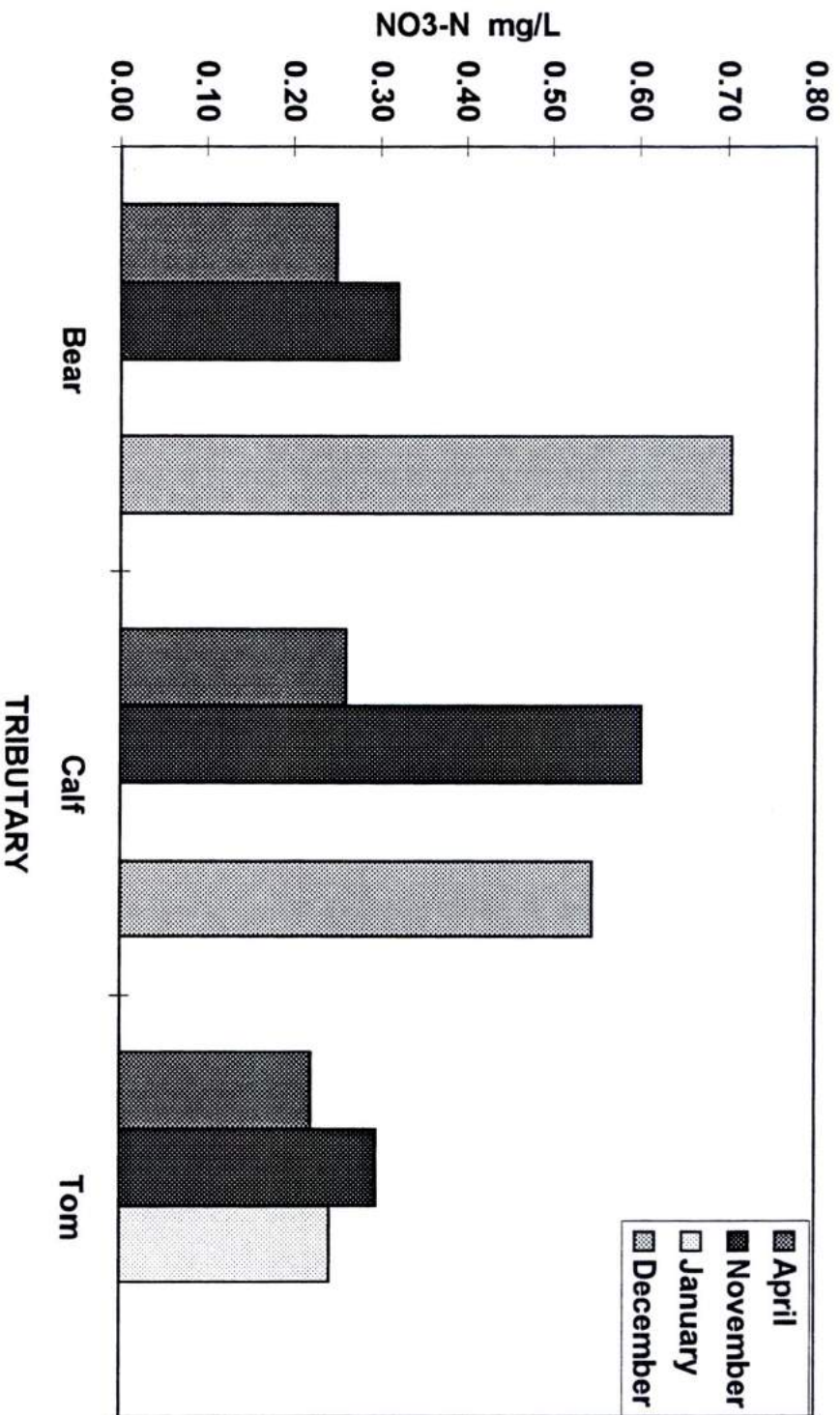


Figure 44. Maximum nitrate concentrations for the tributaries by storm.

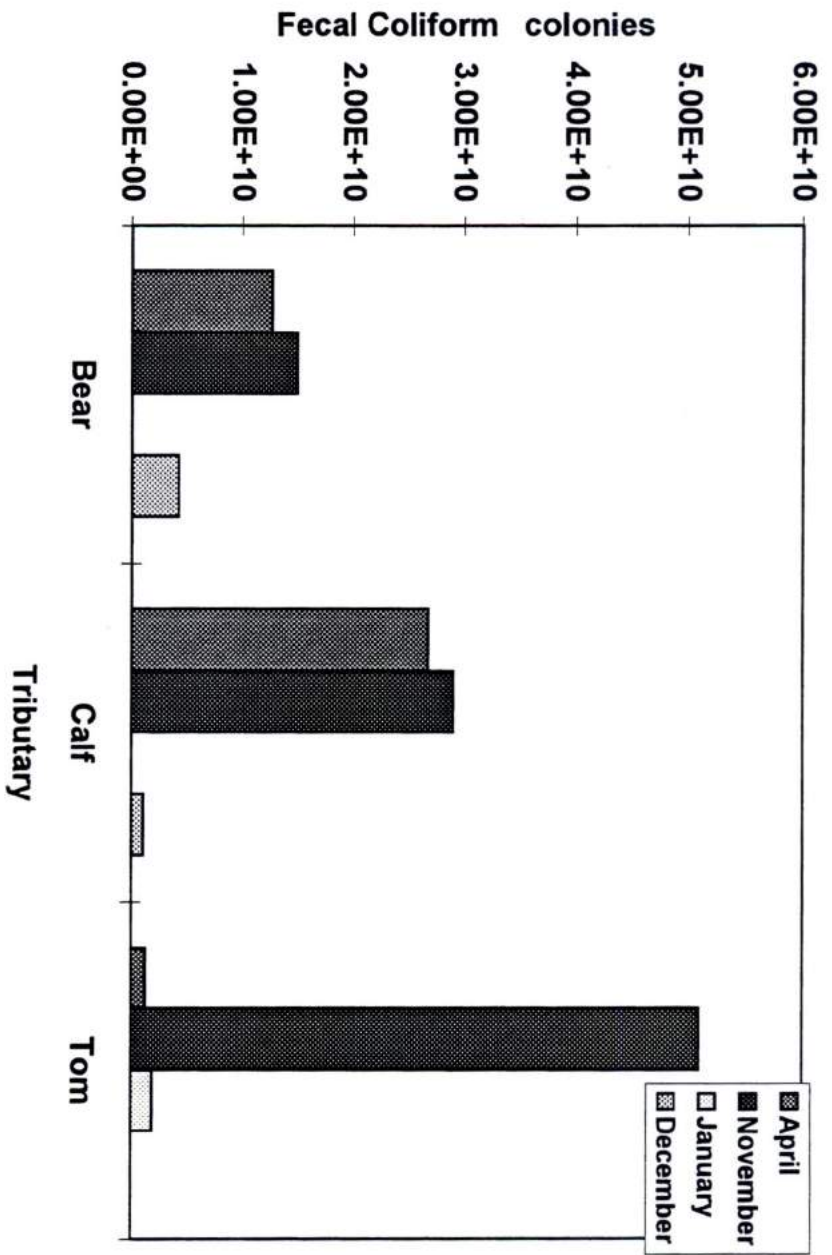


Figure 45. Maximum fecal coliform storm loads for the tributaries by storm.

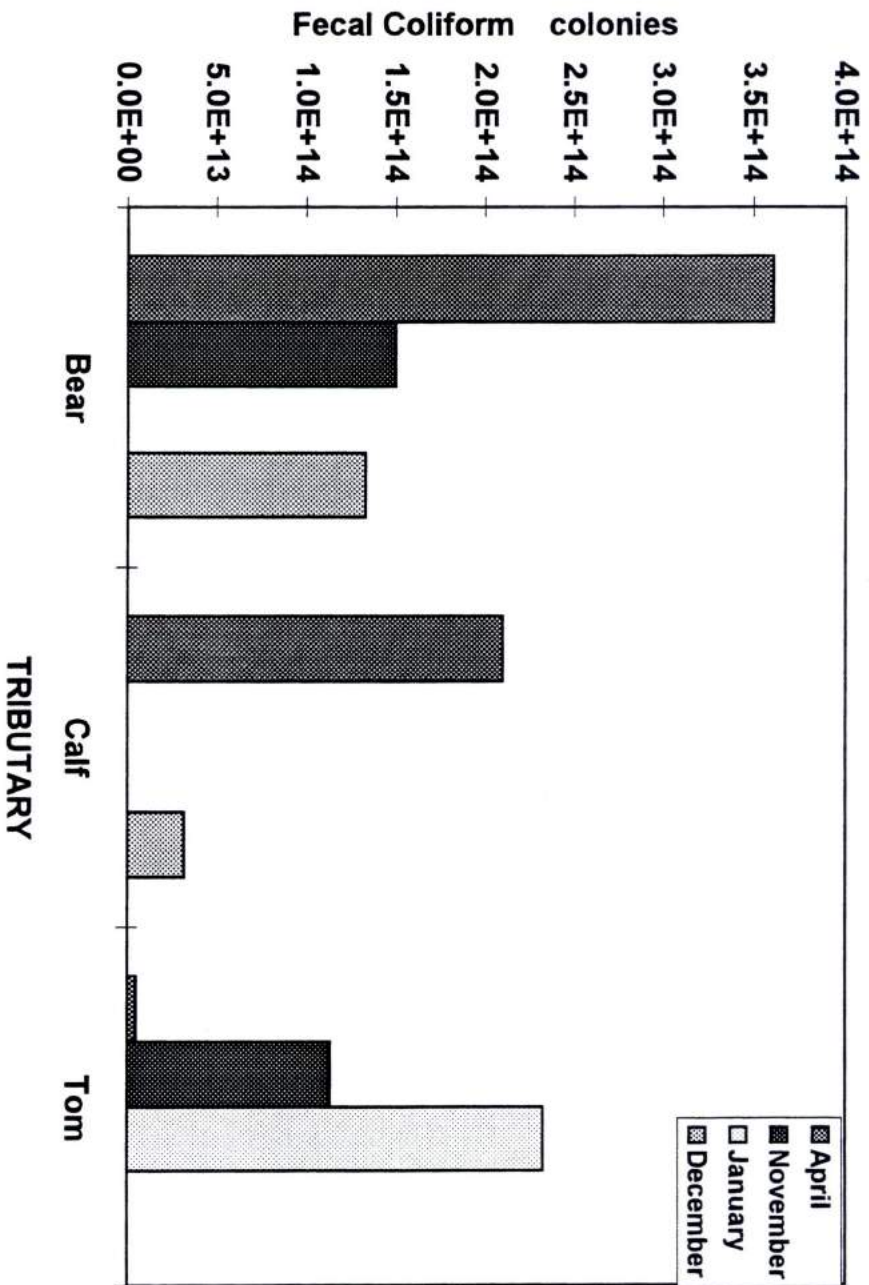


Figure 46. Fecal coliform loads for the tributaries by storm.

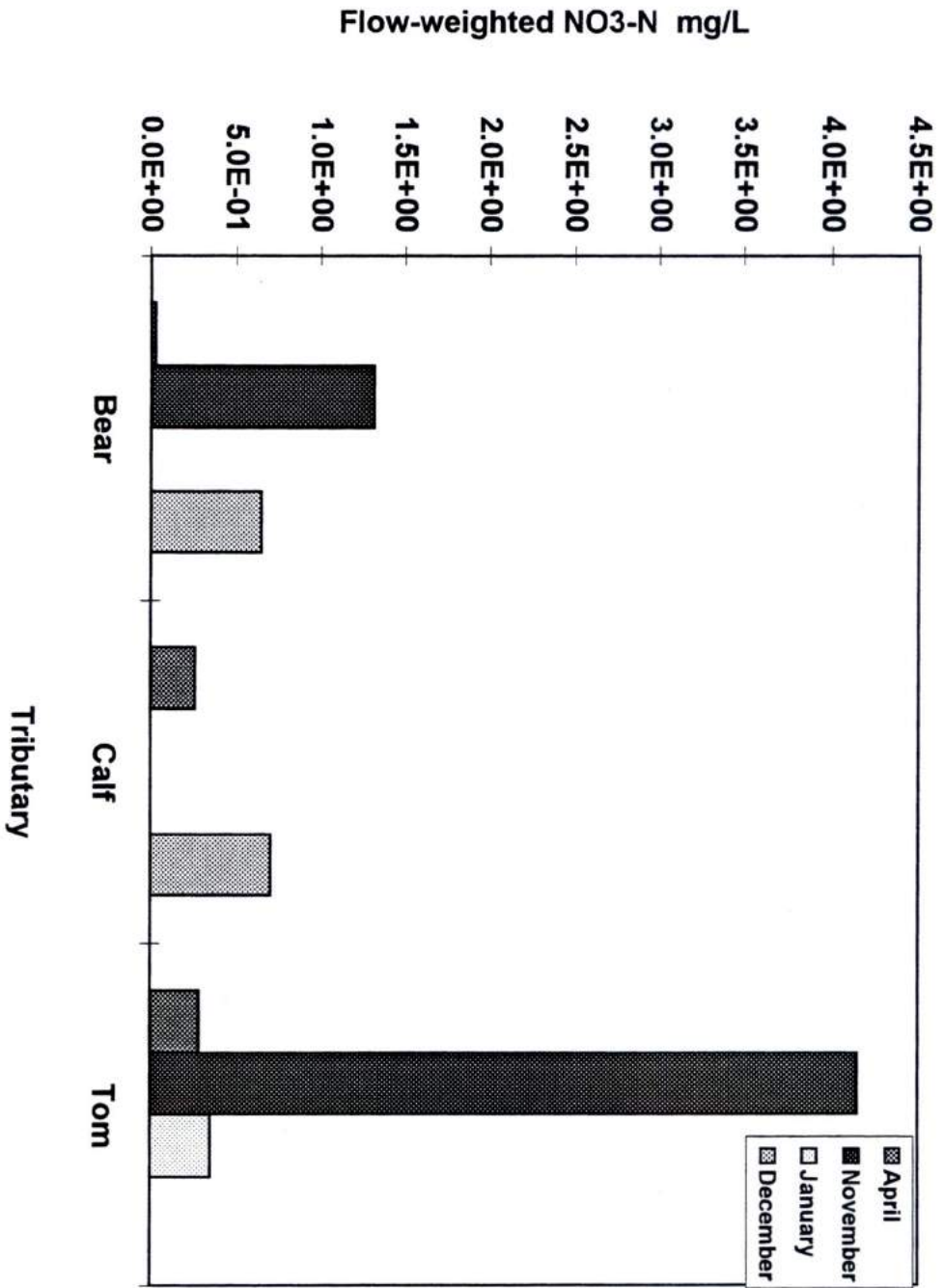


Figure 47. Nitrate-N flow-weighted concentrations for the tributaries by storm.

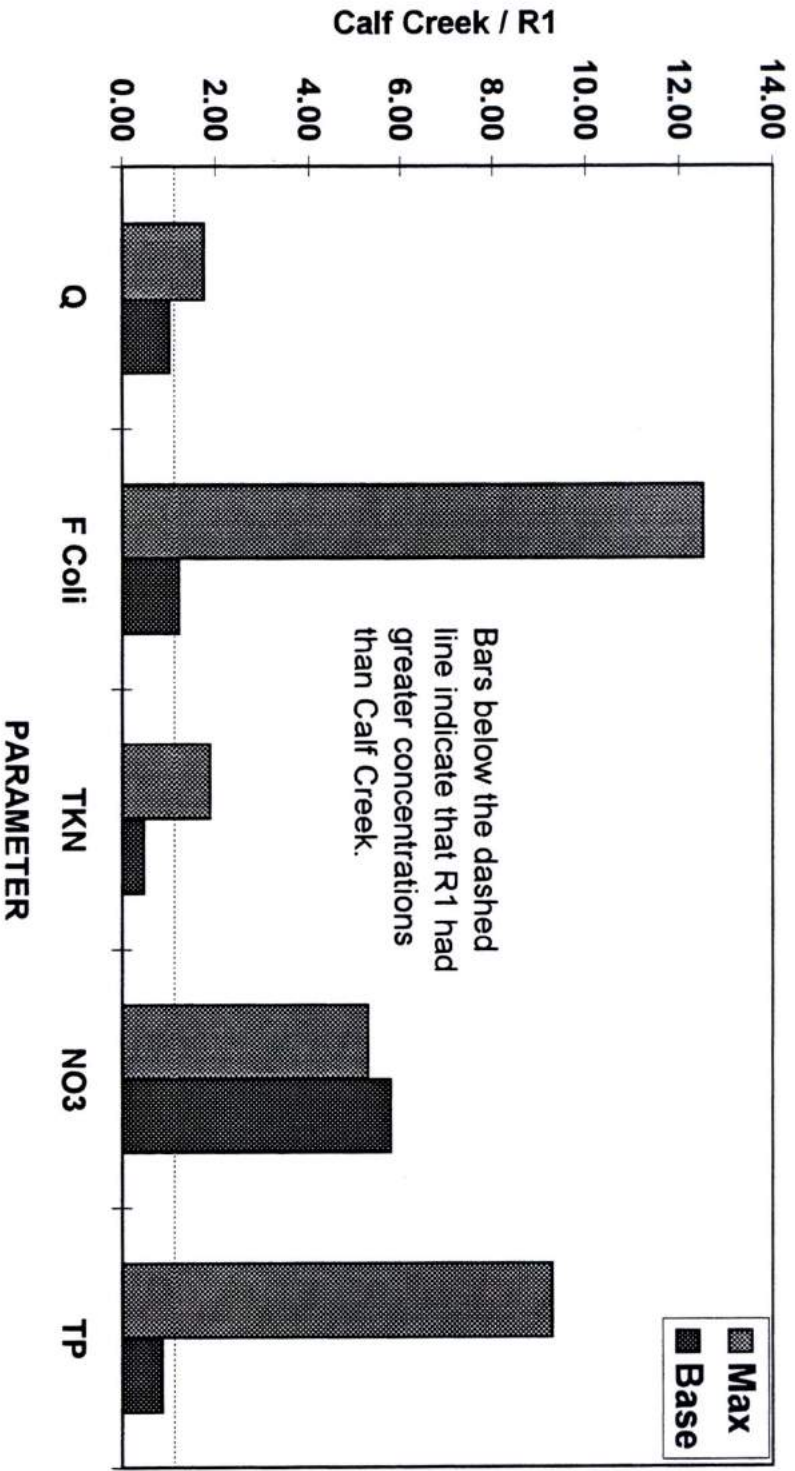


Figure 48. Ratios for Calf Creek to R1 for maximum storm flow and associated concentrations during the second part of the April storm and for average annual base flow and associated concentrations.

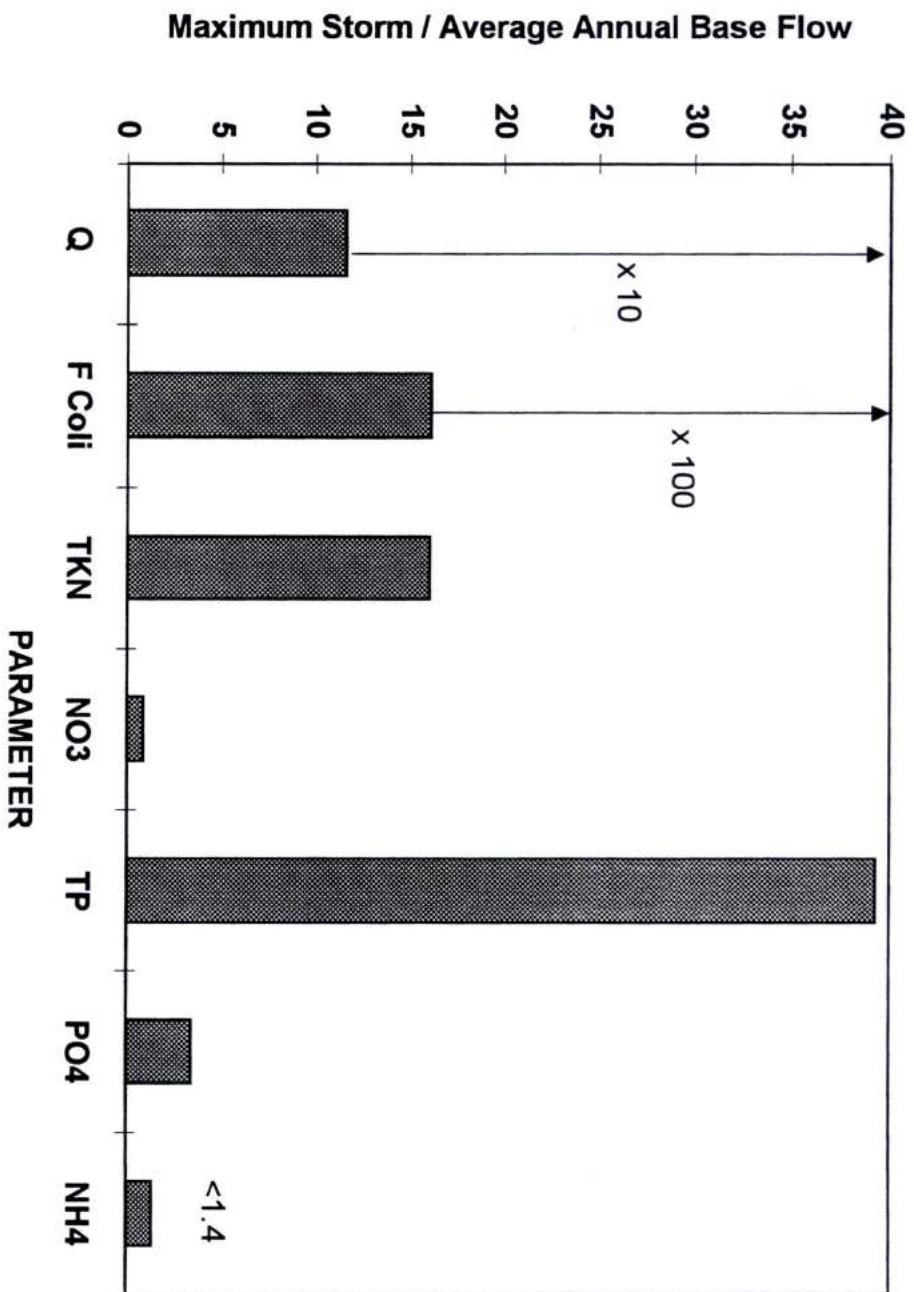


Figure 49. Ratio of maximum storm discharge and associated concentrations for Calf Creek for the second part of the April storm to the average annual base flow and associated concentrations for Calf Creek.

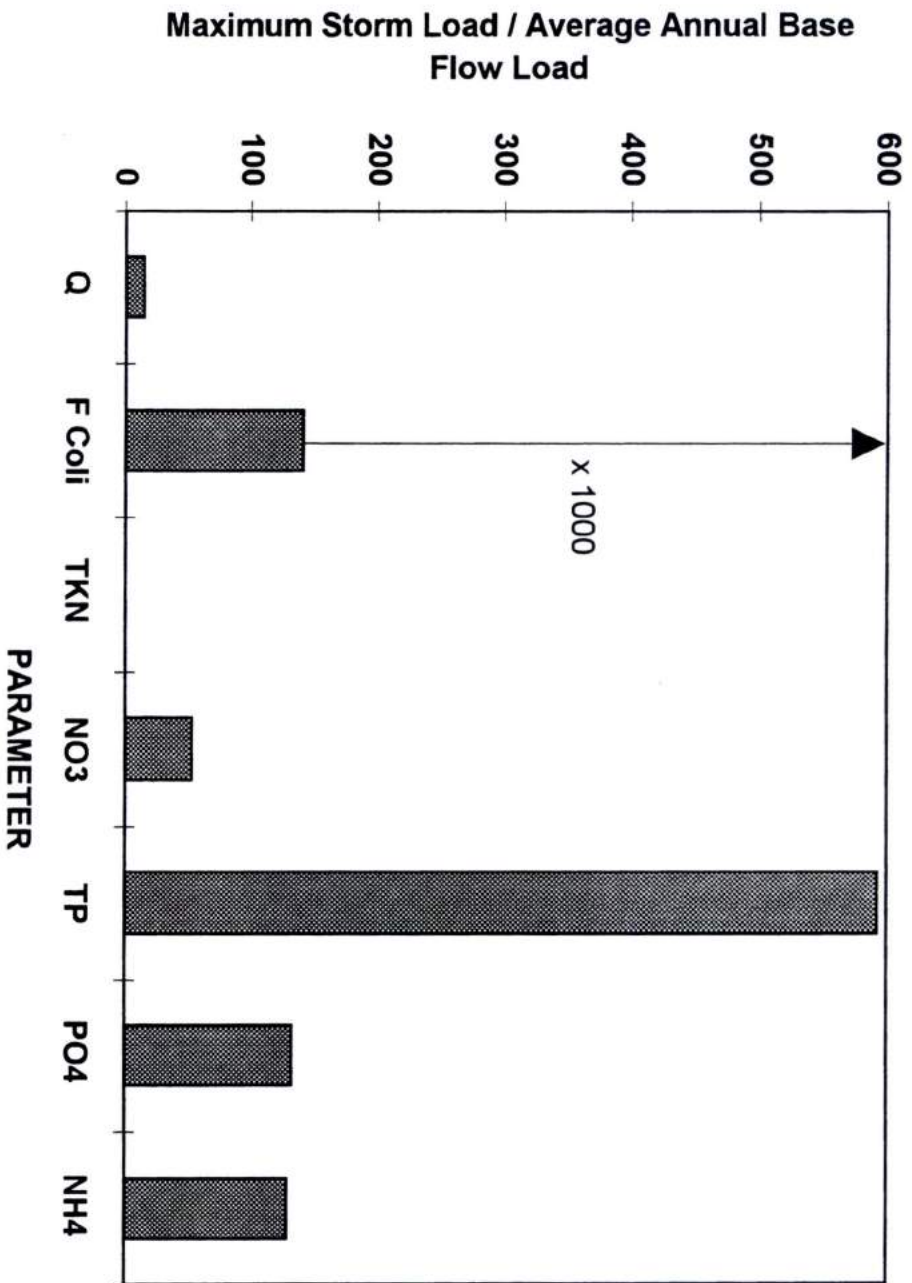


Figure 50. Ratio of maximum storm discharge and associated loads for Bear Creek during the first part of the April storm to the average annual base flow and associated loads for Bear Creek.



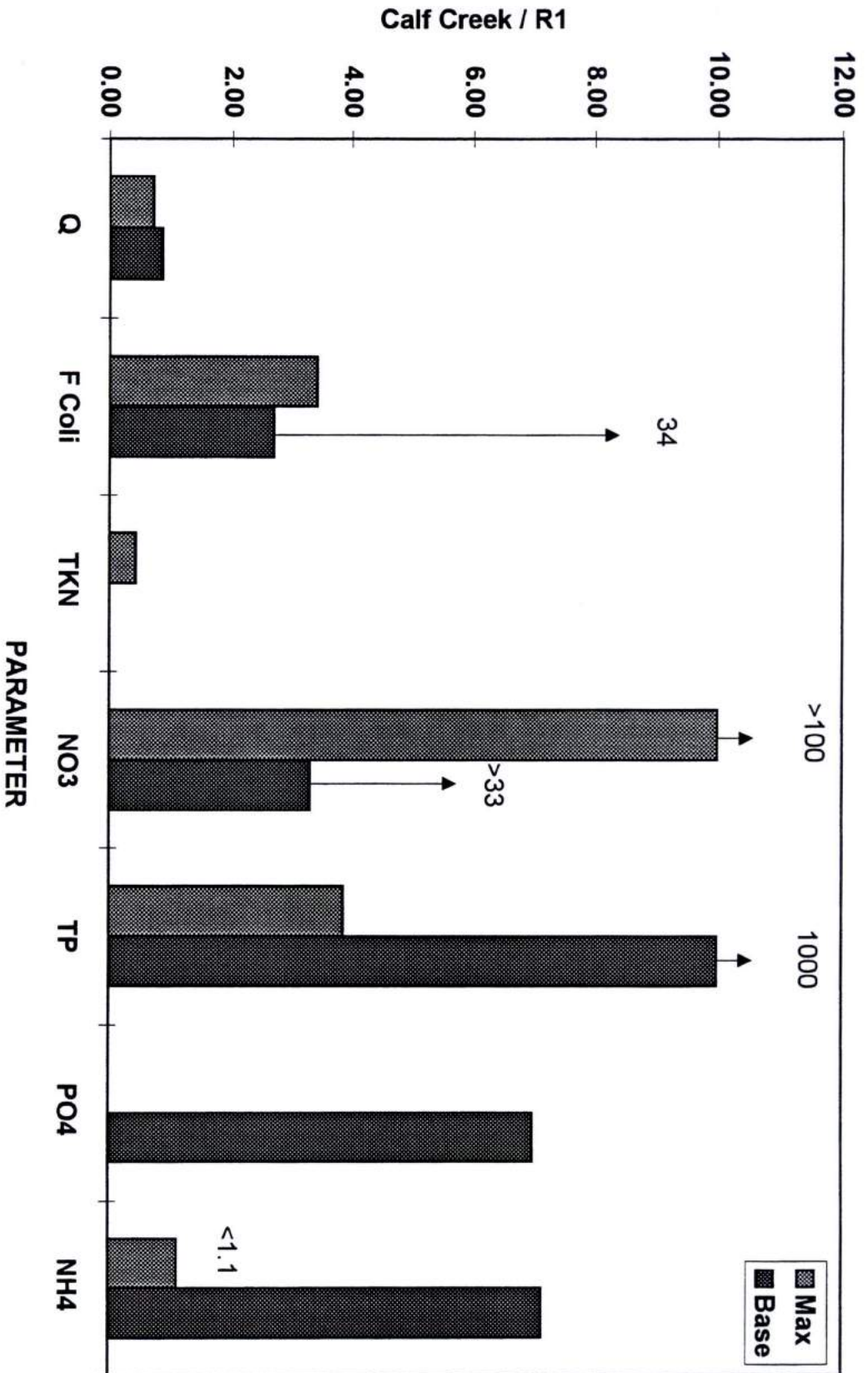


Figure 51. Ratios for Calf Creek to R1 for maximum storm loads and associated loads during the December storm and for average annual base flow and associated loads.

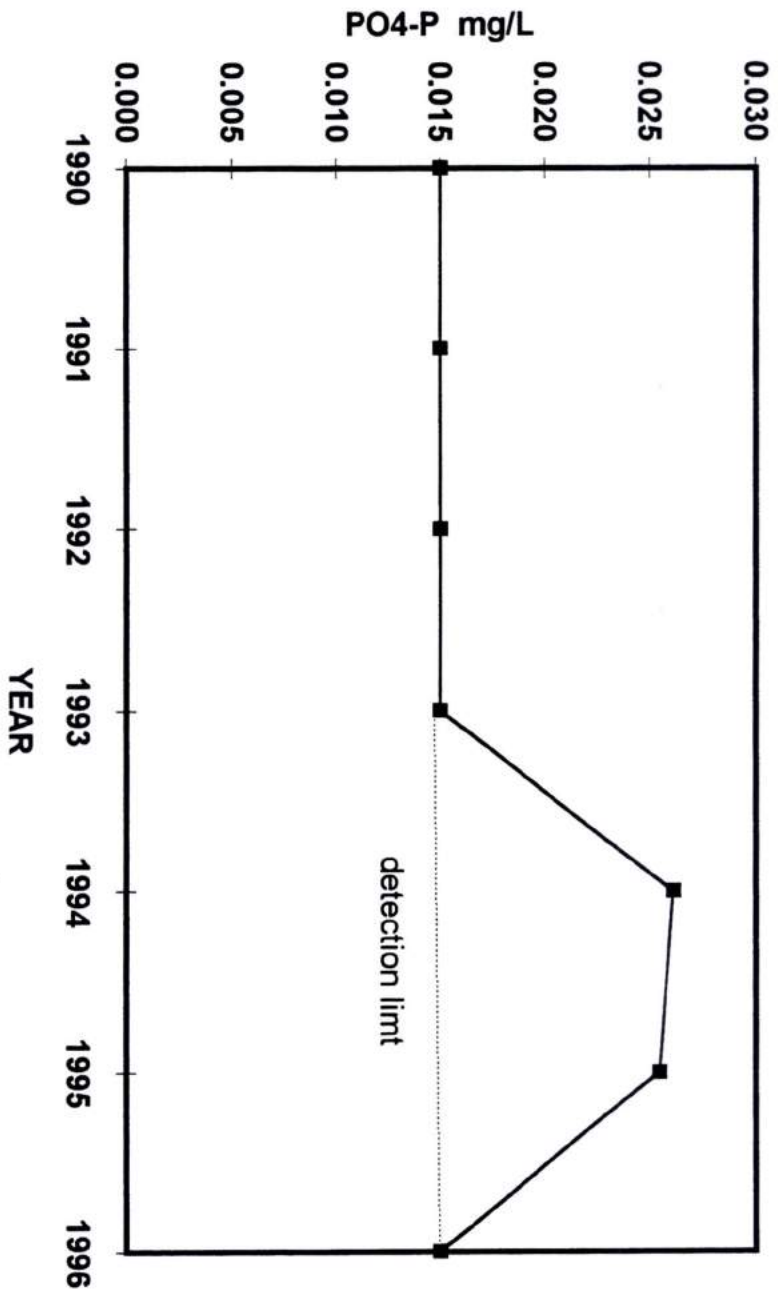


Figure 52. Orthophosphate versus year for Tomahawk Creek.

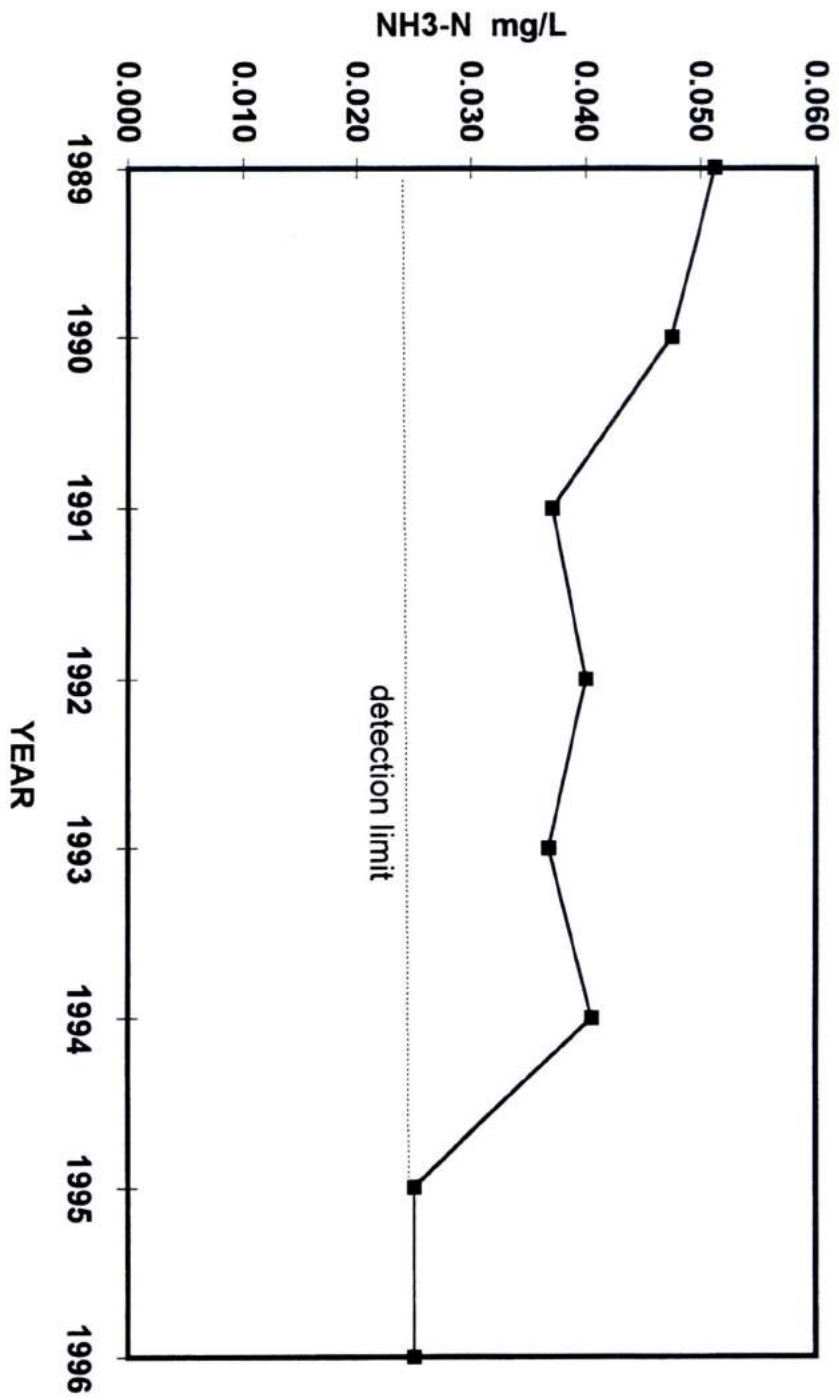


Figure 53. Ammonia versus year for Tomahawk Creek.

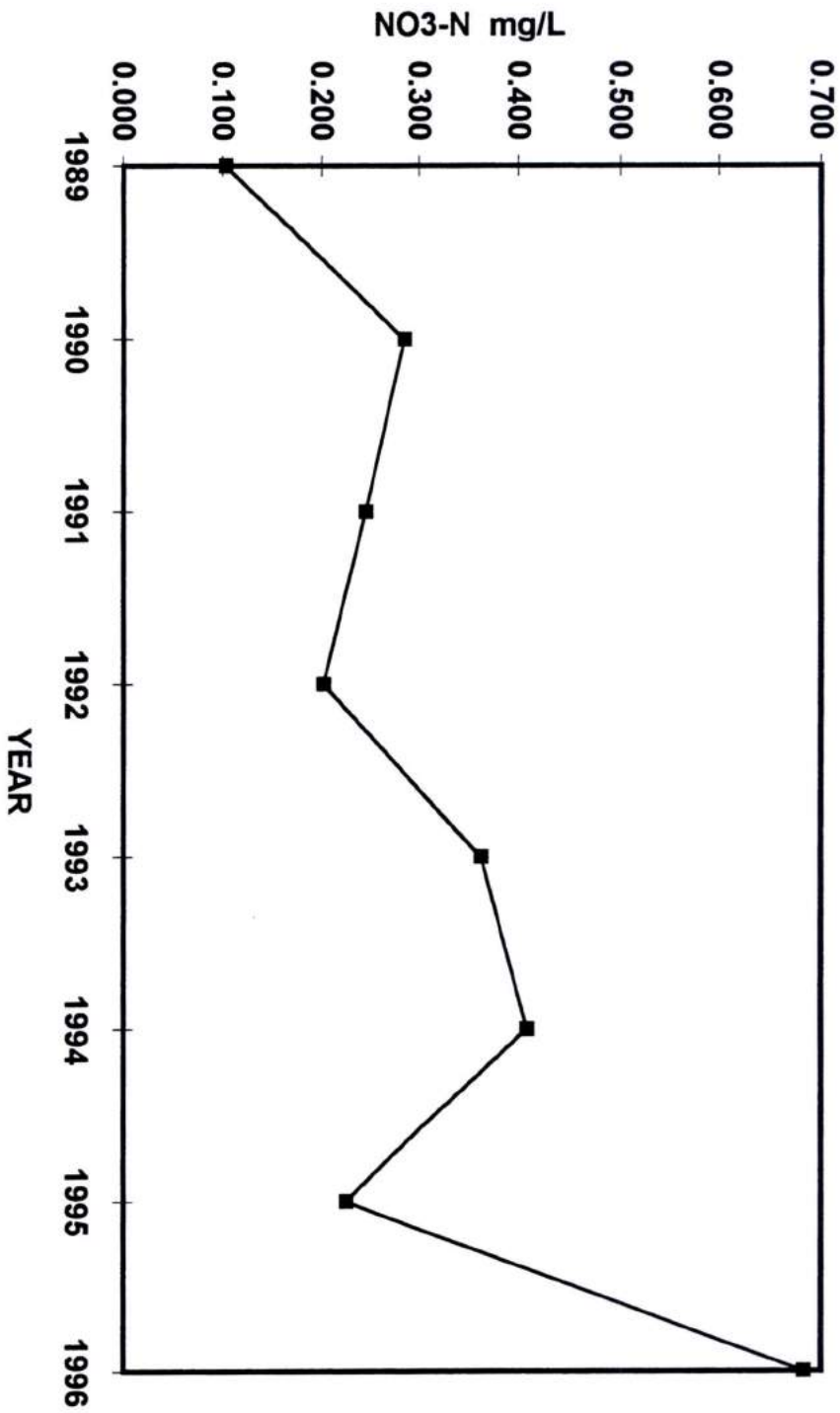


Figure 54. Nitrate versus year for Tomahawk Creek.

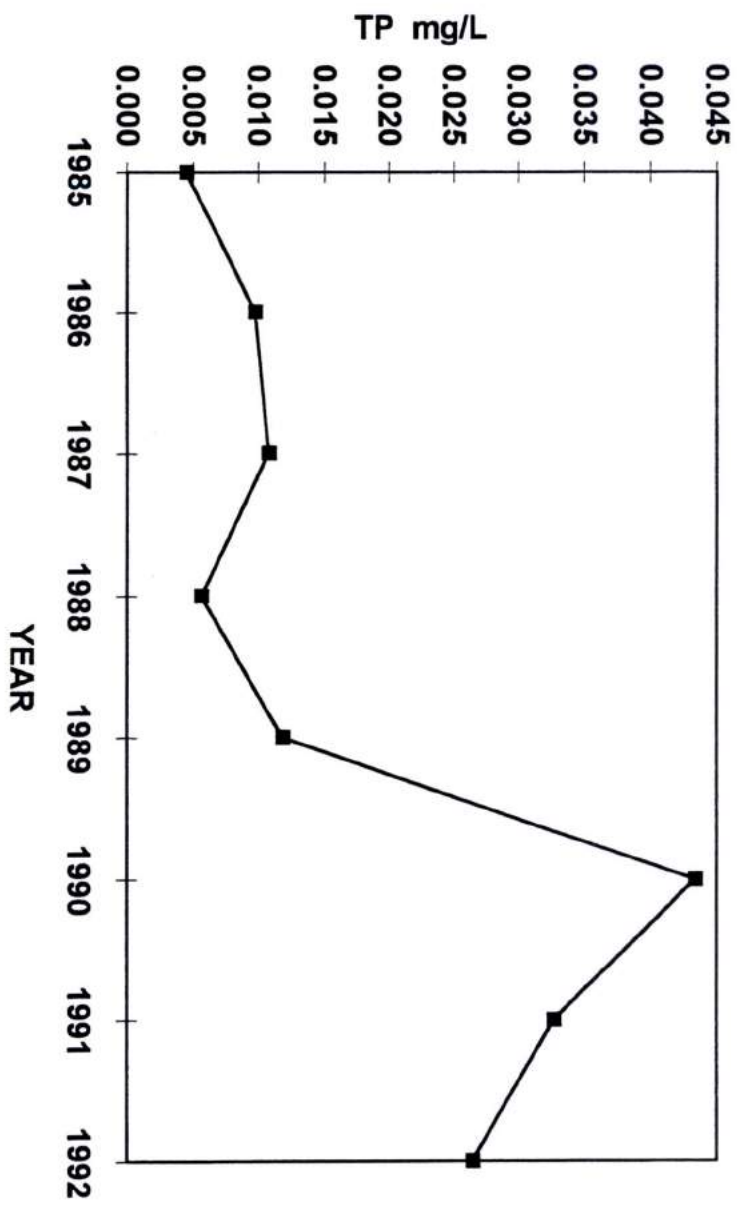


Figure 55. Total phosphorus versus year for R1.

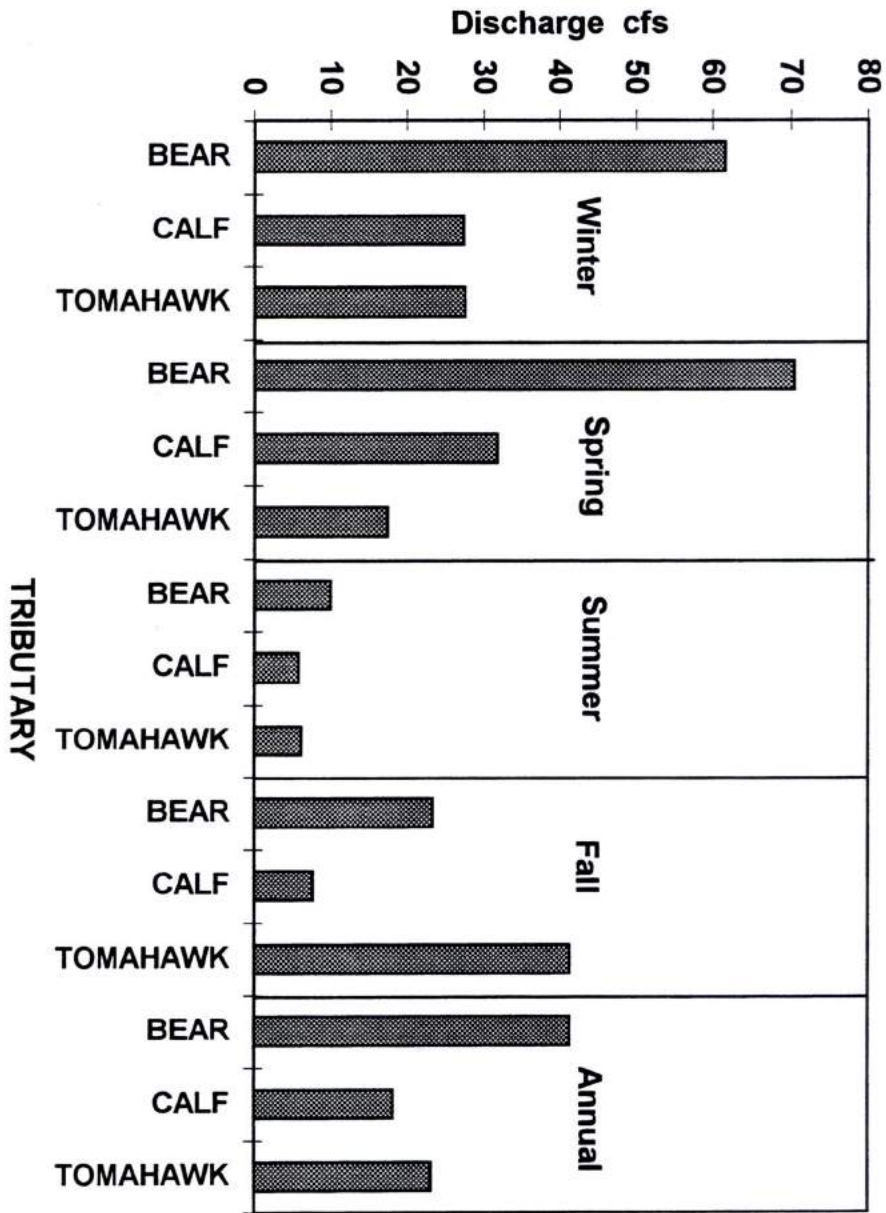


Figure 56. Average annual and seasonal base flow discharge for each tributary.

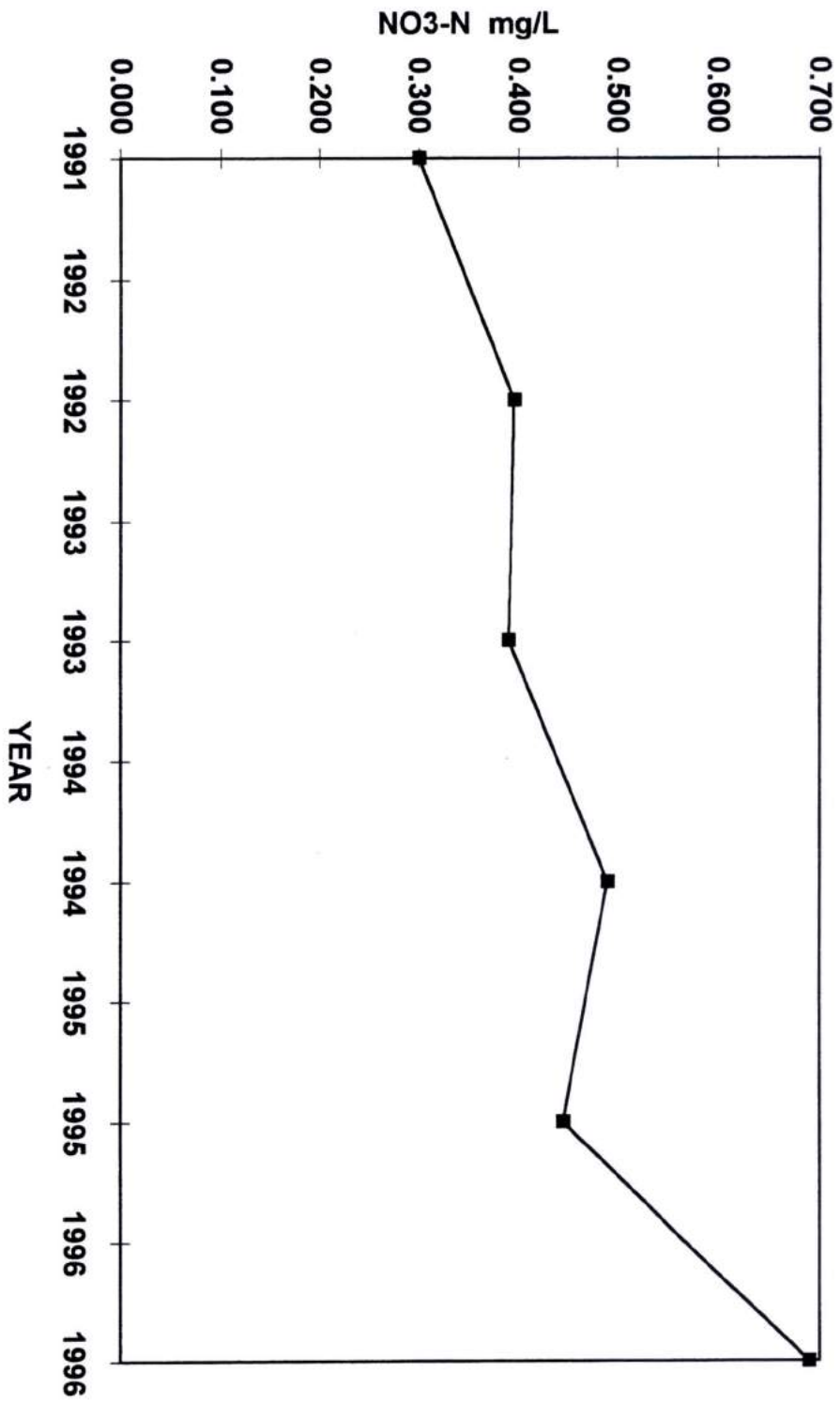


Figure 57. Average annual winter nitrate concentration versus year for Tomahawk Creek.

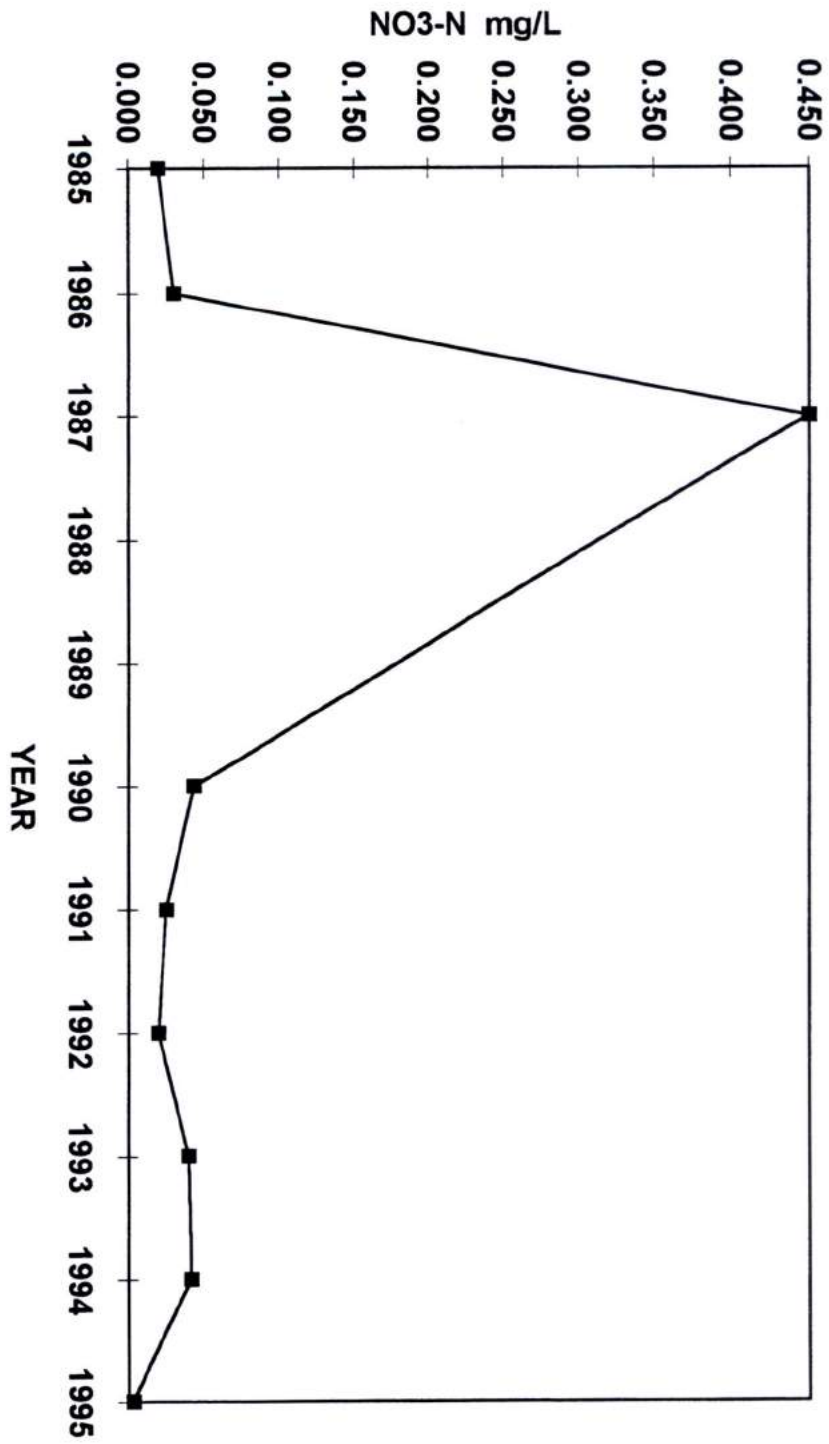


Figure 58: Average annual spring season nitrate concentration versus year for R1.



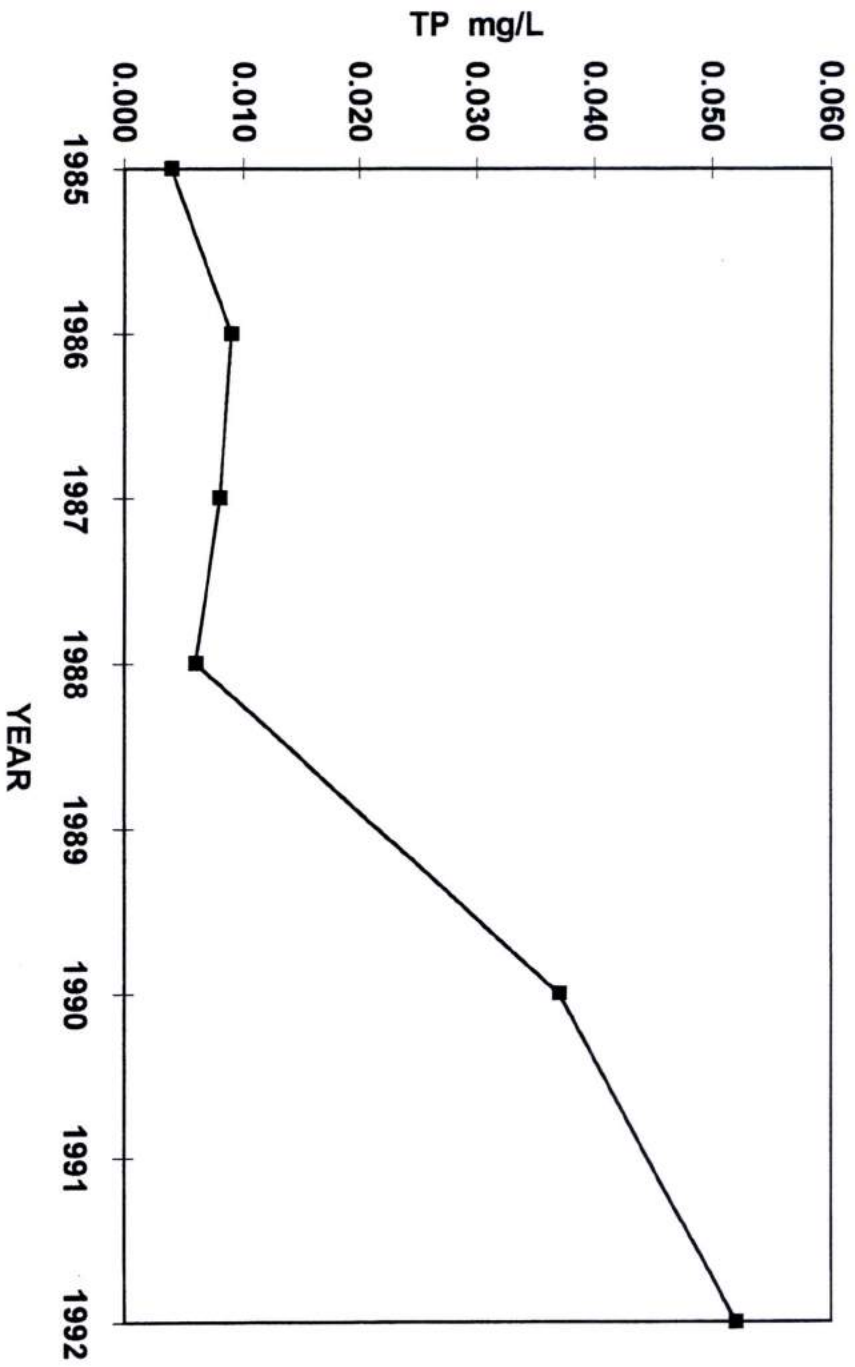


Figure 59. Average annual spring season total phosphorus concentration versus year for R1.

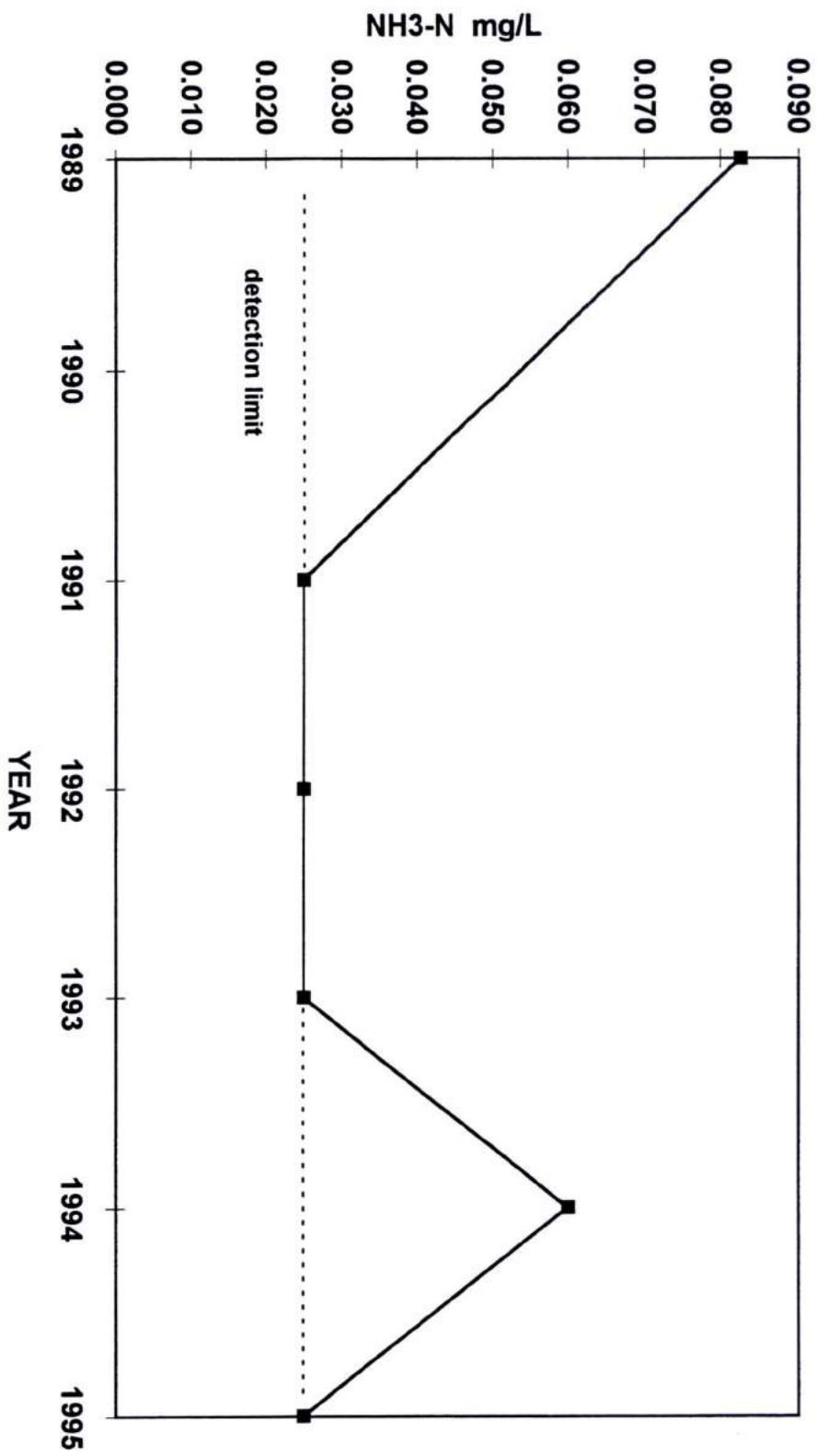


Figure 60. Average annual summer ammonia concentration versus year for Tomahawk Creek.

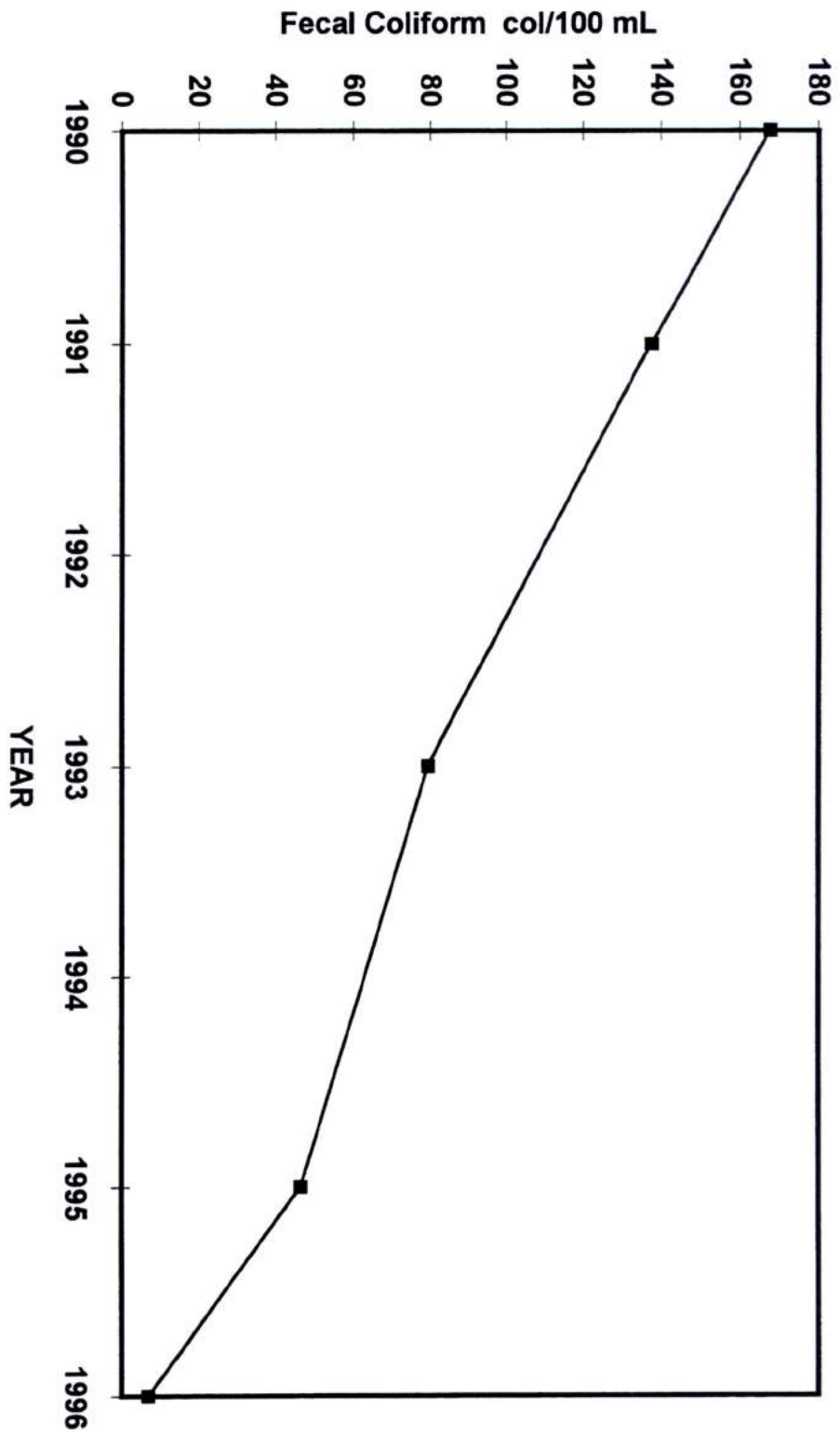


Figure 61. Average annual fall fecal coliform concentration versus year for Tomahawk Creek.

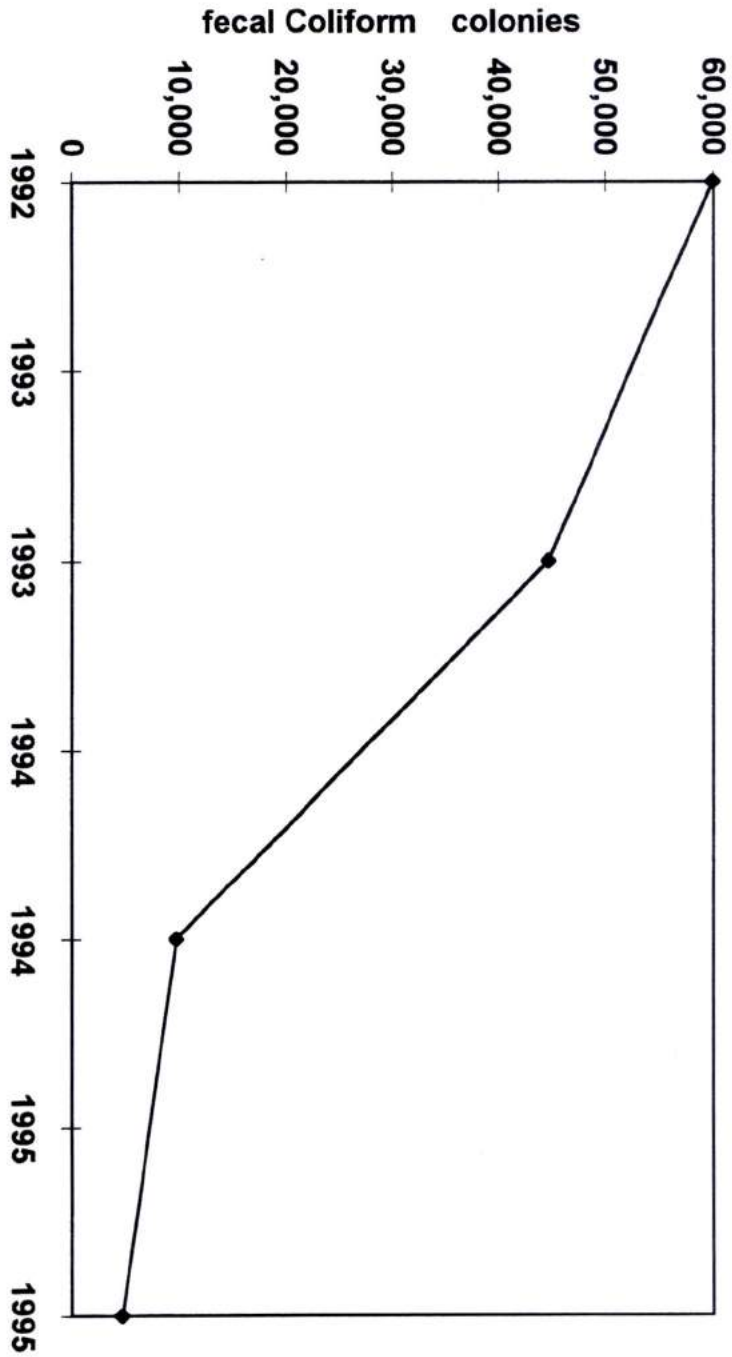
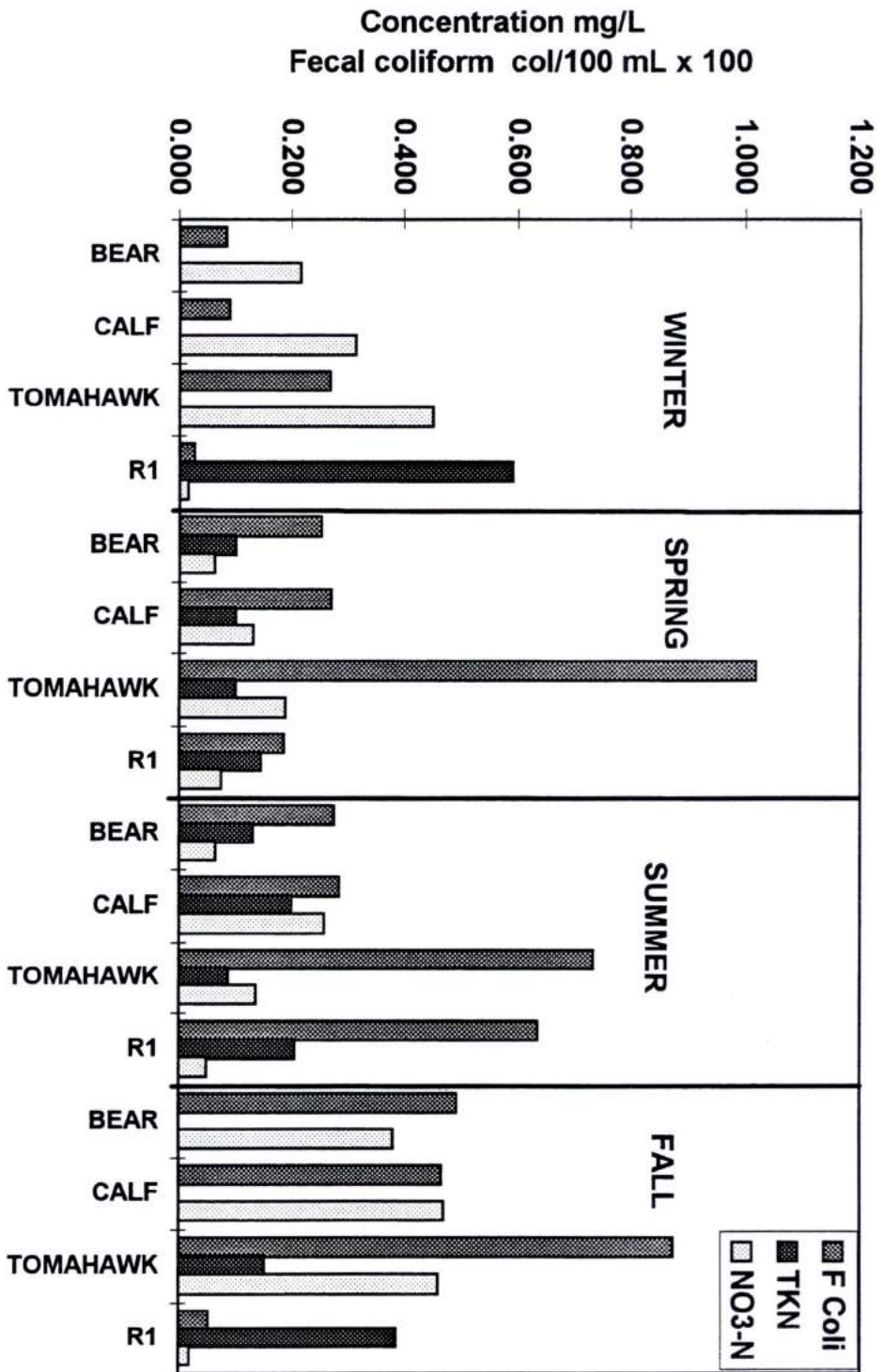


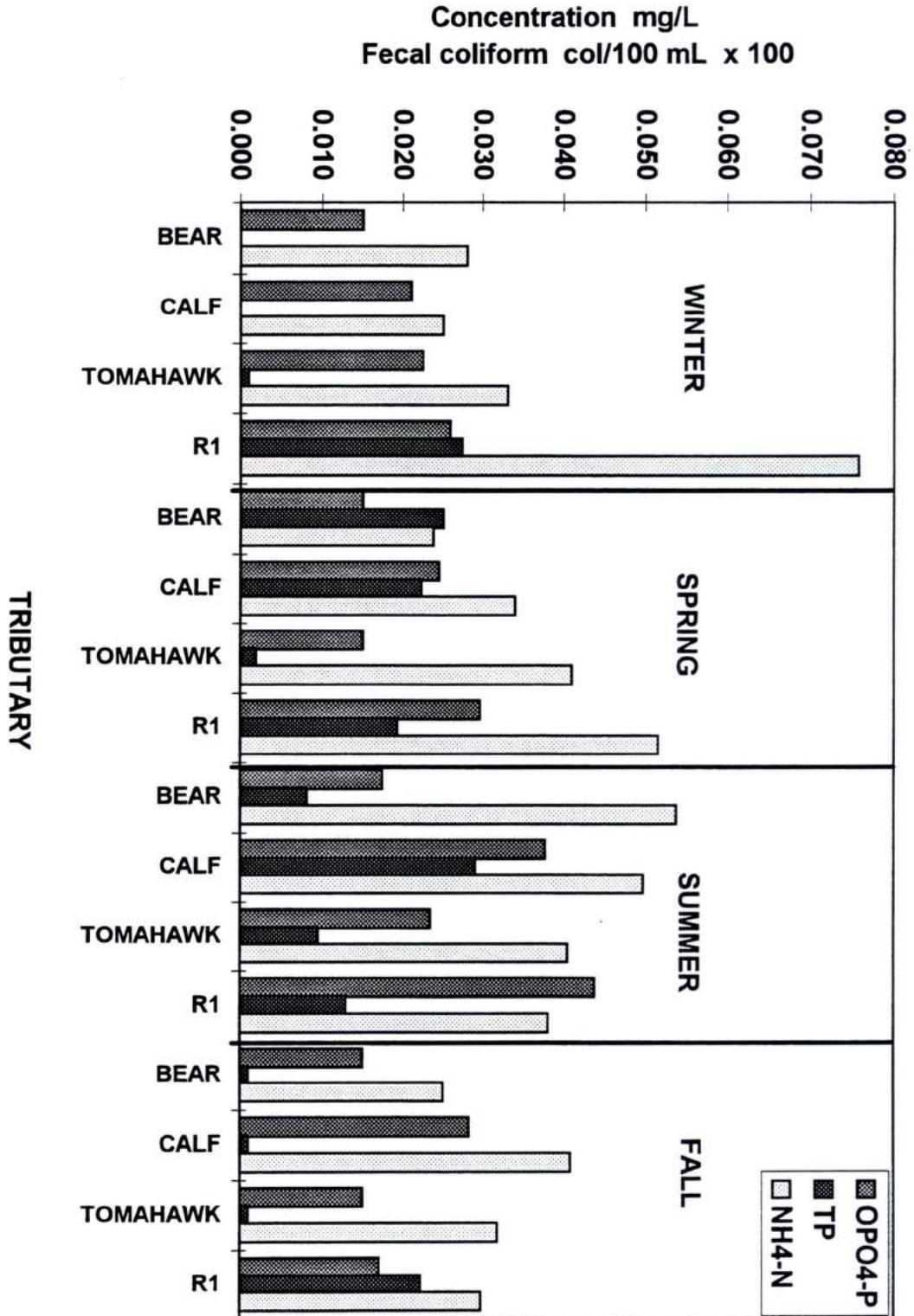
Figure 62. Average annual spring season fecal coliform loads for Calf Creek.



**TRIBUTARY**

Figure 63. Average seasonal and annual base flow concentrations for the tributaries and R1.

Figure 64. Average seasonal base flow concentrations for the tributaries and R1.



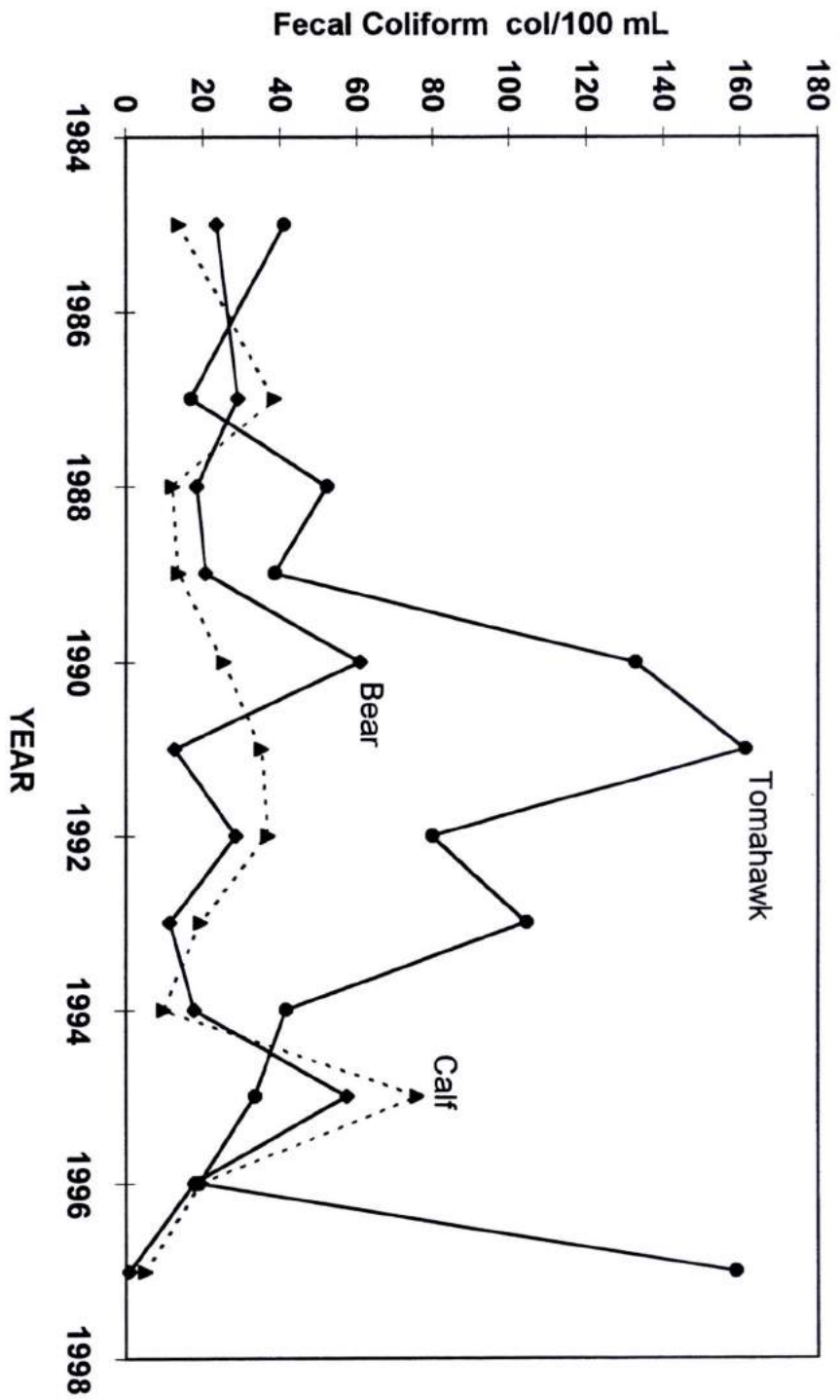


Figure 65. Annual fecal coliform concentrations for the three tributaries.

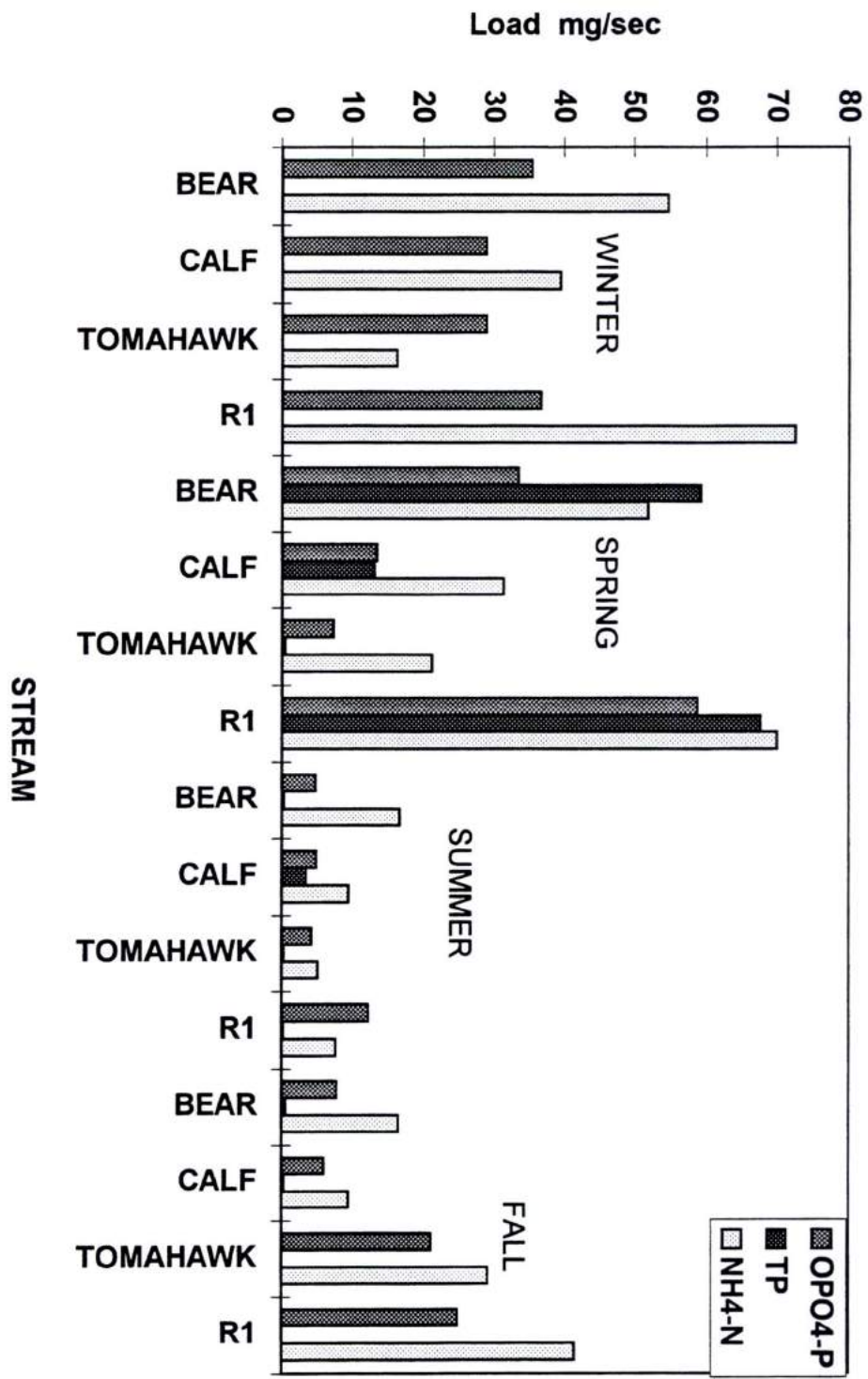


Figure 66. Average seasonal loads for the tributaries and R1.



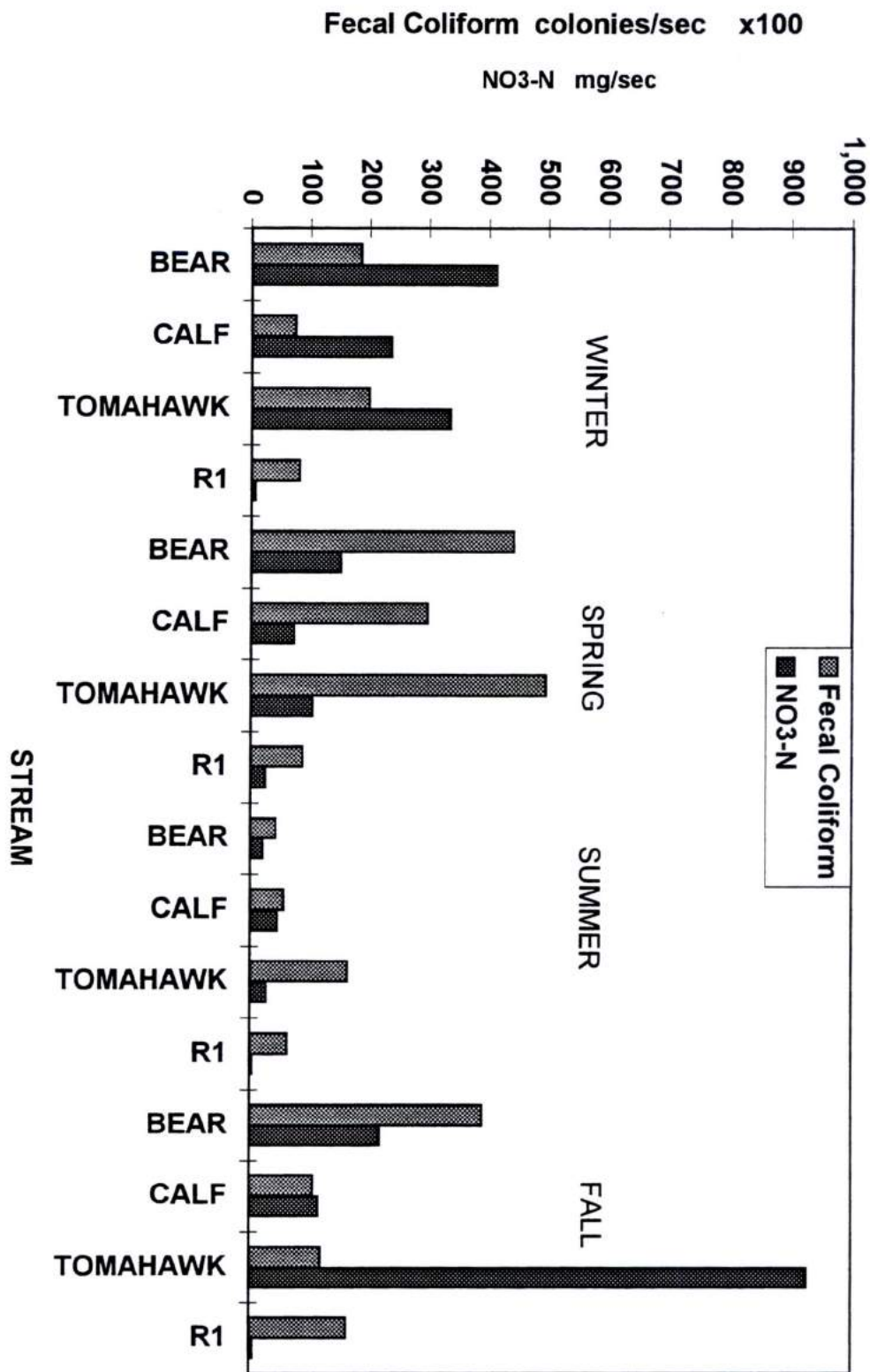


Figure 67. Average seasonal loads for the tributaries and R1.