OXIDIZED NITROGEN AND TOTAL PHOSPHORUS RELATIONSHIPS IN THE HYDROLOGY OF A MIXED PINE-HARDWOOD WATERSHED IN SOUTHEASTERN OKLAHOMA

By

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PREFACE

This study is concerned with the occurrence and movement of two nutrients in the hydrologic cycle of a forested watershed prior to timber harvesting. The primary objective is to provide basic data on the presence and behavior of oxidized nitrogen and total phosphorus in precipitation, throughfall, and streamflow in a manner which will allow statistical comparisons after timber harvesting. Linear, polynomial, and multiple linear regression models are developed.

I would like to express appreciation to my major advisor, Dr. P. J. Wigington, Jr., for his guidance and assistance throughout this study. Appreciation is also expressed to the other committee members, Dr. Sterling L. Burks, Dr. Ronald McNew, and Dr. Robert Wittwer, for their invaluable assistance in the preparation of the final manuscript.

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Finally, special gratitude is expressed to my wife, Kathy, for her understanding, many sacrifices and her excellent typing throughout the study, and to my son Timothy who was born at the start of the study, and endured many hours when "Daddy" was away both physically and mentally. To them I dedicate this thesis. I would also like to acknowledge my faith in Jesus Christ and his word through whom I drew strength during the many difficult times of

this study.

I have seen the task which God has given the sons of men with which to occupy themselves.

Ecclesiastes 3:10 NAS

But he who practices the truth comes to the light, that his deeds may be manifested as having been wrought in God.

John 3:21 NAS

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CHAPTER I

INTRODUCTION

The importance of land-water linkages has in the past been generally underrated in resource management. The output of water, dissolved nutrients, sediment, and particulate matter from the terrestrial ecosystem is the primary input for most aquatic ecosystems. Rivers and streams are the primary links between terrestrial ecosystems and lakes and reservoirs. Therefore the terrestrial ecosystem has a direct effect on the water and biological quality of water downstream (Likens and Bormann, 1974).

The extent and intensity of disturbance within a watershed will affect proportionally streams, lakes, or reservoirs downstream. An increase in eutrophication is the rule rather than the exception as dissolved nutrients, sediment, and particulate matter are increasingly lost from the terrestrial ecosystem and gained by the aquatic ecosystem. Eutrophication is defined as the natural increase in productivity as a stream, lake, or reservoir matures. Because lakes and reservoirs are sinks for materials leaving a watershed, the effects of eutrophication are usually more pronounced in these water bodies than in streams.

Man's activities through logging, mining, urbanization, roadbuilding, and agriculture tend to alter the equilibrium of natural terrestrial ecosystems, increasing the amounts of dissolved substances, particulate matter, and sediment entering streams and creating accelerated eutrophication downstream. The rate at which accelerated eutrophication occurs depends not only upon the type and amount of nutrients entering the aquatic ecosystem, but also upon the eutrophic state of the water body prior to the disturbance (Likens and Bormann, 1974). In general, accelerated eutrophication increases the productivity of a water body, an effect which is indicated by algae blooms, a decrease in aesthetics, a decrease in water quality, an increased cost for use as a water supply, and a decrease in the economic life span of reservoirs. The severity of these effects will govern the type of use and the degree to which the water is used.

Oxidized nitrogen, nitrate and nitrite, and total phosphorus are the main nutrients implicated in the accelerated eutrophication of streams, lakes, and reservoirs. However, total phosphorus is the most important of the two nutrients. Profound increases in aquatic vegetation may occur when the supply of these nutrients is suddenly increased, especially in water bodies which are nutrient poor. Nitrates in excess of 10 mg/l in treated or untreated domestic water supplies have been known to cause the disease methemaglobinemia in infants.

The potential for water quality problems during man's use of the landscape has been recognized and is beginning to be addressed throughout many scientific disciplines. Likens and Bormann (1974) state the key to the wise management of aquatic ecosystems is the wise management of watersheds or landscapes. In forestry this means the selection of Best Management Practices (BMP) to decrease or prevent the amount of material leaving the terrestrial ecosystem and entering the aquatic ecosystem. Best Management Practices are defined as the management of day to day operations to reduce negative impacts on the environment. BMP's may include the proper placement of roads and skid trials, the placement of waterbars and turnouts along roads, the maintenance of streamside protection zones, and the placement of culverts under stream crossings. However, because of variation in watershed characteristics and hydrology, the relative effectiveness of each BMP varies for different watersheds and for different regions. Therefore, in order to apply BMP's that are both economical and effective in a given area, specific BMP's need to be evaluated for their effectiveness in a given region during actual timber harvesting. However, the effectiveness of BMP's can only be compared to the natural conditions of a watershed prior to timber harvesting. Therefore, data are critically needed concerning the movement and behavior of nutrients within undisturbed watersheds. Mixed pine-hardwood watersheds are disappearing rapidly as the clear-cutting of large tracts of forested land continues in the Ouachita Highlands of southeastern Oklahoma. This large scale harvesting and the conversion of the land from mixed pine-hardwood stands to pure pine plantations can be expected to continue because of the economic value of the timber.

There exists in the state of Oklahoma a great deal of concern about the negative effects such harvesting may have on the water quality and aquatic resources in southeastern Oklahoma. Studies have been initiated by the Oklahoma State Division of Forestry and the Department of Forestry at Oklahoma State University to determine the impact of this harvesting on the water quality of streams in southeastern Oklahoma.

The primary objective of the study herein was to provide basic data on the content and movement of oxidized nitrogen and total phosphorus in precipitation, throughfall, and streamflow in a mixed pine-hardwood watershed.

More specific objectives include:

1) To determine the concentrations and loads of both nutrients entering the watershed by precipitation on a storm basis and for a single season.

2) To determine the effect of a forest canopy on the concentration and

loading of both nutrients when precipitation encounters the canopy on a storm and seasonal basis.

3) To determine the concentration and loads of both nutrients leaving the watershed via streamflow on a storm basis and for a single season.

4) To determine the behavior of both nutrients in streamflow during individual storms.

Definitions

Bulk Precipitation: the combination of wetfall (rain, snow, hail) and dryfall (dust, pollen, debris) leaving the atmosphere and impinging on a surface.

Throughfall: that part of wet precipitation falling through the vegetative foliage including water drip from wetted leaves, branches, and stems.

Oxidized nitrogen: the most oxidized and therefore most stable forms of nitrogen. The nitrate (NO_3^-) and nitrite (NO_2^-) ions collectively.

Total phosphorus: all forms of phosphorus including those in solution, bound in organic matter, inorganic solids, and sorbed to soil and clay particles.

Interflow: water flowing beneath the soil surface toward a channel.

Delayed Flow the portion of streamflow during periods of no precipitation.

Ephemeral: a stream which flows only when precipitation occurs.

First Flush: relatively high concentrations of nutrients during the initial stages of streamflow that decline rapidly and remain at a low level as the storm proceeds.

CHAPTER II

LITERATURE REVIEW

Precipitation

Oxidized Nitrogen

The chemistry of precipitation is highly variable across the United States and indeed throughout the earth. The proximity to oceans, to other large bodies of water, and to large industrial areas determines much of the precipitation chemistry of a region (Reid et al., 1981). Industrial areas, for instance, because of the burning of fossil fuels may alter the surrounding chemistry of rain and snow by contributing sulfur dioxides and nitrous oxides to the atmosphere. These chemicals react with water in the atmosphere to form sulfuric and nitric acids (Likens, 1976; Likens et al., 1977; Pierrou, 1976). The presence of these acids in precipitation is indicated by a pH of less than 5.6, the minimum pH of pure water at equilibrium with carbon dioxide in the atmosphere (Snoeyink and Jenkins, 1980; Hem, 1970). The typical pH of precipitation near or downwind from industrial areas is in the range of 3-5 (Likens, 1976). In this pH range nitric acid contributes an average of 36 % of the hydrogen ions (Asman et al., 1981).

There is concern worldwide about the potential effects of acid precipitation on terrestrial and aquatic ecosystems, particularly the effect of the leaching of heavy metals and cations from soils on the terrestrial and aquatic biota. One study has suggested that nitric acid, in most cases, poses no long term problems for forest ecosystems because it is readily assimilated into the internal nitrogen cycle of the forest ecosystem with a concommitant buffering of hydrogen ions (Mclean, 1981). The vegetation canopy is an important factor in the buffering of hydrogen ions in precipitation (Stottlemyer, 1983). Nitrate in the form of nitric acid may also be significant in increasing the productivity of a forest ecosystem (Mclean, 1981). Table I summarizes the range of nitrates observed as inputs from precipitation (Likens et al., 1977; Mclean, 1981). Nitrates are usually found in precipitation at higher concentrations than phosphates (Lewis, 1981; Likens et al., 1977).

Total Phosphorus

Total phosphorus in the atmosphere is more likely to be derived from natural sources than from anthropogenic sources. In general total phosphorus is present as particulates of organic matter, soil colloids such as clays, and sea spray (Wetzel, 1975; Pierrou, 1976). Little is known about the exact forms and fluxes of phosphorus in the atmosphere. The total phosphorus found in the atmosphere is almost without exception in the part per billion range. Table I summarizes total phosphorus concentration in precipitation from various studies across the United States. Sober and Bates (1979) found phosphorus inputs had increased as precipitation, dust, and airborne soil increased. They concluded that dirt roads in Oklahoma contributed the majority of phosphorus found in their precipitation study.

Throughfall

Intact forested ecosystems, as they mature, develop tight nutrient cycles losing only small amounts of nutrients in drainage water (Likens and Bormann, 1974; Vitousek, 1977). Nutrient flux occurs between four general

TABLE I

EXAMPLES OF OXIDIZED NITROGEN AND TOTAL PHOSPHORUS CONCENTRATIONS IN PRECIPITATION, THROUGHFALL, AND STREAMFLOW FROM THE LITERATURE

Source	Precipitation		Throughfall		Streamflow	
	N	P	N	P	N	P
	mg/l					
Likens et al. (1977, New Hampshire)	1.47	.008	.67	.15	2.01	.0023
Asman et al. (1981, Netherlands)	.062	N/M*	N/M	N/M	N/M	N/M
Foster (1974, British Columbia)	.37	.103	.19	.019	N/M	N/M
Verry and Timmons (1977, Minnesota)	.28	.059	.26	.096	N/M	N/M
Bond (1979, Utah)	.063	.09	N/M	N/M	.18	.30
Swank and Caskey (1982)	N/M	N/M	N/M	N/M	.05	N/M
Sober and Bates (1979, Oklahoma)	N/M	.300	N/M	N/M	N/M	N/M
Brozka et al. (1981, Illinois)	N/M	N/M	N/M	N/M	.35/ .52	.02/ .05
Rolfe et al. (1978, Illinois)	1.36	.173	1.66	.246	N/M	N/M
Tammi (1951)	.20	.03	.30	.05	N/M	N/M

*N/M = not measured.

compartments or storage zones: above ground biomass, below ground biomass, soil, and mineral (Likens et al., 1977). Above ground biomass includes all vegetation above the physical soil boundary, not including the litter layer. The below ground biomass includes the litter layer, the organic soil horizon, root systems, microbes, and soil invertebrates. The soil compartment includes the mineral soil body from the soil surface to the start of parent material. The mineral compartment includes soil parent material and bedrock.

The above ground biomass influences the quantity and quality of incoming precipitation in a number of ways and to varying degrees. Precipitation is intercepted, partially evaporated, and partially stored by the leaves and branches that comprise the vegetative canopy of a forested ecosystem. This interception allows only a fraction of the incoming water to reach the forest floor as throughfall. Throughfall varies on the average from 80 % to 95 % of precipitation (Boggess, 1956; Lawson, 1967). Clingenpeel (1980) found throughfall to average 85.6 % of precipitation for a small pine-hardwood watershed in southeastern Oklahoma with a range between 79 % and 93 %. For storms greater than 0.5 inches, factors such as forest plant associations, vegetation canopy density, and rainfall intensity affect the amount and variability of throughfall in a forested ecosystem (Dunne and Leopold, 1978).

Kimmins (1973), in an exhaustive statistical analysis of throughfall collection, concluded most throughfall studies have not given precise and accurate estimates of throughfall volume and chemistry due to inadequate sampling. Kimmins found not only high variability in throughfall volumes, but even higher spatial variabilities for throughfall chemistry. He concluded at least 30 throughfall collectors were needed to obtain a 95 percent confidence interval within 10 % of the mean throughfall chemistry of a 30m by 40m plot. Kimmins noted that various storms may not require the same number of collectors and that sampling for different chemicals may require different numbers of collectors. In addition, the number of collectors needed to achieve a given level of accuracy and precision for throughfall chemistry measurements is independent of throughfall volume.

Many researchers have designed various throughfall sampling schemes in an effort to keep precision and accuracy high and to minimize the number of throughfall collectors. Wilm (1946) first described the use of roving collectors. The collectors are randomly assigned new locations after each storm; the data for each collector is adjusted using the sample covariance to eliminate variation in the volumes collected during each storm, and all data is then used to calculate a mean for the whole study period. However, Wilm concluded roving collectors, cannot be used if a detailed analysis of individual storms is needed, if the experiment is of short duration, or if the chemical trends in throughfall are not similar to precipitation trends (Kimmins, 1973). Increasing the collection area with troughs or larger collector funnels is often used in an attempt to decrease the variability in throughfall collection. However, Stuart (1962) showed only a relatively small decrease in variability with a 350 % increase in sampling area. Czarowski and Olszweski (1970) noted the relative spacing of collectors had no effect on the standard deviations of throughfall chemistry. The use of data on an annual or areal basis (kg/ha) decreases variability and allows the use of a smaller number of collectors (Kimmins, 1973).

Oxidized Nitrogen

Precipitation-leaf interaction can affect the chemistry of incoming water by altering acidity and increasing or decreasing chemical constituents through leaf-wash and ion exchange reactions. Hoffman et al. (1981) noted the total acidity in rainfall is conserved in rain-leaf interactions. He concluded that strong acids (sulfuric and nitric acids) are partially removed from rain while weak acids (amino acids, humic and fulvic acids) are removed from the leaf surface. Mclean (1981) also noted a removal of sulfuric acid by the vegetation canopy. Carlisle et al. (1967) concluded inorganic nitrogen was retained by the forest canopy in an oak woodland in North Lancashire, United Kingdom. They observed rainfall with slightly higher concentrations of inorganic nitrogen than were found in throughfall. Peterson and Rolfe (1982) observed similar behavior for nitrogen in upland forests in Illinois. Rolfe and Peterson concluded microorganisms on leaf surfaces used the nitrogen in rainfall for their metabolic processes. Foster (1974) and Verry and Timmons (1978) observed an increase in throughfall nitrate concentrations from a pine species in Canada, and from black spruce and aspen forests in Minnesota, respectively.

Leaching of the decomposing litter layer by throughfall transports considerable amounts of nutrients to the mineral soil. Rolfe and Peterson (1982) discovered leaf litter retained significant amounts of nitrogen from throughfall, and the release of nitrogen from the litter layer is affected by this input of nitrogen (Gosz et al., 1973). Apparently the rate of organic decomposition is related to the amount of nitrogen which microorganisms receive.

The loss of oxidized nitrogen due to leaching of the litter layer by surface runoff is poorly understood. This lack of knowledge is perhaps due to the popular assumption that no overland flow occurs in forested watersheds (Dunne and Leopold, 1978). However, recent evidence suggests that some overland flow does occur in saturated zones adjacent to channels and swales. Indeed the leaching of the litter layer may be more important than often believed (Dunne et al., 1975).

The processes which regulate the presence of oxidized nitrogen in soil-water appear to be biochemical in origin. The conversion of organic nitrogen in the litter layer to oxidized nitrogen is generally a three step process: deamination, ammonification, and nitrification. Deamination is the microbally mediated removal of amino acids from the organic leaf litter. In the ammonification process, amino acids are oxidized to ammonium, again by microbial activity. Then ammonium is converted through nitrification, to nitrate (NO_3) by the microbes Nitrobacter and Nitrosomonas residing in the soil (Brezonick, 1972; Hem, 1970; Vitousek and Melillo, 1979). The nitrifying bacteria are generally confined to the top 10 cm of soil (Todd, et al., 1975) and the intensity of nitrification depends on the size of soil aggregates (Simon, 1974), vegetation type, and successional stage of the forest (Todd et al., 1975). Bacteria, blue-green algae, and leguminous vegetation may provide additional nitrogen for a watershed through nitrogen fixation, the conversion of nitrogen gas to nitrate (Hem, 1970).

Losses of nitrogen from the ecosystem can occur by denitrification, the conversion of nitrate to nitrogen gas. Denitrification may occur under anaerobic conditions or when tannin and acidity levels in the soil body are high (Vitousek and Melillo, 1979). A soil moisture content of 80 to 100 % is usually sufficient to create anaerobic conditions in the soil (Simon, 1974). The reaction of organic matter with nitric acid in acidic soils may convert nitrates to nitrogen gas which may then leave the ecosystem (Brezonick, 1972).

Total Phosphorous

The vegetation canopy in a forested ecosystem is effective in scavenging dust and particulate matter from the atmosphere (Likens et al., 1977). Phosphorus has been shown to be associated with dust, particulate and organic matter in the atmosphere (Lindsey and Viek, 1977; Sober and Bates, 1979). Phosphorus contributions to the forest floor by throughfall are therefore in a form unavailable for biotic uptake. Rainfall provides a vehicle for moving the insoluble phosphorus from the vegetation canopy to the forest floor. Verry and Timmons (1977) observed total phosphorus concentrations in throughfall which were inversely related to precipitation amounts.

The cycling of phosphorus within a forested ecosystem is controlled by biochemical and geochemical processes. Total phosphorus is tied up mainly in an organic matter pool and an inorganic mineral pool (Pritchett, 1979). Phosphorus release from organic matter to the soil in a forested ecosystem is caused primarily by microbial decomposition of leaf litter (Peterson and Rolfe, 1982). The removal of phosphorus from the leaf litter layer is accomplished through leaching by throughfall and precipitation falling on the litter layer, and by microbial uptake (Gosz et al., 1973; Elmsly, 1980).

Organic matter may be the principal source of phosphorus for vegetation growing on many different soil types. Orthophosphate (PO_4-3) is the primary form of phosphorus taken up by vegetation. The availability of orthophosphate to vegetation depends on the soil acidity and the solubility effects of iron, aluminum, and magnesium. These cations may form insoluble precipitates with orthophosphates in very acid soils (Pritchett, 1979).

The soil body is the major phosphate mineral pool in most forested ecosystems and is the result of pedogenesis involving parent material and bedrock containing phosphate minerals. However, phosphate minerals comprise only a small part of a soil body. The phosphate mineral pool in a forested ecosystem may be represented by any of over 200 known phosphate minerals, or an infinite number of amorphous or transition compounds (Elmsley, 1980; Lindsey and Vlek, 1977). Orthophosphate (PO_4^{-3}) has a very high affinity for cations in the environment. Substitutions involving di and trivalent cations may form many different ion pairs and complexes with orthophosphate. The weathering of primary mineral phosphates may produce many transitory compounds as cation substitution, redox reactions, and other chemical equilibria processes occur in the soil body. Some of the most insoluble phosphate minerals are those as iron and aluminum phosphates (Lindsay and Vlek, 1977).

Streamflow

Streamflow is a combination of overland flow, interflow and baseflow produced by storm events contributing rainfall or snow. The relative importance of each is determined by the intensity, duration, timing, and volume of the precipitation, by the infiltration capacity and permeability of the soil, and by the underlying geology, all of which also determine the duration of streamflow (Dunne and Leopold, 1979).

In most forested watersheds extensive areas of overland flow are uncommon. Therefore interflow and baseflow are usually the dominant components contributing to streamflow (Dunne and Leopold, 1979; Bond, 1979). However, increasing evidence suggests interflow may be diverted to overland flow at water-saturated zones adjacent to channels and swales (Dunne et al., 1975; Hewlett and Troendle, 1975).

Vitousek (1977) suggested that the majority of nutrients carried out of a watershed by streamflow are nutrients unable to be assimilated within the forested ecosystem. Vitousek also hypothesized that as a forested ecosystem matures the conservation of nutrients increases and the leakage of nutrients out of the watershed via streamflow decreases.

Oxidized Nitrogen

The degree of nutrient movement, particularly oxidized nitrogen and total phosphorus, out of a undisturbed forested ecosystem through streamflow depends a great deal on what processes contribute to streamflow during a particular storm event. The oxidized nitrogen in streamflow, for instance, is regulated by biochemical processes in the ecosystem. Therefore if overland flow occurs extensively, ammonium ions from the leaf litter may be removed from the watershed thus reducing the ammonium available for oxidation to nitrate by nitrification in the soil body. This in turn reduces the amount of oxidized nitrogen entering the stream through interflow (Vitousek and Melillo, 1979). Likewise if interflow is impeded due to low permeability of the soil, nitrates in the soil-water are removed more extensively by the vegetation due to the greater residence time in the root zone. Alternatively, if permeability is rapid, nitrate laden soil-water moves rapidly out of the root zone thus contributing more nitrate to streamwater (Vitousek and Melillo, 1979).

The importance of vegetative uptake of nitrate in soil-water is seen in many studies by growing season minima and dormant season maxima for nitrate-nitrogen concentrations in streamwater (Hem, 1970; Likens et al., 1977; Brozka et al., 1981; Reid et al., 1981). Other losses of ammonium available for nitrification in an ecosystem will result in a decrease in oxidized nitrogen leaving the ecosystem in streamflow. Such losses include microbial uptake, cation exchange in soils, volatilization loss of ammonia, and denitrification of ammonium to nitrogen gas (Vitousek and Melillo, 1979). Nitrate losses also occur in streams due to uptake by algae, fungi, and other biota (Swank and Caskey, 1982). Unidentified, short-term nitrogen storage may also occur in streams (Meyer et al., 1981).

The behavior of oxidized nitrogen in streamflow during a storm seems to be variable among different watersheds and under different levels of biotic activity. Bond (1979) concluded oxidized nitrogen did not vary with discharge in a perennial montane watershed in Utah. While Vitousek (1977), and Lewis and Grant (1979) observed a decrease in oxidized nitrogen concentrations with increasing discharge in a perennial stream draining a forested watershed in Colorado. Lewis and Grant (1979) also observed oxidized nitrogen yields that increased at a slower rate than the rate of discharge increase.

Total Phosphorus

During a storm event, overland flow either in the saturated soil zone near channels or sheet flow in other areas of a watershed often carry soil particles, colloids, and coarse particulate organic matter with associated phosphates into a stream channel (Dunne and Leopold, 1979). The materials deposited in the channel are stored there until a critical stream velocity is reached capable of moving a portion of this sediment and organic matter downstream. Wetzel (1975) and Likens et al. (1977) have concluded that most total phosphorus generally moves with sediment. Harms (1977) and Smith (1976) observed that total phosphorus levels in streamflow were associated with suspended sediments derived from stream bed scour.

The behavior of total phosphorus export from an ecosystem in streamflow during a storm event appears to be variable and unpredictable. Bond (1979) indicated phosphorus behavior was variable during stormflow in a perennial stream draining a montane ecosystem in Utah and had little relationship to stream discharge. Jones (1978) found phosphorus concentrations unrelated to stream discharge at low flows and only a weak relationship at high flows in a stream draining a forested watershed in Canada. Lewis and Grant (1979) observed that dissolved organic phosphorus had no relationship to discharge, but orthophosphate increased with increasing discharge. However, phosphorus export via streamflow appears to vary with storm intensity. Mild storms contributed 1 to 2 % more of the total basin load than baseflow, whereas intense storms contributed up to 50 % of the total annual load (Smith, 1976; Jones, 1978). Likens et al. (1977) observed a total phosphorus output that appeared to be highest when streamflow was highest. Duffy et al. (1978), in a study of nutrient export from loblolly pine watersheds, observed sediment concentrations and sediment total P were independent of stormflow but were strongly related to each other. They also observed that 10 % of the storms accounted for 63 % of all the sediment total P, and that clay seemed to carry the most phosphorus.

CHAPTER III

METHODS AND MATERIALS

Study Area

The Clayton Lake Watershed Research Area is the 1000 hectare Peal Creek watershed approximately thirteen kilometers southeast of Clayton, Oklahoma in Pushmataha County (Figure 1). The watershed is the major drainage area for Clayton Lake, a small reservoir operated by the state for recreation. Currently three small watersheds in the research area are being monitored by the Oklahoma State University, Department of Forestry for rainfall, stream flow, and stream chemistry. These three watersheds, designated 1,2, and 3, are owned individually or in combination by Nekoosa Papers, Inc. and Weyerhaeuser Company.

The research presented herein was conducted on watershed 1. Watershed number 1 was relatively undisturbed, but has a history of high-grade timber harvesting. The most recent harvesting occurred 23 to 28 years ago (Vowell, 1980). However, sometime between 1980 and 1981 a thinning operation occurred on three acres in the southeast corner of the watershed.

Climate

The climate at the research area is temperate and typical of the lower coastal region. Mean annual rainfall is 119.5 cm and mean annual temperature is 17.2 C (Bain and Waterson, 1979). Temperature extremes of +40 C in the summer and -7.8 C in the winter may occur, but are usually brief and

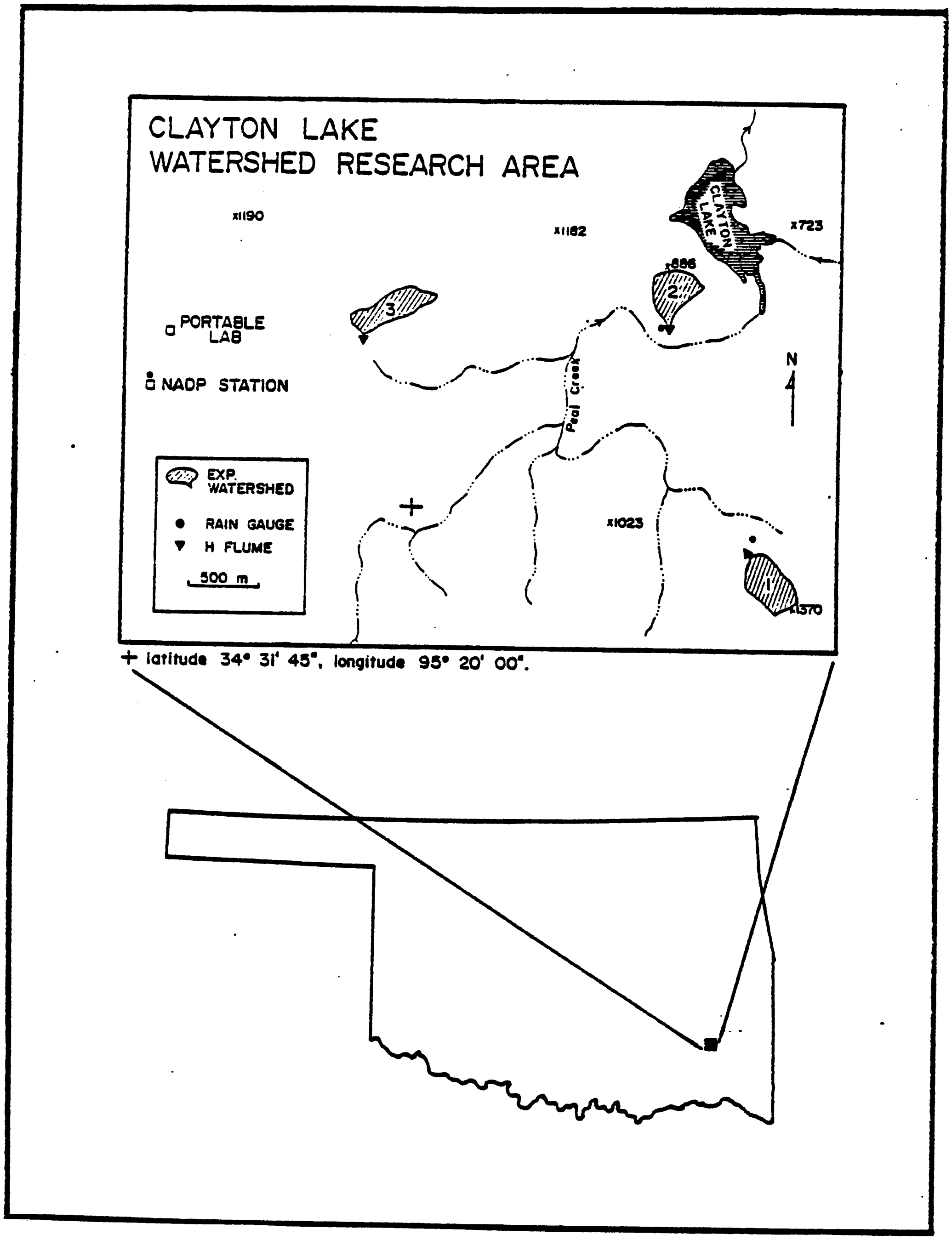


Figure 1. The Location of the Oklahoma State University's Forested Watershed Research area

infrequent. Spring and summer rain storms are usually frontal-convective, producing rainfall of high intensity and short duration. These storms result from prevailing winds from the south or southeast bringing warm moist air from the Gulf of Mexico. Winter precipitation events arise generally from cyclonic systems originating off the Pacific Coast moving west to east into the area or frontal systems moving down from Canada. Most of the precipitation occurs primarily as rain with the majority of the annual precipitation falling from March to June (Figure 2).

Vegetation and Soils

The vegetation and soils reflect the climatic conditions which exist in the region. Vegetation of the study watershed consisted of scattered old and sapling stands of shortleaf pine (*Pinus echinata*) and a mixed hardwood understory. Predominant hardwoods included oak-hickory (*Quercus*-*Carya*) association, and elm (*Ulmus*).

The primary soil type of the study watershed is the Carnasaw series (Bain and Waterson, 1979). This soil (clayey, mixed, thermic typic Hapludult) is characterized as relatively deep and well drained with moderate permeability (1.52 to 5.08 cm/hr.) in the A horizon and low permeability (.51 to 1.52 cm/hr.) in the B horizon. The soil parent material is weathered shale and sandstone. Piram and Stapp soils are found frequently and have less clay in the control section. The depth of the A horizon of Carnasaw soils is 0-18 cm and is a stony, sandy loam. The B horizon depth is 18-90 cm and is predominately clay (Bain and Waterson, 1979).

Hydrology

Streamflow in the study area is ephemeral and occurs generally in

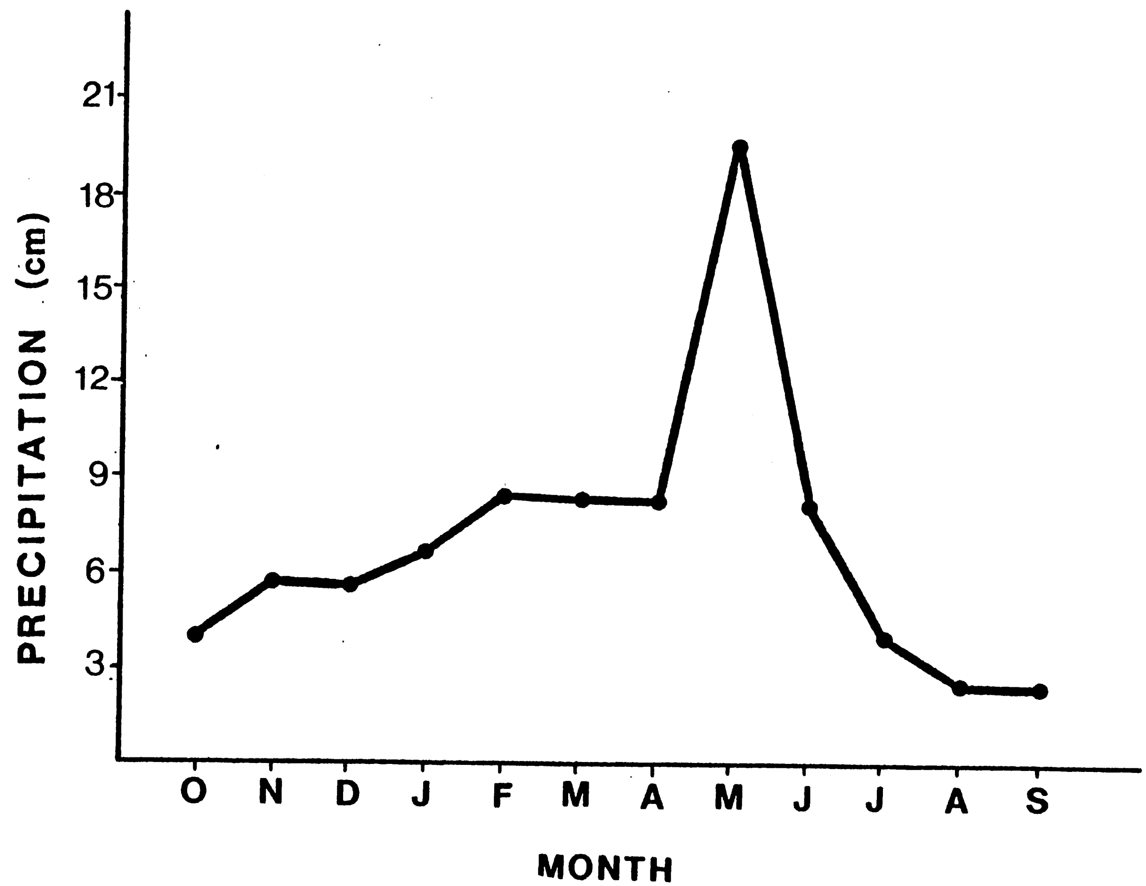


Figure 2. Five Year Average Monthly Precipitation at Watershed One, 1978-1982

response to high intensity convective storms, although cyclonic storms of long duration will also produce streamflow. The response of the watershed to precipitation is quite rapid, producing a hydrograph with a steep rising limb, short crest segment, steep falling limb, and delayed flow of variable length (Figure 3). This type of hydrologic response is characteristic of watersheds with low permeability, little bank storage, and little groundwater storage. Streamflow occurs most frequently during the months of April, May, and June (Figure 4).

Basin configuration is short and broad (Figure 5) and dissected by many small rills and swales that drain into two relatively well-defined channels. This channel development is typical of regional headwater areas. Table II summarizes the watershed characteristics.

Sampling Methods

The sampling methods used in this study were composites of methods gleaned from the literature and methods in use in the watershed at the time this study began. Precipitation, throughfall, and streamflow samples were collected from March 1, 1983 to June 30, 1983.

Precipitation

Two sites were selected for collecting bulk precipitation samples (Figure 5). One in a clearing at the watershed outlet adjacent to a weighing-bucket type recording raingage and the other site in a clearing on the ridge delineating the upper boundary of the watershed. This site was approximately 9 to 12 meters north of an unimproved dirt road which ran along the top of the ridge.

The bulk precipitation collectors (Figure 6) were modifications of a design described by Lewis and Grant (1978). The collector consisted of a four-sided

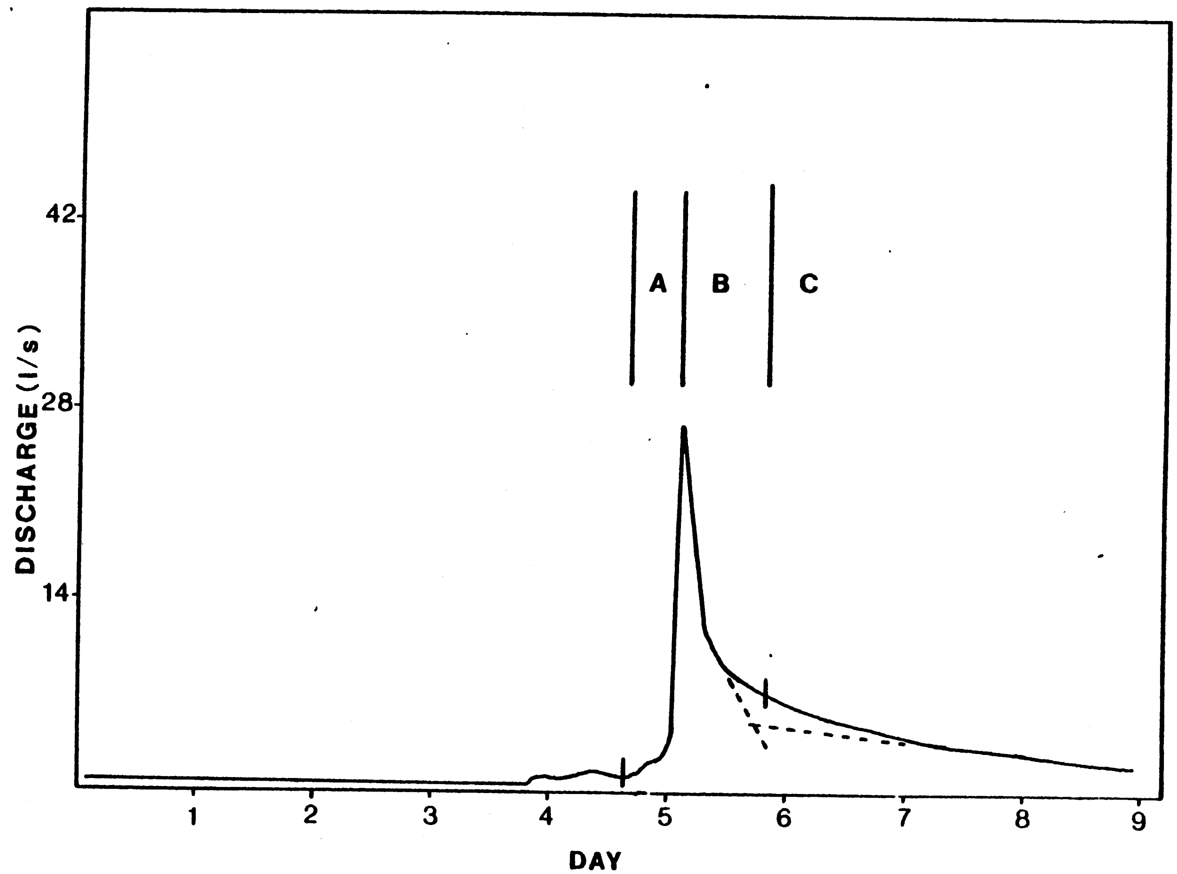


Figure 3. A Typical Stream Hydrograph from Watershed Number One. A, B, C designate the Rising, Falling, and Delayed Flow, respectively

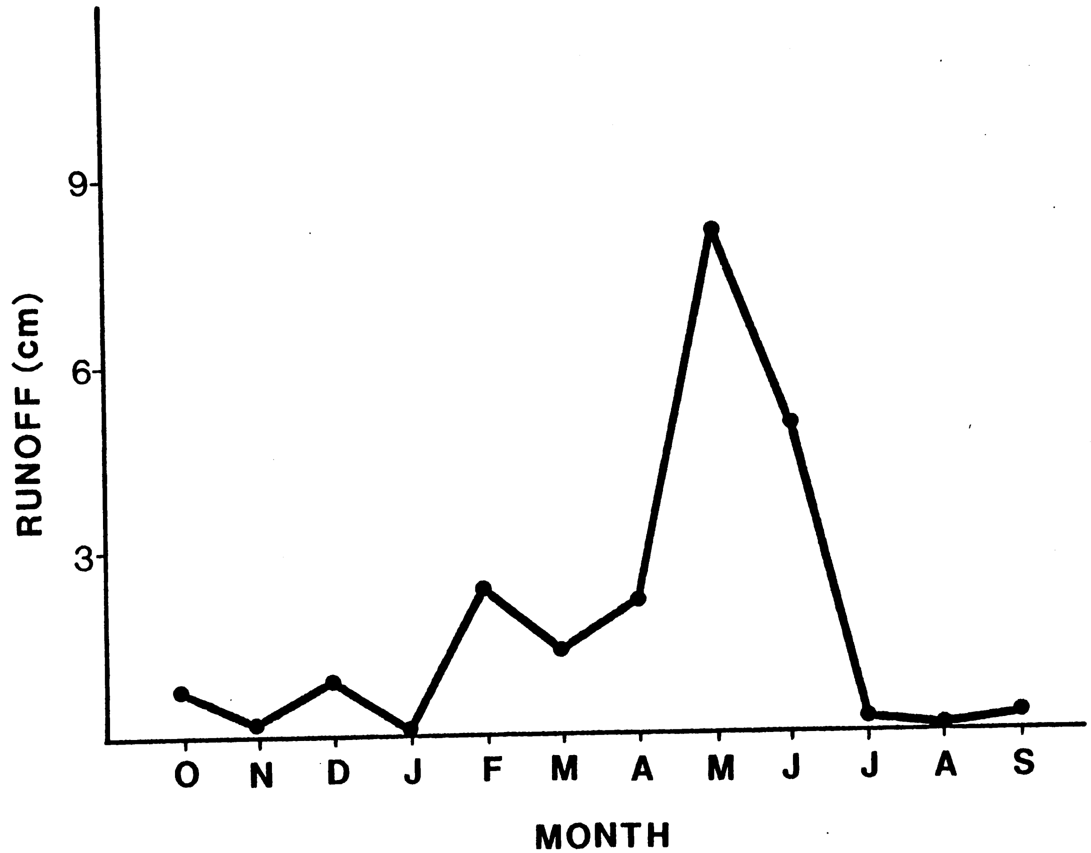


Figure 4. Distribution of the Five-Year Mean Monthly Runoff from Watershed One, 1978-1982

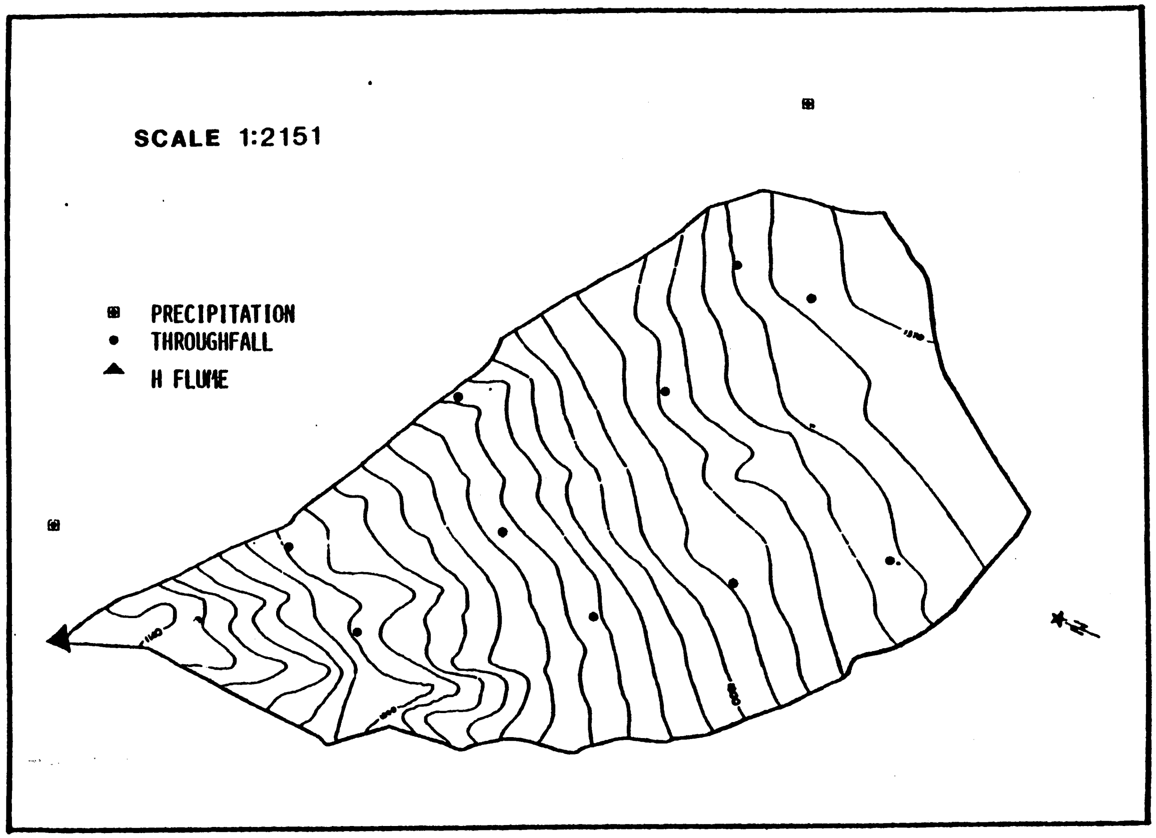


Figure 5. Basin Configuration and Location of Collection Equipment on Watershed One

ERRATA

This Errata Sheet replaces TABLE 2 on page 25; the replacement was made on September 16, 1988.

TABLE II

WATERSHED CHARACTERISTICS

Parameter	Units of Measure	Value
Area	Hectares	7.86
Elevation	Meters	
Maximum		418
Minimum		335
Aspect		NNW
Slope (average[1])	Percent	16
Crown Cover[2]	Percent	90
Ground Cover	Percent	
litter		86
rock		3
tree		6
erosion		1
stream channel		4

[1]Change in elevation divided by watershed length.
[2]Crown cover was estimated from aerial photographs.

TABLE II

CHARACTERISTICS OF WATERSHED ONE[1,2]

Parameter	Unit of Measure	Value
Area	Hectare	7.86
	Acres	19.42
Elevation	Meters	418
		348
Aspect		NW
Slope (Average)	Percent	14
Crown Cover[3]	Percent	90
Pine		65
Hardwood		25
Surface Conditions	Percent	
Litter		86
Rock		3
Tree		6
Erosion		1
Stream Channel		4

[1]Data were collected from sample points at 20 meter intervals on a random grid.

[2]Percent crown cover estimated from aerial photographs.

[3]Most of the table taken from Vowell (1980).

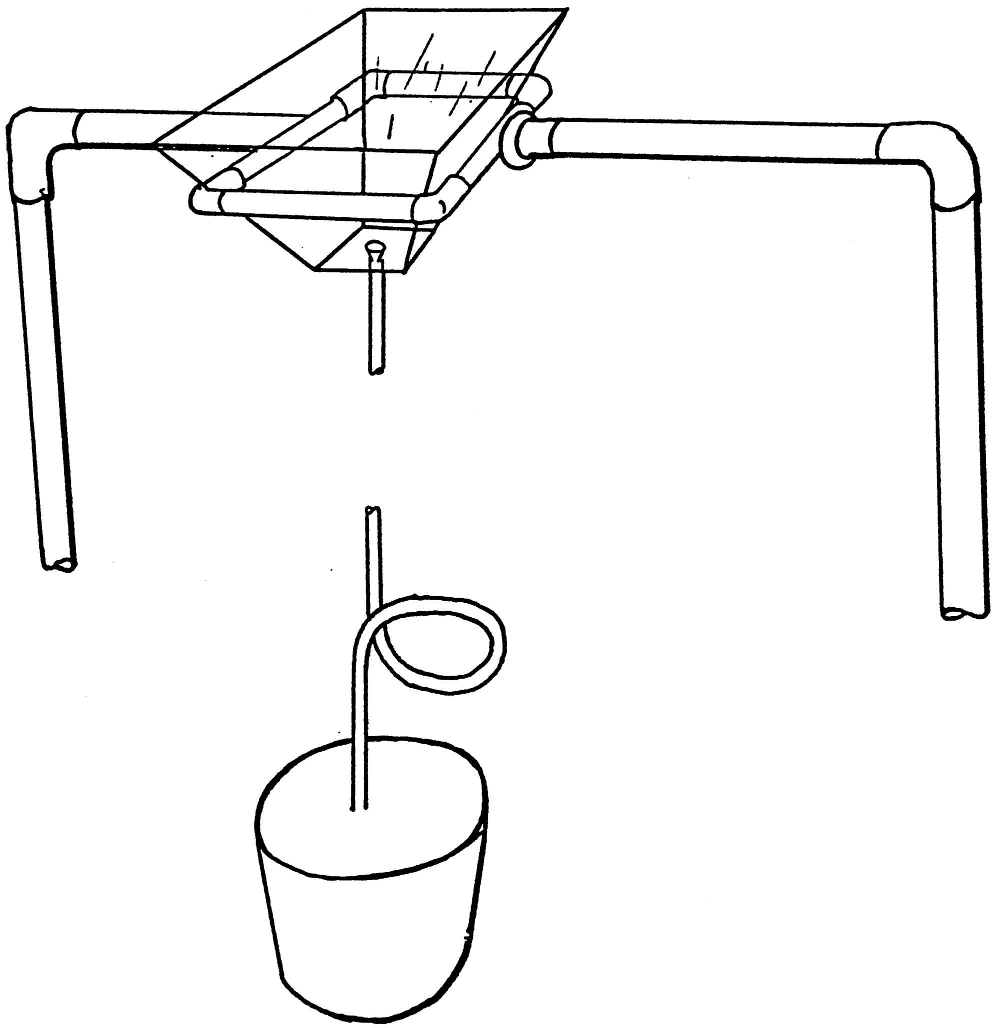


Figure 6. Illustration of the Bulk Precipitation Collector used in the Study

plexiglass funnel (2090.32 cm^2 in area), latex rubber tubing, and two 18 liter polyethylene buckets placed in tandom to assure that any size storm could be sampled without fear of overflow. A one millimeter mesh fiberglass screen was placed in the funnel to keep insects and debris out. No effort was made to keep birds away from the funnel.

Throughfall

Ten sites were selected for collecting throughfall samples (Figure 5). A stratified design was chosen to sample throughfall from the hardwood canopy and the pine canopy according to the percentage of the total vegetation canopy each canopy occupied. Therefore, seven collectors were placed under pine canopy and three were placed under hardwood canopy. The actual placement of the ten collectors in the watershed was determined using a random number table to both assign random numbers to numbered grid stakes in the watershed and to assign a collector to a grid point.

The throughfall collectors (Figure 7) consisted of a 26.67 cm (558.6 cm^2 in area) diameter circular polyethylene funnel, latex rubber tubing, and one 7.6 liter polyethylene bucket. A one millimeter mesh fiberglass screen was placed inside the funnel to prevent insects and debris from falling into the buckets. No effort was made to keep birds away from the funnels.

Subsamples of 500 milliliters (ml) were collected in polyethylene bottles from the precipitation and throughfall buckets and frozen within one to five days after a storm and subsequently transported to Stillwater for analysis. After the subsamples were taken, the total volume collected was measured by pouring the water from the buckets into a two liter polyethylene graduated cylinder. After collection was completed, the funnels and tubing were washed with 6N hydrochloric acid and rinsed with deionized-distilled water in the

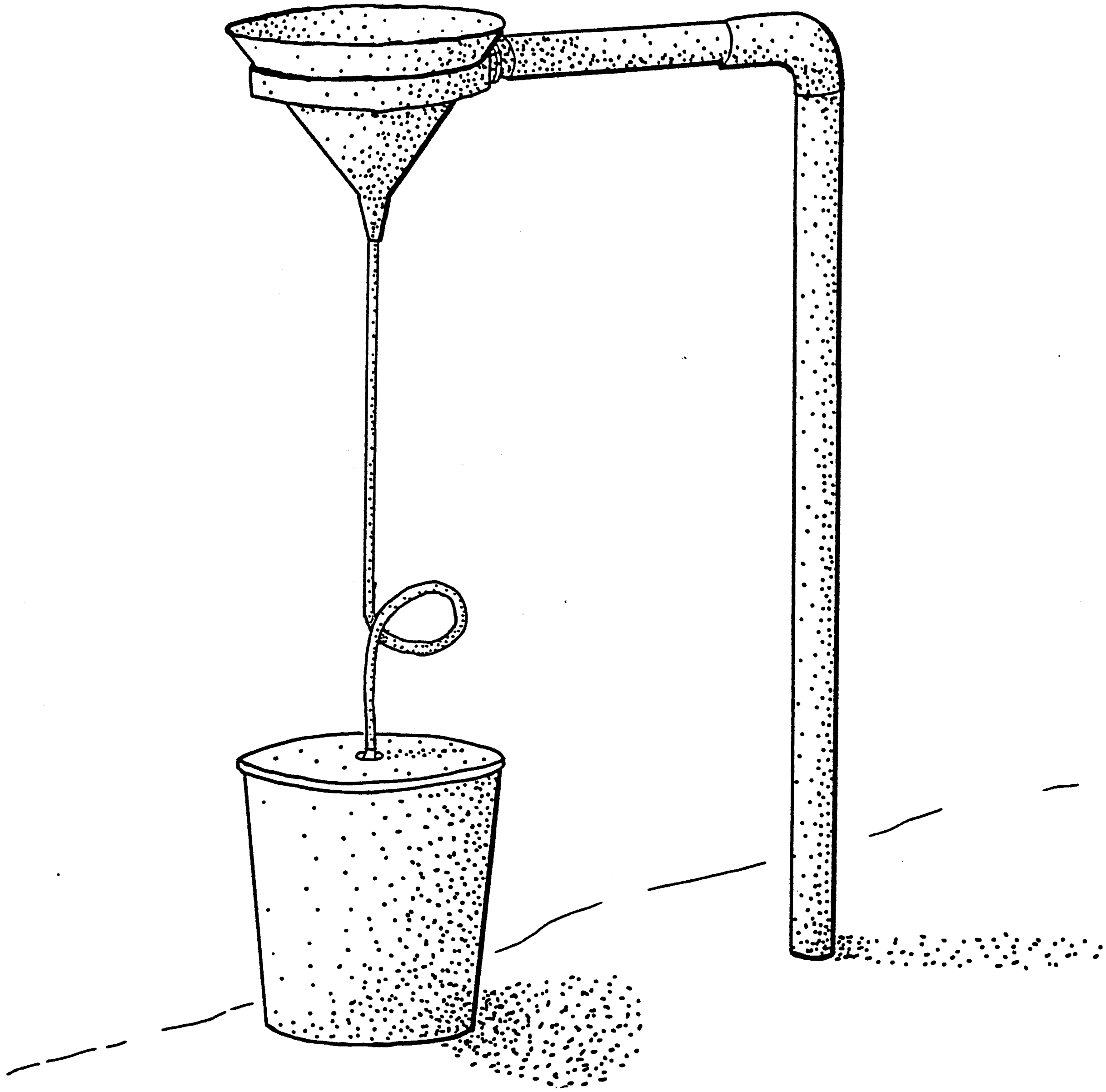


Figure 7. Illustration of the Throughfall Collector used During the Study

field. The buckets were replaced with clean buckets from the lab which had been washed in phosphate-free soap, rinsed in 6N hydrochloric acid, and rinsed with deionized-distilled water.

Streamflow

Stream discharge was determined using a 1.22 meter H flume with a concrete approach section. A water-level chart recorder was used in a stilling-well to record the height of the stream and the associated time in minutes. These values were converted to discharge using equations developed by Gwinn and Parsons (1976).

Four hundred ml water samples were collected at 3.05 cm intervals during stormflow by an automatic sequential sampler (Isco Model 1680) triggered by a magnetic switch column (Turton and Wigington, 1984). The sampler intake was placed just upstream of the concrete approach section to the flume. Samples were taken only when the stage of the stream was greater than or equal to 3.05 cm. These samples were gathered and frozen within one to three days after streamflow began. Grab samples of 500 ml were also collected during delayed flow periods.

Laboratory Analysis

Using Environmental Protection Agency procedures (EPA, 1979), all samples were analyzed for oxidized nitrogen and total phosphorus in the Forest Watershed laboratory at Oklahoma State University (Figures 8 and 9). All analysis were completed as soon as possible after sample collection, but usually within 30 days. Prior to the start of analysis all glassware and other equipment were washed in phosphate-free soap, rinsed with 6N hydrochloric acid, and rinsed with deionized-distilled water.

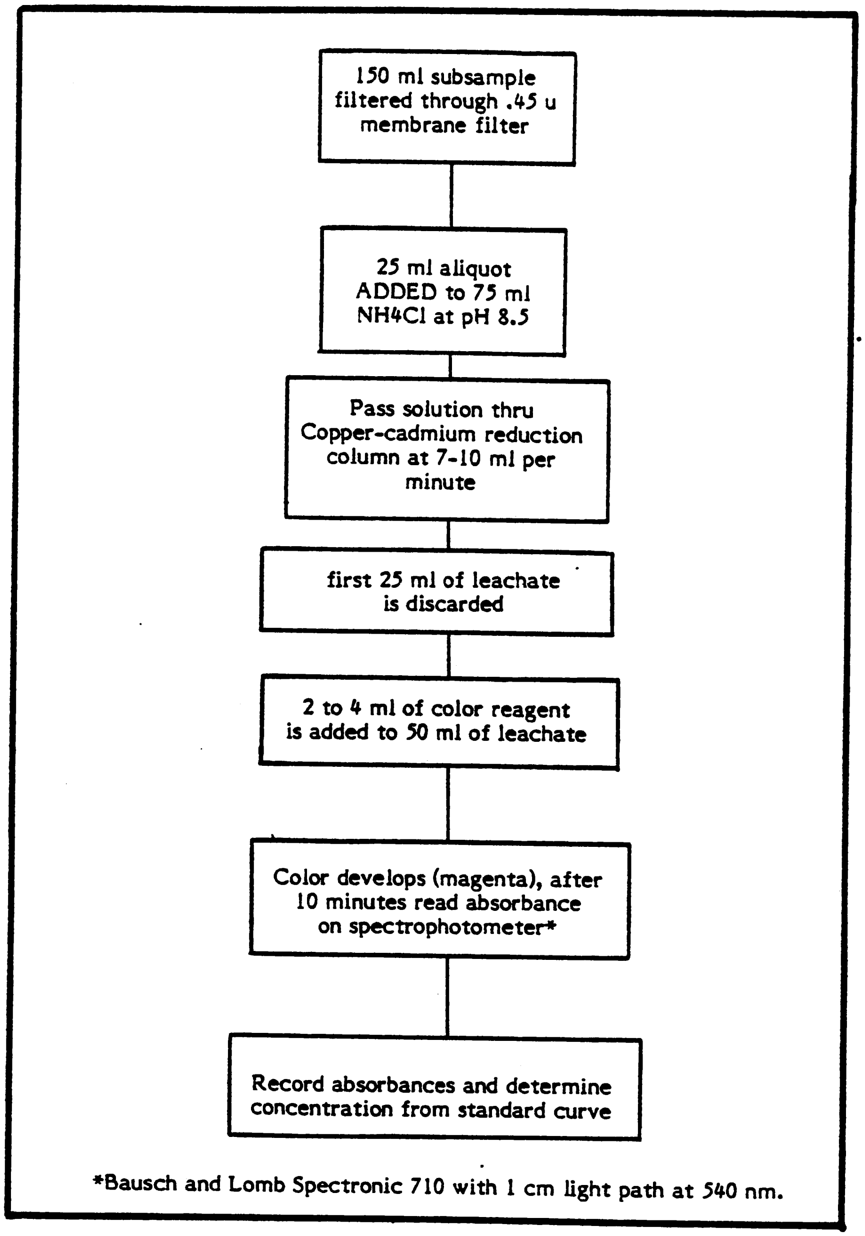
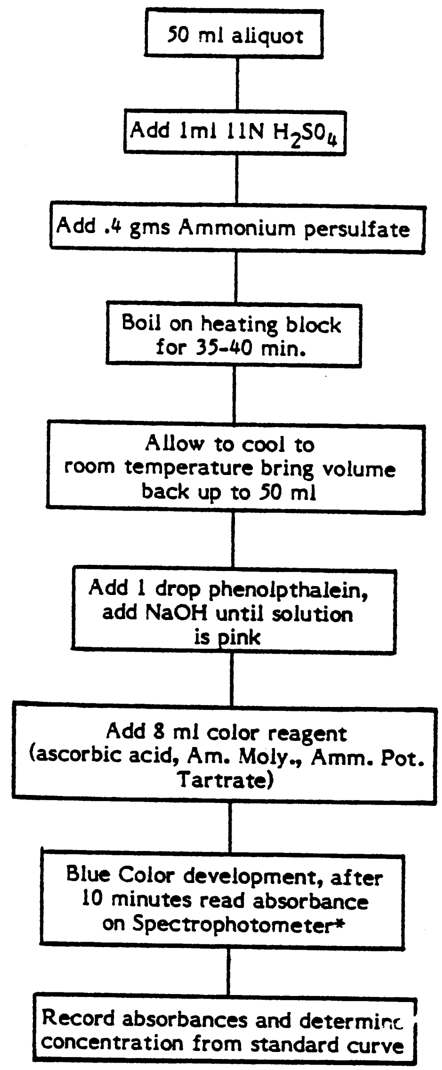


Figure 8. Summary of Methodology used to analyze samples for oxidized nitrogen (EPA, 1979)



*Bausch and Lomb Spectronic 710 with 1 cm path length at 880 nm.

Figure 9. Summary of methodology used to analyze samples for total phosphorus (EPA, 1979)

Quality control during laboratory analysis was maintained by analyzing a standard of known concentration, a spiked sample, and an EPA quality control standard prior to beginning a day's analysis of 15 to 30 samples. Standard curves were constructed when new reagents were mixed or when the cadmium columns were recharged with copper. A Bausch and Lomb Spectronic 710 spectrophotometer with a one centimeter light path was used to measure the absorbances of processed samples.

The limits of measurement were established at 0.01 mg/l and 1.0 mg/l by the EPA (1979) for both the oxidized nitrogen and total phosphorus procedures. Whenever a sample or samples exceeded the upper limit the samples were diluted with deionized-distilled water in volumetric glassware and run through the analysis. Most dilutions ranged from 1:1 to 1:4, although one storm required dilutions for throughfall samples up to 1:200.

Data Analysis

Precipitation and Throughfall

After the oxidized nitrogen and total phosphorus concentrations and the associated precipitation and throughfall volumes were tabulated, the mass per unit area for each nutrient was calculated. The following equation was used:

$$\text{Load (kg/ha)} = CV\,(1\times10^{-6}\ \text{kg/mg}) \div A \qquad (1)$$

where: C = nutrient concentration in mg/l

V = volume of sample collected in liters

A = collector area in hectares

Summary statistics were then calculated for the oxidized nitrogen and total phosphorus concentrations and loads in each storm. Volume-weighted means and standard deviations were also calculated for the study period using the

Statistical Analysis System (SAS, 1979). Indicator variables were used for statistical analysis to describe storm type (convective or frontal) and the dormancy of trees.

A Pearson correlation analysis (Johnson, 1976) was completed among the variables rainfall depth, inverse of rainfall, maximum intensity, storm duration, dormancy of trees, date, oxidized nitrogen concentration, oxidized nitrogen load, total phosphorus concentration, and total phosphorus load. The significance of correlation was tested at =0.05. Those variables found to be significantly correlated with the oxidized nitrogen and total phosphorus concentration and loads were used in a stepwise regression analysis to find the "best" models which describe the relationships found in the correlation analysis. If stepwise regression indicated the resulting model included only one variable, then the appropriate graph was consulted to determine linearity of the relationship. If the relationship was not linear, then either transformations were done to linearize the data or a polynomial regression analysis was completed. Data were dropped from the statistical analysis if more than two storms were represented during a collection and both storms were nearly equal in size, or if after initial regression analysis the data points in question were greater than 2.5 standardized residuals.

Streamflow

Streamflow was assumed to begin when discharge suddenly increased after a period of precipitation, and end when the discharge was less than 0.5 % of the peak discharge. Stream hydrographs were separated into three blocks: rising limb, falling limb, and delayed flow. The rising limb of a storm hydrograph was determined to start at the beginning of stormflow and end at the peak discharge. The falling limb was determined to start at peak discharge and end at a point where a straight line drawin along the falling limb intersected with a straight line drawn along the delayed flow limb (Figure 3). Delayed flow was determined to start at the end of the falling limb and end when discharge was less than 0.5 % of the peak discharge.

After the sampling times, the discharge at sampling, and the oxidized nitrogen and total phosphorus concentrations were tabulated, loads using an equation similar to equation 1, and discharge-weighted summary statistics were calculated using SAS (1979). A total storm load for both nutrients in each storm was determined by using a computer program to integrate, by histogram summation, a curve of load versus time. A Pearson correlation analysis (Johnson, 1976) was completed among stormflow, timing before or after peak flow, total storm runoff, total suspended solids, organic suspended solids, dormancy of trees, date, oxidized nitrogen concentration, oxidized nitrogen load, total phosphorus concentration and load. All variables found to be significantly correlated with oxidized nitrogen concentration and load, total phosphorus concentration and load were included, respectively, in a stepwise regression analysis.

The behavior of oxidized nitrogen and total phosphorus concentrations were observed within each storm by plotting the nutrient concentration versus discharge for consecutive samples beginning with the first sample collected for each storm and continuing to the last sample collected in a storm. Such plots form a loop which Bond (1979) called trajectories, that have a direction (clockwise or counterclockwise), a quantifiable limb slope and limb separation, and usually a concentration difference between the first and last samples (Figure 10). Loops which are clockwise in direction indicate a dilution of the nutrient in question after peak flow, therefore concentrations of the nutrient are higher before peak flow than after. In a similar way, loops which are

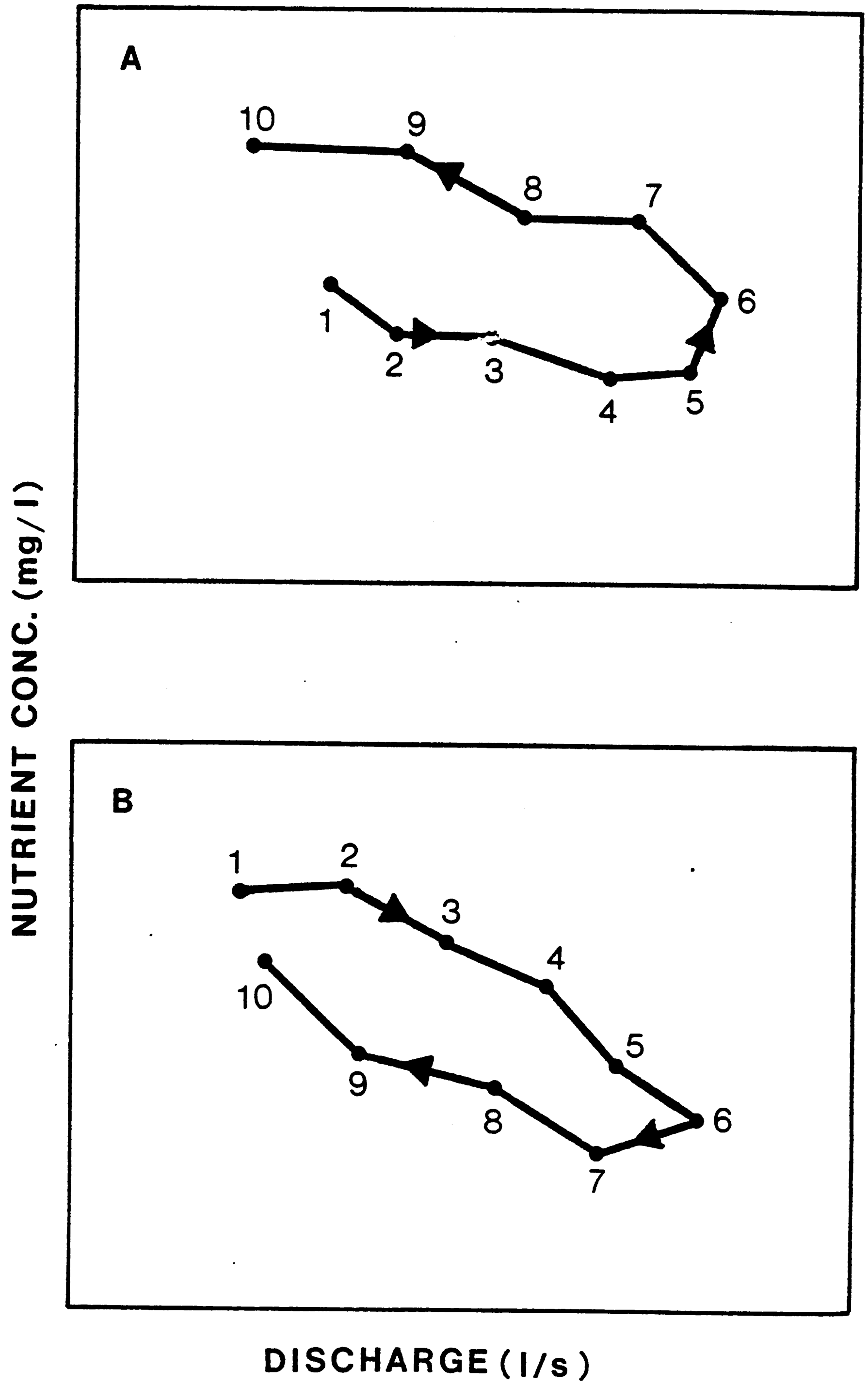


Figure 10. Hypothetical Trajectories Showing A) Counter-clockwise Direction and B) Clockwise Direction

counterclockwise in direction indicate a concentration of the nutrient in question after peak flow, therefore nutrient concentrations are lower before peak flow than after peak flow. Whitfield and Shreier (1981) concluded that these loops represent a hysteresis phenomenon and simple linear regression techniques could not be used with any confidence for predicting nutrient concentrations in response to discharge.

Often the first few minutes or hours of streamflow have a much higher nutrient concentration than the concentrations in the remainder of the storm (Helsel, 1979). This phenomenon has been called the first flush effect. A procedure outlined by Helsel (1979) was used in this study to determine if a first flush of oxidized nitrogen and total phosphorus occurred during stormflow for each storm. The procedure plots the cumulative percentages of total nutrient load and total flow versus the percentage of elapsed time. A first flush is indicated when the incremental load is greater than the incremental flow (Figure 11). A computer program was written to construct these plots and indicate first flush.

Study period comparisons between storms and between the rising, falling, and delayed flow blocks were completed for both nutrients. A graph of oxidized nitrogen and total phosphorus load was constructed for the entire study period by setting peak discharge, end of the falling limb, and end of delayed flow equal to 1.0, respectively. The nutrient concentrations from each storm were plotted with the corresponding discharge as a fraction of peak discharge, end of falling limb discharge, or end of delayed flow discharge depending on which of the blocks the sample was taken. A randomized complete block analysis of variance and Duncans multiple range procedure were completed to test for differences between storms and for differences between rising, falling, and delayed flow blocks.

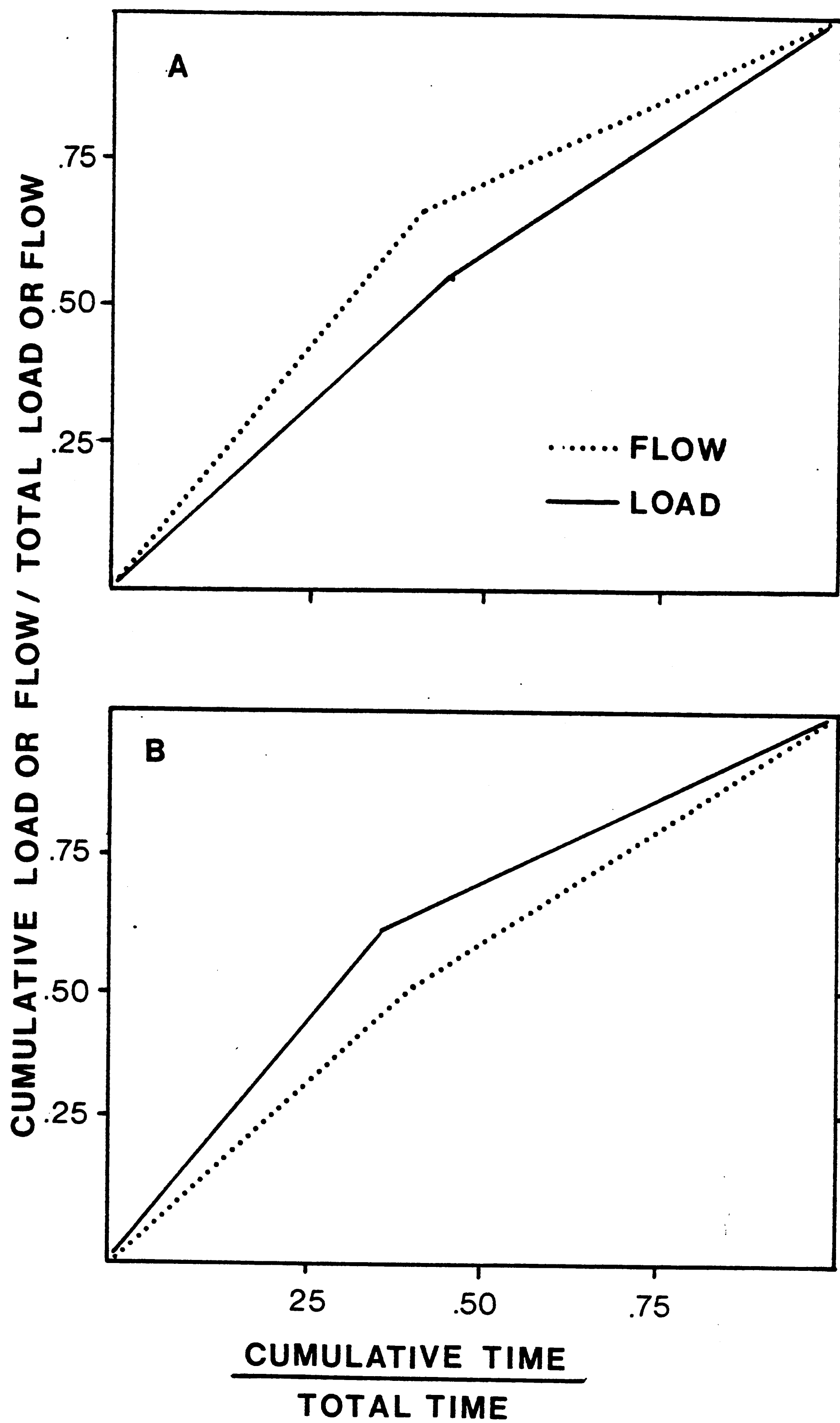


Figure 11. Plots for the Determination of the First Flush Effect. A: No Flush, B: First Flush

A t-test (=.10) was used to compare nutrient concentrations and loads among precipitation, pine throughfall, hardwood throughfall, and streamflow on a storm and total study period basis.

CHAPTER IV

RESULTS

Precipitation

Precipitation for the study period was variable and ranged from 0.254 cm to 6.35 cm per event. The greatest number of storms as well as the largest storms occurred in May, 1983 (Figure 12). Significant correlations were seen among rainfall depth, maximum intensity of rainfall, and storm duration. However, rainfall depth had the highest correlation with maximum intensity (Table III).

Oxidized Nitrogen

Significant correlations were seen among oxidized nitrogen concentrations (mg/l), rainfall depth (cm), and the inverse of rainfall depth (Table III). Oxidized nitrogen concentrations were found to be relatively high during storms with low amounts of rainfall, and low during storms with high amounts of rainfall. Oxidized nitrogen concentrations declined rapidly then remained relatively constant as rainfall amounts increased (Figures 13 and 14).

A clear relationship between rainfall pH and oxidized nitrogen concentration was not evident (Figure 15). Generally precipitation pH was lower than the theoretical pH of pure rain water. The volume-weighted average pH for rainfall during the study period was 4.65. The lowest pH

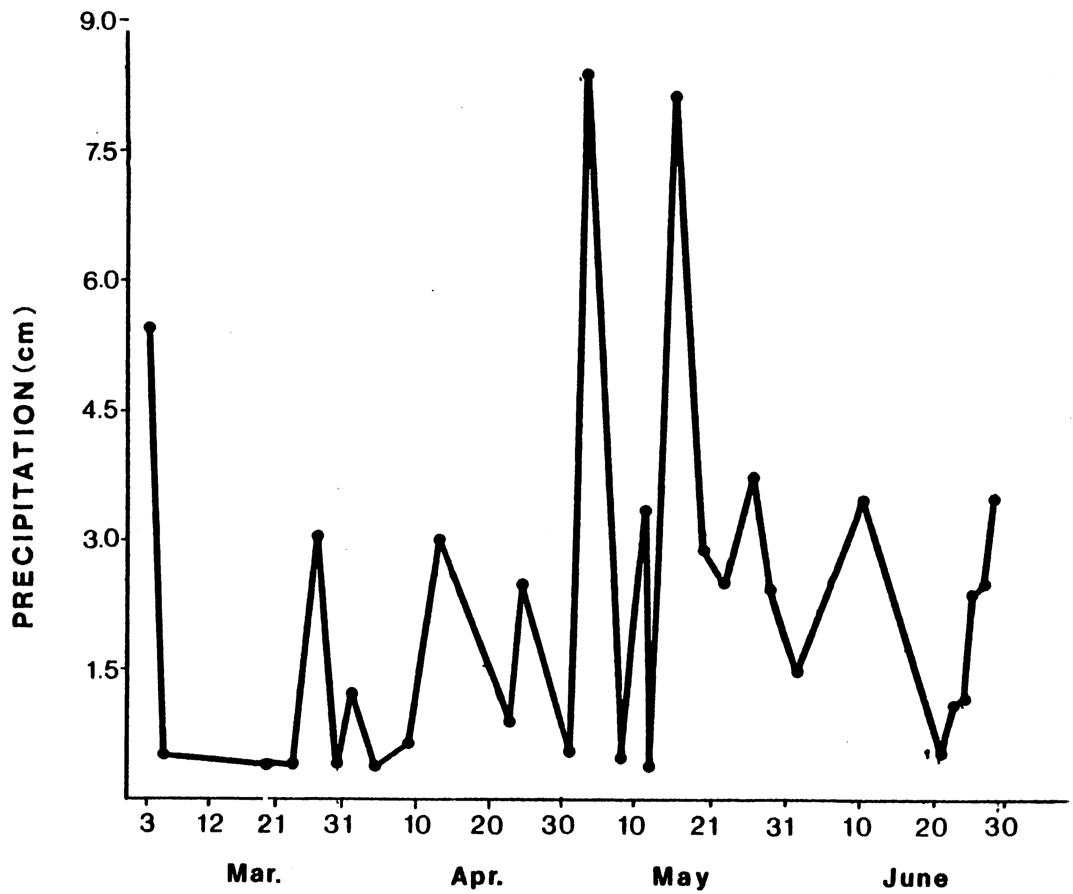


Figure 12. Distribution of Rainfall During the Study Period.
3/1/83 to 7/1/83

TABLE III

CORRELATIONS AMONG OXIDIZED NITROGEN, TOTAL PHOSPHORUS, AND HYDROLOGIC PARAMETERS IN THE BULK PRECIPITATION

	Rain (cm)	Oxidized Nitrogen (mg/l)	Total P. (mg/l)	Oxidized N Load (mg)	Total P Load (mg)	Date	Max. Intensity (cm/hr)	Duration (hours)	Inverse Rain
Rain (cm)		-.523*	-.452	.808*	.673*	.496*	.637*	.609*	-.723*
Oxidized N.			.417	-.120	-.141	-.245	-.375	-.200	.657*
Total P.				-.322	.085	-.170	-.127	-.167	.631*
Oxidized N. Load					.741*	-.549*		-.700*	.598*
-.600*									
Total P. Load						.180	.597*	.743*	-.570
Date							.420	.0264	-.493*
Max. Intensity								.607*	-.611*
Duration									-.341
Oxidized N (CV)	-.1238					-.234	.065	.321	
Total P (CV)	.2230					.681	.155	.257	-.366

*Significant at = .05

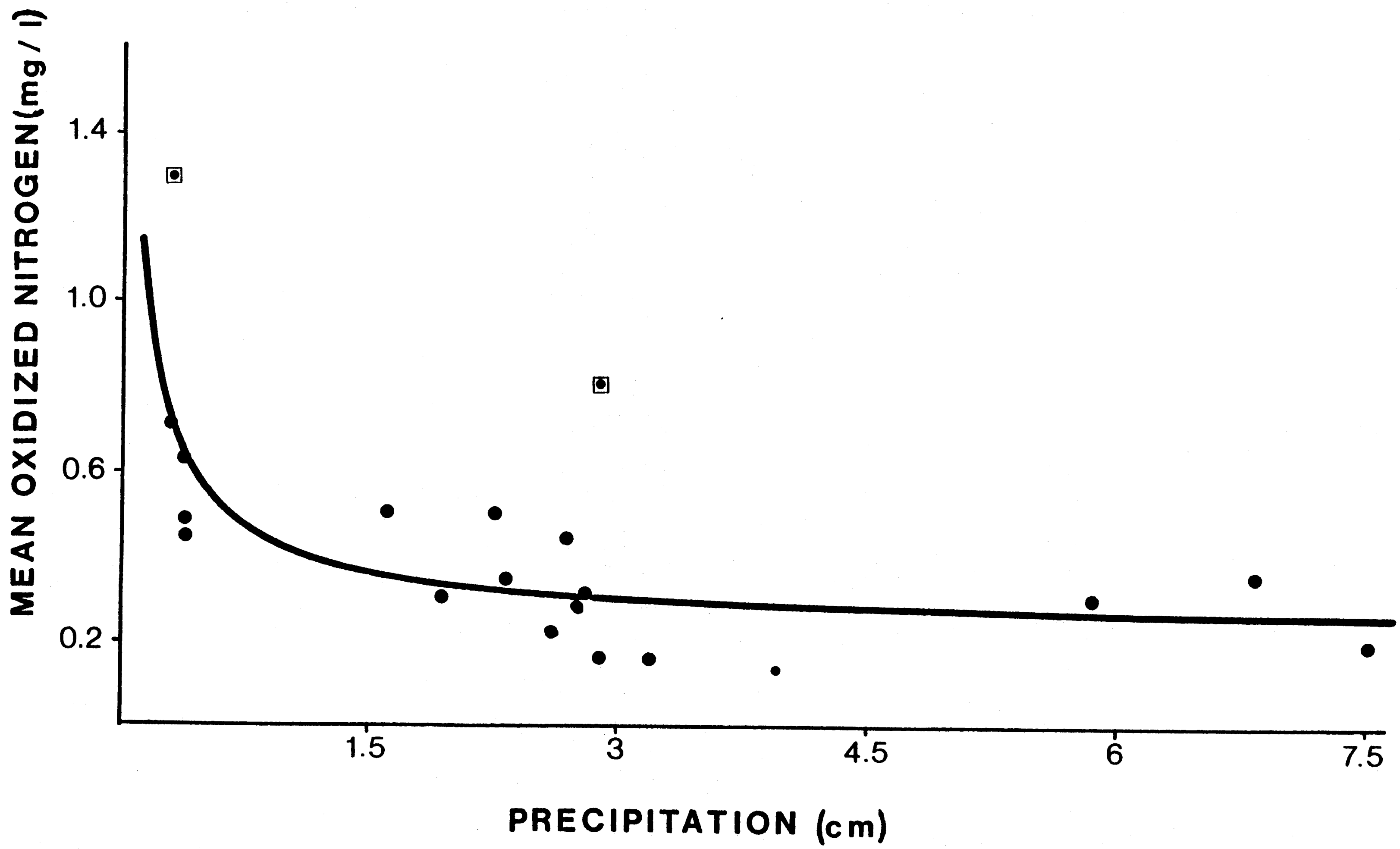


Figure 13. Scattergram of Oxidized Nitrogen Concentrations in Precipitation Collected and the Prediction Line from Figure 14

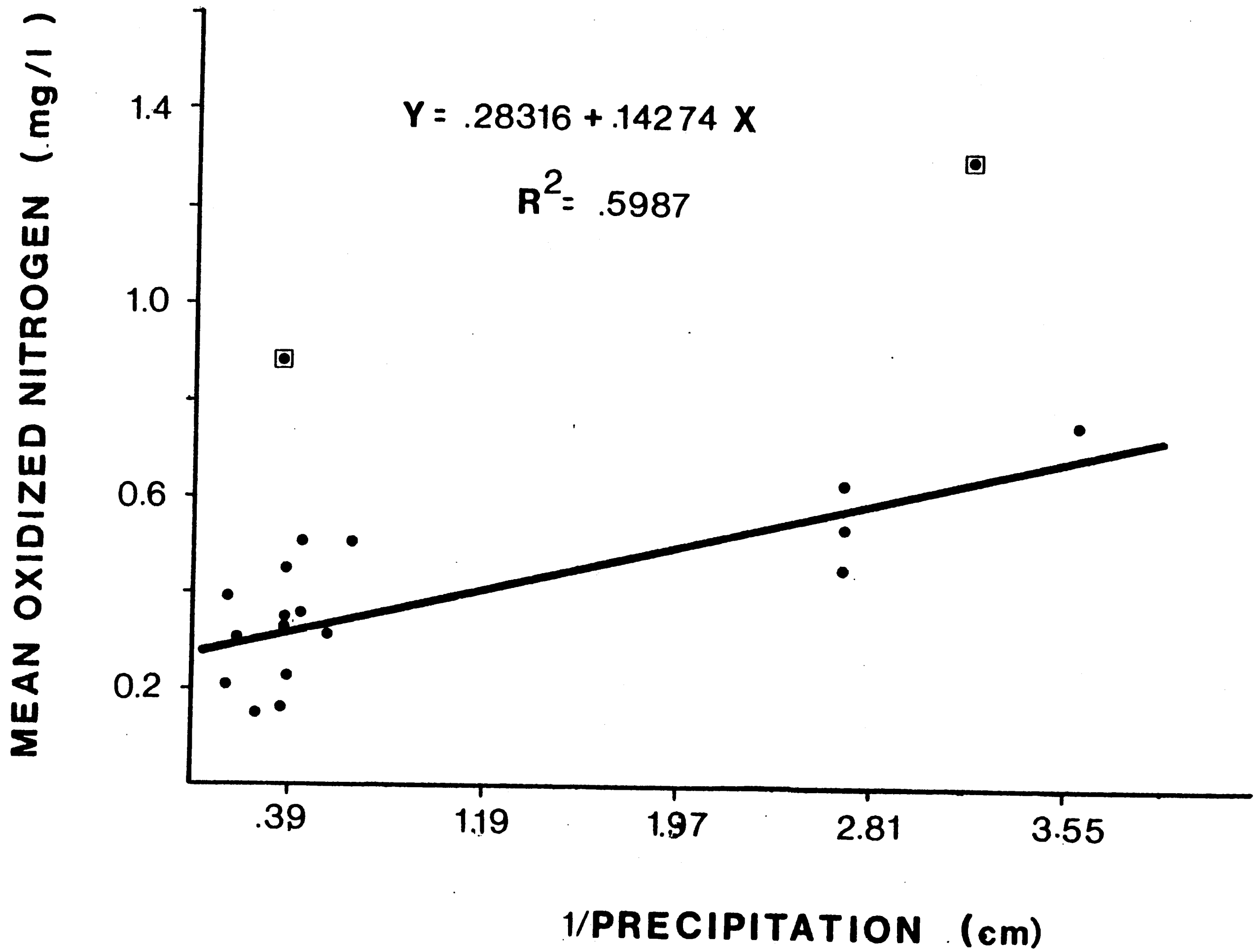


Figure 14. Linear Regression of Oxidized Nitrogen Concentrations with the Inverse of Precipitation

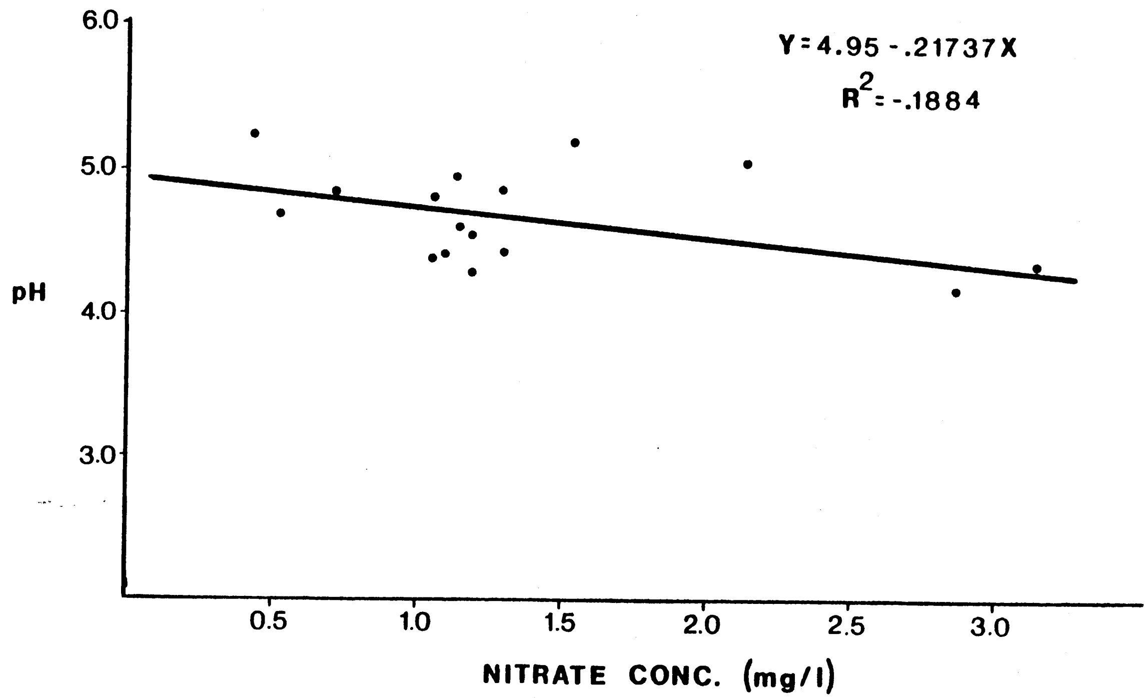


Figure 15. The Relationship Between Oxidized Nitrogen Concentration and pH at the NADP Site During the Study Period

recorded in the field was 3.93.

The oxidized nitrogen loading (mg) into the watershed was highly correlated with rainfall amounts and with the maximum intensity of rainfall (Table III). The oxidized nitrogen loads were observed to increase in a curvilinear fashion as rainfall amounts increased (Figure 16).

Total Phosphorus

Total phosphorus concentrations were significantly correlated with the inverse of rainfall amount only (Table III). As with oxidized nitrogen, total phosphorus concentrations declined rapidly from relatively high concentrations during storms with small amounts of rainfall to relatively constant low concentrations for storms with high amounts of rainfall (Figures 17 and 18).

The total phosphorus load into the watershed was significantly correlated with rainfall amount, maximum storm intensity, and storm duration (Table III). Similar to oxidized nitrogen loads, regression analysis indicated that total phosphorus loads increased curvilinearly as rainfall amounts increased (Figure 19).

Throughfall

Throughfall under the pine canopy was significantly correlated with rainfall depth and maximum intensity (Table IV), but under the hardwood canopy throughfall was correlated with the dormant state of trees (Table V). Mean throughfall depth for both the pine and the hardwood canopies increased proportionally as precipitation depth increased (Figure 20). Throughfall in individual collectors under the pine canopy ranged from 31 % to 130 % of rainfall while storm means ranged from 52 % to 102 % of rainfall. Throughfall under the hardwood canopy ranged from 47 % to 113 % of rainfall while storm

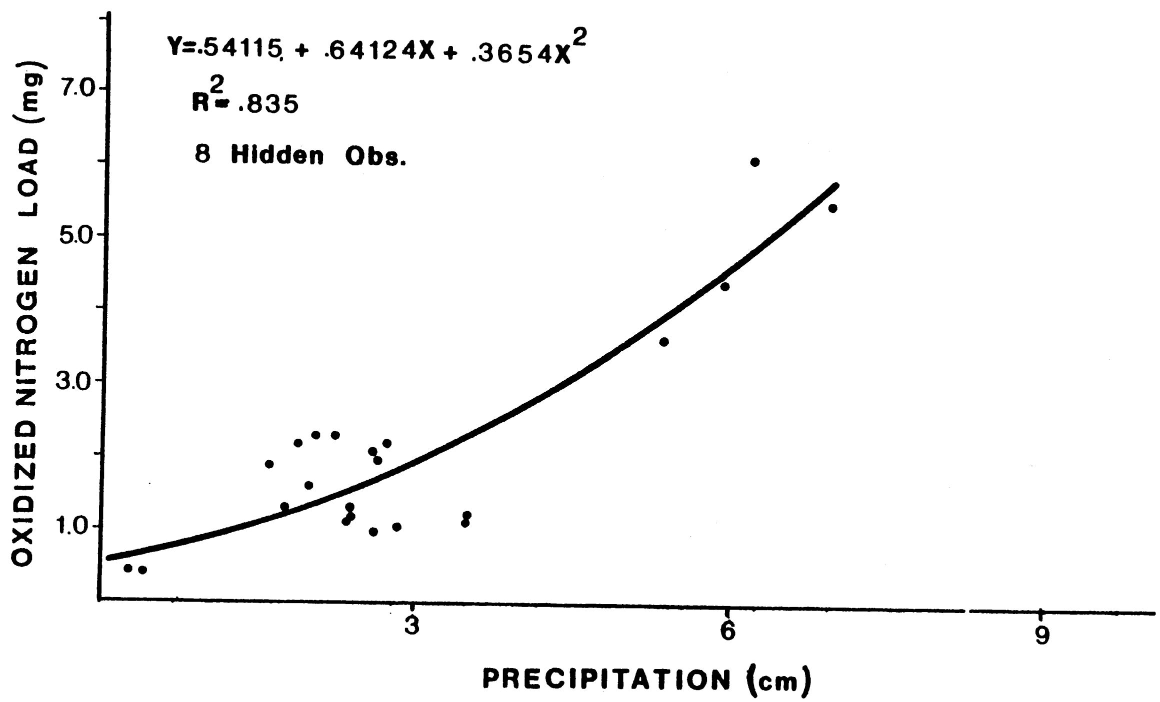


Figure 16. Polynomial Regression Model Relating Oxidized Nitrogen Load as a Function of Precipitation

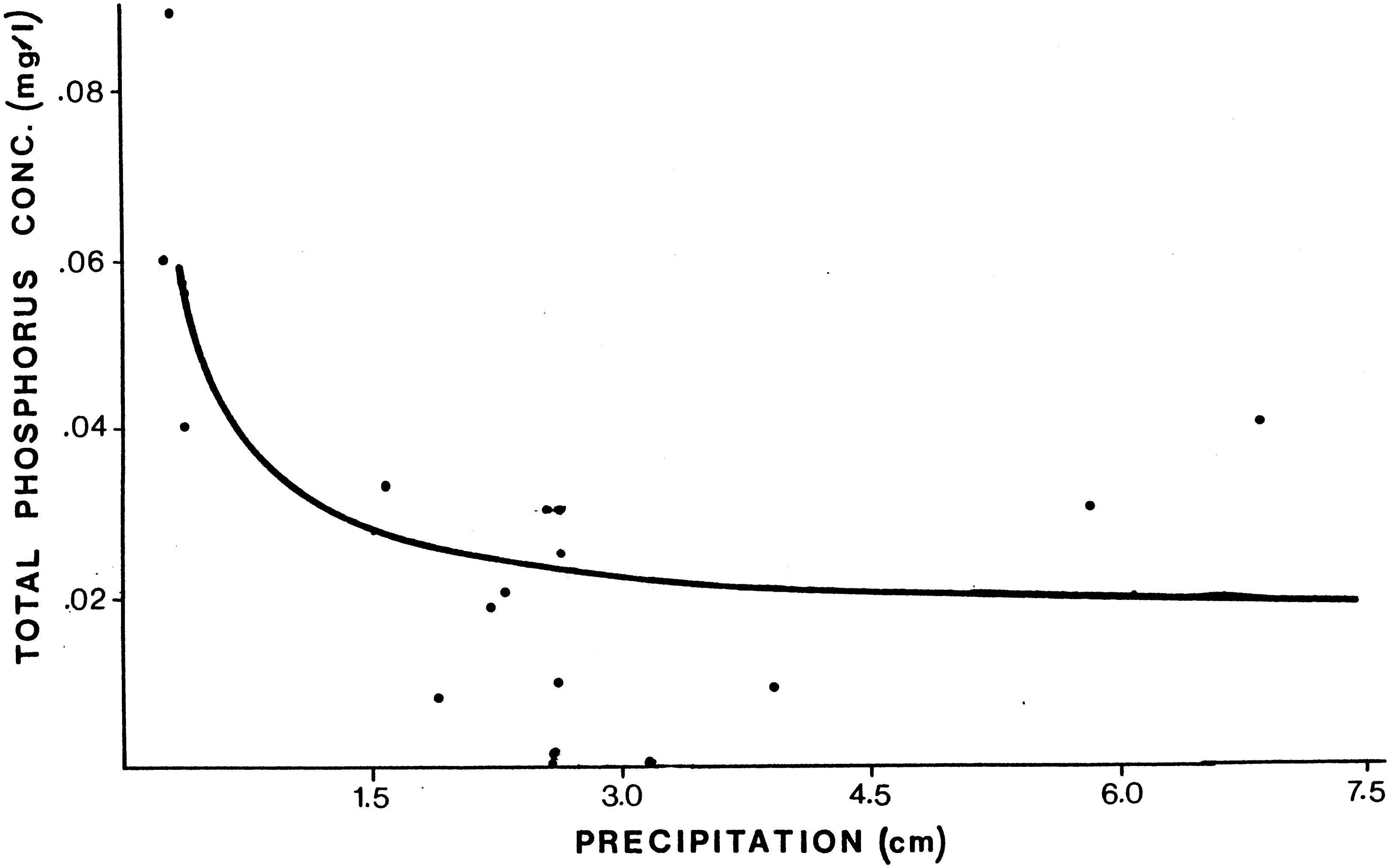


Figure 17. Scattergram of Total Phosphorus Concentrations at Various Precipitation Depths with Prediction Line from Figure 18

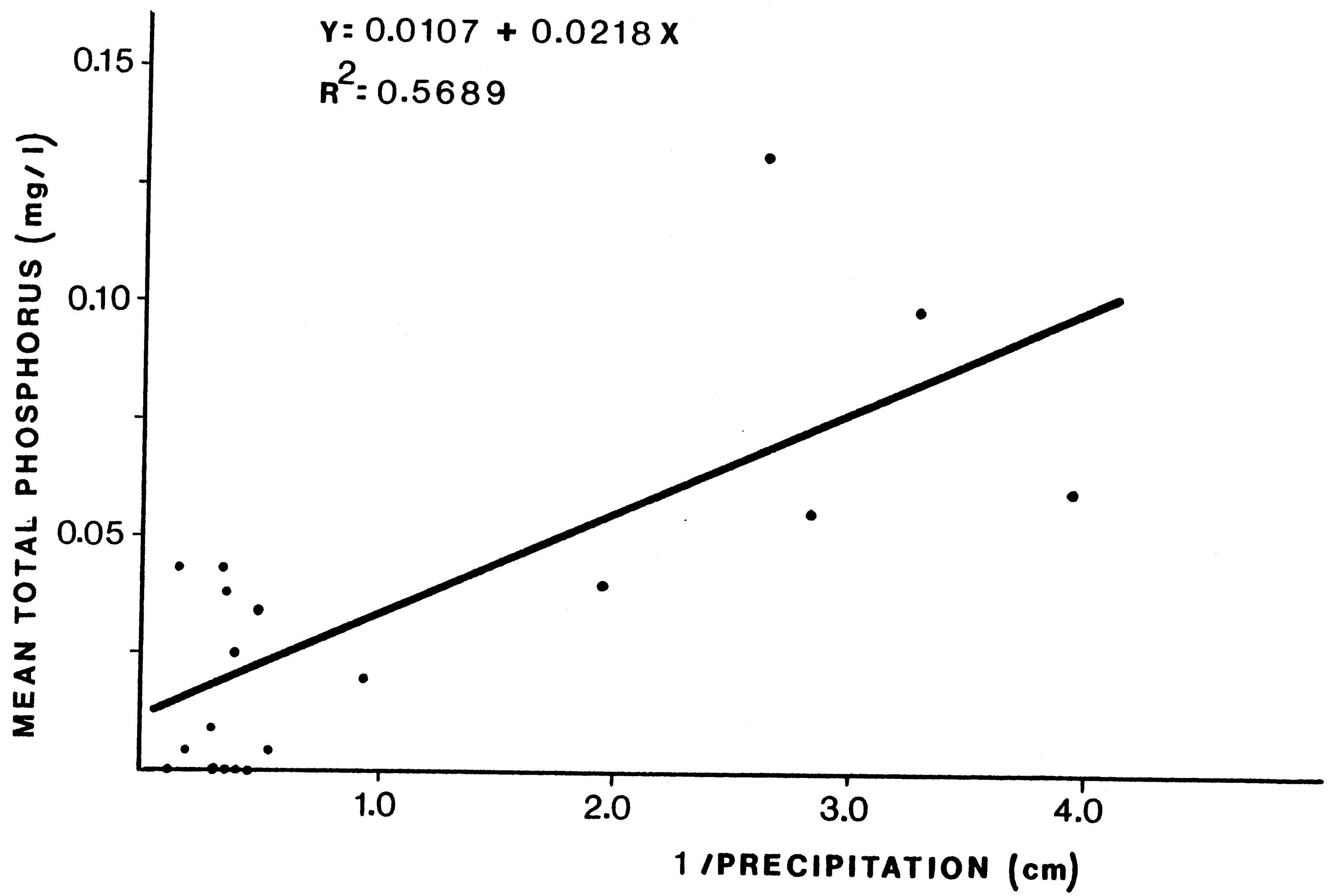


Figure 18. Linear Regression Model Relating Total Phosphorus Concentration in Precipitation as a Function of the Inverse of Precipitation

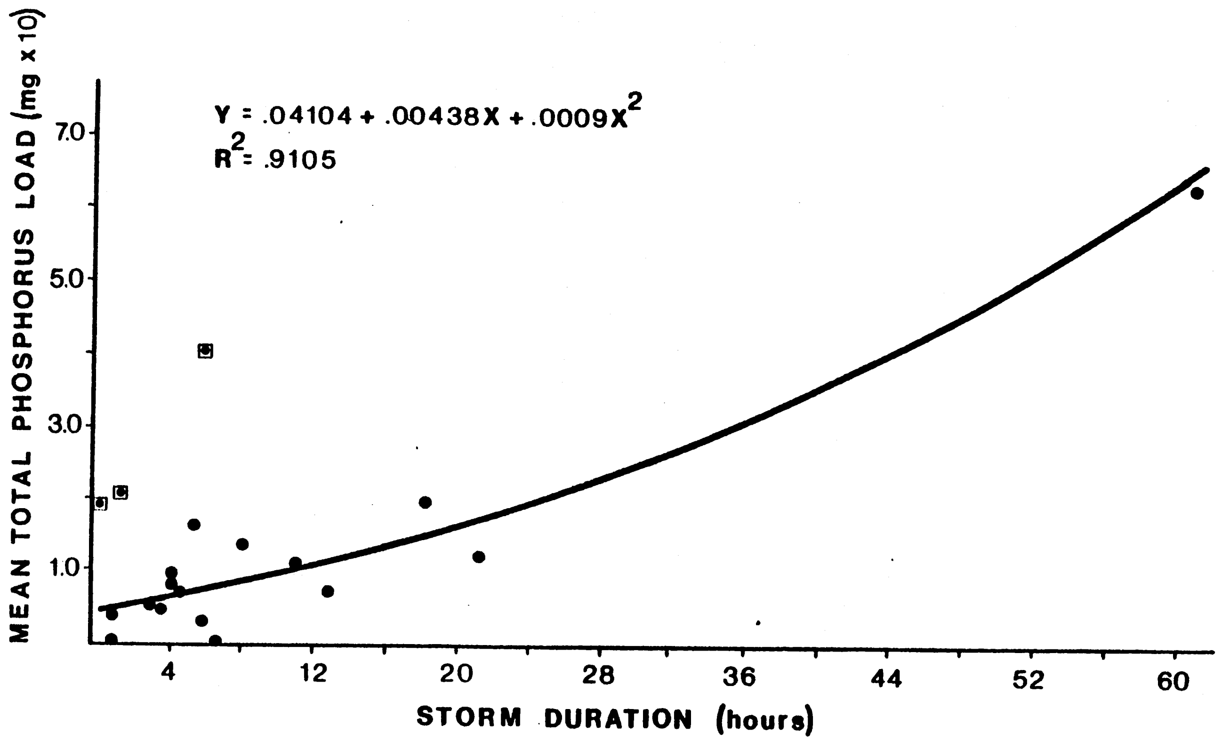


Figure 19. Polynomial Regression Model Relating Mean Phosphorus Load in Bulk Precipitation as a Function of Storm Duration

TABLE IV

CORRELATIONS AMONG OXIDIZED NITROGEN AND TOTAL PHOSPHORUS, AND HYDROLOGIC PARAMETERS IN PINE THROUGHFALL

	Rain (cm)	Nitrogen Load (mg)	Phos. Load (mg)	Oxid. N (mg/1)	Total P (mg/1)	Storm Duration (hr)	Max. Inten. (cm/hr)	% of Rain	Dormant State	Antecedent Storm (days)
Rain		.538*	.852*	-.444*	-.435	.602*	.611*	.573*	.227	-.219
Nitrogen Load			.452*	.216	-.174	.715*	.394	-.300	-.385	.450*
Phosphorus Load				-.250	-.102	.403	.381	.475*	.336	-.267
Oxidized N					.489*	-.133	-.429	-.446*	-.356	.685*
Total Phosphorus						-.234	-.234	.359	.066	.239
Storm Duration							.588*	.096	.154	.088
Max. Intensity								.481	.588*	.047
% of Rain									-.280	.223
Dormant State										-.458*
No. of Days Since Last Storm										

*Significant at α = .05

TABLE V

CORRELATIONS AMONG OXIDIZED NITROGEN AND TOTAL PHOSPHORUS AND HYDROLOGIC PARAMETERS IN HARDWOOD THROUGHFALL

	Oxidized N (mg/l)	Total Phos. (mg/l)	% of Rain	Nitrogen Load (mg)	Phos. Load (mg)	Storm Duration (Hours)	Max. Intens. (cm/hr)	Dormant State	Antecedent Strm. (days)
Rain (cm)	-.573*	-.201	-.045	.816*	.783	.602*	.611*	.227	-.219
Oxidized N		.492*	-.111	-.255	-.345	-.172	-.522*	-.430	.543*
Total P			.373	-.147	.161	-.100	.042	.268	.009
% of Rain				.016	.229	-.308	-.097	.481*	-.077
Nitrogen Load					.630*	.662*	-.559*	.070	-.028
Phosphorus Load						.461*	.350	.352	-.264
Storm Duration							.588*	-.324	.088
Max. Intensity								.154	.291
Dormant State									

*Significant at α = .05

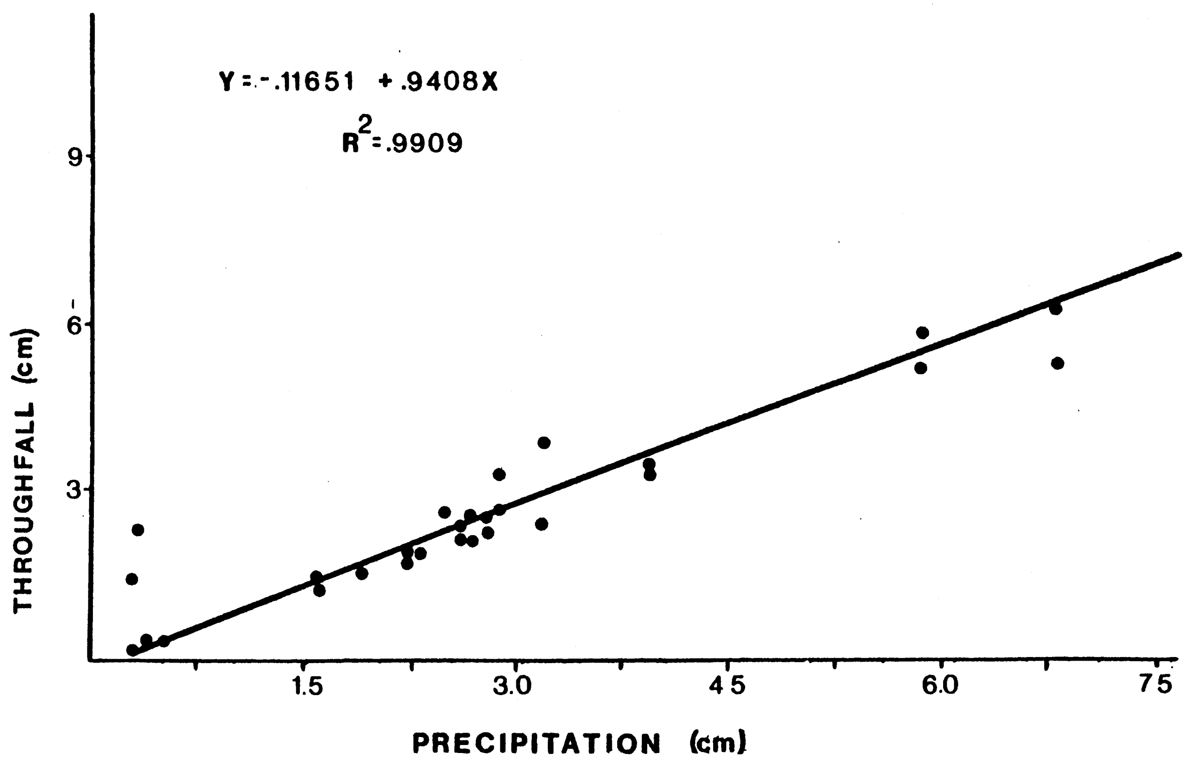


Figure 20. Relationship Between Mean Throughfall Depth and Precipitation Depth for the Study Period

means ranged from 63 % to 95 % of rainfall.

Oxidized Nitrogen

Oxidized nitrogen concentrations in throughfall from the pine canopy were significantly correlated with rainfall amounts, total phosphorus concentrations, inverse of rainfall, throughfall, and the number of days since the last storm (Table IV). About 71 % of the variation in pine throughfall oxidized nitrogen concentrations could be explained by the following model:

$$Y=-1.9014 + .56712(X) + .44663(Z)$$

$$R^2=.71$$

where:

Y=oxidized nitrogen in mg/l

X=inverse of rainfall (cm)

Z=number of days since the last storm

Oxidized nitrogen concentrations from the hardwood canopy were significantly correlated with rainfall amount, maximum intensity of the storm, inverse of rainfall, and the number of days since the last storm (Table V). About 80 % of the variation in oxidized nitrogen concentrations could be explained by the following model:

$$Y=.04449 + .14681(X) + .04834(Z)$$

$$R^2=.80$$

where:

Y=oxidized nitrogen concentration in mg/l

X=inverse of rainfall (cm)

Z=number of days since the last storm

The oxidized nitrogen load entering the watershed by throughfall from the pine canopy was significantly correlated with rainfall amount, phosphorus load, storm duration, and the number of days since the last storm (Table IV). About 66 % of the variation in load could be accounted for using the following model:

$$Y=.3969 + .03084(X) + .06317(Z)$$

$$R^2=.66$$

where:

Y=oxidized nitrogen load in mg

X=storm duration in hours

Z=rainfall in cm

The oxidized nitrogen load from the hardwood canopy was significantly correlated with rainfall amount, phosphorus load, storm duration, and negatively correlated with maximum intensity of rainfall (Table V). The load increased at an increasing rate as rainfall amounts increased (Figure 21).

Total Phosphorus

Total phosphorus concentrations in throughfall from the pine canopy were significantly correlated with the inverse of precipitation (cm) (Table IV). Concentrations were high at low rainfall amounts and decreased rapidly to low concentrations as rainfall amounts increase (Figure 22 and 23). There were no significant correlations between concentrations in hardwood throughfall and any parameter (Table V).

Total phosphorus loads in pine throughfall were significantly correlated with rainfall amounts and throughfall depth (cm) (Table IV). Loads increased at an increasing rate as rainfall amounts increased (Figure 24). Loads in hardwood throughfall are significantly correlated with rainfall amount and storm duration (Table V). Loads from hardwoods increased in a curvilinear fashion as rainfall amounts increased (Figure 25).

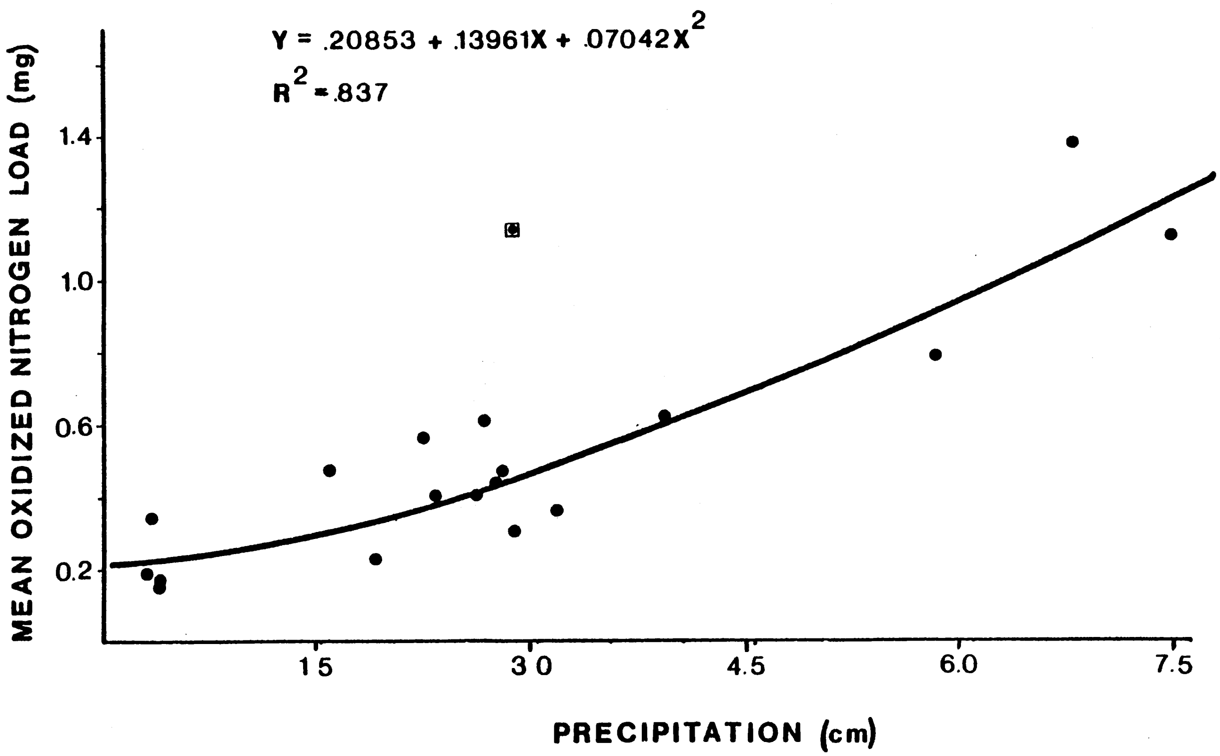


Figure 21. Relationship Between Oxidized Nitrogen Load in Hardwood Throughfall and Precipitation Depth

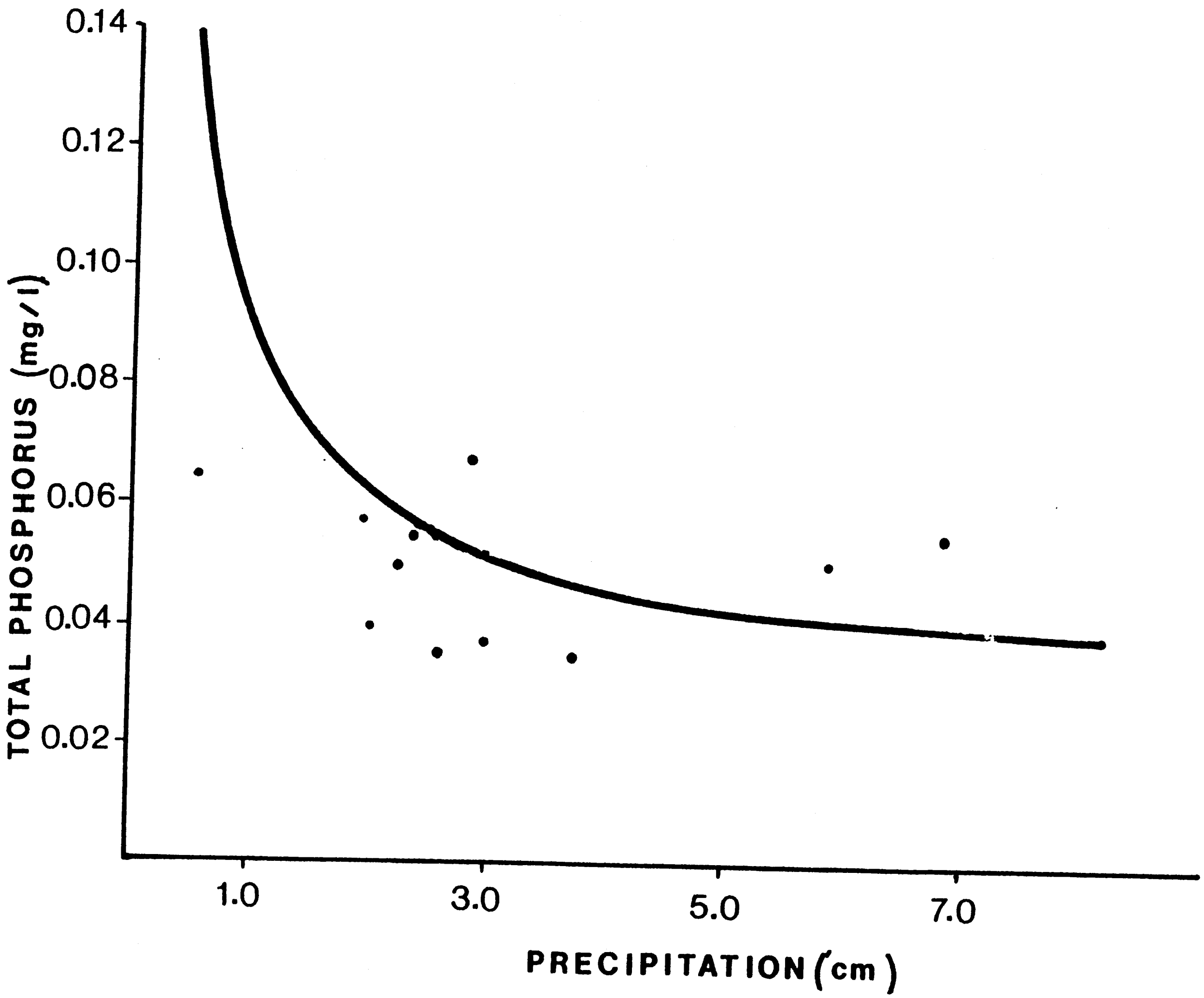


Figure 22. Scattergram of Total Phosphorus Concentration in Pine Throughfall as a Function of Precipitation Depth with a Prediction Line from Figure 23

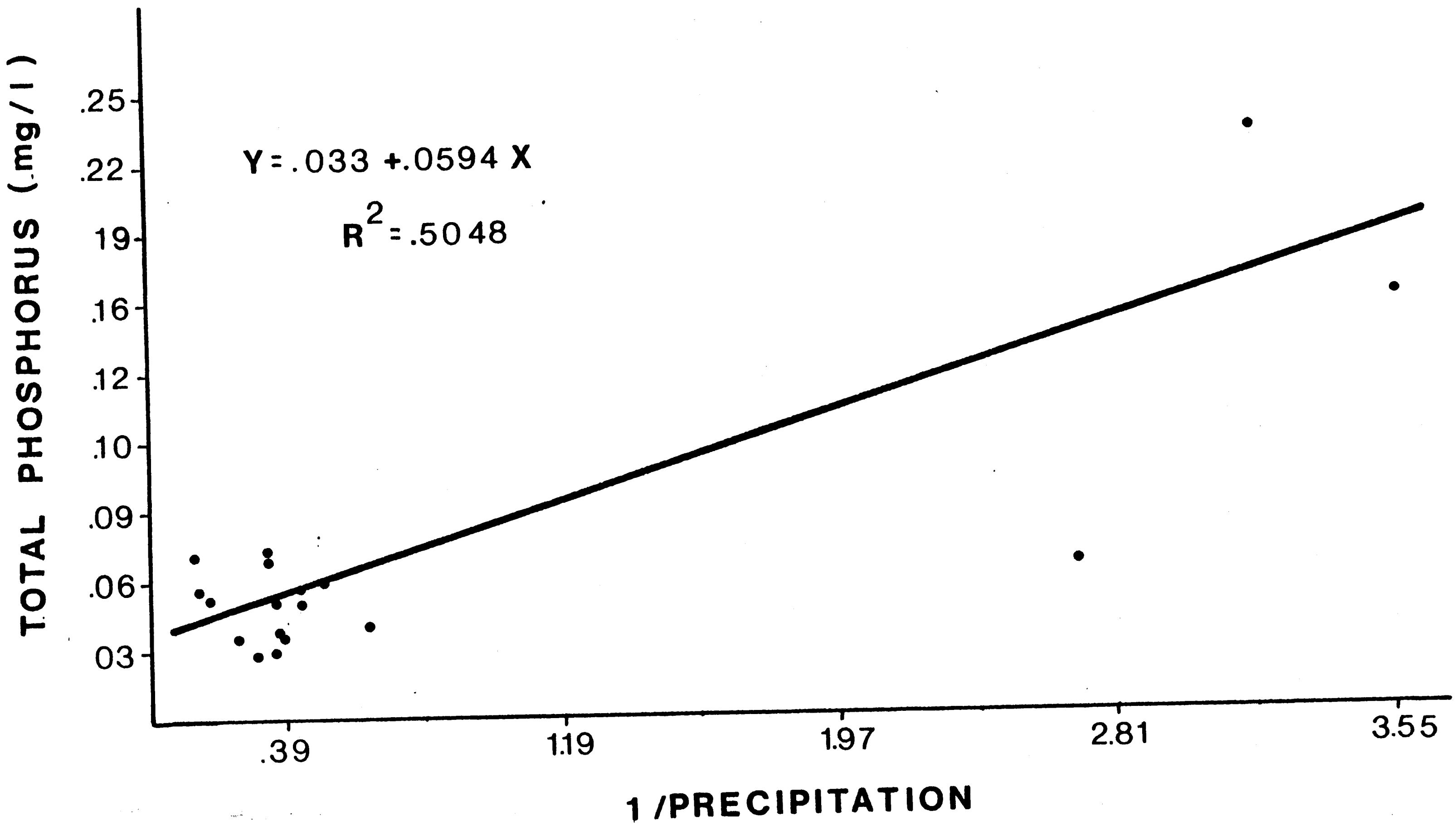


Figure 23. Linear Regression Model Relating Total Phosphorus Concentrations from Pine Throughfall as a Function of the Inverse of Precipitation. ▣ indicates an outlier

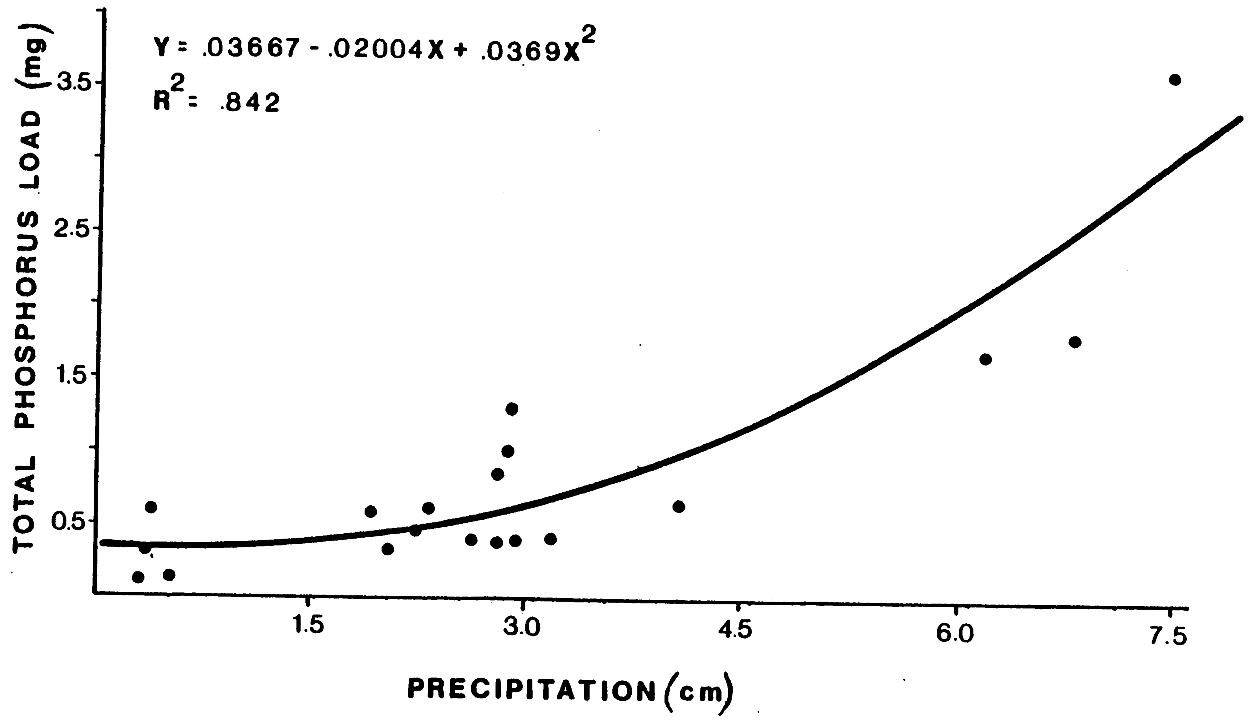


Figure 24. Polynomial Regression Model of Total Phosphorus Load in Pine Throughfall as a Function of Precipitation Depth

Streamflow

Total storm runoff ranged from .31 cm to 4.47 cm per event and was generally associated with high intensity storms greater than 2.03 cm of rain (Table VI). Streamflow was flashy with hydrographs that had very steep rising limbs and falling limbs (Figure 3).

Oxidized Nitrogen

Oxidized nitrogen concentrations in streamflow were significantly correlated with total phosphorus concentrations, streamflow, total suspended solids, timing before or after peak flow, and the interaction between total suspended solids and timing before or after peak flow (Table VII). During small storms, equal to or smaller than the one shown in Figure 26, concentrations remained constant throughout the stormflow. During moderate storms, concentrations were high in the initial stages of stormflow and rapidly declined as the storm progressed. Concentrations were much lower after peak flow than before (Figure 27). During the largest storms, concentrations increased rapidly in the initial stages of stormflow then declined rapidly as the storm progressed and concentrations were much lower after peak flow than before. Trajectories from the largest storms tend to be more complex than trajectories from the smaller storms (Figure 28 and 29). When multiple pulses of rainfall occurred during a storm which produced multiple peaks in flow during stormflow, oxidized nitrogen concentrations briefly increased in response to each peak (Figure 29). Using the method outlined by Helsel (1979), 61 % of all the storms exhibited a first flush of oxidized nitrogen. Those storms which did not show a first flush were the very small (Table VIII).

Oxidized nitrogen loads were significantly correlated with streamflow, total phosphorus load, total suspended solids, timing before or after peak flow,

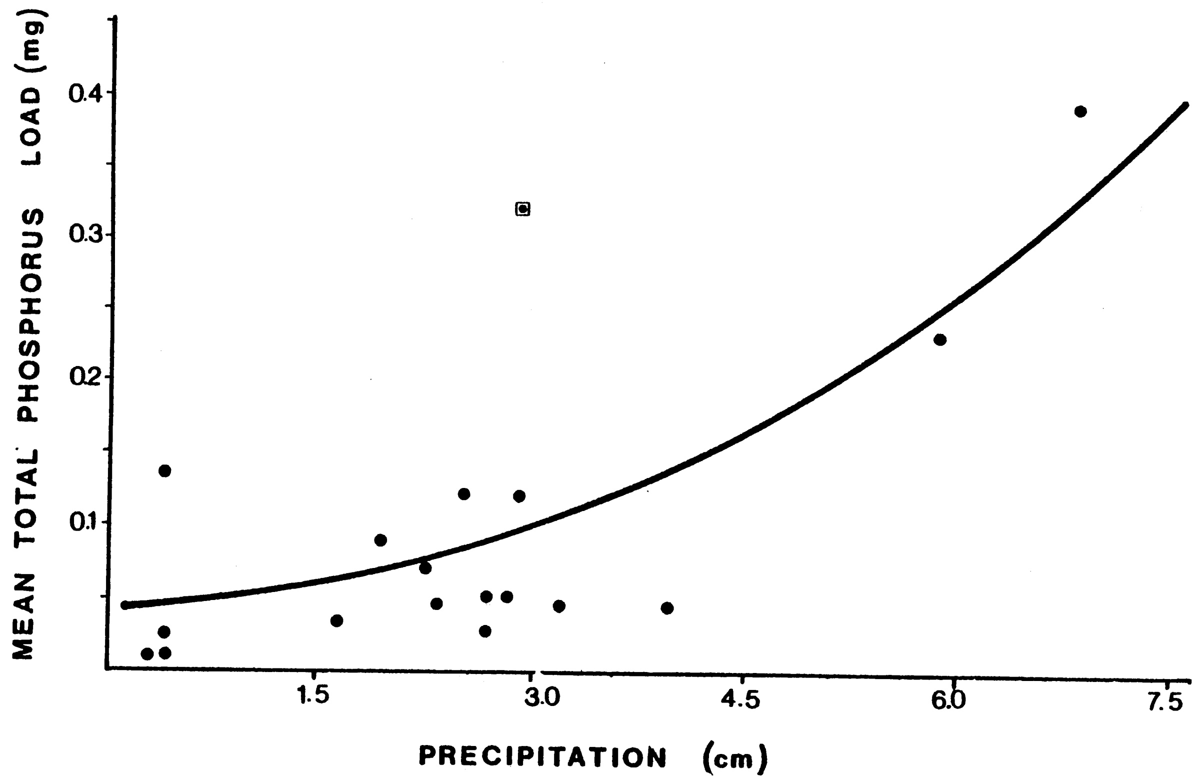


Figure 25. Polynomial Regression Model Relating the Mean Total Phosphorus Load in Hardwoods as a Function of Precipitation

TABLE VI

PRECIPITATION CHARACTERISTICS AND STORM RUNOFF FOR ALL STORMS SAMPLED FROM MARCH 1 TO JULY 1, 1983

Storm Date	Precipitation (cm)	Maximum Intensity (cm/hr)	Storm Duration (hours)	Runoff (cm)
3/3/83	3.94	5.49	12.67	.74
3/5/83	.38	1.22	2.91	N
3/20/83	.32	.38	4.50	N
3/23/83	2.6	1.52	8.10	N
3/30/83	.28	.30	1.00	N
4/1/83-4/5/83	1.6	4.88	21.10	N
4/9/83	.38	.30	3.60	N
4/13/83	2.31	4.88	4.17	.31
4/21/83	2.67	8.53	11.20	N
4/30/83	6.79	12.65	60.67	3.03
5/7//83	.38	4.88	.08	N
5/10/83	2.86	1.96	5.25	.515
5/14/84	5.84	6.86	5.57	4.47
5/17/83	2.22	2.44	5.30	.68
5/21/83	1.91	7.32	4.28	.36
5/25/83	2.87	4.8	1.25	.58
5/28/83	2.79	3.45	6.58	.49
6/6/83-6/9/83	2.74	8.84	.74	.28
6/26/83-6/28/83	10.4	5.49	18.10	.62
6/29/83	--	--	--	.78

TABLE VII

CORRELATIONS AMONG OXIDIZED NITROGEN AND TOTAL PHOSPHORUS AND HYDROLOGIC PARAMETERS IN STREAMFLOW

	Av. Oxidized N conc. (mg/l)	Av. Total P conc. (mg/l)	Oxidized N load (mg)	Total P load (mg)	Total Sus.Sol. (mg/l)	Org.Susp. Solids (mg/l)	Timing	Inter-Action TSS/Timing	Vegetation Dormant State
Av. Flow	-.099	.184	.519*	.811*	.220*	.221*	-.177	-.107	-.168
Av. Oxidized Nitrogen		.318*	.375*	.007	.258*	.021	-.368*	-.331	.210
Av.Total Phosphorus			.363*	.514*	.858*	.518*	.565*	-.477*	
Oxidized N load				.608*	.340*	.190	-.326*	-.277*	
Total P load					.579*	.461*	-.278*	-.210*	
Total Suspended Solids						.671	-.559*	-.441*	
Organic Suspended Solids							-.282*	-.127	
Timing								.907	
Total Runoff	-.140	.255							

*Significant at = .05

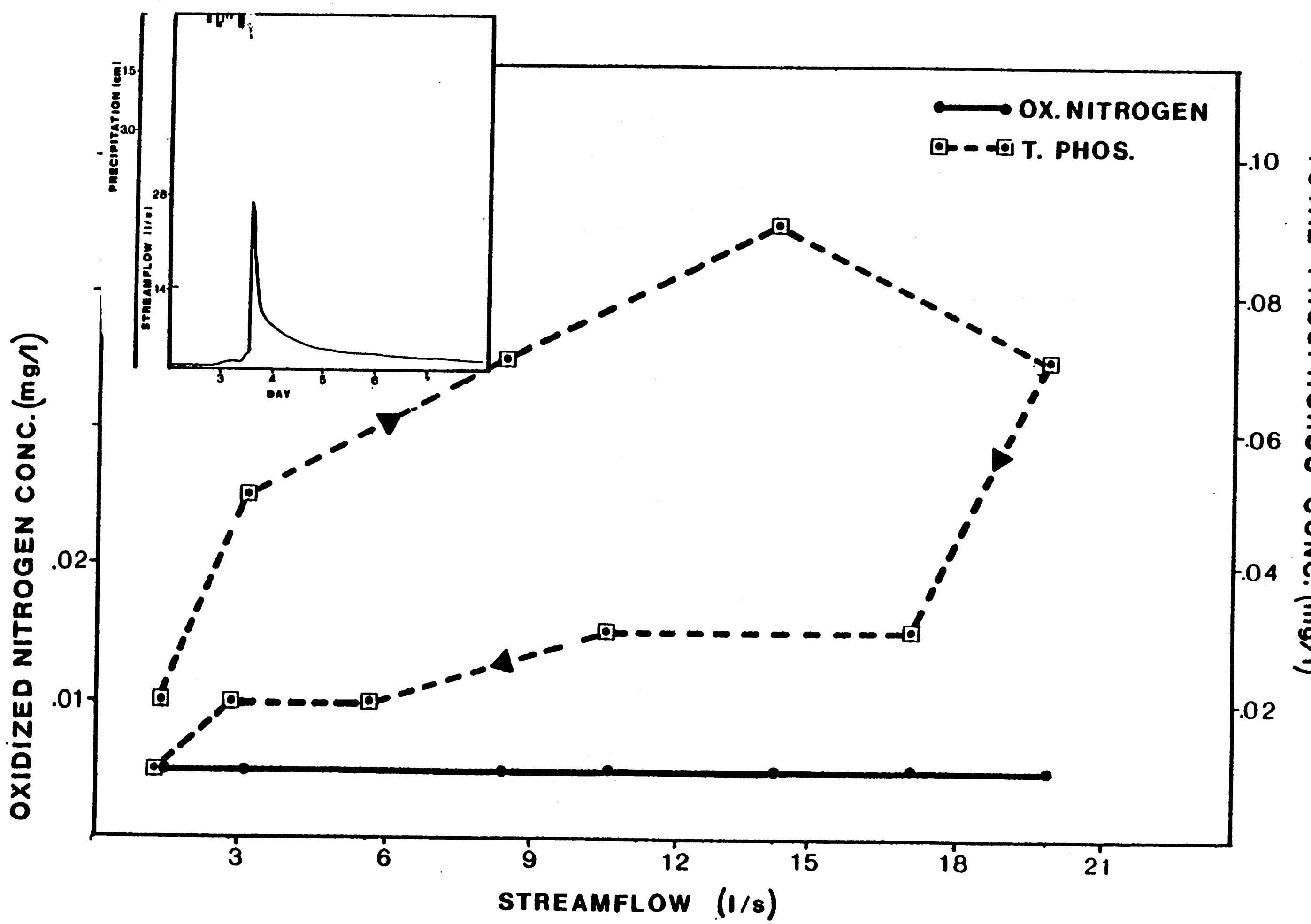


Figure 26. Oxidized Nitrogen and Total Phosphorus Concentration Trajectories in Streamflow during the Storm of 3/4/83. Inset Shows the Hydrograph for the Storm

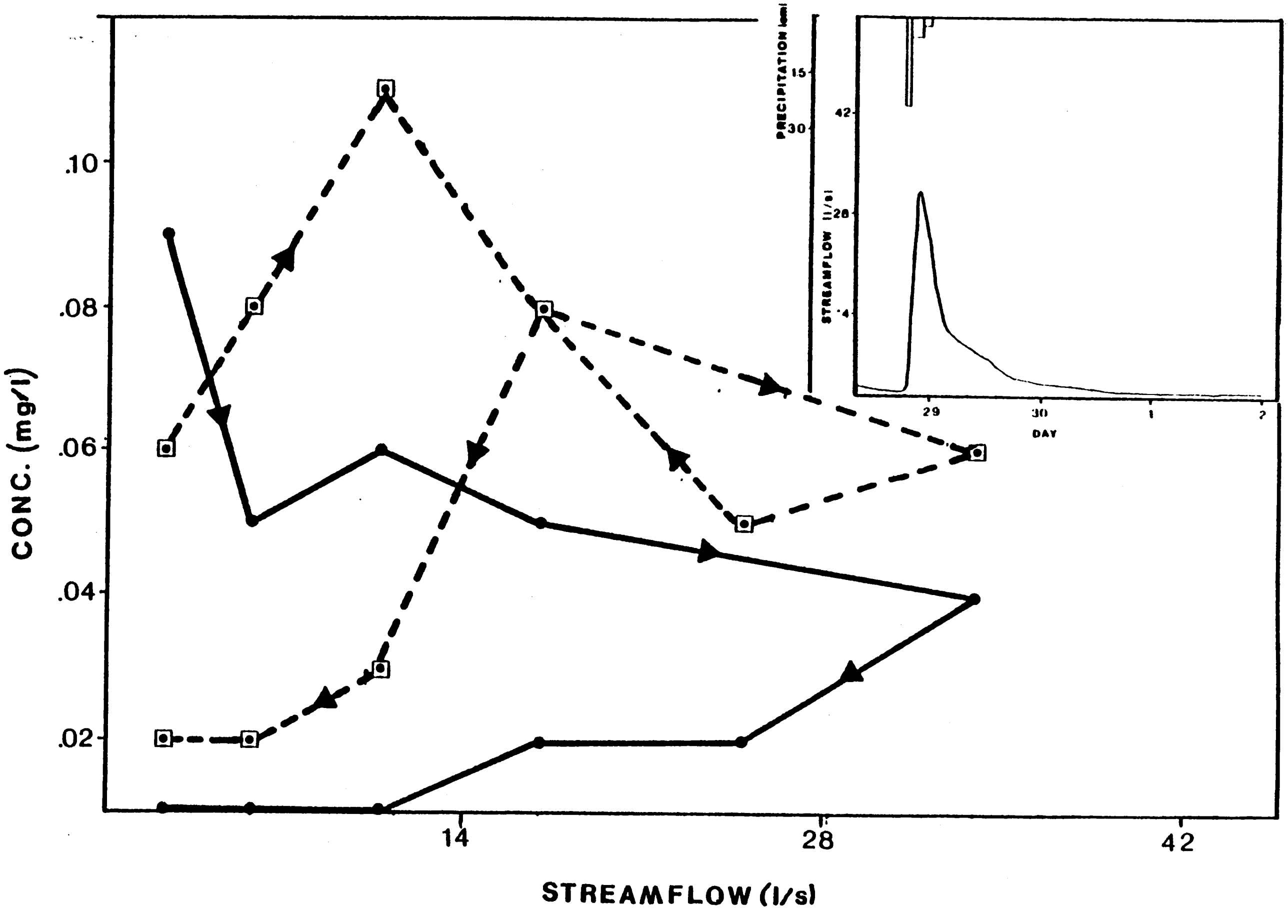


Figure 27. Oxidized Nitrogen and Total Phosphorus Concentration Trajectories in Streamflow During the Storm of 6/28-29/83. Inset Shows Storm Hydrograph

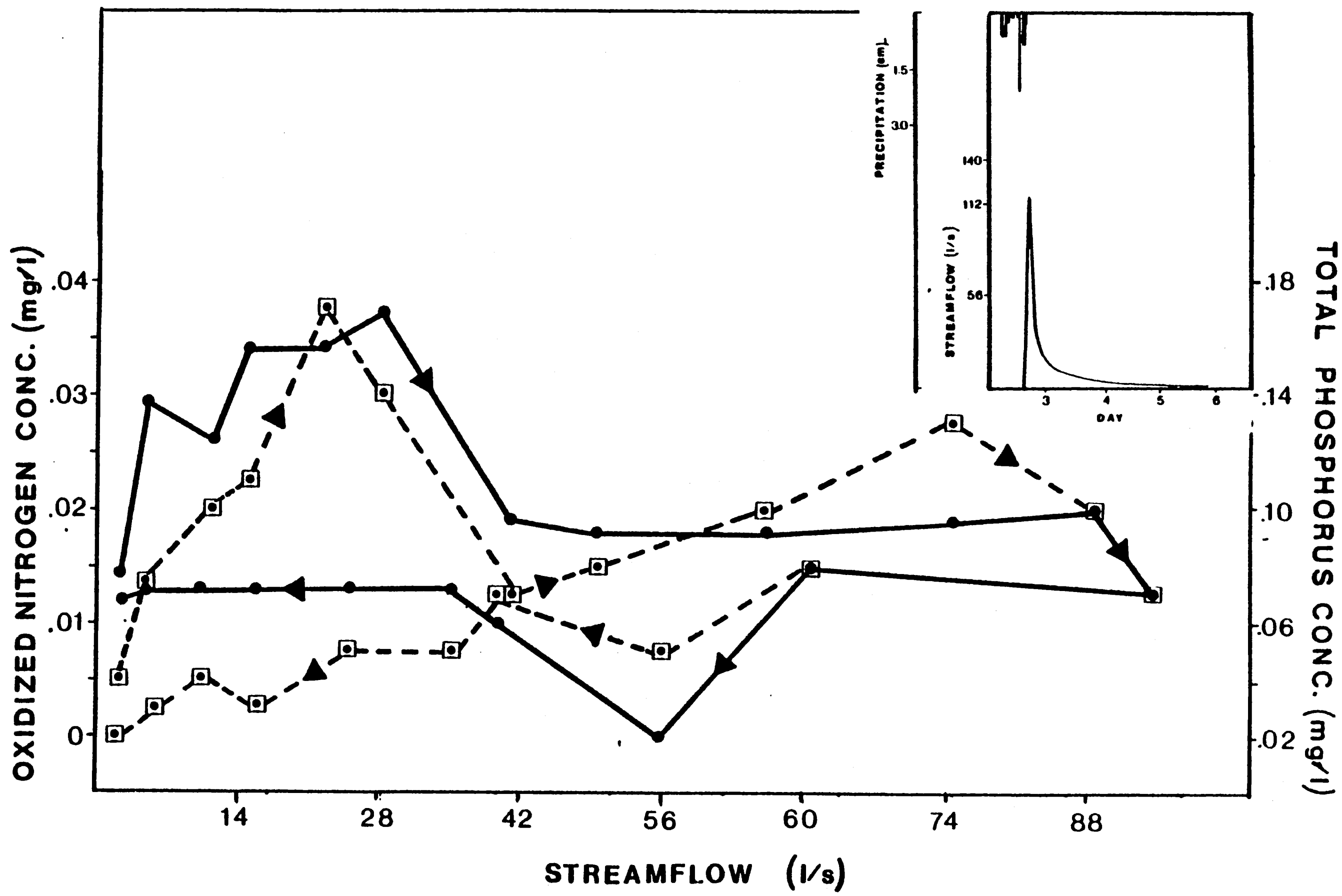


Figure 28. Oxidized Nitrogen and Total Phosphorus Concentration Trajectories in Streamflow During the Storm of 5/2/83. Inset Shows Storm Hydrograph

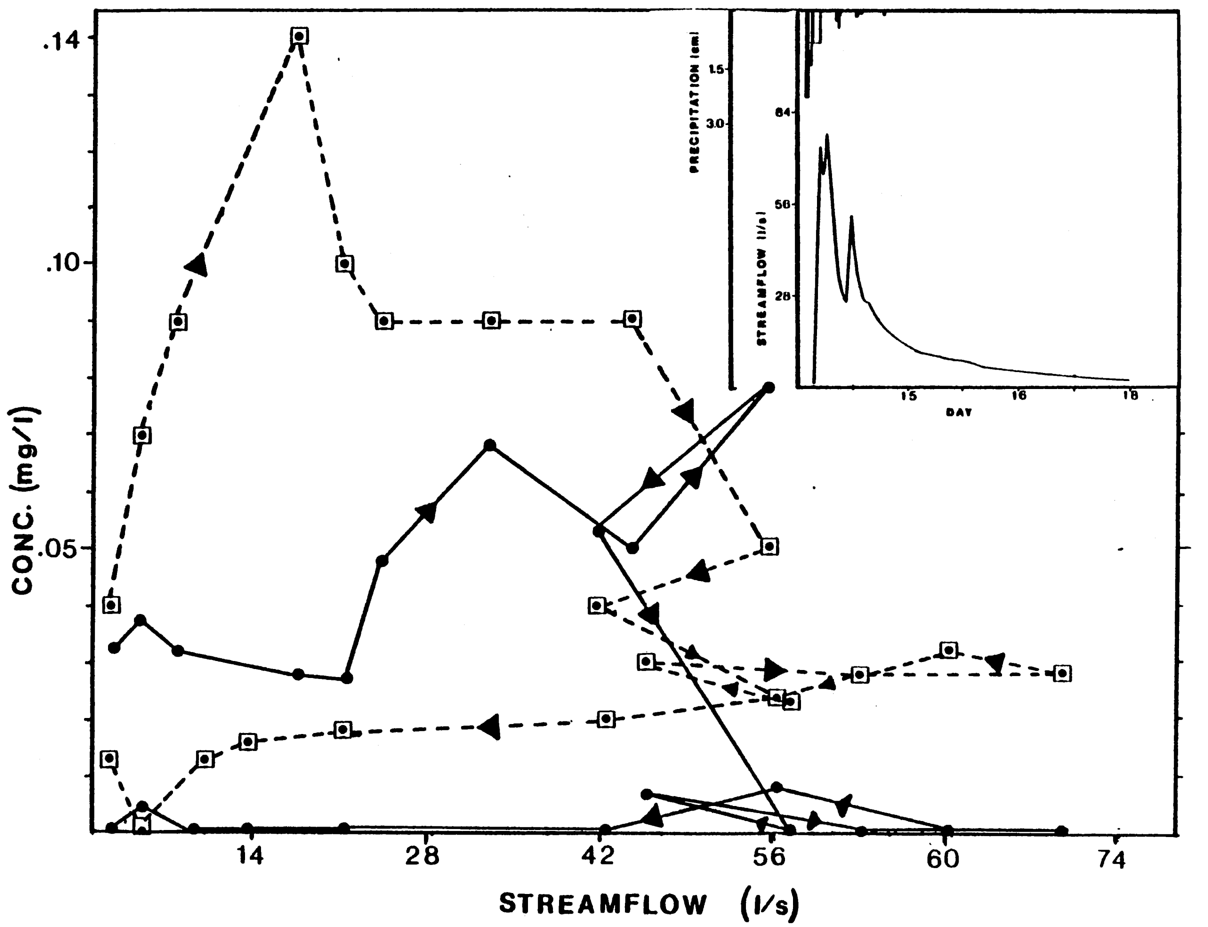


Figure 29. Oxidized Nitrogen and Total Phosphorus Concentration Trajectories in Streamflow During the Storm of 5/14/83. Inset Shows Storm Hydrograph

and the interaction between total suspended solids and timing before or after peak flow (Table VII). During the study period as a whole the rising limb of stormflow transported significantly more oxidized nitrogen than the delayed flow limb (Figure 30 and Table IX). The largest storm produced the greatest transport of oxidized nitrogen (Table X).

Total Phosphorus

Total phosphorus concentrations in streamflow were significantly correlated with total suspended solids, organic suspended solids, timing before or after peak flow, and the interaction between total suspended solids and timing before or after peak flow (Table VII). Concentrations increased at a decreasing rate as total suspended solid concentrations increased (Figures 31 and 32).

Concentrations of total phosphorus increased with increasing streamflow and declined after peak flow during small and moderate storms (Figures 26 and 27). During the largest storms total phosphorus concentrations increased rapidly during the initial stages of streamflow but then declined rapidly as streamflow progressed. Concentrations declined rapidly after peak flow (Figures 28 and 29).

Total phosphorus loads were significantly correlated with streamflow, total suspended solids, organic suspended solids, timing before or after peak flow (Table VII). A first flush of total phosphorus was indicated for 81 % of all storms. Generally the smallest storms did not show a first flush (Table VIII).

For the entire study period as a whole, total phosphorus transport was significantly greatest during the rising limb of streamflow (Figure 33 and Table IX). One storm, the largest, contributed significantly more total phosphorus than the other storms (Table X).

TABLE VIII

STORMDATE AND STREAMFLOW ASSOCIATED WITH THE OCCURRENCE OF A FIRST FLUSH FOR OXIDIZED NITROGEN AND TOTAL PHOSPHORUS

Date	Total Streamflow (cm)	Oxidized Nitrogen Flush*	Total Phosphorus Flush
3/3/83	.74	-	+
4/13/83	.31		
5/2/83	3.03	+	+
5/10/83	.515	+	+
5/14/83	4.47	+	+
5/18/83	.68	+	+
5/21/83	.36	+	+
5/26/83	.58	+	+
5/28/83	.49	+	+
6/4/83	.14	-	-
6/6/83	.14	-	-
6/26/83	.62	-	+
6/29/83	.78	+	+

* + = flush, - = no flush

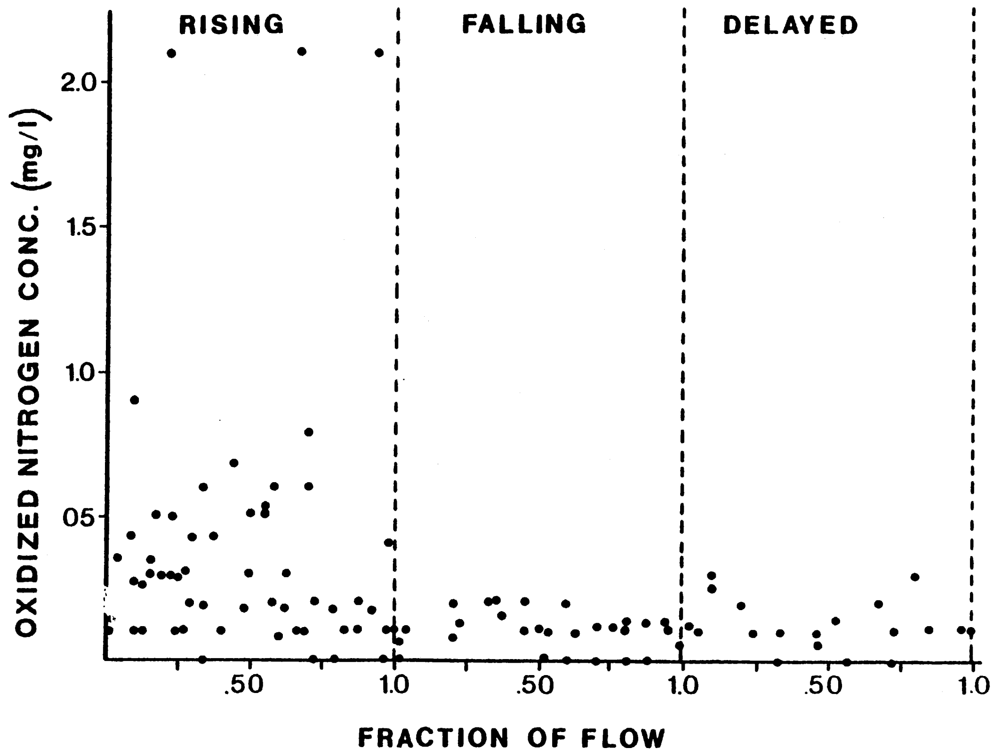


Figure 30. A Seasonal Separation of Streamflow and Oxidized Nitrogen Concentrations During the Three Major Changes in Streamflow

TABLE IX

OXIDIZED NITROGEN AND TOTAL PHOSPHORUS LOAD (kg/ha) COMPARISONS BETWEEN THE COMPONENTS OF STREAMFLOW USING A RANDOMIZED COMPLETE BLOCK ANALYSIS OF VARIANCE AND DUNCAN'S MULTIPLE RANGE PROCEDURE

	Rising	Falling	Delayed Flow
Oxidized Nitrogen	3.5669	.7521	.0731
Total Phosphorus	9.2045	3.662	.0718

TABLE X

OXIDIZED NITROGEN AND TOTAL PHOSPHORUS LOAD (kg/ha) COMPARISONS BETWEEN STORMFLOW USING A RANDOMIZED COMPLETE BLOCK ANALYSIS OF VARIANCE AND DUNCAN'S MULTIPLE RANGE PROCEDURE

	Stormflow Date										
	5/2	5/14	6/29	5/26	6/26	3/3	6/4	5/21	5/18	5/10	4/13
Mean Oxidized Nitrogen	4.897	6.355	2.613	1.454	.4553	.4375	.2137	.1772	.0761	.0418	.0381
Mean Total Phosphorus	24.318	12.994	4.895	.658	1.828	2.017	.204	.139	.218	.416	.187

*Significance level α = .10

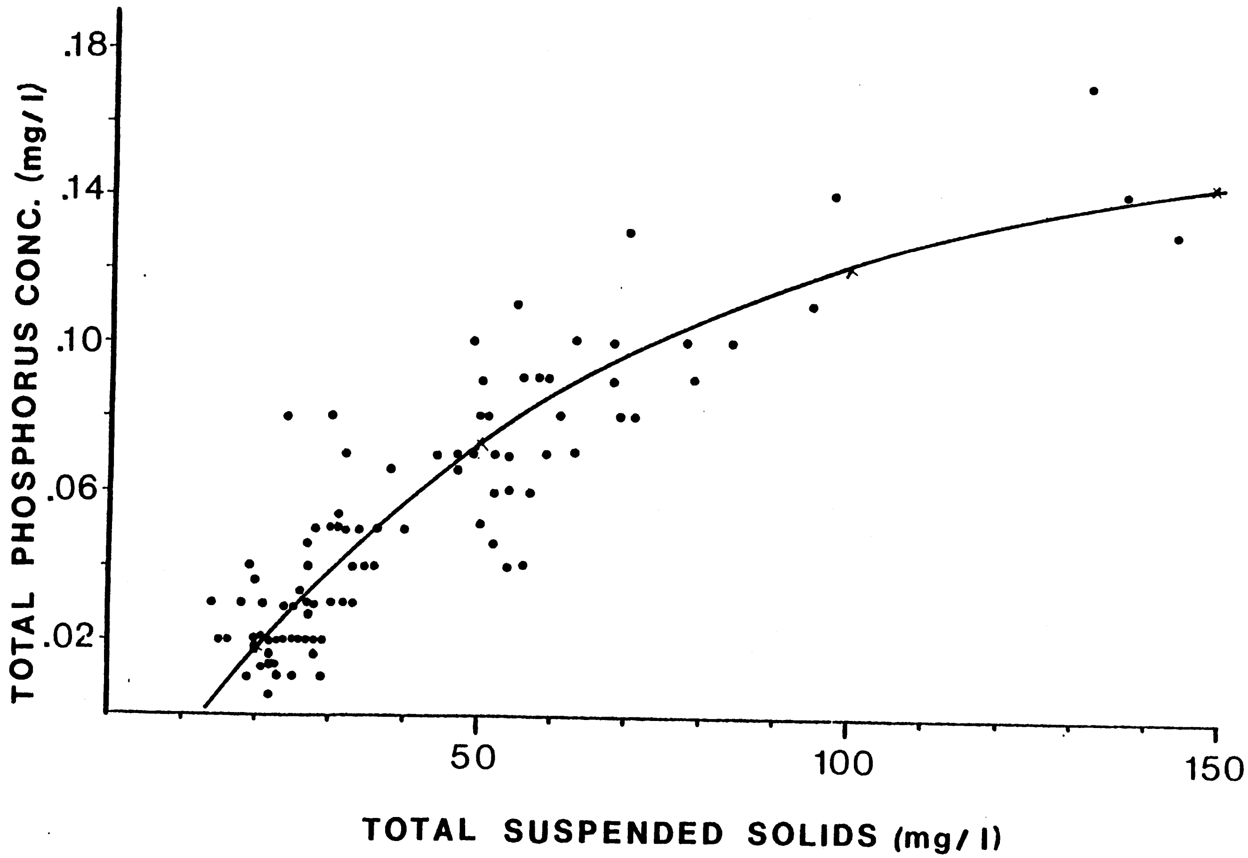


Figure 31. Scattergram of Total Phosphorus Concentrations in Relation to Total Suspended Solids Concentration in Streamflow

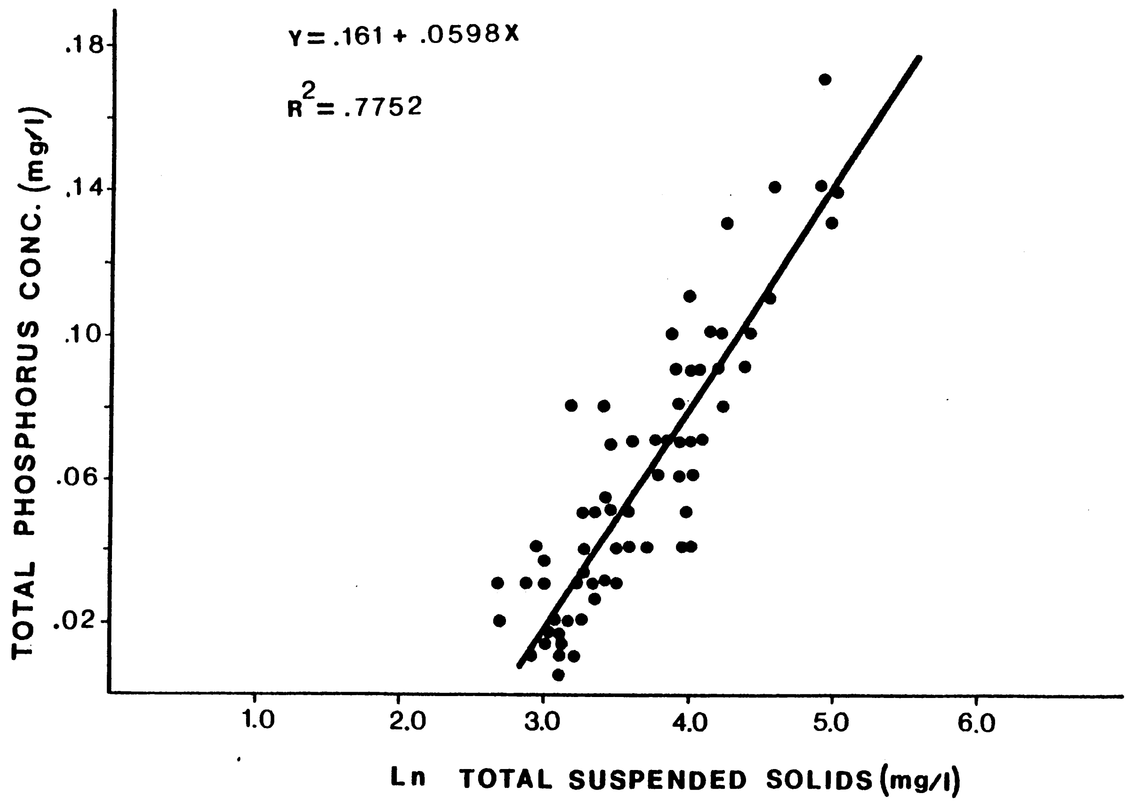


Figure 32. Linear Regression Model Relating Total Phosphorus Concentrations a Function of the Natural Log of Total Suspended Sediment Concentration

Comparisons

On a storm basis prior to May 10, 1983 oxidized nitrogen concentrations were significantly greater in throughfall from the pine and hardwood canopies than concentrations in rainfall and streamflow. However, the concentrations in throughfall paralleled those in rainfall (Figure 34). For the study period as a whole, oxidized nitrogen concentrations were found to be similar among rainfall, pine and hardwood throughfall. These concentrations were significantly greater than concentrations in streamflow (Figure 35). Oxidized nitrogen loads were also similar among rainfall, pine and hardwood throughfall, but were significantly greater than oxidized nitrogen loads in streamflow (Figure 36) for the study period.

On a storm basis there were no significant differences in total phosphorus concentrations between rainfall, pine and hardwood throughfall, and streamflow (Figure 37). For the study period as a whole, concentrations were also not significantly different between rainfall, pine and hardwood throughfall, and streamflow (Figure 38). Total phosphorus loads for the study period as a whole are significantly greater in pine and hardwood throughfall than in rainfall and streamflow (Figure 39).

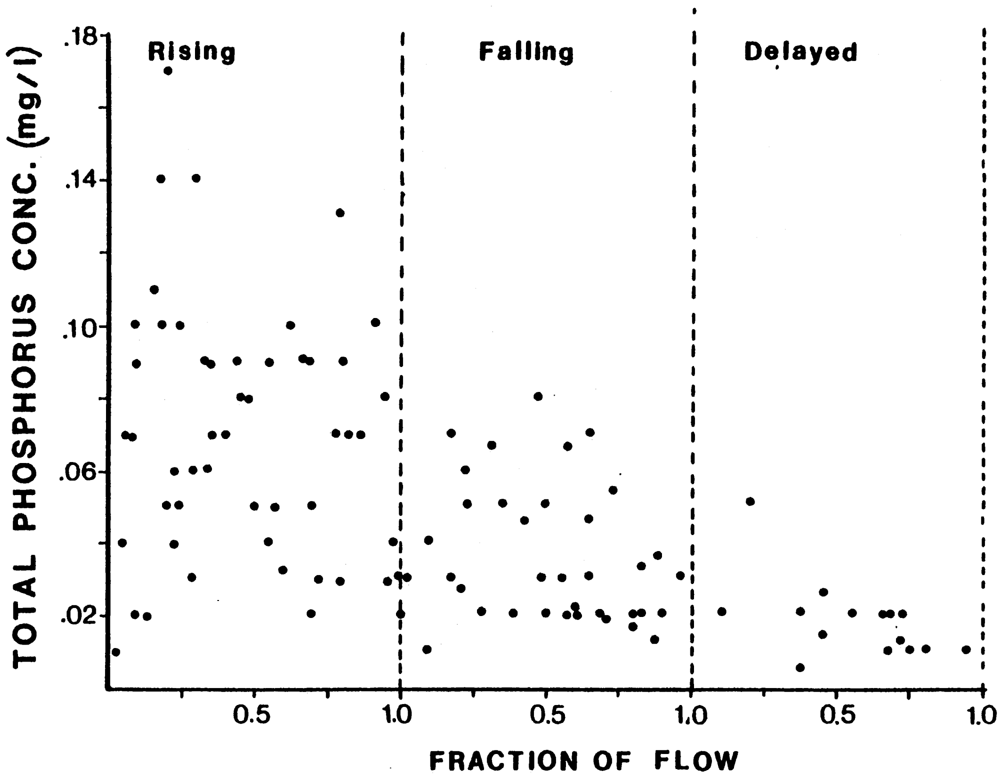


Figure 33. A Seasonal Separation of Streamflow and Total Phosphorus Concentrations During the Three Major Changes in Flow

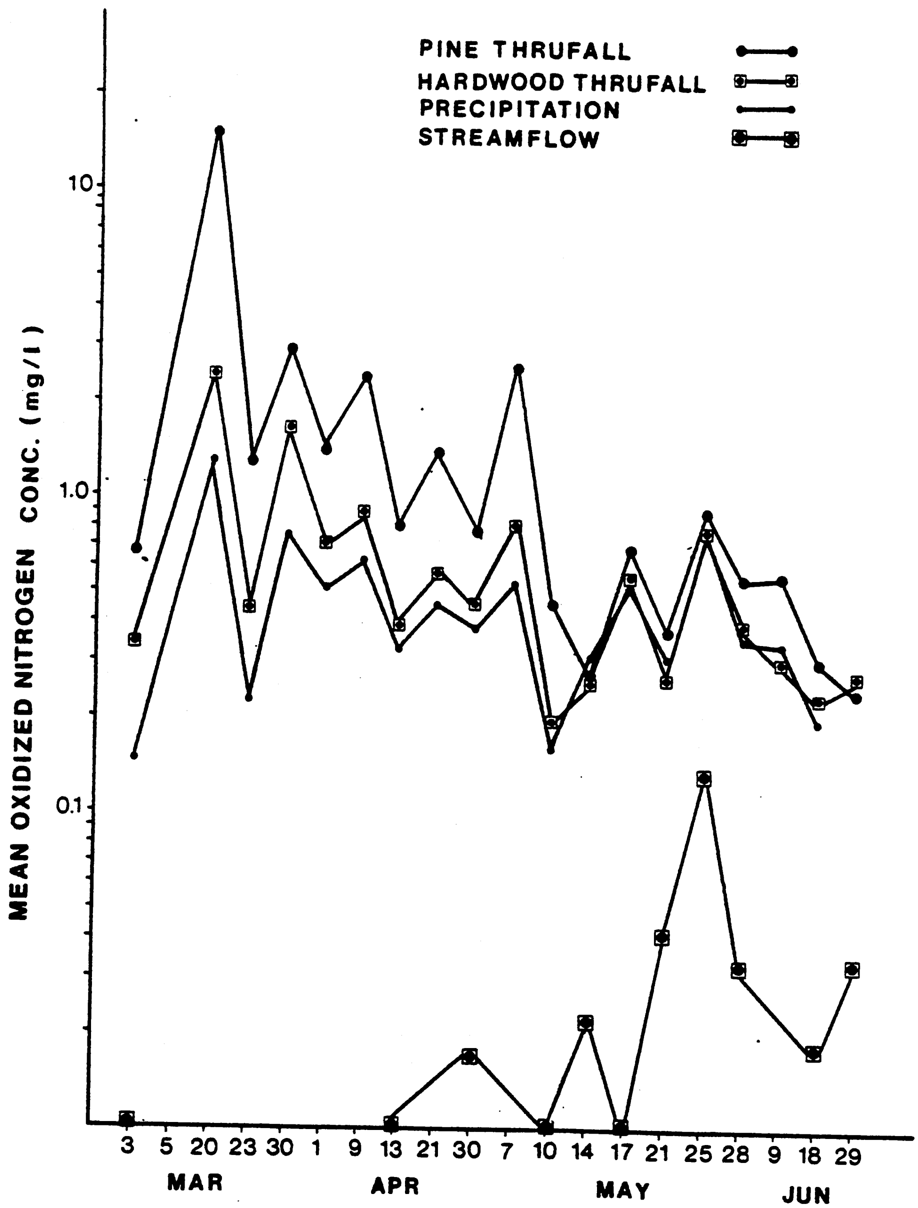


Figure 34. Oxidized Nitrogen Concentrations in Precipitation, Throughfall, and Streamflow for each Storm Sampled

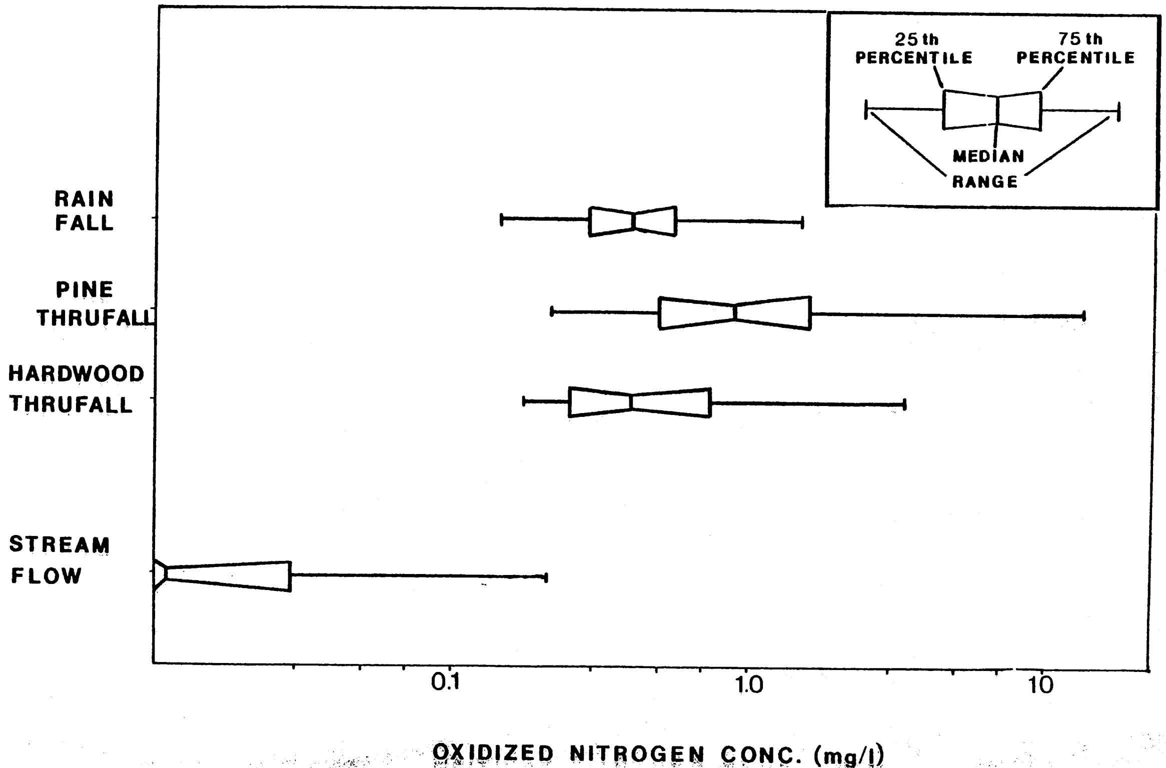


Figure 35. Oxidized Nitrogen Concentrations for the Study Period in the Hydrologic Profile of Watershed One

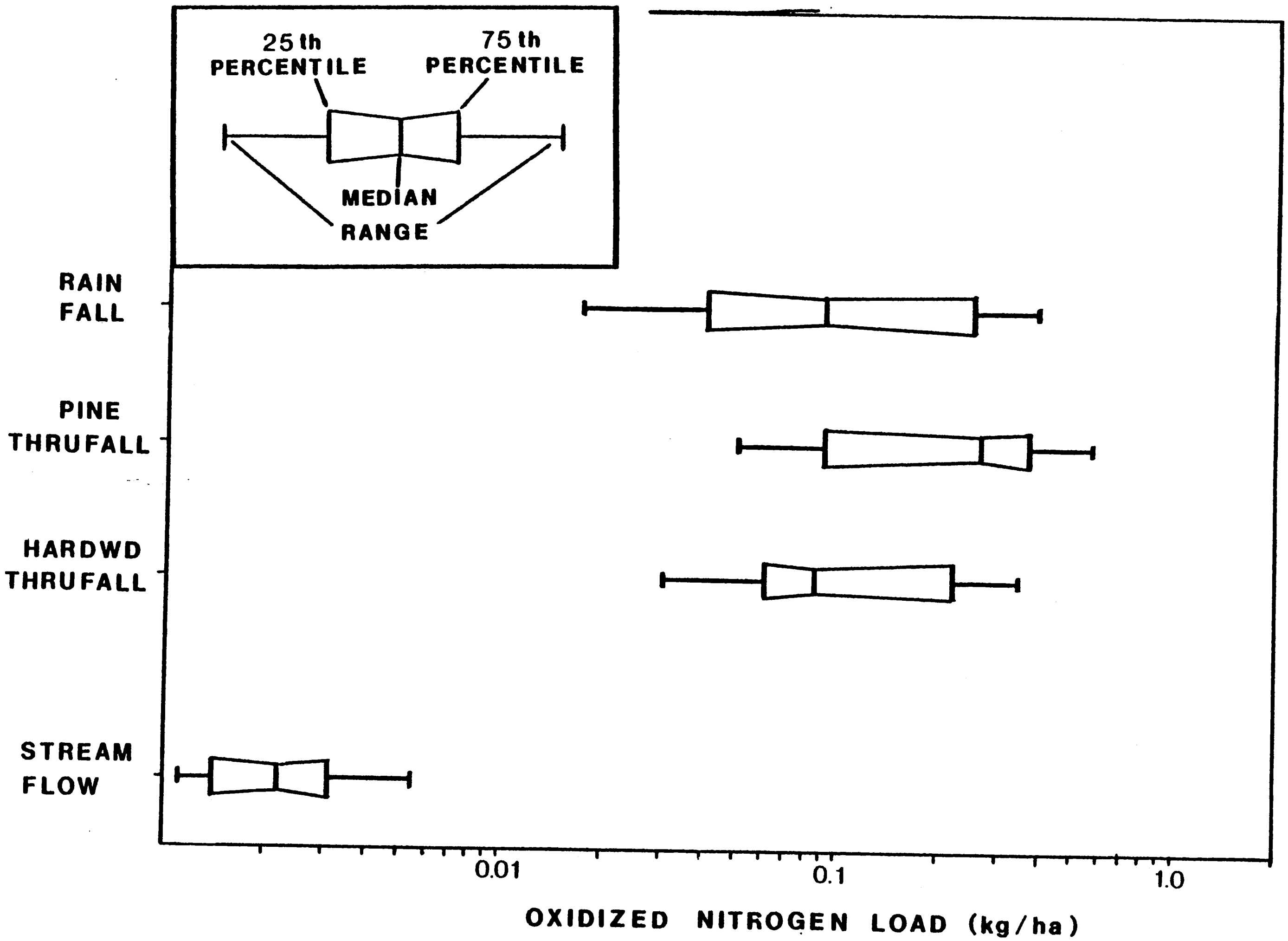


Figure 36. Profile of the Oxidized Nitrogen Load for the Study Period in the Hydrology of Watershed One

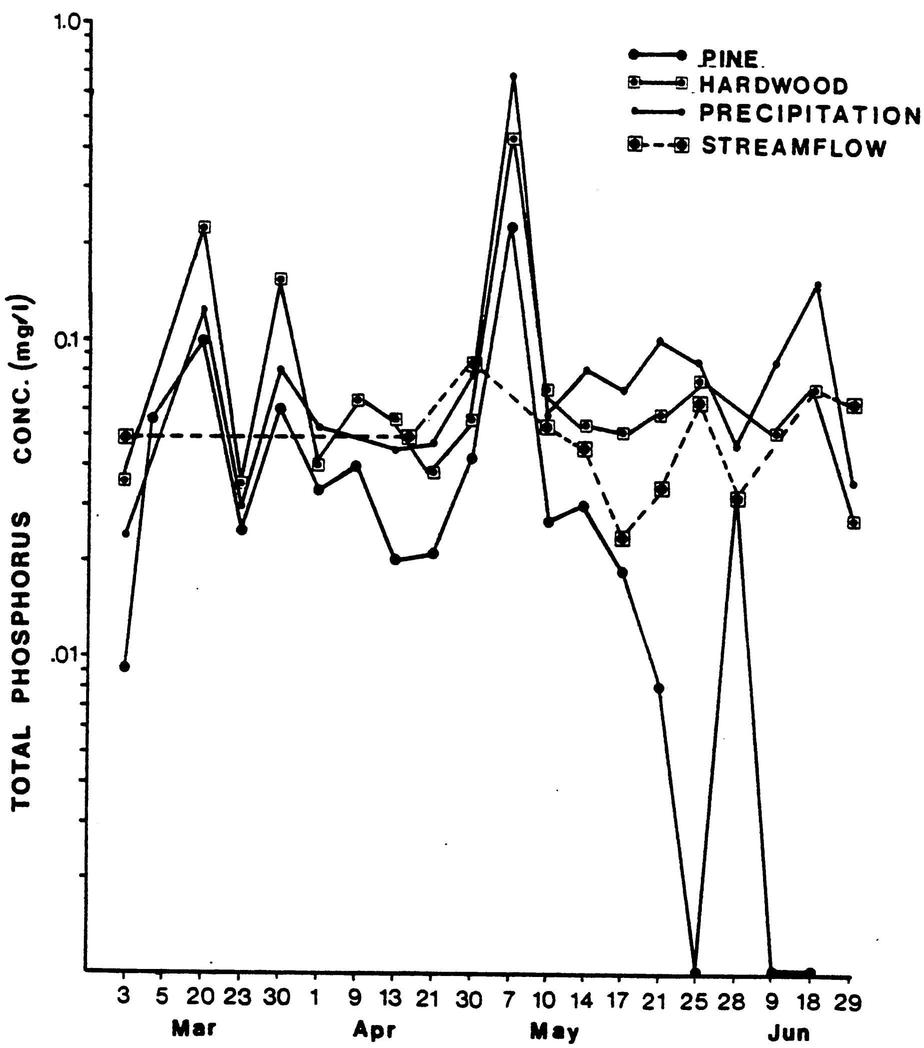


Figure 37. Mean Total Phosphorus Concentrations in Precipitation, Throughfall, and Streamflow for each Storm Sampled

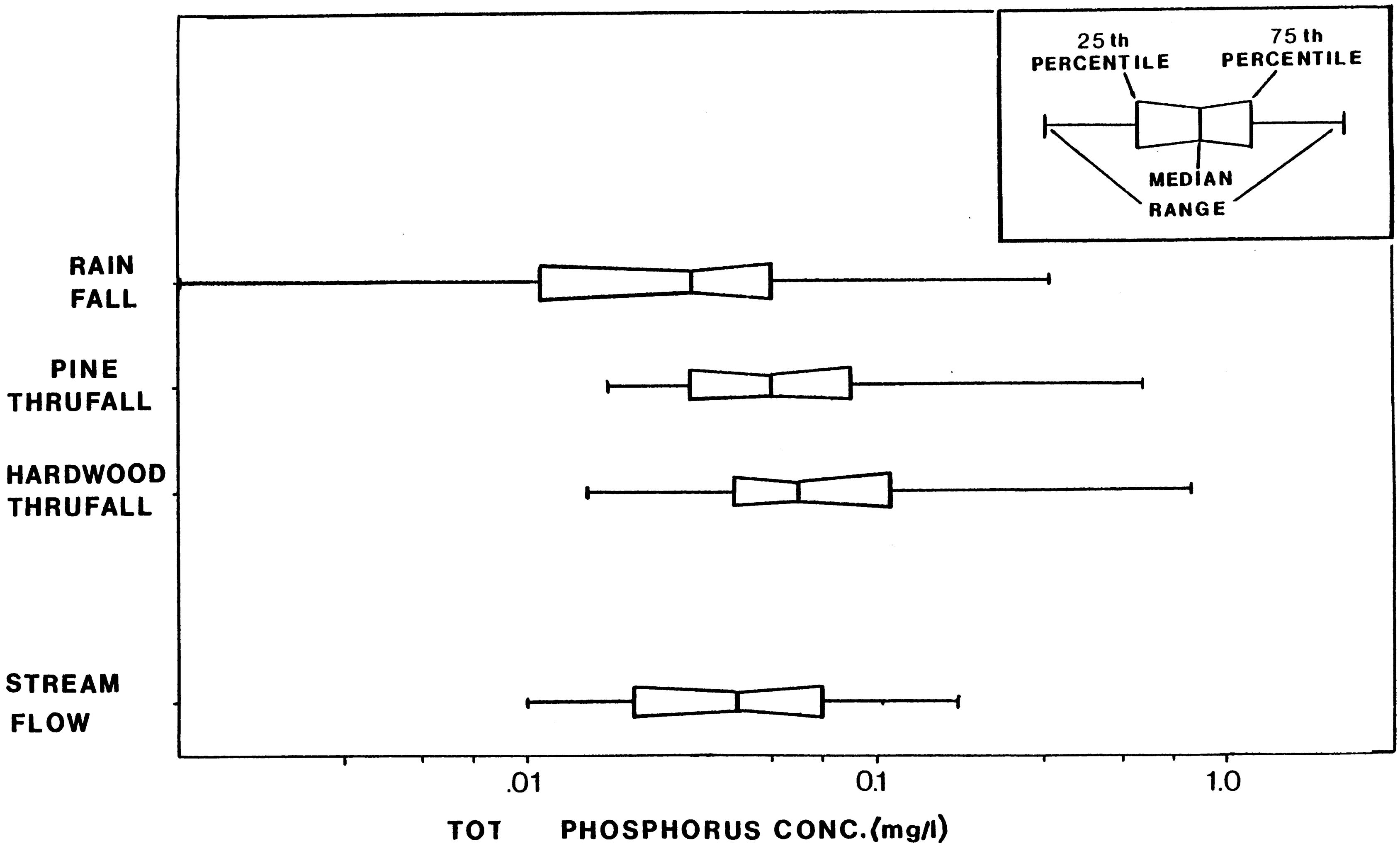


Figure 38. Total Phosphorus Concentrations for the Study Period in the Hydrologic Profile of Watershed One

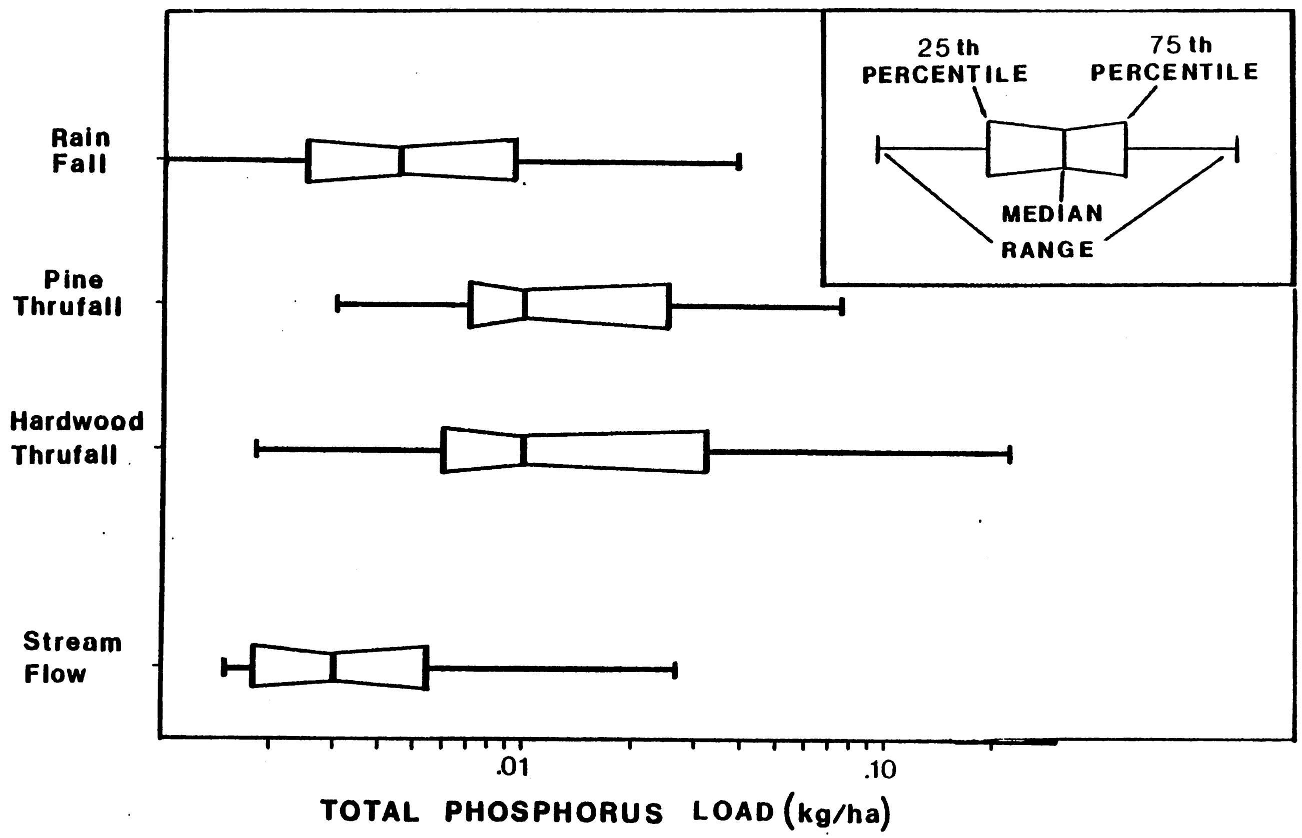


Figure 39. Profile of the Seasonal Total Phosphorus Load in the Hydrology of Watershed One

CHAPTER V

DISCUSSION

Precipitation

Oxidized Nitrogen

The amount of oxidized nitrogen entering this small watershed seemed to be governed by the amount of precipitation deposited during a given storm. Concentrations in bulk precipitation were found to be inversely related to precipitation depth (Figures 13 and 14). Lewis and Grant (1979) and others have observed nutrient concentrations in precipitation that tend be highest during the first few minutes of a storm, and then decrease rapidly as the storm proceeds. This flushing of nutrients out of the atmosphere early in a storm may also have occurred during storm events on the study watershed.

However, the curvilinear increase in load with increasing precipitation, as determined by regression analysis and observed in Figure 17, is somewhat contradictory with precipitation oxidized nitrogen concentration trends. Based on the concentration curves in Figures 13 and 14, the load curve in Figure 16 should have a convex-up shape rather than concave. Findings such as these reflect the dangers associated with empirical curve fitting by regression techniques.

As with many precipitation studies, the precipitation entering the study watershed was found to be slightly acidic. The average pH at the NADP site was almost 10 times more acidic than the pH of water at equilibrium with carbon dioxide. The majority of the published literature on this subject indicates sulfate affects the pH of precipitation to a much greater extent than oxidized nitrogen. However, in this study, neither oxidized nitrogen sulfate was found to be strongly correlated with pH. Of the two, oxidized nitrogen had the better correlation (r= .43 versus r of .22; Figure 15).

The pH levels found during this study are higher than those found in the Northeast part of the United States, but less than those found in the West. There seems to be some uncertainty as to the effects of acidic precipitation on a forested ecosystem when oxidized nitrogen is contributing the majority of hydrogen ions (Mclean, 1981). However, there is general agreement among most atmospheric scientists that acid precipitation is a result of fossil fuel combustion which contributes nitrous and sulfurous oxides to the atmosphere (Likens et. al., 1977; Mclean, 1981). The possible sources of oxidized nitrogen in this study were not addressed. However it appears sulfate and oxidized nitrogen may be arising from the same source because these concentrations were highly correlated (r= .79).

Total Phosphorus

The concentrations of total phosphorus appear to be much higher than those reported in the literature (Table I). There seems to be some indication that a source of phosphorus other than precipitation is contributing to the high total phosphorus concentrations collected (Figure 16 and 17). There were high coefficients of variation seen between the two collectors with the upper collector often having concentrations an order of magnitude greater than the collector at the outlet. The coefficients of variation were significantly correlated with date (Table IV) and seem to increase after May 1, 1983. Traffic on the upper dirt road near the second collector appeared by observation to increase significantly after this date when hunters and logging trucks frequently used the road. Sober and Bates (1977) concluded soil and dust from dirt roads contributed significantly to the high total phosphorus values found in their study in central Oklahoma. The dirt on the upper ridge of the watershed seems to be a significant source of soil-bound phosphorus. The outliers that were left out of the regression analyses were assumed to be due to contamination by road derived soil and dust.

The total phosphorus concentrations in precipitation were inversely related to the amount of precipitation during a storm (Figure 16 and 17). Total phosphorus in precipitation seemed to behave similarly to the flushing of nutrients at the beginning of rainfall described by Lewis and Grant (1979). Phosphorus load appeared to increase curvilinearly as the storm duration increased (Figure 18). The significance of storm duration as opposed to precipitation is uncertain. Perhaps dust, soil, and other particulate matter deposited on the funnel surfaces during dry periods were washed into the collector buckets. The longer the storm duration, the greater the total precipitation falling on the collector and therefore the greater the washing of material deposited on the collector into the bucket. There was also a significant correlation with maximum intensity (Table III) which also supports this conclusion. High precipitation intensities usually mean high velocities on impact with a solid surface, which would tend to dislodge particles sorbed to the funnel surface.

Throughfall

The vegetation canopy in the watershed had a distinct effect on incoming rainfall and nutrient concentrations. Throughfall amounts were linearly related to precipitation amounts (Figure 20) and were similar to relationships found by other researchers (Clinginpeel, 1979). Not only does the amount of precipitation affect the amount of throughfall, but maximum storm intensity and duration, evaporation, windspeed, and the specific vegetation canopy may work in complex ways to affect throughfall. In several storms during this study throughfall amounts, especially at collector number one, were in excess of 100 % of the incident precipitation amounts. The only explanation that seems plausible is that the wind reached high enough velocities during and immediately after a storm to shake additional water from the canopy and into the collectors. If the canopy can be considered a collection surface both horizontally and vertically, it can easily be concluded that a strong wind could dislodge additional amounts of water to give a higher throughfall depth in a given collector. In addition, the lower the maximum storm intensity, the greater the proportion of rain that is held by the canopy to be lost by evaporation or shaken loose by the wind.

Oxidized Nitrogen

The relationships seen among the concentrations, loads, precipitation, storm duration, and days since last storm shed some light on a possible mechanism governing the high concentrations in throughfall. The vegetation canopy, especially pine, has a very high surface area for the retention of water during a storm. Some water will always be retained on the leaves, stems, and branches due to the adhesion of water to these surfaces. Because the adhesive forces are stronger than gravitational forces, the only way this water can be removed is by evaporation. Since evaporation is a distillation process, the water sorbed to the vegetation becomes more concentrated with respect to minerals and nutrients as water is lost. Eventually a film of mineral and nutrient salts remain on the vegetation. Small storms would be expected to produce throughfall of relatively high concentration because a relatively large amount of mineral and nutrient salts will have dissolved in a small amount of water in addition to the nutrients already in the precipitation. The significance of the number of days since the last storm may be explained by considering that dryfall (dust and soil, etc.) is deposited and held in the canopy during periods of no rainfall. The activity of microbes on the leaf, stem, and branch surfaces could also be converting ammonium in rainfall to oxidized nitrogen in addition to decomposing organic material on the leaves, stems, and branches.

Other studies have shown results both similar and dissimilar to the results in this study. Likens et. al. (1977) found greater oxidized nitrogen concentrations in throughfall from hardwoods and pines in their study. But Rolfe and Peterson (1982) and Carlisle et. al. (1967) noted a retention of oxidized nitrogen in the hardwood vegetative canopy in their respective studies.

Total Phosphorus

It seems likely that the majority of total phosphorus in throughfall was a result of the washing of dust, aerosols, and organic matter out of the canopy during storm events. Based on the inverse relationship between phosphorus from the pine canopy and precipitation and the curvilinear relationship between load and precipitation it is possible that a flushing of particulate matter out of the canopy along with associated phosphorus occurred during the initial phases of the storms.

Other studies (Tamm, 1951; Carlisle et al., 1967) have shown total phosphorus concentrations which were higher in throughfall than precipitation and which were also inversely related with the amount of precipitation.

Streamflow

Streamflow from watershed one increased rapidly during moderate to large, high intensity storms (Table VII and Figure 3). The quick response of the watershed to streamflow is indicative of a basin with steep slopes and little deep infiltration and subsequent groundwater recharge. The streamflow, therefore, was probably a result of rapidly moving shallow interflow (and perhaps some surface runoff) which in turn has a strong influence on the behavior of oxidized nitrogen and total phosphorus during any given storm.

Oxidized Nitrogen

The trajectories of streamflow during large storms (Figure 27 and 28) indicate the concentrations rose and fell rapidly during the initial stages of streamflow and a flushing effect was taking place. Bond (1979) and Whitfield and Schreir (1981) observed higher oxidized nitrogen concentrations prior to peak discharge in two different large perennial rivers. But no data were found for small ephemeral headwater streams such as the stream in this study.

For moderate to large storms, initial surface runoff and shallow interflow may have washed oxidized nitrogen out of the litter layer and A horizon of the soil at a relatively fast rate and reduced the amount of time that vegetation and microbes can assimilate the nutrient. As storms progressed oxidized nitrogen dropped to a low level because most of it had been washed out of the litter layer and upper soil surface. This would account for the relatively high concentrations before peak flow and low concentrations after peak flow in moderate and large storms. Small storms on the other hand showed a low concentrations that remained unchanged throughout the storm (Figure 25 and 26). Perhaps only a small part of the watershed was contributing to the streamflow in these small storms. Possibly, the high variabilities and low correlations in oxidized nitrogen concentrations were due to the demand for the nutrient by biota, both in the stream and in the watershed. Several studies have concluded biotic activity is a major factor controlling oxidized nitrogen concentrations in streams (Likens et. al., 1977; Bond, 1979; Lewis and Grant, 1979).

In this study oxidized nitrogen was lost via streamflow at very low rates (Figure 36) and indicates a net accumulation of oxidized nitrogen occurred in the watershed, probably within the biotic pool.

Total Phosphorus

Figures 30 and 31 show, without much doubt, the strong relationship between total phosphorus and total suspended solids. Many other studies have also reported similar relationships (Likens et al., 1977; Dunne and Leopold, 1979; Harms, 1977). With respect to total phosphorus, the relative importance of total suspended solids (TSS) decreased as TSS increased because the lower surface area of the large particles which were found at higher concentrations of TSS. The lower the surface area, the lower the amount of phosphorus associated with those particles. Total phosphorus concentrations showed a first flush effect and trajectories showed concentrations to be greater before peak discharge than after (Figures 25 to 28). Peak concentrations occurred before peak flow in streamflow during the largest storms (Figure 27 and 28). The rapid rise of streamflow during a storm apparently provided enough velocity to suspend and transport stream bed sediments and associated phosphorus. After peak discharge, velocities declined and sediments began settling out. Harms (1977) and Smith (1976) observed that total phosphorus transport in streamflow is related to stream bed scour. In other studies phosphorus transport seems to be variable (Bond, 1979), and unrelated to discharge at low flows (Jones, 1978). Smith (1976) and Jones (1978) concluded intense storms provide up to 50 % of the annual phosphorus transported in streamflow from a forested watershed.

In this study the large amounts of total phosphorus in precipitation and throughfall coupled with the relatively small amounts lost by stream indicated a net accummulation of phosphorus in the watershed (Figures 36 and 38).

Sampling Error

Precipitation

There were several areas where potential errors could have occurred during the data collection. Loss of precipitation by raindrop splash out of the collectors undoubtedly occurred during high intensity storms. However, there was no indication that this loss amounted to more than 5 % of that collected by the recording rain gauge. Loss of sample out of the buckets by evaporation was negligible due to the vapor loop maintained in the latex rubber hose. Some loss of sample took place during the volume measurement as water from the bucket was poured into the graduated cylinder. However, this error was not considered to be any greater than 1 % of the volume collected.

There was no indication that any sample was contaminated by bird feces or insects. Few insects were seen in the collection buckets. There is a possibility that microbial activity could have affected oxidized nitrogen concentrations because samples at times sat during warm weather up to four or five days after a storm. Ammonium could have been oxidized to nitrate or nitrate taken up due to bacterial activity.

Total phosphorus concentrations may have been underestimated for several storms. There was a retention of particulates to the sides of the funnels and bottom of the buckets which were not removed.

Throughfall

There were two very significant potential sources of error in throughfall collection. The fiberglass screens in the funnels were not very efficient in keeping insects and large debris out. There were times when the number of insects and the amount of debris in the buckets were significant. There is no way of knowing to what extent foreign material contaminated the samples.

The funnels often accumulated very fine particulate matter by sorption to the polyethylene. This could have affected the total phosphorus measurements. However, the extent of this error is unknown.

Streamflow

There were only two obvious sources of potential error during the collection of stream samples. Cross-contamination of samples could have occurred while pump samples were taken due to residual water remaining in the hose from a previous sample. It is felt this type of contamination was negligible because every effort was made to assure adequate drainage of any residual water. It is possible that the amount of sediment was underestimated due to the difficulties in collecting all sediment being transported during a storm. This would have underestimated total phosphorus concentrations and transport.

Analysis of Samples

Quality control was rigidly maintained during the laboratory analysis of the samples. However, when nearly all analyses were complete it was noticed that the .45 micron membrane filters were contributing as much as .06 mg/1 of oxidized nitrogen to the precipitation and throughfall samples. Streamflow samples were not affected because they were filtered only through glass fiber filters that were acid washed.

CHAPTER VI

CONCLUSIONS

Oxidized nitrogen and total phosphorus concentrations in precipitation were generally higher for storms with low rainfall amounts and lower for large rainstorms. This observation may be due to a flushing of oxidized nitrogen and total phosphorus out of the atmosphere during the initial stages of a storm and subsequent dilution if precipitation exceeded the volume necessary to remove the atmosphere contaminants. Relationships among pH, oxidized nitrogen, and other precipitation chemical constituents were unclear. Total phosphorus concentrations were relatively large compared to similar studies and may have been caused by collector contamination with dust from nearby dirt roads.

The forest canopy appeared to increase greatly the oxidized nitrogen and total phosphorus concentrations above that found in precipitation. Oxidized nitrogen concentrations appeared to be most related to the number of days since the last storm and inversely with volume of precipitation. It may be that a combination of evaporation and nitrification of precipitation on the leaves, stems, and branches were the mechanisms that increased the oxidized nitrogen in throughfall. Total phosphorus concentrations were inversely related to precipitation amounts in throughfall from the pine canopy. No relationships were seen in throughfall from the hardwood canopy.

The cumulative load of oxidized nitrogen from the canopy increased as rainfall amount and storm duration increased. This is perhaps significant in washing nitrate salts from the canopy. Total cumulative phosphorus loads also increased as precipitation amounts increased. This also may be due to washing of particulate matter out of the canopy.

The export of oxidized nitrogen out of the watershed was extremely small and indicated a net accumulation of the nutrient in the watershed. Large storms transported the greatest cumulative total amounts of oxidized nitrogen out of the watershed. The initial stages of precipitation may have washed much of the oxidized nitrogen out of the litter layer and A soil horizon and into the stream. Oxidized nitrogen concentrations in the stream decreased rapidly as the storm progresses.

Total phosphorus was transported in association with total suspended solids. The first stages of a storm transported the higher concentration of total phosphorus but the larger storms transported the greatest cumulative total of phosphorus on a seasonal basis. Total phosphorus also appeared to accumulate in the watershed.

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APPENDIXES

APPENDIX A

SUMMARY STATISTICS

TABLE XI

MEANS, STANDARD DEVIATIONS (S-D), AND COEFFICIENTS OF VARIATIONS (CV) FOR OXIDIZED NITROGEN AND TOTAL PHOSPHORUS CONCENTRATIONS IN BULK PRECIPITATION

Date	N mean (mg/l)	N SD (mg/l)	N CV (%)	P mean (mg/l)	P SD (mg/l)	P CV (%)
3/3/83	.148	.0028	1.9	.009	0	0
3/5/83	.46	.028	6.1	.056	.016	27.8
3/20/83	1.30	.29	22	.099	.003	2.9
3/26/83	.23	.021	9	.025	.007	28
3/30/83	.755	.035	4.7	.06	0	0
4/1-5/83	.51	--	--	.03	--	--
4/9/83	.630	--	--	.04	--	--
4/13/83	.355	.007	2	.02	--	--
4/21-22/83	.45	--	--	.02	--	--
5/2/83	.385	.064	16.5	.042	.0035	8.4
5/7/83	.54	.071	13.1	.2235	.129	57.9
5/11/83	.16	0	0	.0265	.015	56
5/14/83	.31	.014	4.6	.03	.0368	123
5/17/83	.51	.028	5.5	.02	0	0
5/21/83	.31	.014	4.6	.005	.007	141
5/25/83	.78	.028	3.6	.03	.014	47
5/28-30/83	.355	.007	2	.005	.007	141
6/9/83	.34	.014	4.2	.03	.042	141
6/28/83	.199	--	--	.005	.007	141

TABLE XII

MEANS, STANDARD DEVIATIONS (SD) AND COEFFICIENTS OF VARIATION (CV) FOR OXIDIZED NITROGEN AND TOTAL PHOSPHORUS CONCENTRATIONS IN THROUGHFALL FROM THE PINE CANOPY

Date	N mean (mg/l)	N SD (mg/l)	N CV (%)	P mean (mg/l)	P SD (mg/l)	P CV (%)
3/3/83	.667	.201	30	.036	.015	41.7
3/20/83	14.42	4.26	29.5	.229	.043	18.8
3/26/83	1.27	.423	33	.036	.014	38.8
3/30/83	2.99	.496	16.6	.156	.05	32
4/1-5/83	1.38	.235	17.1	.04	.02	49.6
4/9/83	2.37	.564	23.8	.065	.016	23.9
4/13/83	.78	.24	30.6	.056	.016	28.9
4/21-22/83	1.37	.267	19.5	.038	.009	23.1
5/2/83	.773	.165	21.3	.056	.0125	22.4
5/7/83	2.52	.921	36.5	.431	.194	45
5/11/83	.46	.220	47.3	.07	.036	51.8
5/14/83	.272	.04	14.8	.054	.016	29.6
5/17/83	.692	.086	12.4	.051	.027	53.1
5/21/83	.372	.045	12.1	.058	.021	36
5/25/83	.883	.103	11.6	.074	.022	30
5/28-30/83	.547	.130	23.8	.029	.018	63.4
6/9/83	.559	.122	21.9	.051	.032	62.6
6/28/83	.302	.051	16.9	.071	.05	70.5
6/29/83	.249	.024	9.6	.027	.015	57

TABLE XIII

MEANS, STANDARD DEVIATIONS (SD), AND COEFFICIENTS OF VARIATION (CV) FOR OXIDIZED NITROGEN AND TOTAL PHOSPHORUS CONCENTRATIONS IN THROUGHFALL FROM THE HARDWOOD CANOPY

Storm Date	N mean (mg/l)	N SD mg/l)	N CV (%)	P mean (mg/l)	P SD (mg/l)	P CV (%)
3/3/83	.343	.200	58.3	.024	.009	37.6
3/20/83	2.48	1.28	51.7	.125	.004	3.4
3/26/83	.44	.243	55	.03	.02	57.7
3/30/83	1.67	.802	48	.08	.01	12.5
4/1-5/83	.71	.120	16.9	.053	.002	4
4/9/83	.89	.092	10.3	.065	.007	10.9
4/13/83	.385	.007	1.8	.045	.007	15.7
4/21-22/83	.572	.063	11.1	.047	.014	29.5
5/2/83	.462	.039	8.5	.149	.123	82.8
5/7/83	.83	.08	9.4	.689	.095	13.8
5/10/83	.197	.019	9.5	.221	.282	127
5/14/83	.267	.03	11.2	.081	.041	50.6
5/17/83	.549	.03	5.4	.07	.008	10.9
5/21/83	.264	.008	3	.104	.023	22.2
5/25/83	.791	.034	4.3	.086	.014	15.9
5/28-30/83	.390	.063	16.2	.047	.029	62
6/9/83	.303	.036	11.9	.087	.068	78.5
6/28/83	.235	.04	17.1	.154	.104	67.6
6/29/83	.274	.008	2.9	.036	.015	42.2

TABLE XIV

DISCHARGE-WEIGHTED MEANS, STANDARD DEVIATIONS (SD), AND COEFFICIENTS OF VARIATION (CV) FOR OXIDIZED NITROGEN AND TOTAL PHOSPHORUS CONCENTRATIONS IN STREAMFLOW

Date	N			P		
	mean (mg/l)	SD (mg/l)	CV (%)	mean (mg/l)	SD (mg/l)	CV (%)
3/3/83	.01	0	0	.05	.02	33.1
4/13/83	.01	0	0	.05	.01	16.3
5/3/83	.02	.01	56.0	.08	.04	47.3
5/10/83	.01	.002	30.4	.05	.01	18.5
5/14/83	.02	.03	148	.05	.04	76.7
5/18/83	.01	.001	12.0	.02	.002	8.7
5/21/83	.04	.01	13.2	.03	.01	32.7
5/28/83	.13	.04	33.0	.06	.01	17.1
5/28/83	.03	.01	27.3	.03	.01	18.3
6/28/83	.02	.003	14.2	.07	.01	13.8
6/29/83	.03	.01	42.3	.06	.02	28.5

TABLE XV

STORM INPUTS, OUTPUTS, AND FLUX FOR OXIDIZED NITROGEN (kg/ha) DURING THE STUDY PERIOD

Storm	Precipitation	Throughfall Pine	Throughfall Hardwood	Streamflow	Flux
1	.0071	.226	.110	.0011	+.006
2	.0200	---	---	---	+.020
3	.044	.315	.061	---	+.044
4	.058	.261	.071	---	+.058
5	.021	.044	.033	---	+.021
6	.089	.203	.084	---	+.089
7	.031	.081	.028	---	+.031
8	.079	.158	.071	.0001	+.079
9	.112	.283	.108	---	+.112
10	.292	.467	.243	.0044	+.288
11	.020	.066	.03	---	+.020
12	.047	.123	.053	.0002	+.047
13	.175	.157	.137	.0022	+.173
14	.111	.120	.100	.0012	+.110
15	.059	.060	.040	.0021	+.057
16	.238	.279	.202	.0017	+.236
17	.089	.129	.083	.0008	+.088
18	.081	.148	.077	.0012	+.080
19	.281	.197	.210	.0004	+.281
Total	1.854	3.317	1.740	.0172	+1.839

Storm	Date	Storm	Date	Storm	Date
1	3/4/3	7	4/9/83	13	5/14/83
2	3/6/83	8	4/13/83	14	5/17/83
3	3/20/83	9	4/21/83	15	5/21/83
4	3/23-26/83	10	4/30-5/2/83	16	5/25/83
5	3/30/83	11	5/7/83	17	5/28-30/83
6	4/1-5/83	12	5/10/83	18	6/9/83
				19	6/28/83

TABLE XVI

STORM INPUTS, OUTPUTS, AND FLUX FOR TOTAL PHOSPHORUS (kg/ha) DURING THE STUDY PERIOD

S	Precipitation	Throughfall		Streamflow	
		Pine	Hardwood		
1	.0004	.0118	.0627	.0031	-.0027
2	.0025	---	---	---	+.0025
3	.003	.006	.005	---	+.003
4	.006	.007	.005	---	+.006
5	.002	.0023	.0017	---	+.0058
6	.0058	.0057	.0062	---	+.0058
7	.002	.002	.0021	---	+.002
8	.004	.001	.008	.0005	+.0035
9	.005	.008	.009	---	+.005
10	.03	.033	.069	.0166	+.013
11	.005	.011	.025	---	+.005
12	.011	.018	.057	.0014	+.0096
13	.03	.041	.002	.0132	+.0168
14	.004	.0086	.013	.0023	+.0017
15	.0008	.009	.015	.0013	-.0005
16	.013	.023	.022	.0018	+.0112
17	0	.007	.009	.0008	-.0008
18	0	.014	.022	.0009	-.0009
19	0	.065	.120	.0013	-.0013
Total	.1245	.273	.432	.0475	+.0809

Storm	Date	Storm	Date	Storm	Date
1	3/3/83	7	4/9/83	13	5/14/83
2	3/6/83	8	4/13/83	14	5/17/83
3	3/20/83	9	4/21/83	15	5/21/83
4	3/23-26/83	10	4/30-5/2/83	16	5/25/83
5	3/30/83	11	5/7/83	17	5/28-30/83
6	4/1-5/83	12	5/10/83	18	6/9/83
				19	6/28/83

APPENDIX B

TABULATED DATA

TABLE XVII

OXIDIZED NITROGEN AND TOTAL PHOSPHORUS CONCENTRATIONS FOUND IN BULK PRECIPITATION FROM MARCH 1, 1983 TO JUNE 30, 1983

Date	Collector	N	P	Volume (l)
		mg/l		
3/3/83	1	.146	.009	8.0
	2	.150	.009	7.95
3/5/83	1	.48	.067	.920
	2	.44	.045	.925
3/20/83	1	1.09	.101	.740
	2	1.50	.097	.680
3/26/83	1	.21	.02	5.37
	2	.24	.03	5.46
3/30/83	1	.73	.06	.60
	2	.78	.06	.60
4/1-5/83	1	.51	.03	.69
	2	--	--	--
4/9/83	1	.630	.040	1.025
	2	--	--	--
4/13/83	1	.36	.02	4.52
	2	.35	--	4.83
4/21-22/83	1	--	--	--
	2	.45	.02	5.18
5/2/83	1	.43	.044	14.25
	2	.34	.039	15.90
5/7/83	1	.49	.132	.860
	2	.59	.315	.825
5/11/83	1	.16	.037	5.97
	2	.16	.016	6.41

TABLE XVII (Continued)

Date	Collector	N mg/l	P	Volume (1)
5/14/83	1	.30	.004	12.16
	2	.32	.056	13.57
5/17/83	1	.49	.02	4.69
	2	.53	.02	4.24
5/21/83	1	.300	.01	4.140
	2	.32	.01	4.00
5/25/83	1	.80	.04	6.22
	2	.76	.02	6.78
5/28-30/83	1	.36	.01	5.87
	2	.35	---	5.97
6/9/83	1	.33	.01	6.00
	2	.35	.06	6.20
6/28/83	1	.199	.01	21.75
	2	---	---	---

TABLE XVIII

OXIDIZED NITROGEN, TOTAL PHOSPHORUS CONCENTRATIONS (mg/l),
AND VOLUME (V) IN LITERS COLLECTED IN THROUGHFALL FROM
THE PINE CANOPY (COLLECTORS 1,2,5,6,7,8,9) AND
HARDWOOD CANOPY (COLLECTORS 3,4,10) FROM
MARCH 1, 1983 TO JUNE 30, 1983

Date		Collector 1	2	3	4	5	6	7	8	9	10
3/3/83	N	.73	.62	.29	.17	.57	1.09	.61	.48	.58	.56
	P	.03	.03	.03	.02	.03	.04	.05	.02	.06	.03
	V	2.1	1.415	1.605	1.85	1.675	2.05	1.83	2.02	1.945	1.87
3/20/83	N	13.6	9.0	3.38	1.57	20.0	18.77	16.97	12.41	10.17	---
	P	.23	.24	.20	.21	.44	.26	.21	.23	.26	---
	V	.162	.156	.143	.126	.091	.140	.082	.100	.160	---
3/23-26/83	N	1.43	1.44	.36	.25	1.03	2.05	.96	.77	1.18	.715
	P	.02	.03	.02	.02	.03	.05	.05	.02	.05	.05
	V	1.44	.84	1.33	1.24	1.11	1.21	1.18	1.16	1.10	1.23
3/30/83	N	3.7	3.3	1.61	.90	2.72	3.00	3.00	2.00	3.10	2.50
	P	.14	.12	.07	.09	.14	.26	.11	.17	.15	.08
	V	.099	.068	.152	.132	.07	.048	.098	.120	.080	.074

TABLE XVIII (Continued)

4/1-5/83	N	1.65	1.58	.79	.62	1.38	1.60	1.13	1.11	1.19	---
	P	.03	.03	.05	.05	.04	.03	.04	.04	.08	---
	V	.960	.650	.760	.550	.630	1.055	.865	.780	.770	---
4/9/83	N	2.78	2.28	.95	.82	3.04	2.98	1.88	2.04	1.62	---
	P	.04	.05	.07	.06	.07	.06	.09	.07	.07	---
	V	.298	.204	.194	.158	.094	.200	.134	.156	.270	---
4/13/83	N	.70	.67	.39	.38	.76	1.27	.86	.59	.58	---
	P	.03	.05	.04	.05	.07	.07	.06	.04	.07	---
	V	1.35	1.10	1.01	1.04	.900	1.28	1.06	.815	1.35	---
4/21-22/83	N	1.64	1.44	.64	.52	1.28	1.74	1.18	.96	1.33	.56
	P	.03	.04	.03	.06	.05	.04	.04	.03	.05	.06
	V	1.34	1.03	1.04	1.24	.98	1.12	1.29	1.09	1.20	.90
4/30-5/2	N	.82	.68	.51	.43	.82	.98	.95	.63	.54	.45
	P	.04	.06	.07	.29	.07	.05	.07	.06	.05	.08
	V	4.95	3.85	3.77	2.30	2.6	3.80	2.2	2.4	4.02	2.06
5/7/83	N	2.47	2.00	.89	.85	3.53	4.04	2.04	1.50	2.06	.74
	P	.32	.56	.66	.61	.50	.49	.04	.58	.53	.80
	V	.246	.184	.240	.204	.062	.086	.26	.134	.134	.16

TABLE XVIII (Continued)

5/10/83	N	.55	.46	.21	.21	.43	.90	.28	.24	.4	.18
	P	.06	.06	.04	.55	.05	.15	.04	.06	.08	.08
	V	1.59	1.23	1.67	1.45	1.395	1.495	1.635	1.435	1.495	1.355
5/14/83	N	.33	.29	.30	.27	.23	.30	.28	.21	.26	.24
	P	.05	.03	.04	.11	.05	.08	.07	.05	.05	.10
	V	4.01	3.55	3.11	2.98	2.75	3.27	2.45	2.57	3.67	2.47
5/18/83	N	.85	.71	.52	.56	.69	.63	.75	.60	.62	.58
	P	.02	.04	.06	.07	.03	.07	.08	.03	.09	.08
	V	1.225	.88	1.24	1.05	.920	.86	1.00	.84	.94	.78
5/21/83	N	.45	.41	.26	.27	.35	.39	.33	.35	.33	.27
	P	.02	.05	.08	.11	---	.08	.06	.05	.08	.12
	V	1.10	.79	1.04	.76	.81	.84	.90	.94	.86	.75
5/25/83	N	.86	.79	.81	.75	.91	.80	1.09	.91	.82	.81
	P	.05	.10	.07	.10	.06	.10	.08	.05	.08	.09
	V	2.33	1.63	1.43	1.33	1.70	1.77	1.66	1.59	1.69	1.51
5/30/83	N	.51	.43	.36	.35	.75	.68	.56	.51	.39	.46
	P	.01	.01	.02	.04	.03	.03	.04	.01	.06	.08
	V	1.84	1.60	1.51	1.12	1.02	1.36	1.18	1.06	1.36	1.00

TABLE XVIII (Continued)

6/9/83	N	.66	.56	.31	.27	.68	.68	.36	.49	.49	.34
	P	.04	.04	.01	.15	.02	.05	.10	.03	.09	.10
	V	1.99	1.40	1.56	1.45	1.10	1.53	1.36	1.17	1.70	1.30
6/28/83	N	.33	.34	.25	.19	.32	.37	.24	.25	.28	.27
	P	.03	.06	.13	.06	.07	.18	.05	.04	.09	.27
	V	6.27	5.05	5.33	5.41	4.77	5.57	5.75	5.11	3.78	3.60
6/29/83	N	.23	.27	.28	.27	.25	.23	.21	.28	.27	.27
	P	.01	.03	.02	.05	.02	.03	.05	.02	.04	.04
	V	2.26	1.37	1.29	1.32	1.59	1.97	1.59	1.44	1.70	1.21

TABLE XIX

OXIDIZED NITROGEN AND TOTAL PHOSPHORUS CONCENTRATIONS IN SAMPLES COLLECTED DURING STREAMFLOW

Storm Date	Sample	Discharge (cfs)	N	P
			mg/l	
3/3/83	1	0.0806	0.01	0.02
	2	0.2203	0.01	0.05
	3	0.3771	0.01	0.07
	4	0.6257	0.01	0.09
	5	0.8180	0.01	0.07
	6	0.9403	0.01	0.03
	7	0.6779	0.01	0.03
	8	0.4386	0.01	0.03
	9	0.2680	0.01	0.02
	10	0.1507	0.01	0.02
	11	0.0316	0.01	0.01
	12	0.0061	0.01	0.02
4/13/83	1	0.0709	0.01	0.03
	2	0.2054	0.01	0.07
	3	0.1016	0.01	0.03
	4	0.0253	0.01	0.01
5/3/83	1	0.1130	0.01	0.04
	2	0.2357	0.03	0.07
	3	0.3771	0.03	0.10
	4	0.6257	0.03	0.11
	5	0.9088	0.03	0.17
	6	1.213	0.04	0.14
	7	1.607	0.02	0.07
	8	1.967	0.02	0.08
	9	2.586	0.02	0.10
	10	3.303	0.02	0.13

TABLE XIX (Continued)

	11	3.837	0.01	0.07
	12	3.303	0.01	0.07
	13	2.699	0.02	0.07
	14	2.163	0	0.05
	15	1.65	0.01	0.07
	16	1.363	0.01	0.05
	17	1.005	0.01	0.05
	18	0.6515	0.01	0.03
	19	0.4386	0.01	0.04
	20	0.2203	0.01	0.03
	21	0.2203	0.01	0.01
	22	0.1103	0.01	0.02
5/10/83	1	0.1250	.01	0.09
	2	0.2680	0.01	0.07
	3	0.2357	0.01	0.04
	4	0.1130	0.01	0.03
	5	0.0619	.01	0.02
5/14/83	1	0.1016	0.03	0.04
	2	0.2357	0.04	0.07
	3	0.3771	0.03	0.09
	4	0.6257	0.03	0.14
	5	0.9088	0.03	0.10
	6	1.213	0.04	0.09
	7	1.607	0.07	0.09
	8	2.015	0.05	0.09
	9	2.586	0.08	0.05
	10	1.967	0.05	0.04
	11	2.163	0.01	0.03
	12	2.932	.01	0.03
	13	3.564	.01	0.03
	14	3.303	.01	0.03
	15	2.642	0.01	0.03
	16	1.324	.01	0.02

TABLE XIX (Continued)

5/14/83	17	1.005	.01	0.02
	18	0.6515	.01	0.02
	19	0.4386	.01	0.01
	20	0.2516	0.01	0.01
	21	0.1130	.01	0.01
	22	0.113	0.01	0.01
5/18/83	1	0.0806	0.02	0.03
	2	0.2054	0.01	0.03
	3	0.2357	0.01	0.02
	4	0.1130	0.01	0.02
	5	0.0908	0.01	0.02
5/21/83	1	0.0806	0.03	0.08
	2	0.1130	0.06	0.02
	3	0.0908	0.03	0.01
5/26/83	1	0.0806	0.21	0.06
	2	0.2356	0.21	0.09
	3	0.3387	0.21	0.08
	4	0.2680	0.02	0.05
	5	0.1130	0.01	0.02
	6	0.0455	0.01	0.02
5/28/83	1	0.0806	0.05	0.04
	2	0.2054	0.06	0.05
	3	0.2516	0.02	0.02
	4	0.1250	0.01	0.02
	5	0.0316	.01	0.02
6/28/83	1	0.1375	0.02	0.10
	2	0.2030	0.02	0.06
	3	0.3971	0.02	0.08
	4	0.6771	0.02	0.09
	5	0.5757	0.01	0.06
	6	0.3771	0.02	0.05
	7	0.2516	0.02	0.07

TABLE XIX (Continued)

	8	0.0806	0.02	0.05
6/29/83	1	0.1250	0.09	0.06
	2	0.2640	0.05	0.08
	3	0.4601	0.06	0.11
	4	0.7048	0.05	0.08
	5	1.3630	0.04	0.06
	6	1.0050	0.02	0.05
	7	0.7048	0.02	0.08
	8	0.4601	0.01	0.03
	9	0.2680	0.01	0.02
	10	0.1250	0.01	0.02

VITA

Stephen John Lawrence

Candidate for the Degree of

Master of Science

Thesis: OXIDIZED NITROGEN AND TOTAL PHOSPHORUS RELATIONSHIPS IN THE HYDROLOGY OF A MIXED PINE HARDWOOD WATERSHED IN SOUTHEASTERN OKLAHOMA

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