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PATTERNS AND PROCESSES OF VARIATION IN NITROGEN AND PHOSPHORUS CONCENTRATIONS IN FORESTED STREAMS

TECHNICAL BULLETIN NO. 836

DECEMBER 2001

by
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Acknowledgments

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PRESIDENT'S NOTE

Nutrient concentrations are often important factors determining the quality of water. Concentrations that are too low can produce unproductive fish habitat. Concentrations that are too high can create excessive, undesirable plant growth and water quality deterioration associated with eutrophication.

EPA has developed draft protocols for setting water quality standards for nutrients in different ecoregions. One of the approaches recommended in these protocols is setting nutrient criteria equal to the lowest 25th percentile values in distributions of nutrient concentrations for waterbody categories within ecoregions. Thus, all waterbodies with nutrient concentrations above 25th percentile values could be considered impaired by excess nutrients. NCASI and others have noted in comments to EPA that this practical but simplistic approach could force states to list as impaired many streams in which nutrients do not have any significant adverse impacts but merely occur at concentrations above arbitrary limits. In many streams, violations of nutrient criteria will occur naturally for various reasons (e.g., presence of nitrogen fixing plants in riparian zones or naturally high concentrations of phosphate in bedrock).

This technical bulletin reviews forest water quality data from undisturbed forest watersheds to determine whether there are spatial and temporal patterns in nitrogen and phosphorus concentrations that should be recognized as the nation considers new water quality standards. The report was prepared by Dr. Dan Binkley, Professor in the Department of Forest Science at Colorado State University. Dr. Binkley and his colleagues used their extensive contacts to secure data from forest watersheds throughout the United States, and those scientists contributing to this effort are identified in the extensive acknowledgements. The results are both timely and profound. The project was jointly funded by NCASI and the USDA Forest Service.

There is wide variation in stream nitrogen concentrations both within and among forested watersheds. Temporal variation in nutrient concentrations within the same stream can be substantial and should be considered carefully when developing monitoring protocols and water quality criteria. Some of the variation among streams can be explained by rates of atmospheric deposition. Forest vegetation can also be important. The forms of nitrogen in streamwater can vary between different forest cover types (hardwood versus conifer). In the West, streams with nitrogen-fixing alder can have very high nitrate-nitrogen concentrations. Phosphorus concentrations are strongly influenced by geology. There are differences between some ecoregions in mean nutrient concentrations, but there is more variability in stream nutrient concentrations within ecoregions than between ecoregions.

Distributions of nutrient concentrations found for small forested watersheds appear to be substantially different than distributions found for larger forested watersheds included in national monitoring programs such as the USGS National Water Quality Assessment Program. Streams in small forested watersheds tend to have a lower frequency of low concentrations of nutrients and a higher frequency of high concentrations compared to streams in larger forested watersheds.

Ron Yeske

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December 2001

PATTERNS AND PROCESSES OF VARIATION IN NITROGEN AND PHOSPHORUS CONCENTRATIONS IN FORESTED STREAMS

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ABSTRACT

Water is one of the most fundamental and important renewable resources. Between 70 and 80% of the water flowing in rivers in the United States originates as precipitation falling on forests. Water quality in forested streams is usually among the best in the nation. In the United States, laws and regulations provide for states and Native American tribes to develop standards for designated uses (or beneficial uses) of water, and to establish criteria for water quality based on those standards. The overall goals are to protect public health or welfare, enhance water quality, and serve the purposes of the Clean Water Act (USEPA 1994, 2000a). This overall system entails definition of designated uses for water systems by states (or tribes), development of criteria that describe the quality of water relative to these uses, and the promulgation (and EPA approval) of standards for the criteria that will meet the water quality goals.

This report summarizes concentrations of compounds of nitrogen (N) and phosphorus (P) across the US as a basis for the development of appropriate water quality criteria and standards. Based on published water chemistry for over 300 streams in small forested watersheds, nitrate concentrations averaged 0.31 mg N/L (median = 0.15 mg N/L), with some streams averaging ten times this level. Nitrate concentrations tended to be higher in the northeastern US, in watersheds dominated by hardwood forests (especially hardwoods other than oaks), and in recently harvested watersheds. Concentrations of dissolved organic N (mean 0.32 mg N/L, median 0.08 mg N/L) were similar to those of nitrate, whereas ammonium concentrations were much lower (mean 0.05 mg N/L, median 0.01 mg N/L). The nitrogen loads of streams draining hardwood forests are dominated by nitrate, whereas streams in conifer forests are dominated by dissolved organic N. Concentrations of inorganic phosphate were typically much lower (mean 12 μg P/L, median 4 μg P/L) than dissolved organic phosphate (mean 84 μg P/L, median 35 μg P/L).

The frequencies of chemical concentrations in streams in small forested watersheds differs substantially from the frequencies found in national monitoring programs of larger, mostly forested watersheds. At a national scale, streams draining small forested watersheds averaged about twice the concentrations of nitrate reported for larger, forested basins monitored by the US Geological Survey (Hydrologic Benchmark Network and National Water Quality Assessment Network). At a local scale, no trend in nitrate concentration with stream order or basin size was consistent across studies. Downstream changes in land use from forest to agriculture are typically associated with substantial increases in concentrations of N and P compounds.

Variations in streamwater chemistry were analyzed in depth for eight small watersheds within days, within months, within years, and across years. Variations between months within years tended to be higher than variation for other time periods, with coefficients of variation commonly exceeding 100% for nitrogen compounds and 50% for inorganic phosphate. Many streams in the northeastern US have shown dramatic reductions (more than 60%) in nitrate concentrations over the past 20 years, despite sustained high rates of atmospheric deposition.

One approach to the establishment of standards and criteria has been the idea of ecoregions. At the broadest level some regions do differ substantially in nutrient concentrations, but variations within regions are commonly larger than difference between regions. The differences in regional averages tended to be on the order of twofold, whereas the ranges found within regions typically spanned a fivefold (or greater) range.

The concentrations of N and P reported for forested streams are generally much lower than concentrations found in streams with agricultural or urban land use, and these low concentrations have not been shown to represent a threat to designated (or beneficial) uses of forest streams. Streamwater chemistry varies over time within streams and among streams, with varying impacts on biotic processes in streams, but these differences are probably small relative to the dynamics associated with light, temperature, sediment load, and other factors.

KEYWORDS

ammonium, eutrophication, nitrate, nitrite, nitrogen, nonpoint source pollution, organic nitrogen, orthophosphate, phosphorus, stream water quality, water quality criteria and standards

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 820 (January 2001). *Forest operations and water quality in the Northeastern states: Overview of impacts and assessment of state implementation of nonpoint source programs under the federal Clean Water Act*.

Special Report No. 99-06 (December 1999). *Silviculture and water quality: A quarter century of Clean Water Act progress*.

Technical Bulletin No. 782 (May 1999). *Water quality effects of forest fertilization*.

Technical Bulletin No. 672 (July 1994). *Forests as nonpoint sources of pollution, and effectiveness of Best Management Practices*.

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PATTERNS AND PROCESSES OF VARIATION IN NITROGEN AND PHOSPHORUS CONCENTRATIONS IN FORESTED STREAMS

1.0 INTRODUCTION

Water is one of the most fundamental and important renewable resources. Between 70 and 80% of the water flowing in rivers in the United States originates as precipitation falling on forests (USEPA 2000a; Sedell et al. 2000). The quality of the water that flows from forests is generally among the best in the nation; the concentrations of nutrients in forested streams is usually less than 15% of the levels found in streams that run through agricultural or urban areas (Omernik 1976, 1977). The quality of water from forested streams is generally so high that a recent report by the Ecological Society of America on nonpoint pollution of surface waters with phosphorus and nitrogen did not even mention forests or forest practices as areas of concern (Carpenter et al. 1998). Maintaining this high quality of water in forested streams is important, and a variety of laws, regulations, and criteria have been established in the past 30 years.

In the United States, laws and regulations provide for states and Native American tribes to develop standards for designated uses (or beneficial uses) of water, and to establish criteria for water quality based on those standards. The overall goals are to protect public health or welfare, enhance water quality, and serve the purposes of the Clean Water Act (USEPA 1994, 2000a). This overall system entails definition of designated uses for water systems by states (or tribes), development of criteria that describe the quality of water relative to these uses, and the promulgation (and EPA approval) of standards for the criteria that will meet water quality goals.

The designated uses for water in forested streams may require criteria to support fish and wildlife or protect drinking water for communities. The geography and ecology of streams is not identical across the country, and the standards for water quality (which derive from designated uses) may also vary among regions. The US Environmental Protection Agency recently produced a technical guidance manual to help with the development of criteria for use in evaluating water quality standards by states and tribes (USEPA 2000b). The manual explicitly recognizes variations across the country, and describes approaches for classifying streams and rivers and accounting for normal differences that relate to geography, physical features, or other natural factors. One approach would classify water bodies into 84 “nutrient ecoregions” (Omernik 2000) within which water quality standards might be established.

A great deal of information on water quality in forested streams has been developed in the past four decades (Binkley and Brown 1993). This base of knowledge provides an opportunity to examine patterns in streamwater quality in forests, and how these patterns relate to regions of the country, forest types and conditions, and management activities. The present concentrations of nutrients in streamwaters also reflects a legacy of long-term changes in land use, including, in some cases, historic deforestation, agriculture and reforestation, and substantial changes in species composition; any long-term trends in nutrient concentrations may reflect “recovery” from these legacies (Krug and Winstanley 2000). The purpose of this report is to synthesize existing information on variations in streamwater nitrogen and phosphorus compounds, and identify patterns and processes that would be useful in establishing standards and criteria for maintaining the high quality of water in forested streams.

The core of this report is a summary of water chemistry data from more than 300 forest streams, mostly from small headwater streams that drain watersheds of less than 1000 ha. Section 2 summarizes the overall (synoptic) patterns among these streams, examining patterns in relation to regions, forest type and age, and geology. Streamwater chemistry varies substantially over periods of hours, day, months, and years, and Section 3 describes these patterns of variation over time for eight intensively studied watersheds (detailed information on each of these eight watersheds is provided in Appendix B). Section 4 examines sources of variation in streamwater chemistry within local areas, including changes in streamwater chemistry from headwaters to larger streams, and responses to management activities. Section 5 builds a synthesis from this information base and presents major implications for establishing water quality standards and criteria.

2.0 SYNOPTIC PATTERNS

At a local scale, the chemistry of streamwater may be influenced by a wide array of factors including recent weather, land use, and vegetation change. A synoptic view of water quality in forest streams subsumes all these sources of variation to describe the overall patterns for large regions and long periods of time. In this section, information from small watershed studies (typically <250 ha in size) in forest ecosystems is summarized. Information was collected for more than 300 streams from the published literature for forested streams in the United States, and histograms were compiled to illustrate the ranges of chemical concentrations. This section includes all streams in the database (Appendix A) except those that were fertilized. For the broadest coverage, these studies examined relatively undisturbed watersheds, as well as watersheds that were harvested or burned. The magnitudes of the effects of recent disturbances is discussed in Section 4. Averages and medians were estimated simply from the number of studies reported, without regard to the number of studies reported by region or forest condition class. The effects of fertilization are discussed in Section 3. At the end of this section, the chemistry for these headwater streams is compared to that reported for larger, forested basins in the USGS Hydrologic Benchmark Network and the National Water Quality Assessment Program.

2.1 Nitrate

Across the United States, forested streams averaged 0.31 mg N/L as nitrate, with a median value of 0.15 mg N/L (Figure 2.1). Concentrations reported for streams in the Northeast were much higher (mean 0.50 mg N/L, median 0.30 mg N/L) than in the Southeast (mean 0.18 mg N/L, median 0.05 mg N/L) or the West (mean 0.20 mg N/L, median 0.03 mg N/L). Extreme values (>1 mg N/L) were reported for forests in the Northeast and for forests containing nitrogen-fixing alders in the West.

The regional pattern in nitrate concentrations relates well to the concentrations of nitrate in precipitation across the country (Figure 2.2). Concentrations across the Northeast average about 1.5 mg NO_3^-/L (0.33 mg N/L), about double the concentrations in precipitation for the Southeast and West.

The regional pattern is also confounded by patterns in vegetation. Northeastern forests are dominated by hardwoods, whereas conifers are more common in the Southeast and West. Across all hardwood forests, nitrate concentrations averaged 0.46 mg N/L (median 0.31 mg N/L), compared with a mean of 0.15 mg N/L (median 0.03 mg N/L) for conifers (Figure 2.3). This trend was consistent even when broken down by vegetation types within regions; nitrate concentrations in streams draining hardwood forests exceeded those for streams draining coniferous forests in each region.

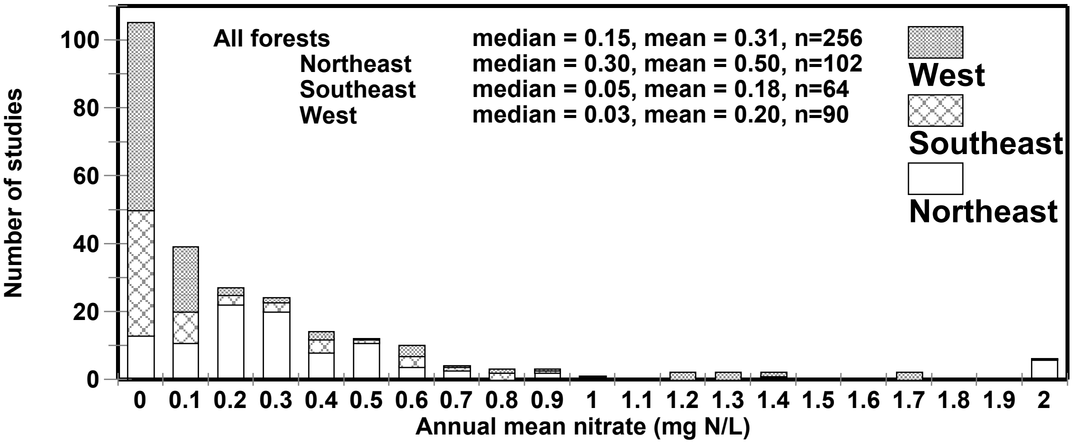
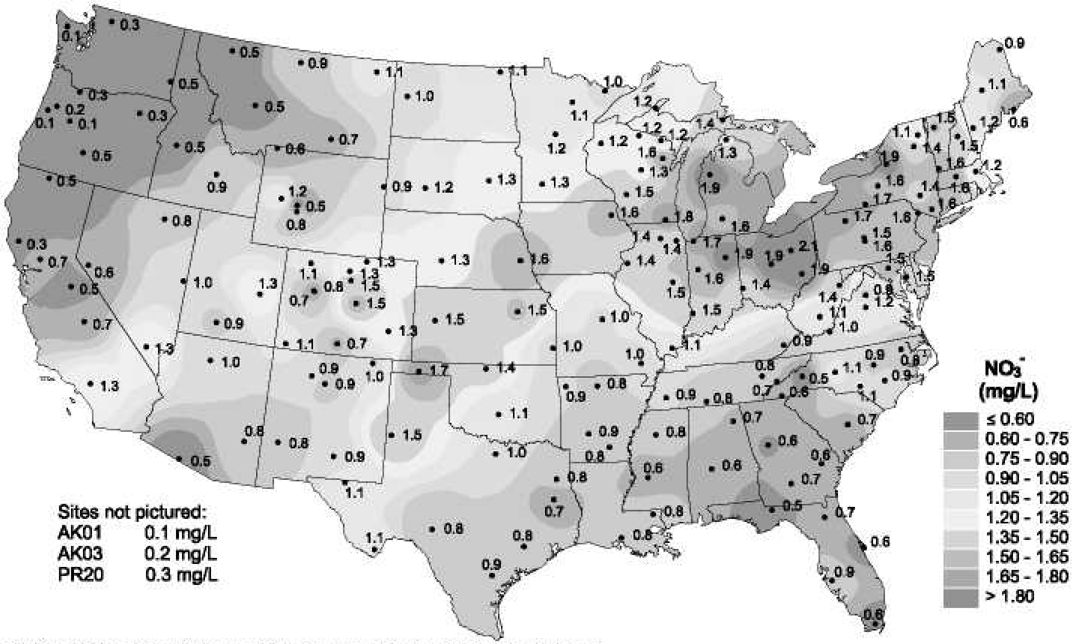


Figure 2.1. Average Annual Concentrations of Nitrate for Small Forested Watersheds

Nitrate ion concentration, 1994



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Figure 2.2. Concentrations of Nitrate (mg NO_3^-/L) for 1994 in Atmospheric Deposition

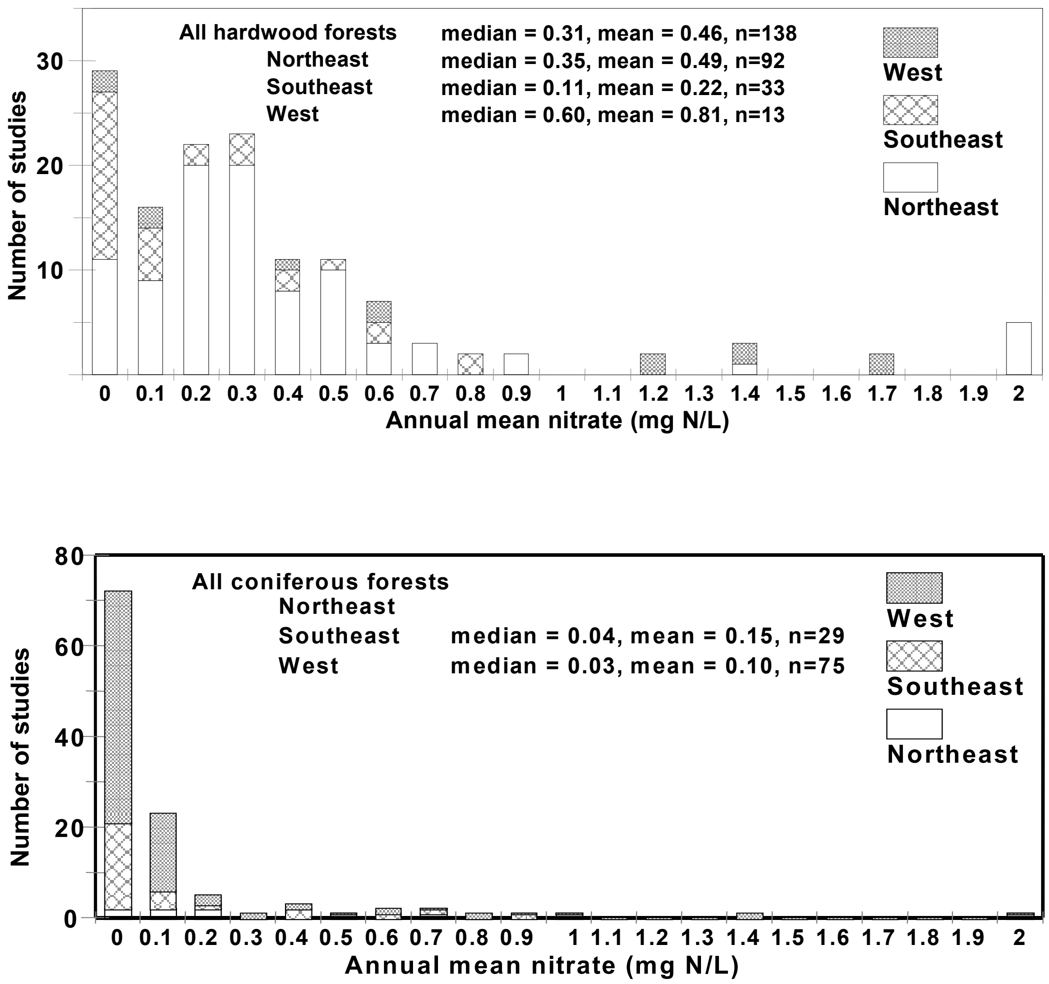


Figure 2.3. Average Annual Concentrations of Nitrate by Forest Type and Region

Little trend in nitrate concentrations was evident based on the age of the forests (Figure 2.4). Forests older than 100 years tended to have lower concentrations of nitrate, but most of these old forests were from the West where concentrations tended to be lower for all age classes, so this apparent age-related effect is probably geographical. A more detailed analysis of forest stand age and nutrient concentrations in runoff is provided in Section 4.

The influence of parent materials on nitrate concentrations was examined by grouping the streams by bedrock types (Figure 2.5). Glacial till deposits were combined regardless of mineralogy (most were igneous), and very old soils (Ultisols) were grouped with sedimentary parent materials owing to a low content of weatherable primary minerals. Streams draining sites with glacial till soils showed the highest nitrate concentrations; most of these were again from the Northeast, where any effect of geology is confounded by higher rates of nitrate deposition and hardwood dominated vegetation types. Igneous and volcanic parent materials showed the lowest concentrations, and these geologic types were confounded by their occurrence primarily in the West.

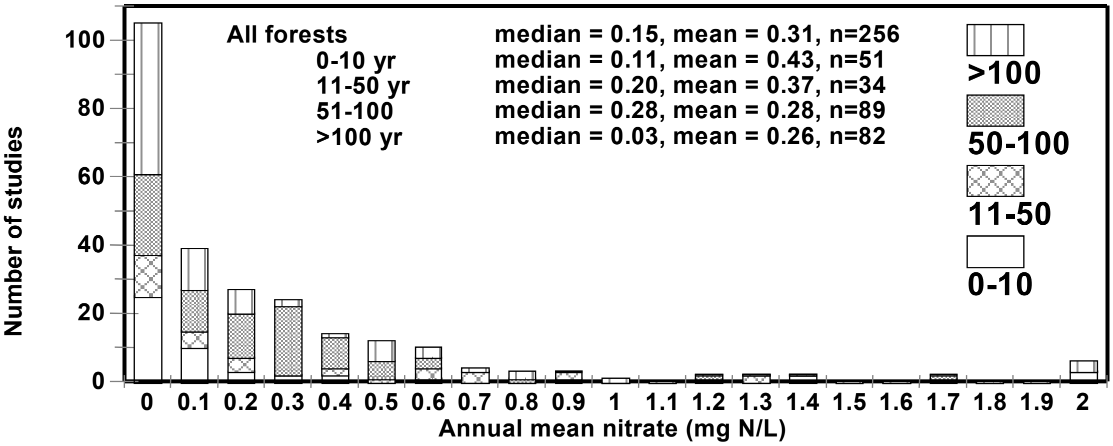


Figure 2.4. Average Annual Concentrations of Nitrate by Forest Age Class

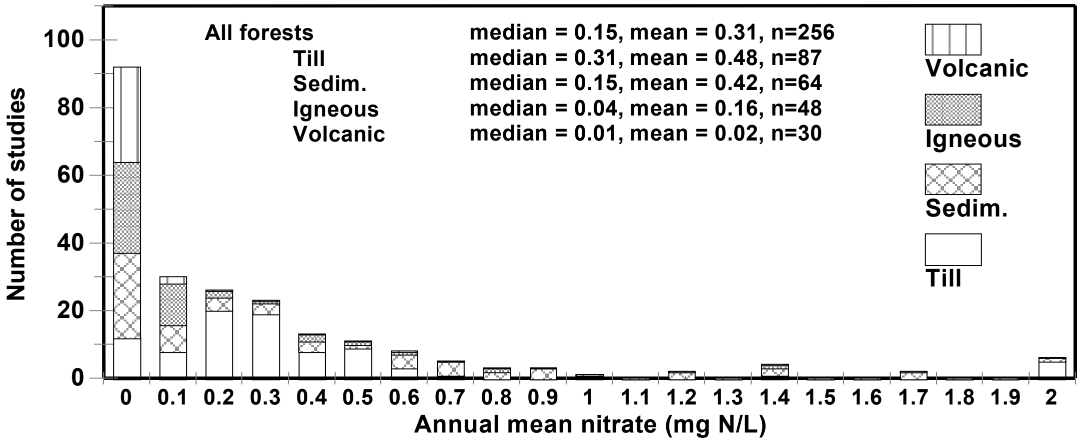


Figure 2.5. Average Annual Concentrations of Nitrate by Geologic Substrate

The maximum reported concentrations of nitrate were higher for sites with high annual average concentrations (Figure 2.6). Across all sites, the maximum nitrate concentration tended to be about 80% higher than the annual average.

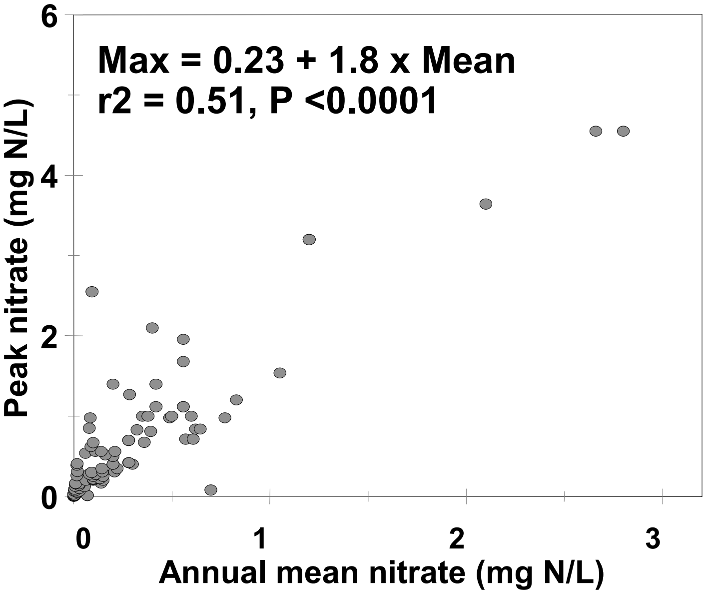


Figure 2.6. Maximum Reported Concentration of Nitrate as a Function of Annual Average Concentration

2.2 Ammonium

Across the United States, concentrations of ammonium in streamwater are much lower than nitrate concentrations (Figure 2.7). The average across the country was 0.05 mg N/L (median 0.01 mg N/L). Concentrations were lower for streams in the West (mean 0.02 mg N/L, median <0.01 mg N/L) than in the Northeast (mean 0.09 mg N/L, median 0.03 mg N/L) and Southeast (mean 0.05 mg N/L, median 0.04 mg N/L). Unlike nitrate, the pattern in ammonium concentrations does not relate to the pattern of ammonium concentrations in precipitation (Figure 2.8).

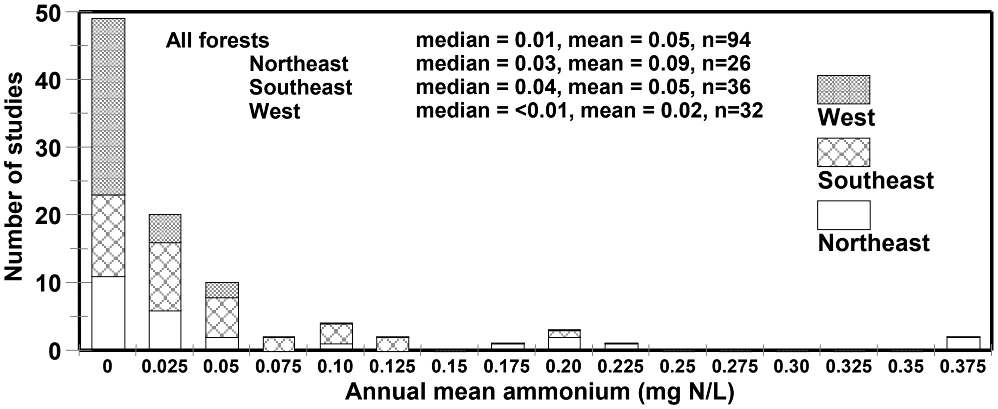
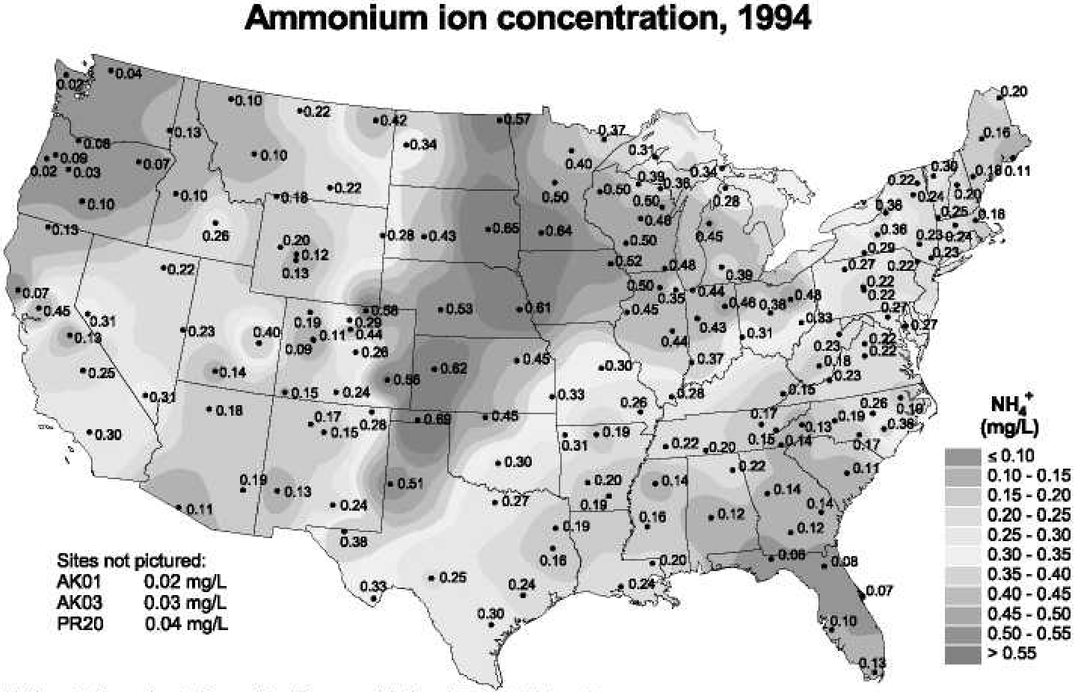


Figure 2.7. Average Annual Concentrations of Ammonium for Small Forested Watersheds



Sites not pictured:

AK01	0.02 mg/L
AK03	0.03 mg/L
PR20	0.04 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Figure 2.8. Concentrations of Ammonium (mg NH_4^+/L) for 1994

Forest type had less effect on streamwater concentations of ammonium than nitrate. Across the country, hardwood forests averaged 0.07 mg N/L (median 0.02 mg N/L) compared with a mean of 0.03 mg N/L (median 0.01 mg N/L) for coniferous forests (Figure 2.9).

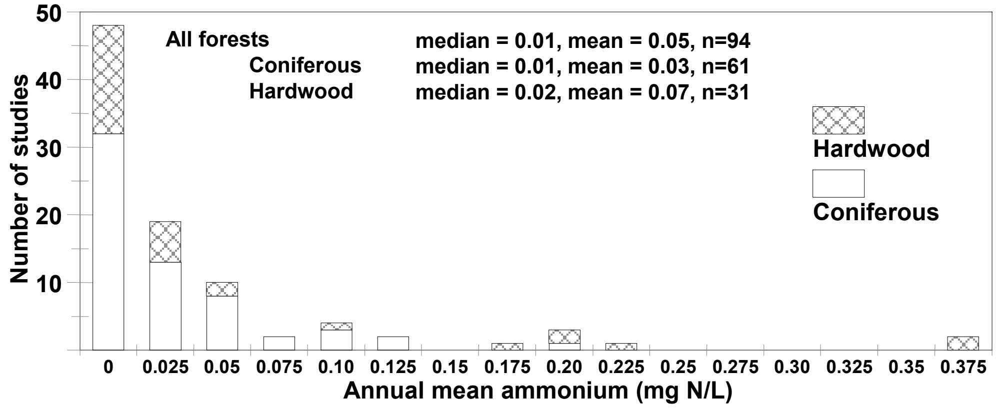


Figure 2.9. Average Annual Concentrations of Ammonium by Forest Type

Ammonium concentrations tended to be lower in streams from older forests (Figure 2.10). Forests less than 10 years old averaged 0.09 mg N/L (median 0.05 mg N/L), compared with a mean of 0.02 mg N/L (median 0.01 mg N/L) in forests older than 100 years.

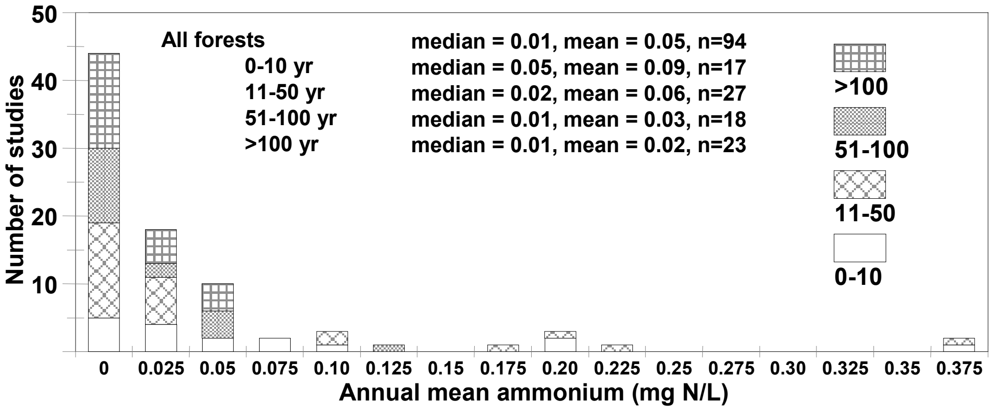


Figure 2.10. Average Annual Concentrations of Ammonium by Forest Age Class

The influence of geology on ammonium concentrations was similar to the effect on nitrate; soils derived from glacial tills and sediments had higher ammonium concentrations than those from igneous or volcanic substrates (Figure 2.11).

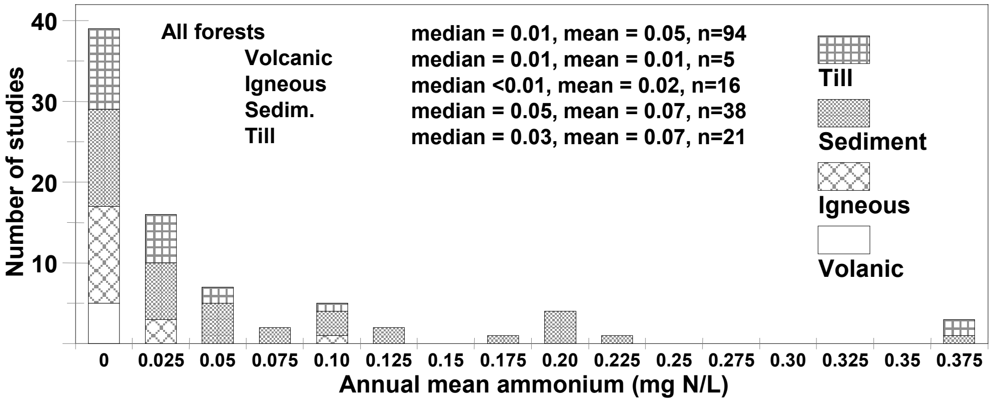


Figure 2.11. Average Annual Concentrations of Ammonium by Geologic Substrate

The maximum observed concentrations of ammonium were higher in streams with higher annual average concentration (Figure 2.12), and the slope of the relationship (maximum = three times average) was much steeper than for nitrate.

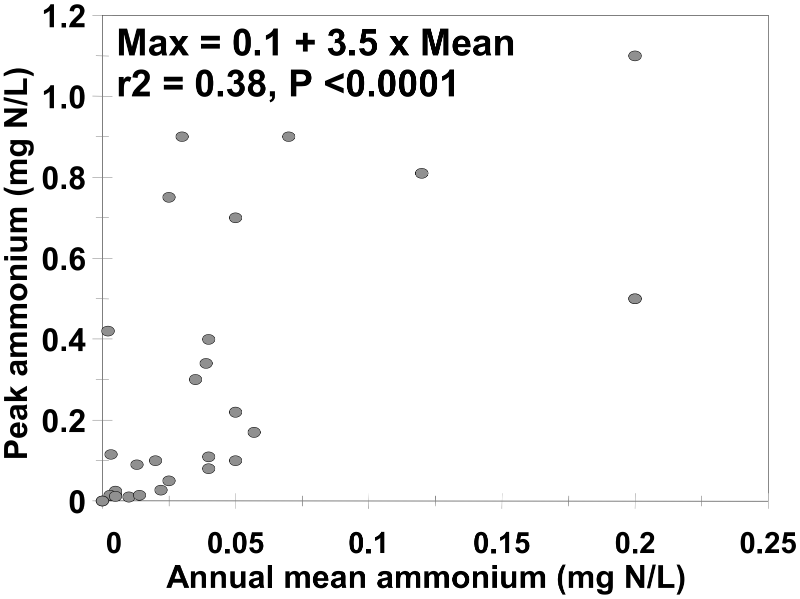


Figure 2.12. Maximum Reported Concentration of Ammonium as a Function of Annual Average Concentration

2.3 Organic Nitrogen

Across the country, the concentrations of dissolved organic nitrogen (DON) were similar to the concentrations of nitrate, averaging 0.32 mg N/L (median 0.08 mg N/L) (Figure 2.13). Most of the studies that measured DON were in the Northeast, where the values were about half those reported in the few studies in the Southeast and West. As a generalization, the nitrogen forms in streams in the Northeast are about 45% nitrate, 10% ammonium, and 45% DON. In the Southeast and West, nitrate comprises about 30% of the streamwater N, ammonium 10%, and DON about 60%. For comparison, Lewis et al. (1999) characterized streamwater nitrate concentrations from tropical streams in the Americas and found that DON comprised about 50% of the dissolved N load, with nitrate contributing 40% and ammonium just 10%.

In contrast to nitrate, coniferous forests showed much higher concentrations of DON (mean 0.7 mg N/L, median 0.7 mg N/L) than hardwood forests (mean 0.2 mg N/L, median 0.1 mg N/L) (Figure 2.14). Overall, streamwater N in hardwood forests was dominated by nitrate (60% of all dissolved N forms), followed by DON (30%) and ammonium (10%). In conifer forests, DON accounted for 80% of all dissolved N forms, followed by nitrate (17%) and ammonium (3%).

The maximum observed concentration of DON was about 30% greater than the annual average DON, which is notably less than the differences between maximums and means for nitrate and ammonium (Figure 2.15). Streams that had high annual average nitrate concentrations also showed high annual average concentrations of DON. No pattern was apparent between DON concentrations and stand age or geology (data not shown).

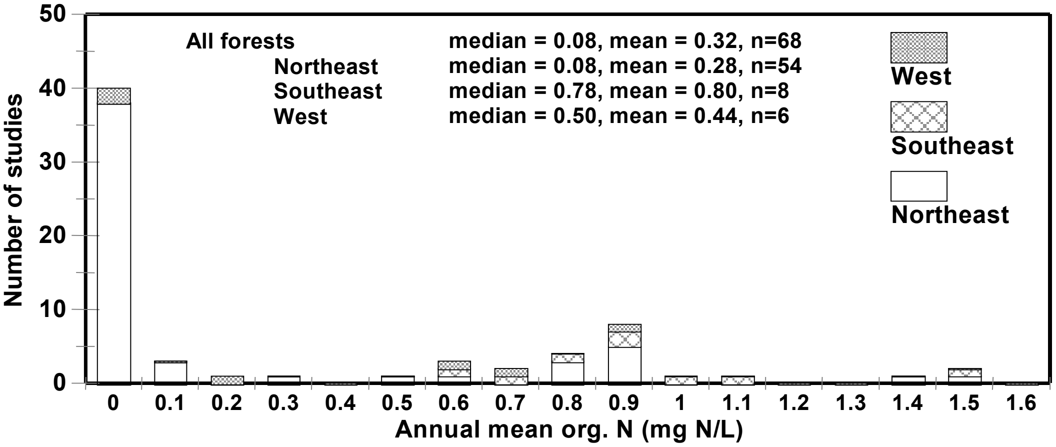


Figure 2.13. Average Annual Concentrations of Organic Nitrogen for Small Forested Watersheds

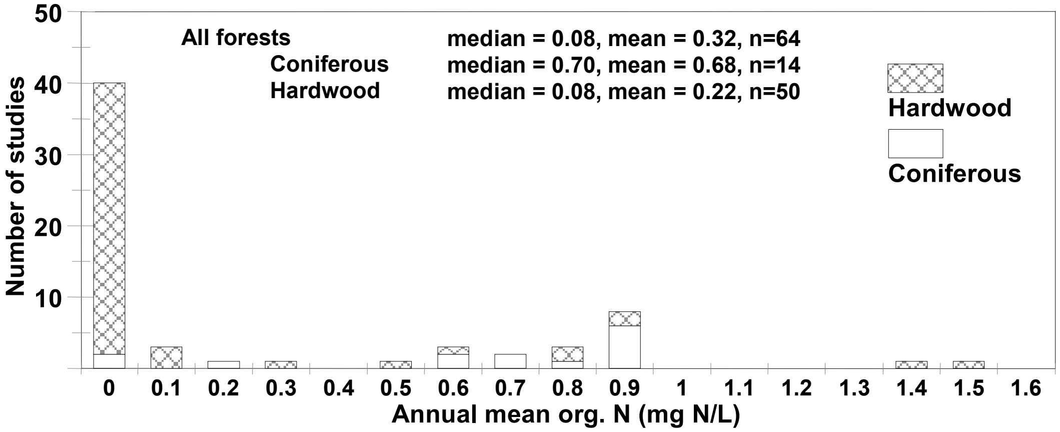


Figure 2.14. Average Annual Concentrations of Dissolved Organic Nitrogen by Forest Age Class

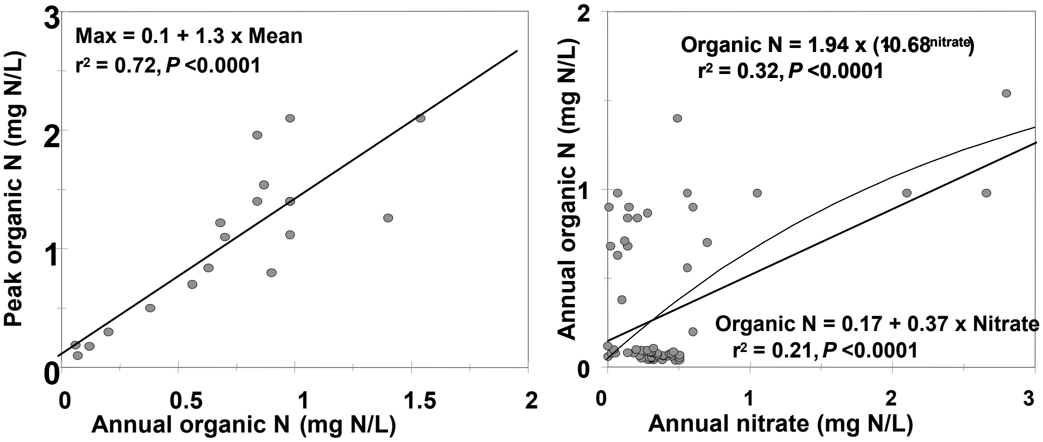


Figure 2.15. Maximum Observed Concentration of Dissolved Organic N (DON) in Relation to Annual Average DON (left), and Annual Average DON in Relation to Annual Average Nitrate (right); the relationship between annual average nitrate and DON was significant either with a linear relation ($r^2 = 0.21$), or with a curvilinear relation ($r^2 = 0.32$)

2.4 Particulate Nitrogen

Too few studies reported concentrations of suspended particulate N to analyze the patterns, but particulate N may contribute a substantial portion of the total N found in streamwaters. For example, the total streamload of N in the control Watershed #9 at the H.J. Andrews Experimental Forest was comprised of 30% particulate N, 60% dissolved organic N, and ammonium+nitrate contributed just 10%.

2.5 Inorganic Phosphate

Across the United States, the average concentration of inorganic P in forested streams is 12 µg P/L, with a median of 4 µg P/L (Figure 2.16). Concentrations are higher in streams from the Northeast (mean 35 µg P/L, median 15 µg P/L) than for the Southeast (mean 14 µg P/L, median 7 µg P/L) or the West (mean 8 µg P/L, median 3 µg P/L).

Phosphate concentrations appeared to be two to four times higher for streams in hardwood forests (mean 20 µg P/L, median 15 µg P/L) than in coniferous forests (mean 10 µg P/L, median 4 µg P/L), but the number of hardwood streams was too small (n = 16) for high confidence in the effects of forest type (Figure 2.17).

Concentrations of phosphate tended to be twice as high in younger forests than in forests over 100 years of age (Figure 2.18). This pattern could result from more productive (higher phosphorus) soils being the site of more frequent timber harvesting. Geology appeared to have a strong influence on phosphate concentrations, with the lowest average of 2 µg P/L (median 2 µg P/L) on igneous parent materials, and the highest average of 22 µg P/L (median 10 µg P/L) on glacial till materials (Figure 2.19). In contrast to the patterns for nitrogen compounds, the maximum observed concentrations of inorganic phosphate did not relate to the annual average concentrations (Figure 2.20).

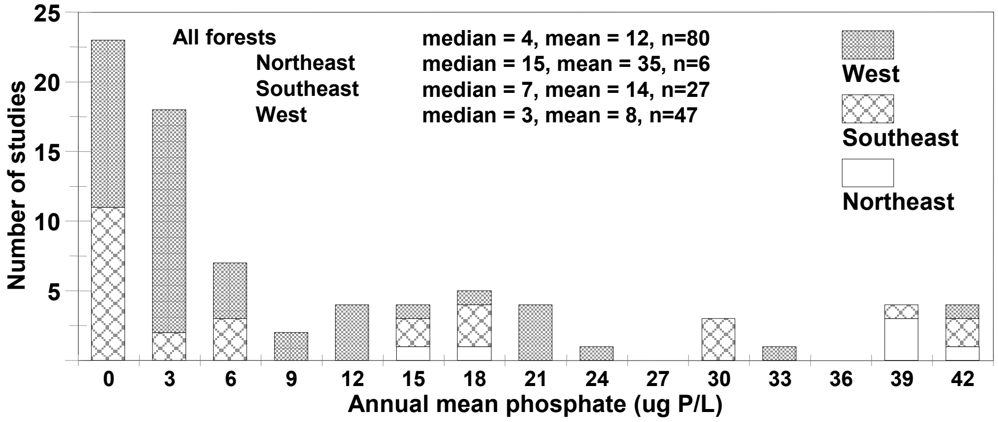


Figure 2.16. Average Annual Concentrations of Inorganic Phosphate for Small Forested Watersheds

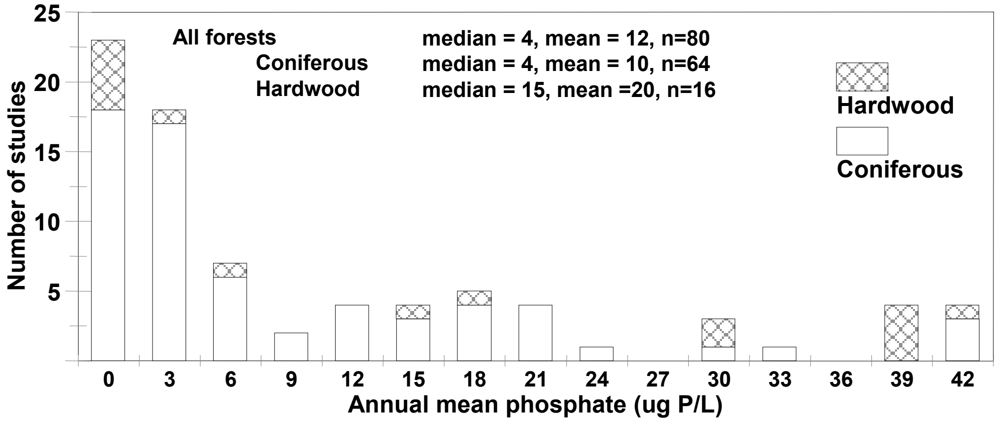


Figure 2.17. Average Annual Concentrations of Inorganic Phosphate by Forest Type

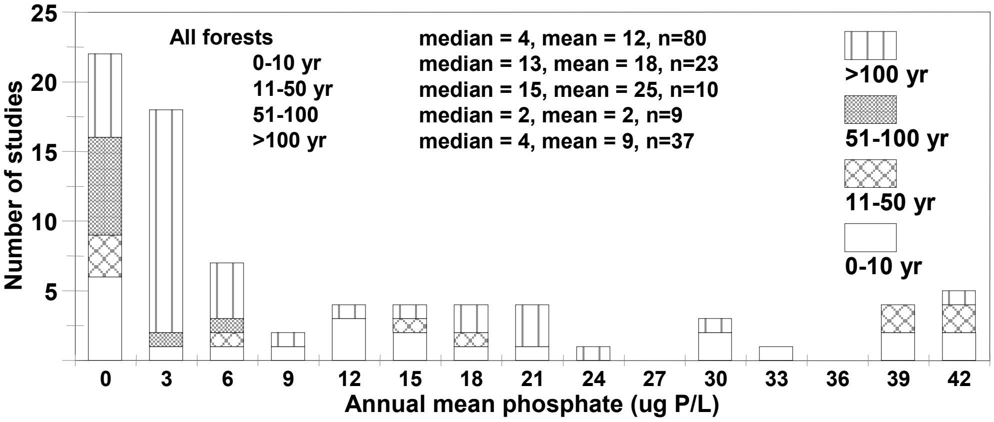


Figure 2.18. Average Annual Concentrations of Inorganic Phosphate by Forest Age Class

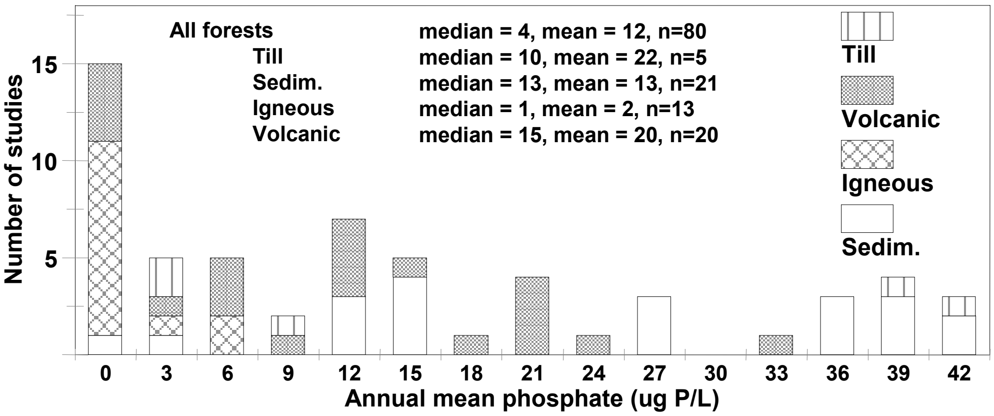


Figure 2.19. Average Annual Concentrations of Inorganic Phosphate by Geologic Substrate

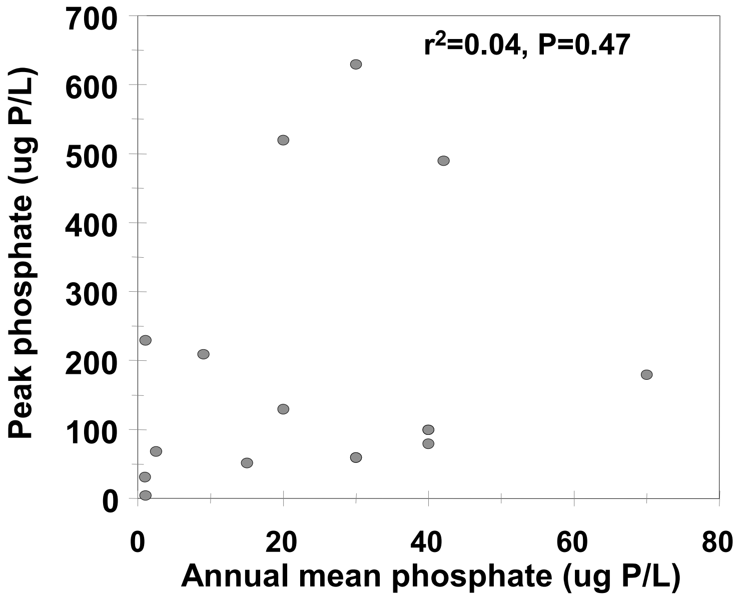


Figure 2.20. Maximum Reported Concentration of Inorganic Phosphate as a Function of Annual Average Concentration

2.6 Dissolved Organic Phosphate

Only 26 studies provided annual average data for dissolved organic phosphate, and the averages for these streams were about double the national average for inorganic phosphate (Figure 2.21). Within individual streams, average concentrations of dissolved organic phosphate showed no correlation with annual average inorganic phosphate, but all (except one) of the data showed higher concentrations of organic forms (Figure 2.22). The available data show that dissolved organic phosphate probably dominates the pool of dissolved phosphate in forested streams.

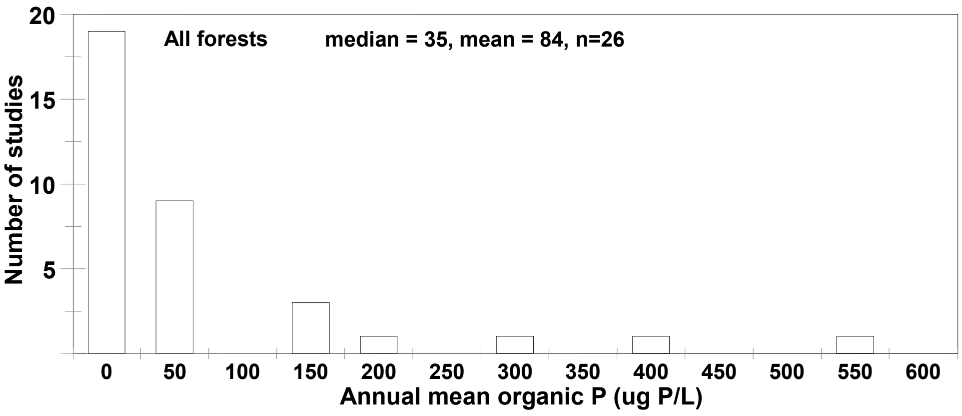


Figure 2.21. Average Annual Concentrations of Dissolved Organic Phosphate for Small Forested Watersheds

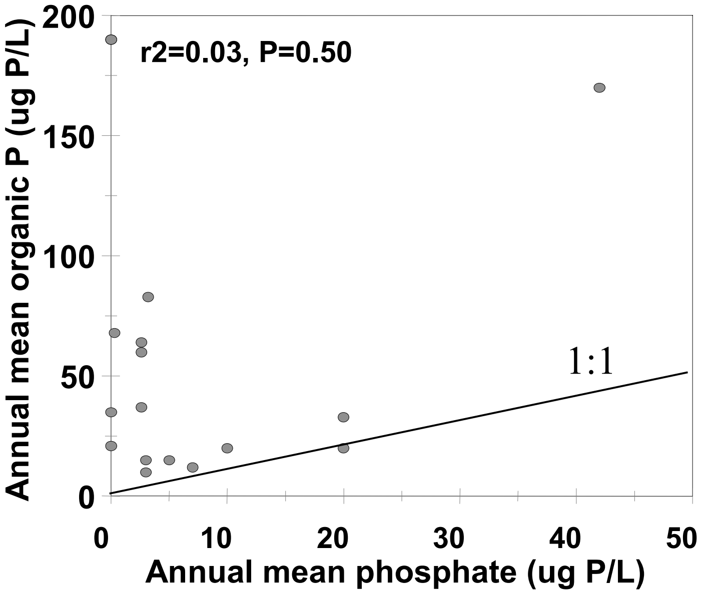


Figure 2.22. Mean Annual Concentration of Dissolved Organic Phosphate in Relation to Annual Average Inorganic Phosphate Concentration

2.7 Particulate Phosphate

Few studies have measured concentrations of suspended particulate phosphate in forested streams. In the control Watershed #9 at the H.J. Andrews Experimental Forest in Oregon, particulate P accounted for about 20% of the streamwater P, compared with 40% for dissolved inorganic phosphate and 40% for dissolved organic phosphate.

2.8 Patterns in Streamwater Chemistry in Larger Basins

The research watersheds described in this section were all relatively small, <500 ha and most <100 ha. Streamwater chemistry in larger basins may differ substantially from small watersheds as a result of integrating larger areas and changing physical and ecological characteristics of higher stream orders (Vannote et al. 1980).

The USGS has maintained two major monitoring programs for water quality. The USGS Hydrologic Benchmark Network (HBN) was started in 1958 to track changes in water quality in major basins (areas in wildland basins ranged from 6 to 2500 km^2) (Cobb and Biesecker 1971). The more recent NAWQA program included a broader range of land uses, and the wildland basins ranged in size from 18 to 2700 km^2. Clark, Mueller, and Mast (2000) summarized patterns in streamwater chemistry for wildland basins in the HBN and NAWQA programs and compared them with a set of 20 research watersheds (RW) that ranged in basin size from 0.1 to 22 km^2. G.M. Clark provided a copy of their data, and the trends identified in the HBN, NAWQA, and RW sites were compared with those of the small watersheds examined earlier in this section. Ten of the 43 HBN basins and two of the 22 NAWQA basins used by Clark, Mueller, and Mast that were primarily dominated by grasslands or shrublands were omitted, and it was noted that eight of Clark, Mueller, and Mast's research watersheds were also included in this group of small watersheds.

All data sets showed roughly similar distribution frequencies for streamwater concentrations of nitrate, ammonium, and phosphate (Figure 2.23). The HBN sites had the highest frequency of streams with <0.01 mg N/L, followed by the RW streams, the small watershed studies summarized in this report, and then the NAWQA sites. All of the HBN sites had nitrate concentrations <0.5 mg N/L, compared with 94% of the NAWQA and RW sites, and 82% of the small watershed sites. The higher frequency of streams with higher nitrate concentrations in the small watersheds derived from three types of sites with nitrate concentrations that exceeded 0.75 mg N/L: northern hardwood forests in New Hampshire, mixed hardwood forests at the Fernow Experimental Forest in West Virginia, and forests dominated by nitrogen-fixing red alder in Oregon. These high nitrate systems did not fall within any of the HBN or NAWQA sites (and the RW group included only one high nitrate stream at Hubbard Brook, NH), so the lack of high nitrate streams in the larger basins could result either from factors that relate to basin size, or the lack of sampling of large basins in high-nitrate areas (discussed further in Section 4).

The patterns for ammonium concentrations were remarkably similar across the three types of sites (Figure 2.23; Clark, Mueller, and Mast 2000 did not include ammonium or phosphate concentrations for the RW group); only a few of the small watersheds showed higher ammonium concentrations than any of the large basins, and the overall distribution of ammonium concentrations appears to be largely consistent in small and larger basins.

Concentrations of inorganic phosphate were also similar among the sets of data, with the exception that the small watersheds had a higher proportion of sites with concentrations above 10 μg P/L. Values below 10 μg P/L are not precise, given detection limits of about 10 μg P/L in the HBN and NAWQA data sets. The small watersheds with phosphate concentrations >20 mg P/L included five southern pine forests on wet sites, seven old-growth conifer forests on volcanic or marine-origin parent materials in the Northwest, and eight hardwood forests in Kentucky, West Virginia, and Minnesota on sandstone or shale parent materials.

These frequency patterns in streamwater chemistry averaged to show higher concentrations of nitrate in the RW and small watershed streams, with means 50 to 300% higher (medians 200% higher) than the HBN and NAWQA streams (Table 2.1). Ammonium averages were again higher for the small watersheds, but the median concentration was not. Phosphate concentrations averaged about 50% higher in small watersheds than in the HBN or NAWQA streams, but median values were similar.

The NAWQA basins are not representative of small, upland, mostly forested streams in New England and the Catskill Mountains of New York (Hornbeck et al. 1997; Lovett, Weathers, and Sobczak 2000) (see Section 4).

The overall low concentration of N compounds in forested streams results primarily from low inputs of N from terrestrial ecosystems. In addition, the rate of removal of N from forest streams is generally high, contributing to further reductions in streamwater N concentrations. For example, Alexander, Smith, and Schwarz (2000) examined the rate of loss of streamwater nitrogen as a function of stream size. As water flows downstream, nitrogen compounds may be removed through biotic uptake, movement into sediments, or conversion to gas. Small streams (with flows of less than 28 m^3/second) tended to lose about half of their N load daily, whereas larger streams lost about 5 to 10% of their N load daily, and rivers lost less than 1% daily.

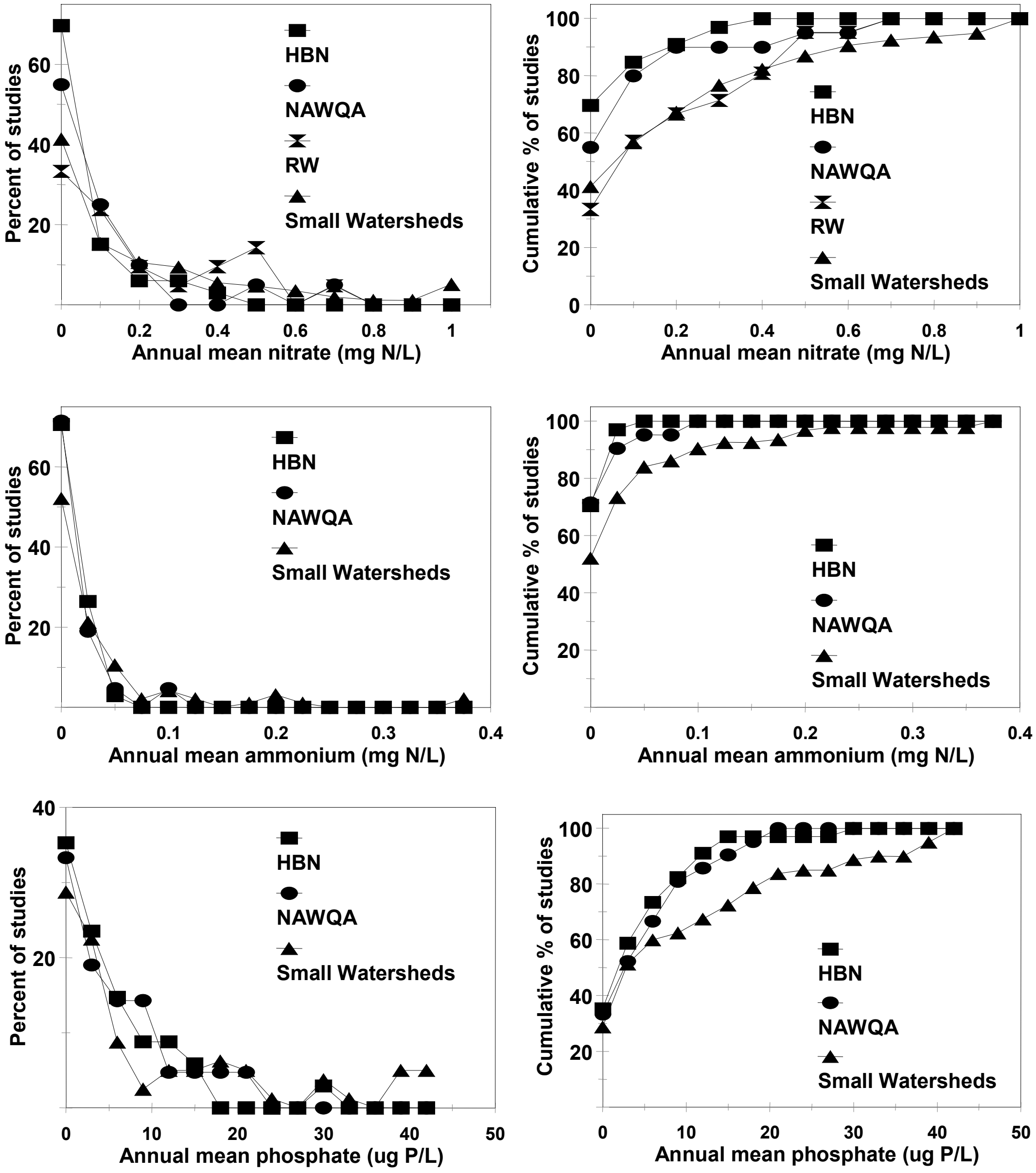


Figure 2.23. Frequency Diagrams for Concentrations of Nitrate (upper), Ammonium (middle), and Inorganic Phosphate (lower) for Three Sets of Forested Streams [HBN is the USGS Hydrologic Benchmark basins, NAWQA is the USGS National Water Quality Assessment basins, RW is the set of research watersheds from Clark et al. 2000, and Small Watersheds is the group of streams described earlier in this chapter (and in Appendix A); HBN, NAWQA and RW data were compiled and provided by G.M. Clark, USGS (Clark, Mueller, and Mast 2000)]

Table 2.1. Mean and Median Concentrations of Nitrate, Ammonium, and Inorganic Phosphate for the HBN, NAWQA, RW, and Small Watershed Series of Streams

	Nitrate (mg N/L)		Ammonium (mg N/L)		Inorganic phosphate (μg P/L)	
	Mean	Median	Mean	Median	Mean	Median
HBN (n = 33)	0.10	0.07	0.02	0.01	9	7
NAWQA (n = 20)	0.15	0.09	0.03	0.02	8	5
RW (n = 20)	0.23	0.18				
Small Watersheds (n = 256 nitrate, 94 ammonium, 80 phosphate)	0.31	0.15	0.05	0.01	12	4

Data for the HBN, NWQA, and RW streams provided by G.M. Clark; data for small watersheds from this report

3.0 TEMPORAL VARIATION IN STREAMWATER CHEMISTRY

The patterns of variation in streamwater chemistry were analyzed for eight intensively studied watersheds spanning the geography and vegetation types of the contiguous United States (Figure 3.1). Four locations were dominated by hardwood vegetation (Isle Royale National Park, Calumet Watershed, Hubbard Brook Experimental Forest, and Coweeta Hydrologic Laboratory), and four were dominated by conifers (H.J. Andrews, Beaver Creek, Fraser, and Santee Experimental Forests). The period of record ranged from one to three decades, and sampling intensity ranged from daily (for short periods) to monthly. This section presents a summary of variations over time, and more detail is available in Appendix B.

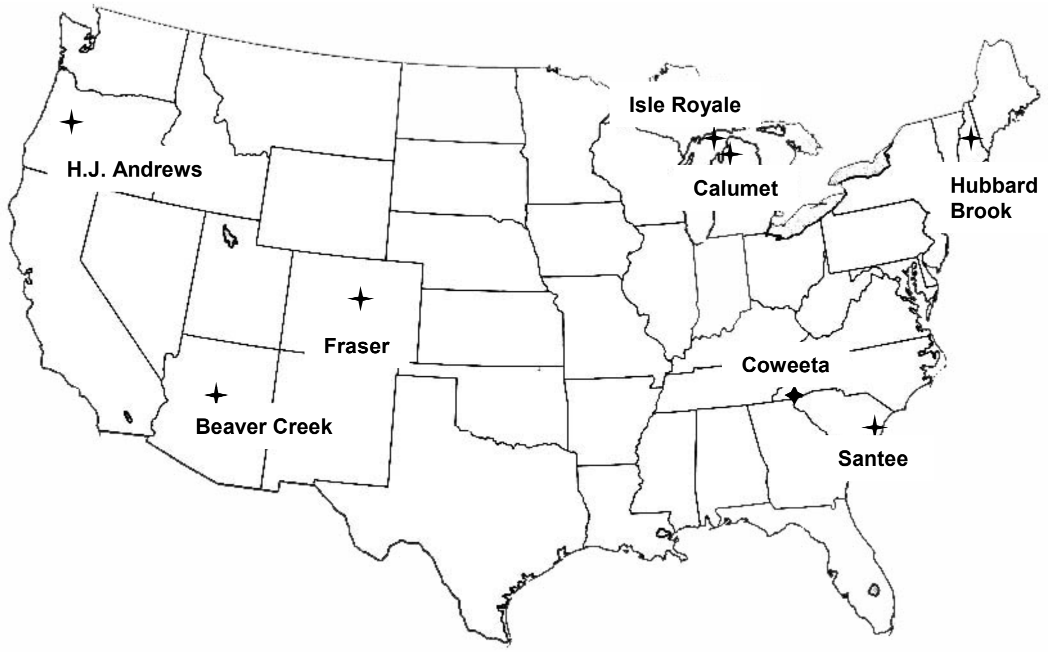


Figure 3.1. Locations of Intensive Watershed Studies for Section 3 and Appendix A

3.1 Site Descriptions

3.1.1 *H.J. Andrews Experimental Forest, Oregon*

The H.J. Andrews Experimental Forest is in the western-central Cascade Mountains of Oregon, within the drainage of the McKenzie River. The experimental forest was established in the l940s, and the landscapes were dominated by old-growth (>400 year old) forests of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco), western hemlock (*Tsuga heterophylla* (Raf.) Sarg.), and western red cedar (*Thuja plicata* Donn ex D. Don), with younger forests that established after fires in the 1800s. Watershed #9 is a reference, old-growth forest, similar to Watershed #10 that was the site of intensive ecosystem studies (Sollins, Grier, et al. 1980; Sollins, Cromack, et al. 1981). Elevations of these watersheds range from about 430 m to 670 m, with an average slope of 25°. Soils are gravelly silty clay loam Typic Disrochrepts, formed in andesitic tuffs and breccias. Annual precipitation is concentrated in fall through spring, and averages 2500 mm/yr with mean air temperatures of 8°C. Streamwater chemistry for Watershed #9 from 1968 through 1998 was analyzed, with data provided by D. Henshaw, USDA Forest Service. The information presented here is a modified version and not the original data or documentation distributed by the Andrews Long-Term Ecological Research group. The Andrews LTER is not liable for damages resulting from any use or misinterpretation of data sets. Data sets were provided by the Forest Science Data Bank, a partnership between the Department of Forest Science, Oregon State University, and the USDA Forest Service Pacific Northwest Research Station, Corvallis, Oregon. Significant funding for these data was provided by the National Science Foundation Long-Term Ecological Research Program (NSF Grant number BSR-90-11663 and DEB-96-32921).

3.1.2 *Fraser Experimental Forest, Colorado*

The Fraser Experimental Forest was established by the USDA Forest Service in 1937 (Stottlemyer and Troendle 1987). The Forest is about 140 km west of Denver, Colorado, and includes subalpine and alpine ecosystems on gneiss and shist bedrocks, with some overlying sandstone cas at the upper elevations (Stottlemyer, Troendle, and Markowitz 1997; Stottlemyer and Troendle 1999). Lexen Creek is an east-facing, 124 ha watershed that drains into West St. Louis Creek. The top of the watershed is the 3515 m summit of Bottle Mountain, and the stream gauging station is at 2984 m. The soils of the Lexen Creek watershed are gravelly sandy loam lnceptisols. The lower and mid-elevation portions of the watershed are dominated by old-growth (>200 yr) forests of lodgepole pine (*Pinus contorta* Dougi.), and the upper elevations by mixed forests of Engelmann spruce (*Picea engelmannii* Parry ex Engelm.) and subalpine fir (*Abies lasiocarpa* (Hook.) Nutt.). The mean annual temperature for the watershed is near 0°C, ranging from –11°C in December to 10°C in July. Precipitation averages about 600 mm/yr, increasing about 20% per 300 m rise in elevation. The peak snowpack averages about 400 mm of water content, and hydrology is dominated by snowmelt, which passes primarily through subsurface flow to the stream. Stream flow typically peaks between 50 and 200 L/sec. Patterns in streamwater chemistry were analyzed for original data provided by R. Stottlemyer (USGS Biological Resources Division) for the period of June 1982 to June 1998. Major funding for these investigations came from the Rocky Mountain Research Station, USDA Forest Service, Ft. Collins, Colorado.

3.1.3 *Beaver Creek Watershed, Arizona*

A series of experiments was initiated along the Mogollon Rim in Central Arizona in the late 1950s and early 1960s to examine changes in water yield when ecosystems dominated by trees and shrubs were converted into grasslands. Deforestation was advocated as a means to increase water yield in the Salt and Verde River systems, and the USDA Forest Service and the University of Arizona examined the relationships between the density of trees and shrubs and water yield and other resources (Baker 1999). Watershed #13 was a control, untreated area of 368 ha, dominated by multiple age-class stands of ponderosa pine *(Pinus ponderosa* Dougl. Ex Laws.) with a bunchgrass understory, at an elevation of about 2200 m. The soils are rocky and variable in depth, formed on basalt parent material. Precipitation averages about 600 mm/yr, with a bimodal distribution of winter snow and rain, and mid-summer thunderstorms. The stream draining Watershed #13 is not perennial, and flows commonly occur only from January through May. Sampling for water quality analyses reflected the variable flows among years. Original data for this analysis were supplied for 1974 to 1981 by M. Baker, USDA Forest Service. The data used here were obtained by scientists of the Beaver Creek Watershed Project and have not been reviewed by those scientists. The Beaver Creek Experimental Watershed is operated and maintained by the Rocky Mountain Research Station, USDA Forest Service, Ft. Collins, Colorado.

3.1.4 *Wallace Lake Watershed, Isle Royale National Park, Michigan*

The National Park Service established a watershed research program in 1982 to quantify ecosystem structure and function, and to determine the response of watersheds to atmospheric inputs and climate change (Stottlemyer, Toczydlowski, and Herrmann 1998). Isle Royale National Park was chosen as a research site because of its remote location (in Lake Superior about 130 km north of Houghton, Michigan), minimal impact of direct human activities, and relatively high inputs of nitrogen (0.3 to 0.4 g N g m^{-2} yr^{-1}) and sulfur (0.4 g S m^{-2} yr^{-1}) in precipitation. The Wallace Lake watershed comprises 115 ha in the northeastern third of Isle Royale National Park, ranging in elevation from 195 m to 275 m. The watershed is relatively flat, with small ridges (<5 m high). Soils are sandy to mixed loamy Alfic Haplorthods from 0.3 to 0.9 m in depth, formed in metamorphosed volcanic parent materials. Annual precipitation averages 750 mm/yr, with about 40% failing as snow. Mean monthly temperatures range from -9°C in January to 16°C in July. The four major tree species in the watershed are aspen *(Populus tremuloides* Michx.), paper birch *(Betula papyrifera* Marsh.), balsam fir *(Abies balsamea* (L.) Mill.), and white spruce *(Picea glauca* (Moench.) Voss). About 10% of the watershed burned in 1936, and the rest of the forest was at least 125 years old. Wallace Lake is about 5 ha in size, and streamwater chemistry was sampled by R. Stottlemyer and colleages above and below the lake. The original data presented here were supplied by R. Stottlemyer, USGS Biological Resources Division, and are from the outlet of the watershed below the lake, from June 1982 through 1996. Major funding for these investigations came from the USDI National Park Service's Watershed Research Program and the USGS Biological Resources Division.

3.1.5 *Calumet Watershed, Michigan*

The Calumet Watershed is adjacent to Lake Superior at the north end of the lower peninsula of Michigan (Stottlemyer and Toczydlowski 1996, 1999). The 176 ha watershed has a northwesterly aspect with moderate topographic relief. The soils are 1.5 to 2.0 m deep (underlain by an ortstein layer and bedrock of metamorphosed volcanics), classified as Typic Haplorthods. The upper end of the watershed has an elevation of 385 m, and the lower end reaches the shoreline of Lake Superior at 183 m. Precipitation averages about 800 mm/yr, with streamflow of about 300 mm/yr. Lake Superior does not freeze in winter, keeping the soils warmer than more inland sites. About one-third of the snowpack melts throughout the winter, unlike inland areas where snowmelt occurs only in the spring. The vegetation is dominated by 60 to 80 year old sugar maple *(Acer saccharum* Marsh.) and paper birch *(Betula papyrifera)*. The original data used here were provided for the period of June 1983 through 1996 by R. Stottlemyer, USGS Biological Resources Division. Major funding for these investigations came from the USDI National Park Service's Watershed Research Program and the USGS Biological Resources Division.

3.1.6 *Coweeta Hydrologic Laboratory, North Carolina*

The Coweeta Experimental Forest was established in the Appalachian Mountains of western North Carolina in 1933 to examine the effects of land use (including livestock grazing) on forest hydrology (Swank and Crossley 1988). Precipitation averages 1900 mm/yr, with streamflow of 1000 mm/yr. Watershed #18 (data summary: http://landscape.ecology.uga.edu/cwtqis/map/ws/wsl8.html) is a northeast-facing control area of 13 ha with an average slope of 52° (125%) (elevation from 726 m to 993 m), with Typic Hapludult soils formed in metasandstone parent materials. The vegetation in Watershed #18 is dominated by oaks *(Quercus prinus* L.*, Q. coccinea* Muenchh., *Q. rubra* L., and *Q. velutina* Lam.), red maple *(Acer rubrum* L.), and other hardwoods. Extensive logging occurred in the Coweeta basin in the early 1900s, but Watershed #18 has remained undisturbed since 1924. Original data for 1972 through 1992 were provided by J. Vose and J. Moore, USDA Forest Service. Coweeta and the principal investigators who provided the data disclaim any responsibility for errors that may or may not exist within the online data used in this report. Significant funding for these data was provided by the National Science Foundation Long-Term Ecological Research Program.

3.1.7 *Hubbard Brook Experimental Forest, New Hampshire*

The Hubbard Brook Experimental Forest in the White Mountains of New Hampshire includes about 3000 ha, and ranges in elevation from 200 to 1000 m (Bormann and Likens 1979; Johnson et al. 2000). The sandy loam Haplorthod soils average 0.6 m in depth (ranging from 0 on ridges to several meters downslope), and are developed in glacial till comprised of medium- to coarse-grained schist. Annual precipitation averages 1400 mm/yr with an even distribution through the year, and streamflow averages 870 mm/yr. Watershed #3 is a 42 ha reference watershed for the Forest, with vegetation that developed following intensive logging in 1909 and 1917. The overstory is dominated by sugar maple *(Acer saccharum)*, American beech *(Fagus grandifolia* Ehrh.), and yellow birch *(Betula alleghaniensis* Britt.), with a variety of other species. Variation in original datasets covering June 1972 through June 1992 (data provided by G. Likens, Institute for Ecosystem Studies) were examined. Significant funding for these data was provided by the National Science Foundation Long-Term Ecological Research Program.

3.1.8 *Santee Experimental Forest, South Carolina*

The Santee Experimental Forest is in the coastal flatwoods of the Francis Marion National Forest, about 25 km from the coast and 50 km north-northeast of Charleston (Richter, Ralston, and Harms 1982, 1983). The climate is mild and wet, with a mean annual temperature of 18°C and annual rainfall of 1200 mm. The soils of the control Watershed #80 are primarily strongly acidic, infertile Aquults with seasonally high water tables. Some calcareous soils are present along the stream. Relief in the 200 ha Watershed #80 is less than 5 m, and water tables are near the surface in winter. Before Hurricane Hugo in 1989, the vegetation on Watershed #80 was mostly old (>80 year) loblolly pine *(Pinus taeda* L.). The hurricane destroyed over 80% of the overstory trees, and forest recovery has been dominated by newly established seedlings of loblolly pine and resprouting hardwoods. Streamwater monitoring stopped in 1982, but resumed in 1989 after the hurricane. The original data analyzed here were provided by C. Trettin, USDA Forest Service. These investigations were supported by the USDA Forest Service.

3.2 Overall Variability Within Days, Months, and Years and Across Years

The coefficients of variation (CV, standard deviations divided by means) in streamflow (discharge) were consistently higher for months within a year than they were for annual averages across years (Figure 3.2). For example, the Calumet Watershed stream had a CV of about 100% across years, whereas the CV among the 12 months of the year averaged almost 300%. Variability within months tended to be lower than variability among months, and the two sites that had repeated samplings within single days (Calumet and Fraser) showed lower variations within days than within months.

The variability in streamwater within single days may increase as concentrations decline to near detection limits (W. Lewis, pers. comm.); a daily change of 0.01 mg N/L would be low variability compared with an average of 0.2 mg N/L, but high variability in a stream with an average of 0.02 mg N/L. This relative concentration feature may explain the much higher daily variation in nitrate at Fraser (CV = 104%, mean = 0.016 mg N/L) relative to Calumet (CV = 18%, mean = 0.09 mg N/L).

No consistent pattern appeared for the relative variability of the N compounds across time scales (Figure 3.3). For example, the CVs for within days changes in streamflow and nitrate concentrations were similar at Calumet, whereas the daily CV for ammonium concentrations was several times higher. The CVs for nitrate and ammonium concentrations were similar within days for Fraser, and both of these were much higher than the variability in streamflow. The CV for ammonium concentrations across years at Fraser was higher than for nitrate, even though the variabilities of these two compounds were similar for shorter timescales.

At an annual scale, the relative variability among months did not relate to the annual average concentrations of nitrate. For example, the CVs for nitrate at Coweeta and Hubbard Brook were both near 90% among months, but Hubbard Brook averaged 25 times greater concentrations of nitrate.

In some streams, patterns in streamflow and nitrate were related. For example, nitrate concentrations in the stream in Watershed #18 at Coweeta declined exponentially as streamflow increased (Figure 3.4). Streamflow was consistently lower in the summer and nitrate concentrations were higher. The relationship between streamflows and nitrate concentrations was reversed at Hubbard Book, where nitrate concentrations increased significantly as streamflow increased. Nitrate concentrations also declined during the summer at Hubbard Brook, in contrast to rising concentrations during the summer at Coweeta.

Some of the variation across years was explained by long-term trends in streamwater concentrations of nitrate. At Coweeta, nitrate concentrations increased slightly (but significantly) over the period of record (N deposition also increased), whereas concentrations at Hubbard Brook declined markedly (Figure 3.5). Over the 12 to 30 year period of record analyzed here, streamwater concentrations of some compounds at some sites showed no change, significant increases, and significant declines (Table 3.1). Of the 23 compounds with sufficient data across the sites, fourteen showed no trend, six showed significant declines, and three showed significant increases in concentrations. All of these watersheds remained undisturbed through this period, except for the hurricane destruction of 80% of the dominant trees at the Santee Experimental Forest. Interestingly, the Santee plots show no significant changes over time. The Hubbard Brook watershed is in the region with the highest rates of N deposition, yet this stream showed strong declines in streamwater nitrate concentrations. This decline in nitrate has also been reported across New England, and is discussed in Section 4. Overall, trends in nutrient concentrations are not uncommon even in streams in undisturbed forests. Some possible factors in these long-term trends are discussed Section 4.

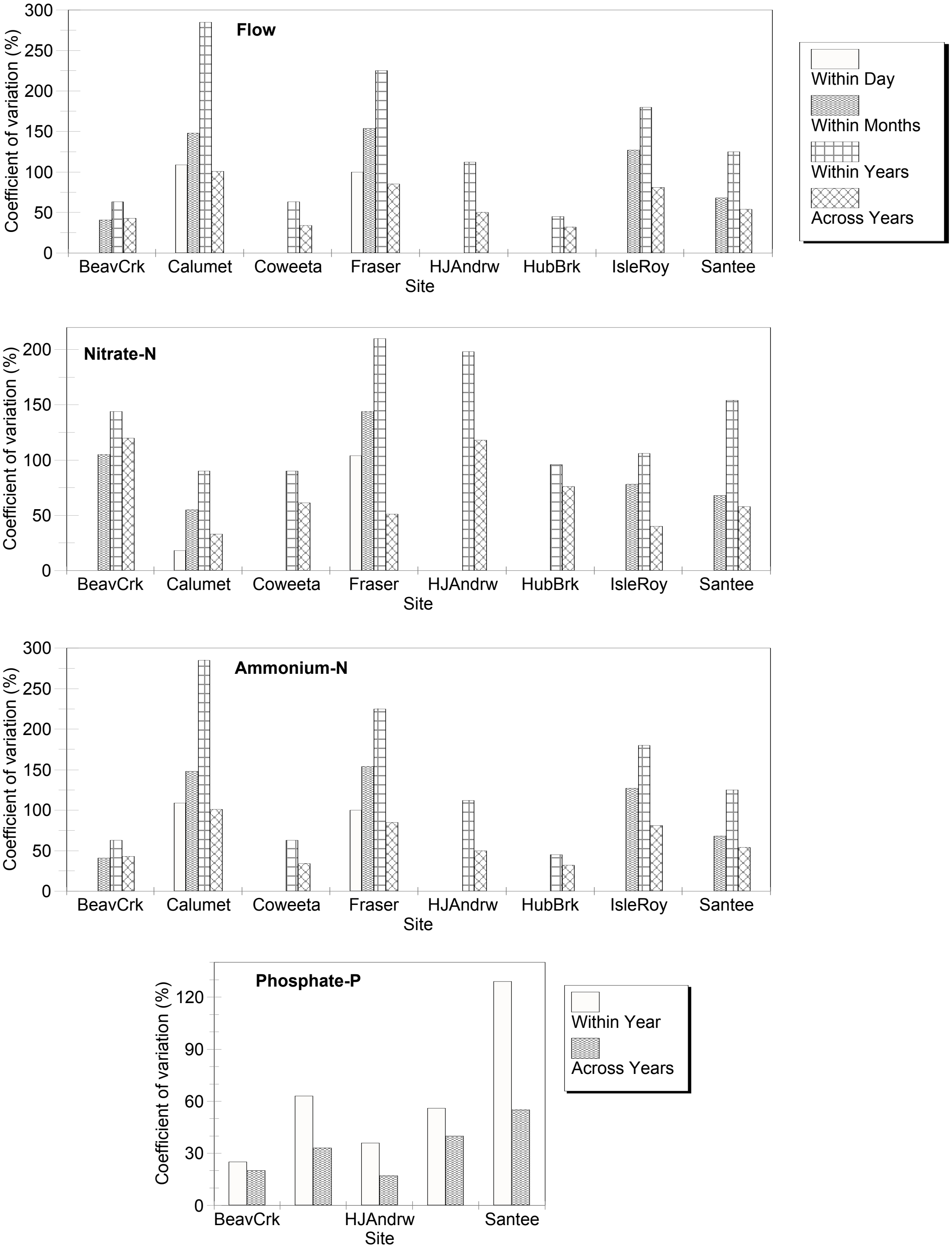


Figure 3.2. Coefficients of Variation for Streamflow, Nitrate, Ammonium, and Inorganic Phosphate by Time Scale

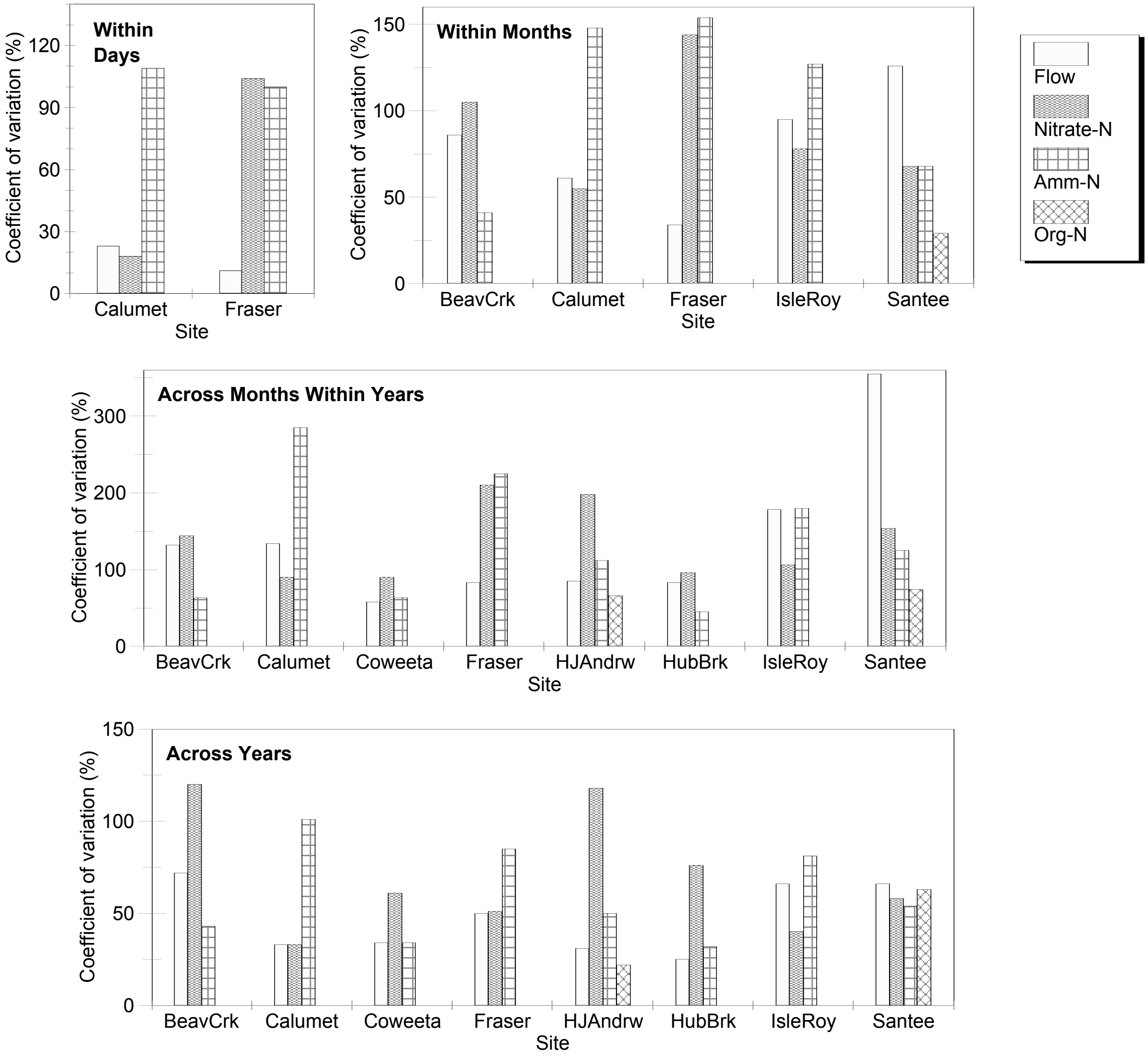
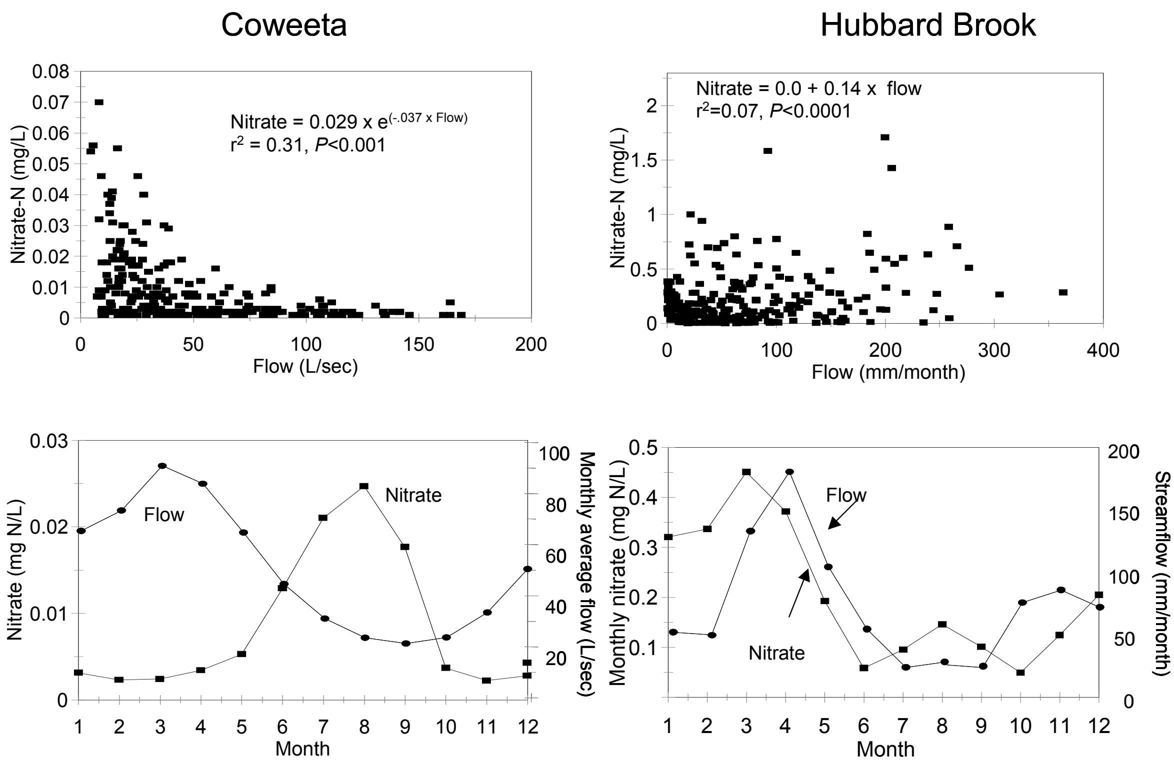


Figure 3.3. Coefficients of Variation in Streamflow and Nitrogen Compounds Within Days, Across Days, Within Months, Across Months, Within Years, and Across Years (see Appendix A for more details)


Coweeta

Hubbard Brook

Figure 3.4. Patterns in Nitrate Concentrations for Coweeta Watershed #18 and Hubbard Brook Watershed #6 in Relation to Streamflow (see Appendix A for more details)

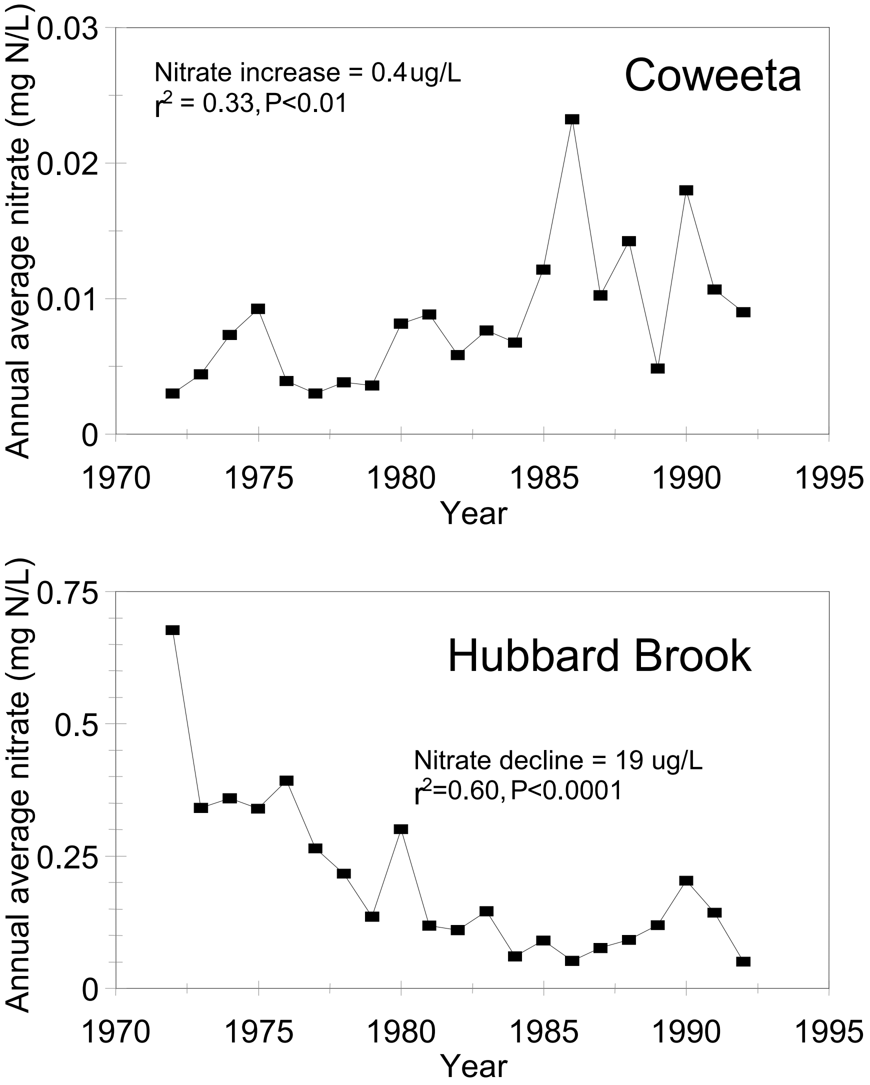


Figure 3.5. Long-Term Trend in Streamwater Nitrate Concentrations at Coweeta Watershed #18 and Hubbard Brook Watershed #6; atmospheric deposition of N doubled over this period at Coweeta (Swank and Vose 1997), but no deposition trend was apparent at Hubbard Brook

Table 3.1. Long-Term Trends in Streamwater Nutrient Concentrations for Intensive Watersheds[1]

Site	Record length (yr)	Nitrate	Ammonium	Organic N	Particulate N	Inorganic P	Organic P	Particulate P
H.J. Andrews	30	0	0	--	0	0	--	--
Fraser	14	0	0					
Isle Royale	14	0	0					
Calumet	14	0	0					
Coweeta	20	+	--			--		
Hubbard Brook	20	--	+			+		
Santee	12	0	0	0		0		

[1] Beaver Creek not included because of shorter record

+ = significant increase (P <0.1); 0 = no significant trend; and -- = significant decline

4.0 FACTORS ACCOUNTING FOR VARIATION IN PATTERNS OF STREAMWATER CHEMISTRY

Broad-scale synoptic patterns were summarized in Section 2, and some of the patterns may have developed from differences in vegetation type (higher nitrate concentrations of nitrate in hardwood streams), age (higher concentrations of some elements from streams draining younger forests), or geological substrate, or from differences associated with stream order and basin size (such as higher frequency of high nitrate streams in small watersheds than in the larger basins of USGS HBN or NAWQA). All of these tendencies may include confounding effects of differences in geography, such as higher N deposition in areas dominated by hardwood forests. This section focuses more narrowly on patterns found at local scales by examining patterns in water quality within local areas of a few tens of kilometers. The synoptic view of Section 2 provides the best nationwide description of water quality in forested streams, while this section gives more insight about the processes that underlie the patterns. These sources of variation in chemistry among streams within local regions may be fundamentally important in establishing appropriate standards and criteria for water quality.

4.1 Variations in Streamwater Chemistry Within Local Watersheds

Patterns of variation in streamwater chemistry among small watersheds in a local (10 to 100 km) area may not resemble patterns from across the US, or from large basins in the same region. Lovett, Weathers, and Sobczak (2000) monitored 39 first- and second-order streams in the Catskill Mountains of New York, and found remarkable variation among streams despite similarities of geology, vegetation, and environments. Nitrate concentrations averaged 0.32 mg N/L, with a 17-fold range between the lowest and highest streams. Few streams had less than 0.1 mg N/L (Figure 4.1). This Catskills pattern differs substantially from that of 159 small, upland, mostly forested streams across Massachusetts, Vermont, New Hampshire, and Maine (Hornbeck et al. 1997). The New England streams averaged 0.1 mg N/L as nitrate, with about two-thirds of the streams falling below 0.1 mg N/L. The pattern for the NAWQA basins clearly could not represent the concentrations for small streams in these regions of New York and New England.

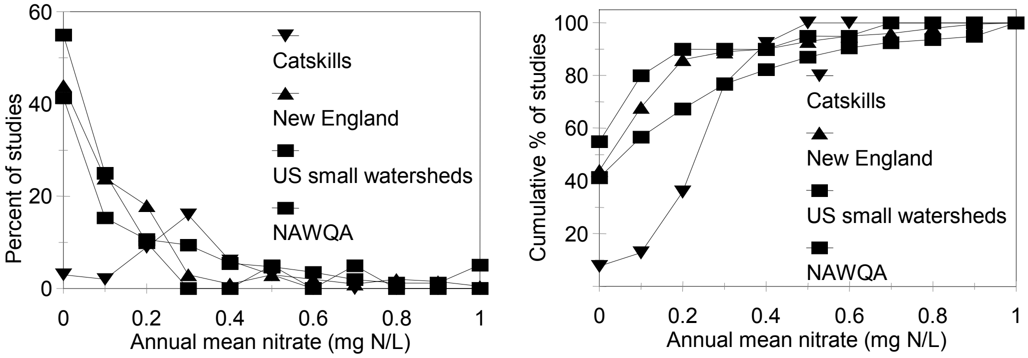


Figure 4.1. Frequency Distributions for 39 First- and Second-Order Forested Streams in the Catskill Mountains of New York (Lovett, Weathers, and Sobczak 2000); 159 Small, Upland, Mostly Forested Streams Within Massachusetts, Vermont, New Hampshire, and Maine (Hornbeck et al. 1997); 256 Small Watersheds Across the US (including the Catskills streams); and 20 Forested NAWQA Basins

What accounts for the ranges in nitrate concentrations in streams within these local areas? Potential factors include local differences in basin size (and stream order), vegetation type, time trends associated with climate or vegetation age, year of measurement, age, disturbance history (including harvest, fire, and fertilization), and geology. The state-of-knowledge does not allow a full accounting for the importance of each of these features, so the rest of this section uses case studies to illustrate the likely influences of these factors. Most case studies focus on nitrate concentrations because of the greater quantity of information available for this compound.

4.2 Longitudinal Trends in Stream Chemistry Within Basins

Wigington et al. (1998) examined nutrient concentrations during a two day period in November 1991 for 48 streams and rivers in the Coast Range of Oregon. Concentrations of nitrate showed a strong, exponential decline in relation to watershed area, and a linear decline in relation to stream order (Figure 4.2). The authors hypothesized that vegetation was responsible for most of the variation in streamwater chemistry, with higher values for smaller streams draining watersheds with substantial influences of nitrogen-fixing red alder. However, they found little association between nitrate concentration and the proportion of watershed area covered by hardwoods (mostly red alder), but they noted the resolution of their vegetation mapping may have been too coarse to detect the real pattern. They did not note whether the proportion of watershed area covered by hardwoods declined as basin size (and stream order) increased, so the effect of vegetation type cannot be separated from the effect of basin size and stream order.

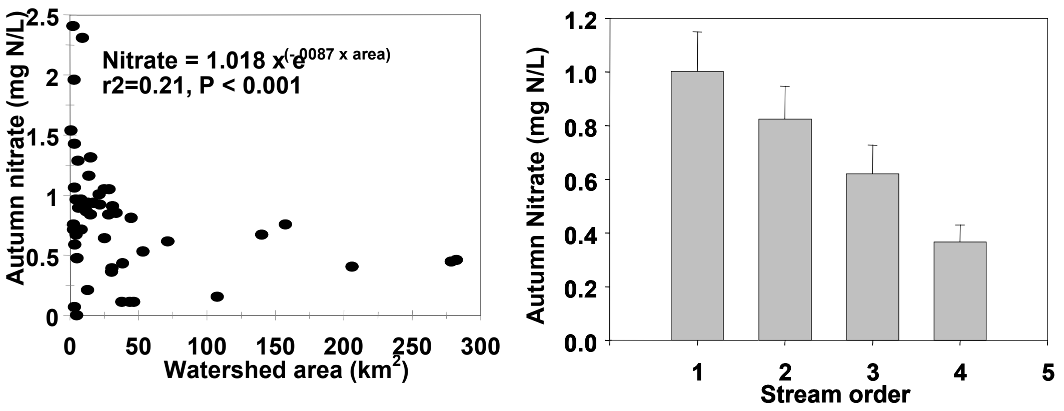


Figure 4.2. Streamwater Nitrate Concentrations in the Oregon Coast Range Declined with Increasing Watershed Area and Increasing Stream Order (from data in Wigington et al. 1998)

This pattern of declining nitrate concentration with increasing watershed size and stream order are reversed in western Oregon as the larger watersheds become large enough to include land suitable for agriculture. Rinella and Janet (1998) examined water quality in the 31,000 km^2 Willamette Basin, and found that watersheds that were entirely in forest land use had median values of 0.36 mg N/L for nitrate and 0.45 mg N/L for total nitrogen (concentrations of inorganic phosphate and total phosphate measured for forest sites were less than the minimum reporting limit of 10 µg P/L). These values for forested streams were about one-third of the median value for other watersheds in the Willamette Basin (nitrate 1.0 mg N/L, total N 1.5 mg N/L), and far lower than the basin-wide median concentration of 60 µg P/L of inorganic P and 100 µg P/L of total P. The higher values in non-forested watersheds were associated with agricultural land use, or point sources of N and P.

Stednick and Kern (1992) reported on detailed monitoring of three of the streams included in Wigington et al. (1998). Subbasin sampling and chemical and isotopic analyses were used to determine the origin and residence time of water contributing to streamflow. Stednick and Kern concluded that the areal distribution of alder was less important in losses of nitrate than where the alder occurs. Subbasins with abundant alder in the riparian area or a contribution zone will have greater nitrate concentrations and fluxes. Basnyat et al. (1999) found a similar pattern in Alabama, where nitrate concentrations were largely determined by the land use and vegetation adjacent to the stream, not the entire watershed.

Streamwater concentrations of nitrate declined from 0.75 mg N/L at 1600 m elevation in Great Smoky Mountains National Park to 0.2 mg N/L below 800 m elevation (Flum and Nodvin 1995) (Figure 4.3). This decline was associated with declining N deposition from the atmosphere, a shift from coniferous to hardwood vegetation, and a decrease in forest age. For vegetation type and stand age, this is a pattern opposite that found for national trends. Old, unlogged forests averaged about twice the nitrate concentrations in streams of those found in watersheds with more than 75% of the forest in post-harvest, regrowing forests (Silsbee and Larson 1982). Flum and Nodvin (1995) consider the upper elevation forests to be saturated with nitrogen, citing a deposition rate of 27 kg N/ha annually. If the concentration of 0.75 mg N/L represents an annual average and streamflow equals 1000 mm/yr, the output of N would be just 7.5 kg N/ha annually, only a quarter of the deposition rate. Either deposition is much lower than the rate cited, or these forests retain three-fourths of the deposited N and are far from being N saturated.

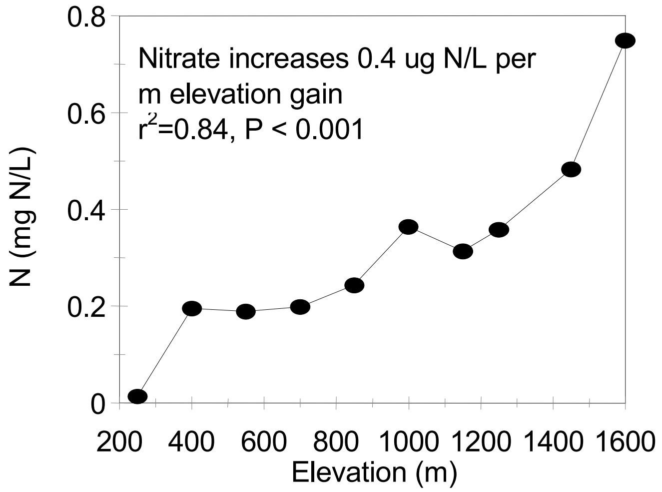


Figure 4.3. Streamwater Nitrate Concentrations Decline with Elevation in the Great Smoky Mountains National Park, Mirroring the Trend in N Deposition, Forest Age (lower forests are younger), and Vegetation Type (lower forests are hardwood, higher forests are coniferous); from 236 streams sampled twice annually for two years (Flum and Nodvin 1995)

Intriguingly, Lawrence, Lovett, and Baevsky (2000) reported an opposite trend in nitrate concentrations with elevation in the Catskill Mountains of New York. They examined the trend with elevation within a single watershed, and found that winter nitrate concentrations decreased from about 0.35 mg N/L at 800 m elevation to 0.22 mg N/L at 1060 m elevation. Summer concentrations showed no pattern with elevation. Atmospheric deposition of N increased from 14 kg N/ha annually at low elevation to 20 kg N/ha annual at high elevation. Lawrence, Lovett, and Baevsky concluded that streamwater nitrate concentrations probably declined with increasing elevation (despite increasing N deposition) as a result of a shift from low elevation hardwood forests to high elevation coniferous forests and an associated increase in forest floor mass. This pattern is consistent with the national pattern of increased nitrogen for hardwood dominated watersheds compared to watersheds dominated by conifers.

Stottlemyer, Troendle, and Markowitz (1997) followed changes in nitrate concentrations from the upper reaches of Lexen Creek in the Fraser Experimental Forest in Colorado (see Appendix B). Annual average concentrations of streamwater nitrate declined ($P < 0.05$) from 0.11 mg N/L at 3415 m elevation to 0.04 mg N/L at 2985 m elevation. Stottlemyer, Troendle, and Markowitz attributed the decline to uptake within the soil system in the watershed, rather than to retention within the aquatic ecosystem.

Johnson et al. (2000) also noted patterns in streamwater chemistry with elevation within Hubbard Brook WS#6 (a 13 ha watershed), with monthly data from 1982 to 1992. The upper 20% of the watershed (750 m elevation) was dominated by red spruce (*Picea rubens*), and the streamwater nitrate averaged about 0.10 mg N/L. The middle 30% of the watershed (700 m elevation) was dominated by mixed hardwood species (especially sugar maple, beech, and yellow birch), and had the highest nitrate concentration of about 0.15 mg N/L. The lower part of the watershed (down to 550 m) was dominated by mixed hardwoods and had nitrate concentrations of about 0.10 mg N/L. These concentrations are very similar to the values for the entire 30 km^2 Hubbard Brook Valley (a fourth-order stream) (Figure 4.4), indicating relatively minor changes across this range of stream sizes.

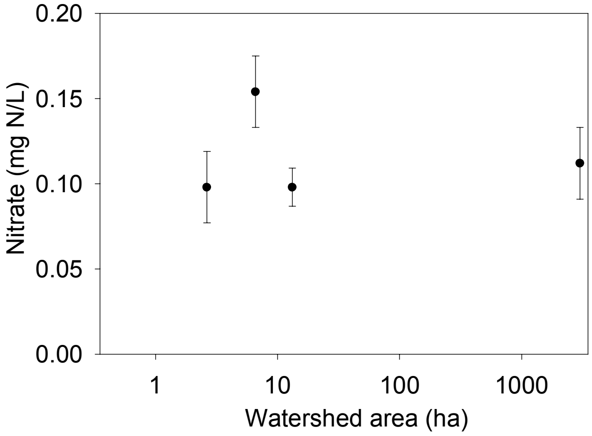


Figure 4.4. Nitrate Concentration and Watershed Area for WS#6 and the Entire Hubbard Brook Valley (based on data from Johnson et al. 2000, assumes streamflow/area is the same for WS#6 and the entire valley; bars are standard errors)

Canajoharie Creek is a fourth-order stream in the USGS NAWQA site, with a gauging station about 30 km from the watershed divide. The upper third of the watershed is forested, and the lower two-thirds is used for row crops, dairy cattle, and hayfields. Annual average concentrations of nitrate were about 1 mg N/L, but summer concentrations decline to near detection limits of 0.05 mg N/L. The concentrations of nitrate in upstream reaches have been assessed only in the summer, when concentrations averaged about 0.5 mg N/L. The summer concentration trend showed high concentrations in the undeveloped, forested reaches, and extremely low nitrate in the agricultural area in the lower reaches. The summer decline in nitrate mirrored a decline in silicate concentrations and an increase in chlorophyll-a concentration; the authors attribute the N removal to uptake by diatoms. The winter trend in nitrate was not assessed in the forested upper reaches, but this incomplete picture emphasizes important differences in nitrate concentrations (and N cycling) from first-order to fourth-order streams.

A similar pattern was found for tributary streams of the Clackamas River, Oregon. Carpenter (in press) monitored water quality in the Clackamas River Basin during the summer of 1998. He found very low nitrate concentrations for upper basin tributaries that were characterized as having narrower buffers and greater erosion. The light and sediment-related phosphorus stimulated algae growth with uptake of available nitrogen. In contrast, the more densely shaded and well-buffered tributaries were found to have higher nitrate losses in the summer. Uptake of nitrogen by algae can be an important process altering the concentrations downstream. Carpenter also found cases where instream nitrogen-fixing algae were present in headwater streams.

An intensive case study from Quebec examined changes in streamwater N from first-order forested headwaters to fifth-order agricultural landscapes along the Riviére de l'Achigan (Cattaneo and Prairie 1995). No trends were apparent within the pristine reaches of the river system (Figure 4.5), and concentrations above and below small lakes showed no effect of the lakes in altering streamwater N concentrations. As the downstream land use shifted to agriculture, nitrate concentrations rose by several fold.

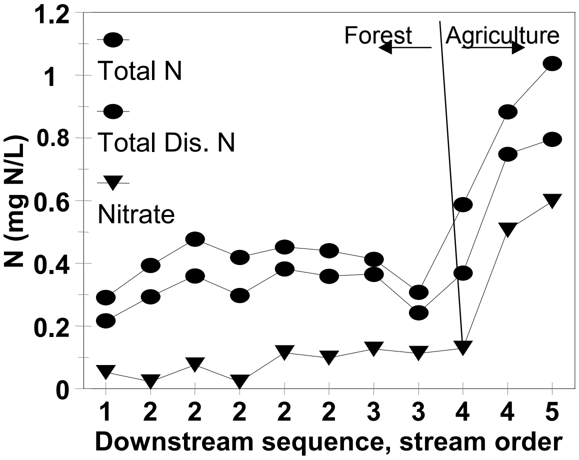


Figure 4.5. Concentrations of Nitrogen Compounds Showed No Pattern Downstream Along the Riviére de l'Achigan, Quebec, Until Land Use Changed from Pristine Forest to Cottages and Agriculture (from Cattaneo and Prairie 1995)

4.3 Effects of Vegetation Type on Streamwater Chemistry Within Local Watersheds

Tree species differ substantially in their effects on nutrient cycling. Experimental plantations of tree species in pure stands within the same site have shown that rates of nitrogen mineralization commonly differ by 50% (and sometimes by >100%), along with substantial differences in soil pH, base saturation, and forest floor masses (Binkley and Giardina 1998; Fisher and Binkley 2000). The influence of tree species on streamwater chemistry may be very large, but available information is sparse. The synoptic patterns in Section 2 showed that nitrogen loads in streams in hardwood dominated forests were dominated by nitrate, with concentrations exceeding those of streams in coniferous forests. The nitrogen loads of streams from coniferous forests were dominated by organic forms of nitrogen. These generalizations had notable exceptions, and the general trend confounded the effects of species and geography; hardwood forests tend to occupy more fertile portions of landscapes.

The influence of tree species on streamwater chemistry may also differ among hardwoods. Lovett, Weathers, and Sobczak (2000) found a broad range of nitrate concentrations in 39 streams in the Catskill Mountains of New York. They concluded that the influences of atmospheric deposition, geography, and hydrology probably did not account for the variations in streamwater chemistry, but that species compositions of the forests showed some consistent trends. The three watershed with the lowest concentrations of nitrate were dominated by red oak (*Quercus rubra*), and the five watersheds with the highest concentrations of nitrate had no oaks. Both oaks and beech (*Fagus grandifolia*) have poorer quality litters than maples, and streamwater concentrations of nitrate may be influenced by the relative influences of these species (Lovett and Rueth 1999; Lovett, Weathers, and Sobczak 2000). A shift in dominance from maple to beech through successional change, or from beech to maple from beech bark disease, might decrease or increase streamwater nitrate concentrations (Lovett, Weathers, and Sobczak 2000).

Lewis and Likens (2000) also examined streamwater nitrate concentrations in relation to species composition of 20 forests in the Allegheny National Forest of northwestern Pennsylvania. Watersheds with at least 10 to 20% cover of red oak averaged about 0.15 mg N/L as nitrate, compared with 0.4 mg N/L for comparable watersheds without red oak. Longer-term studies are needed to account for these changes in forest composition and their influence on streamwater chemistry.

The only watershed-scale, unconfounded experiment with species composition in the US comes from the Coweeta Hydrologic Laboratory in North Carolina, where two watersheds were intentionally converted to white pine (*Pinus strobis*) to compare water use and streamflow with hardwood dominated watersheds. Reported values for streamflow and nutrient output in streams (kg/ha) were combined to estimate nutrient concentrations. The values for nitrate came from Swank and Vose 1997; the ammonium and phosphate data for the white pine watersheds (WS#1, WS#17) came from Table 25.4 in Swank and Crossley (1988); and the values for ammonium and phosphate for the hardwood watersheds (WS#2 and #18) came from the Coweeta web site on January 18, 2001 (http://landscape.ecology.uga.edu/cwtgix/map/cwtbase.html). These data sets indicate less streamflow in watersheds with white pine (740 mm/yr vs. 1050 mm/yr for hardwoods), and higher nitrate concentrations (0.084 mg N/L pine, 0.005 mg N/L hardwood), ammonium concentrations (0.003 mg N/L pine, 0.002 mg N/L hardwood), and phosphate concentrations (6 μg P/L pine, 2 μg P/L hardwood). If this set of calculations is accurate for Coweeta, the higher concentrations of nutrients in streamwater from the white pine watersheds would be the opposite of the national synoptic trend of higher nutrient concentrations in hardwood streams (Section 2). Among conifers, white pine has been noted to accelerate N cycling and N leaching losses (Nadelhoffer, Aber, and Melillo 1983; Binkley 1995), so the effect of white pine on streamwater at Coweeta might not represent the entire group of conifers.

Until more watershed-scale studies examine the effects of different vegetation under local conditions, the synoptic view of higher concentrations in hardwood streams cannot be separated from potentially confounding effects of site factors that have favored the establishment and success of hardwoods or conifers.

4.4 Decadal Time Trends in Streamwater Chemistry Within Local Watersheds

Streamwater chemistry has been monitored in many watersheds across the U.S. for several decades, providing insights on decadal trends. As noted in Section 3, some of these streams have shown increasing or decreasing trends, and many have shown no trends. Earlier assessments anticipated that concentrations of nitrate would rise in streams draining forests that receive high atmospheric inputs of nitrogen. For example, Smith, Alexander, and Wolman (1987) looked for trends in nitrate concentrations from 1974 to 1981 in 383 streams in the US, and about half showed increases. Most of the streams were in agricultural areas, and streamwater chemistry was heavily influenced by fertilizer applications. The early years of monitoring at the Hubbard Brook Experimental Forest showed substantial increases in nitrate concentrations (Appendix A); Stoddard (1994) concluded there was no long-term trend, and continued declines in more recent years have shown a substantial overall decline for the full period of record. Stoddard concluded that headwater streams as well as third- and fourth-order streams in the Catskill Mountains of New York showed increasing concentrations of nitrate through the 20th Century, especially in the 1970s and 1980s. Stoddard also noted increasing trends in lakewater nitrate in the Adirondacks, whereas Driscoll et al. (1995) noted an increasing trend during the 1980s followed by a decline in the early 1990s, for no overall trend.

As noted above, long-term trends in streamwater chemistry could be influenced by changes in atmospheric deposition and species composition. Vitousek and Reiners (1975) also suggested that the net rate of biomass increase could be important; if increasing biomass were the only net sink for nitrogen in forests, then forests with low rates of biomass accumulation would be expected to retain little if any added nitrogen. Vitousek (1977) examined streamwater nitrate concentrations in 57 streams on Mt. Moosilauke and Mt. Washington in New Hampshire. Nitrate concentrations in streams that drained young forests (<80 yr old) averaged about 0.3 mg N/L as nitrate, compared with significantly higher concentrations (about 0.7 mg N/L) in older forests. Similarly, the old-growth hardwood forest in the Bowl Natural Area in the White Mountains had about twice the nitrate concentrations found in the younger forests at Hubbard Brook (Martin 1979). The same trend was reported by Silsbee and Larson (1982) for streams in the Great Smoky Mountains National Park. Streamwater nitrate concentrations were about twice as high in streams draining old, unlogged forests as in streams from post-logging forests.

Four case studies have shown that this biomass accretion model was insufficient for describing trends in nitrate concentrations in New Hampshire:

1. Hornbeck et al. (1997) found near-zero concentrations of nitrate in Cone Pond stream, which drains an old-growth northern hardwoods forest near Hubbard Brook. This old growth forest was among the lowest nitrate streams in the region.
2. As noted in Section 2 and Appendix B, nitrate concentrations declined substantially in the 70 to 90 year old forests at Hubbard Brook during a period when the forest showed a surprising small net biomass increment (averaging 0.5 Mg/ha annually, with mortality almost matching growth) (Johnson et al. 2000; T. Siccama, pers. comm.).
3. In the 1990s, Martin, Driscoll, and Fahey (2000) resampled the stream in the Bowl Natural Area, which had been monitored in the 1970s. They found declines of more than 50% in nitrate concentrations as the old-growth forests aged 20 years.
4. Goodale (1999) and Goodale, Aber, and McDowell (2000) resampled 28 of the streams sampled in the White Mountains by Vitousek (1977). After 23 years of forest aging, nitrate concentrations in streams declined by 68% in both younger (<100 year) and older forests. The trend of higher nitrate concentrations in streams draining older forests (including streams sampled by Vitousek and additional old-growth forests sampled by Goodale) remained consistent over time, but the dramatic decline in streamwater nitrate concentrations could not be explained as a function of expected rates of net biomass accumulation.

What factors account for these unexpected patterns in streamwater concentrations of nitrate in New Hampshire? Atmospheric deposition of N is relatively uniform across this local area, and no trend in deposition occurred over this period (Goodale, Aber, and McDowell 2000). Deposition of sulfate declined, but no mechanistic connection between sulfate deposition and nitrate losses is apparent. If N deposition continued and N outputs declined, then either the net accumulation of biomass has been negative across all these forests over 20 years (which seems unlikely), or the idea that N retention is a simple function of biomass accumulation is insufficient; a change in the stoichiometry of ecosystem C and N needs to be invoked.

Hornbeck et al. (1997) explain the pattern for Cone Pond as a consequence of a severe wildfire at the turn of the century that volatilized the nitrogen in the forest soil and has resulted in a persistent effect on nitrogen losses in runoff.

The region-wide pattern remains unexplained, but two possibilities are climatic trends and trends in vegetation composition. Mitchell et al. (1996) found that peak nitrate concentrations in watersheds in New York and New England were about 30% higher following an unusually cold period. Fitzhugh (2000) examined the relationship between several indexes of frost severity and streamwater chemistry. Between 1970 and 1987, the frost indexes accounted for about 25% of the variation ($P < 0.05$) in the three year running mean concentration of nitrate. When the same trends were examined for the longer period of 1970 to 1997, the associations between frost severity and streamwater nitrate were weaker and largely non-significant. Major frost impacts in the early 1990s (the most severe three years in the period of record) showed particularly low concentrations of nitrate in streamwater (Figure 4.1 in Fitzhugh 2000). If soil freezing played a substantial role in the patterns of streamwater nitrate concentrations, some other factor (or factors) confound the relationship.

Other climatic factors could influence long-term trends in streamwater nitrate concentrations. Aber and Driscoll (1997) used a model to suggest that drought in the 1960s could have led to high nitrate concentrations in the 1970s through a legacy of effects on nitrogen mineralization and plant uptake and storage of N. However, the model failed to account for the very low concentrations of nitrate in Hubbard Brook streams in the 1990s. The vegetation at Hubbard Brook showed surprising changes over the past 30 years, including a cessation of net accumulation of biomass, high mortality of old sugar maples (*Acer saccharum*) and beech, and major recruitment of understory beech seedlings (T. Siccama, pers. comm.). Such changes in the forests may influence rates of both nitrogen mineralization in soils (e.g., Lovett and Rueth 1999) and nitrogen increment in biomass, and patterns in net N mineralization appear to relate well with streamwater nitrate concentrations in this region (Goodale, Aber, and McDowell 2000).

Overall, the current state of science has shown substantial decadal trends in streamwater chemistry in some cases, but mechanistic explanations remain incomplete. The streams in New Hampshire appear to have declined by 50% or more in the past two decades; if these trends were reversed over the next 20 years, could the causes be identified with confidence?

4.5 Variations in Streamwater Chemistry from Forest Disturbances

Disturbances are a normal part of forest landscapes, and disturbances may strongly alter streamwater chemistry. Some disturbances affect tree vigor or growth without major mortality of trees. For example, insect defoliation may increase streamwater nitrate concentrations by an order of magnitude or more for several months or years, without substantial mortality of trees (Swank et al. 1981; Eshleman et al. 1998b). This section examines the effects of disturbances associated with forest management: harvesting, burning, and fertilizing forests.

4.5.1 *Harvesting*

The effects of forest harvesting on streamwater chemistry have been investigated in a wide range of small watersheds. Most of these have documented increases in streamwater nitrate concentrations, but others have found no effect or even declines in concentrations (Figure 4.6). In the 43 harvesting experiments tabulated in Appendix A, control or unlogged watersheds averaged 0.21 mg N/L as nitrate, compared with 0.44 mg N/L for one to five years after logging. Thirty studies showed increases in nitrate concentrations (although only four increased to more than 0.5 mg N/L), nine showed no change, and five declined by 24 to 95%. The effect of logging was not significant when analyzed by analysis of variance ($P = 0.12$). The post-harvest nitrate concentrations did correlate with the control values ($r^2 = 0.14$, $P = 0.01$), but the slope of 0.8 did not differ significantly from 1.0. The streams with high nitrate concentrations after logging either had high nitrate concentrations before logging (site with nitrogen-fixing alders), or were from the Hubbard Brook Experimental Forest (Figure 4.6). The only other exception of nitrate increasing by >1 mg N/L after logging resulted from logging a 100 year old mixed conifer forest along Benton Creek near Priest River, Idaho (Snyder, Haupt, and Belt 1975).

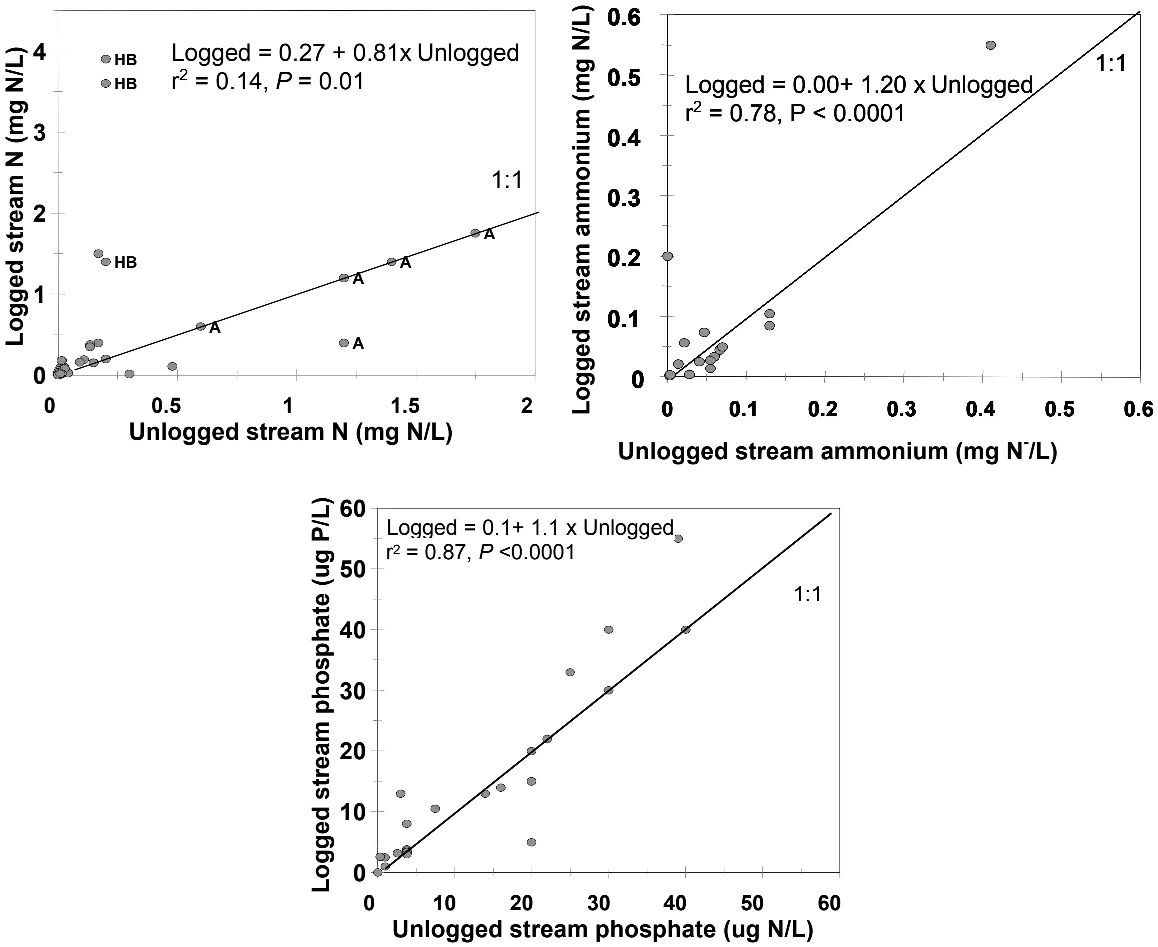


Figure 4.6. Annual Average Concentrations of Nitrate (left), Ammonium (right), and Inorganic Phosphate (bottom) in Logged Watersheds in Relation to Prelogging (or Control) Watershed Concentrations; in the nitrate graph HB = Hubbard Brook, A = Alder

Forest harvesting appeared to have little effect on concentrations of ammonium in streamwater, with averages of 0.07 mg N/L for unlogged watersheds and 0.08 mg N/L for logged watersheds (*P* = 0.81). The regression between concentrations in logged and unlogged streams was strong (r^2 = 0.78, *P* <0.0001), but the slope of 1.2 was not significantly different from 1. The pattern was similar for phosphate, with average concentrations for unlogged watersheds of 12 µg P/L compared with 13 µg P/L for logged watersheds (*P* = 0.77). Phosphate concentrations in unlogged and logged watersheds correlated highly (r^2 = 0.87, P<0.0001), but the slope of 1.1 did not differ significantly from 1.

Forest harvesting may alter streamwater chemistry, but the effects should not be expected to be consistent across forest types and regions. Any initial increase in nitrate concentrations in streams following harvesting may be followed by longer-term declines as forest regeneration increases ecosystem N retention as observed at Hubbard Brook (Pardo, Driscoll, and Likens 1995). Given the high variations in streamwater chemistry among streams and over time (Section 3), very intensive sampling designs would be needed to detect any changes that were less than about twofold.

4.5.2 *Burning*

Fire is a major factor in most forests of the United States, including both wildfires and prescribed management fires (DeBano, Neary, and Ffolliott 1998). Burning typically increases streamwater nutrient concentrations, but these increases are usually too small and too short in duration to substantially impair water quality.

Richter, Ralston, and Harms (1982) found no differences in concentrations of nitrate (0.02 mg N/L), ammonium (0.03 mg N/L), or inorganic phosphate (30 µg P/L) in streams draining control or burned watersheds dominated by old loblolly pines. Williams and Melack (1997) found significant increases in streamwater nitrate concentrations following prescribed fires in mixed conifer forests of the Sierra Nevada in California. Nitrate concentrations in streamwater increased dramatically in the first two years after fire, rising from near 0 before the fire to annual averages of about 0.5 mg N/L. The increase declined in the third year after burning, and was down to background levels in the fourth year. Concentrations of ammonium rose from near 0 to 0.3 mg N/L shortly after the burn, but returned to background levels within several months.

A severe windstorm in the Experimental Lakes Area of Ontario preceded a very intense fire which consumed all understory vegetation <2.5 cm in diameter and oxidized most of the forest floor (and even some organic matter within mineral soil horizons in some places) (Schindler et al. 1980). This fire may represent the upper end of fire severity, and streamwater nutrient concentrations after the fire rose by about five- to ninefold. Before the fire, nitrate concentrations averaged 0.07 to 0.20 mg N/L, compared with 0.2 to 1.1 mg N/L for at least two years after the fire. Concentrations of ammonium also increased, but by less than a factor of two.

Hauer and Spencer (1998) followed the effects of a wildfire in Glacier National Park and the Flathead National Forest in Montana, beginning during the time period of the fire and continuing for four to five years after the fire. Four of the sampling locations in burned watersheds were in fourth-order streams, and one was in a first-order stream. Shortly after the firestorm, ammonium levels in the stream rose from near 0 to 0.26 mg N/L and then declined sharply, reaching background levels within about two years. Nitrate concentrations were highest in the first spring runoff period after the fire, reaching maximum concentrations of about 0.3 mg N/L.

Wright (1976) examined the effects of a severe wildfire in Minnesota on the chemistry of streams and lakes. His sampling began in the second year after the fire, so the largest effects that might be expected to occur in the first year were not included. He found that inorganic P concentrations in streams from a control watershed averaged about 7 µg P/L, compared with 12 to 20 µg P/L for two streams in burned watersheds. The highest observed concentration of 91 µg P/L was in a stream in a burned watershed.

A severe wildfire in eastern Washington increased streamwater concentrations of nitrate from background levels of about 0.02 mg N/L to about 0.5 mg N/L for three years (Tiedemann, Helvey, and Anderson 1978). Concentrations of inorganic phosphate increased from 7 µg P/L to 20 µg P/L, and total phosphorus increased from 12 µg P/L to 33 µg P/L. The variable effects of fire may depend in large part on the amount of sediment moved to streams by erosion. In the case of the eastern Washington fire described above, extensive erosion contributed to high nutrient concentrations in runoff (Helvey 1980). But in many cases the available studies of fire and water quality do not appear to have included fires that were followed by substantial sediment transport to streams (or at least this factor was not highlighted in the publications). The influence of post-fire erosion on streamwater chemistry would be worth direct investigation. These studies also did not include any fires in wetlands with organic soils (DeBano, Neary, and Ffolliott 1998); fires have major effects on these ecosystems and increases in availability of P to plants has been documented (Wilbur and Christensen

1985), but the effects on streamwater chemistry remain unexplored. A summary paper on wildfires and nutrients is provided by Tiedemann (1981).

4.5.3 *Fertilizing*

The effects of forest fertilization have been examined in several dozen case studies in North America (reviewed by Binkley, Burnham, and Allen in NCASI 1999). Forest fertilization commonly leads to moderate, short-term increases in streamwater nutrient concentrations. Average annual nitrate concentrations of fertilized forests remained below 0.5 mg N/L for most cases (Figure 4.7). About 15% of the studies showed nitrate concentrations above 0.5 mg N/L after fertilization. The peak observed concentrations of nitrate were much higher in fertilized forest streams; about half of the studies found peak nitrate in excess of 1 mg N/L, and some exceeded 10 mg N/L for short periods of time (mostly in situations where fertilizer fell directly into streams). Fertilization had no effect on annual average ammonium concentrations (Figure 4.8), though short-term peak concentrations reached 10 mg N/L in cases where fertilizer application to streams occurred. Most of the streams in the fertilization studies had less than 10 μg P/L, and fertilization either had no effect on the annual average concentration, or increased the concentrations up to about 20 μg P/L (Figure 4.9). Short-term peak concentrations of phosphate rose to 25 to 150 μg P/L for short periods in about half of the cases.

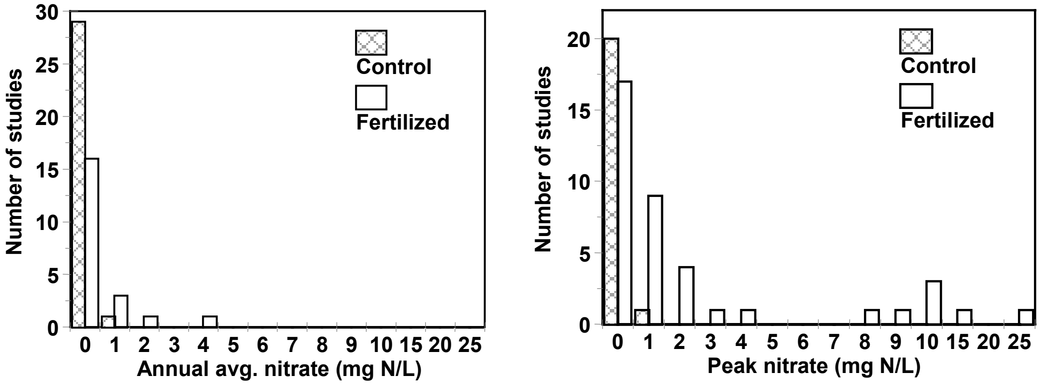


Figure 4.7. Average and Maximum Concentrations of Nitrate N for Control and Fertilized Watersheds; X axis divisions are 1 mg N/L up to 10, then 5 mg N/L divisions; most studies are from the US, but a few are from Canada and Europe (from NCASI 1999)

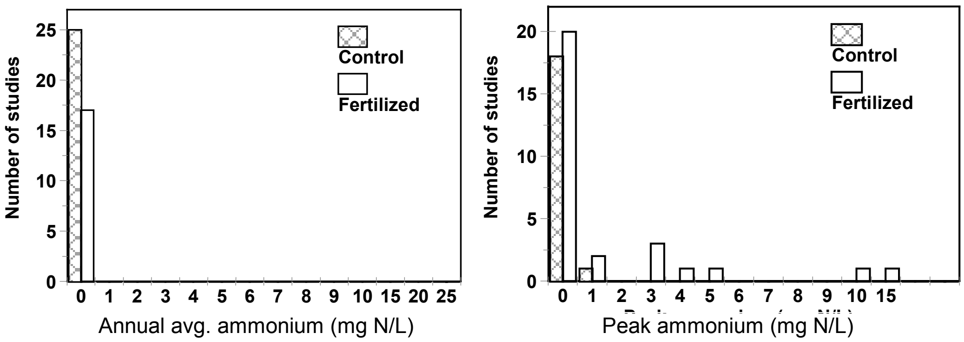


Figure 4.8. Average and Maximum Concentrations of Ammonium N for Control and Fertilized Watersheds; X axis divisions are 1 mg N/L up to 10, then 5 mg N/L divisions (from NCASI 1999)

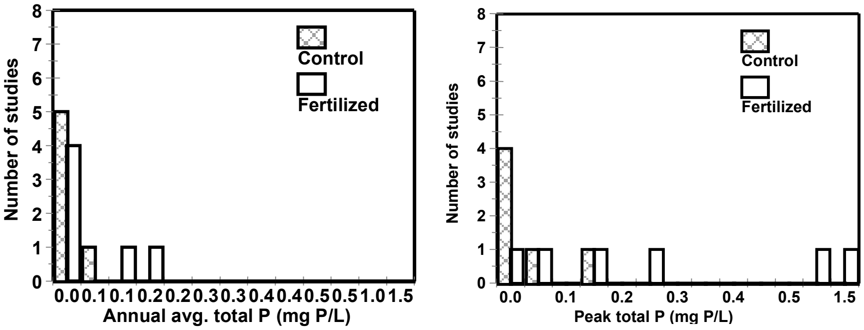


Figure 4.9. Average and Maximum Concentrations of Total P for Control and Fertilized Watersheds; X axis divisions are 0.05 mg P/L up to 0.5, then 0.5 mg P/L divisions (from NCASI 1999)

4.5.4 *Other Disturbance Patterns*

Insect outbreaks have been found to influence nitrogen loss from forest watersheds (Eshleman, Morgan, et al. 1998a, Eshleman, Gardner, et al. 2000). In some cases, heavy nitrogen discharge has been linked to gypsy moth caterpillar droppings. At the peak of an infestation in the Chesapeake Bay as much as 12% of the forest was defoliated, which may have also contributed to the increased nitrogen losses.

4.6 Effects of Local Differences in Parent Material

Although nitrogen is a minor constituent of most parent materials, exceptional situations have been reported where geologic substrates provide large amounts of nitrate to streams. For example, Holloway and Dahlgren (1999) found that some rocks in the Mokelumne watershed of California contained 250 to 1000 mg N/kg of rock, and that about half of this N was released during weathering and soil formation. They estimated that weathering of N provided about half as much N (about 2500 kg N/ha) as the current soil contained, although the balance between N retention in the soil and loss to streams remained unquantified.

Holloway et al. (1998) emphasized bedrock sources of nitrate in explaining the high concentrations of nitrate in lower reaches of the Mokelumne River in California. Headwaters of the river had nitrate concentrations <0.1 mg N/L, whereas tributaries draining areas dominated by metasedimentary and metavolcanic rocks averaged 0.3 to 1.5 mg N/L. Rates of N loss from the grassland/oak savannahs averaged about 20 kg N/ha annually, or ten times the rate of atmospheric deposition.

Rock types influence streamwater nitrate concentrations in the Fernow Experimental Forest in West Virginia. Streams in the Fernow area have shown high concentrations of nitrate export, and have been characterized as nitrogen saturated (inputs = outputs) (Gilliam, Adams, and Yurish 1996). Wooten, Preer, and Edwards (1999) reported that streams influenced by the Greenbriar limestone formation have higher nitrate concentrations than streams influenced by shale and sandstone rocks. For example, Big Spring Run had concentrations of 4 mg N/L where the stream emerged from a cave in Greenbriar limestone, and concentrations declined to less than 3 mg N/L within 0.5 km as the water was diluted by ground water from the Pocono sandstone formation. Streams receiving water from the Greenbriar formation show high concentrations, whether or not the streams orginate in a cave. Wooten, Preer, and Edwards suggest that the N concentration of the limestone itself is too low to support this high concentration in drainage water, and they suggest the likely source is bat guano. The high nitrate in streams influenced by the Greenbriar limestone cannot account for the high nitrate concentrations in the long-term watershed monitoring at the Fernow Experimental Forest, as these watersheds are underlain by acidic sandstones and shales with no influence of Greenbriar limestones (M.B. Adams, pers. comm.).

Bedrock and subsoil can also provide substantial quantities of phosphate to streams in some situations. Kelly, Lynch, and Rounds (1999) intensively characterized the mass balance of water and phosphorus for the Tualatin River in Western Oregon. During low-flow periods, much of the river water is derived from groundwater sources that are in contact with phosphorus bearing minerals (particularly vivianite and iron phosphate). Their mass balance showed that this ground water source of mineral derived phosphate contributed about 25% of the river phosphate. Most forest streams would probably be influenced less by ground water sources of phosphate from minerals, but this case study illustrates the potential importance of unexpected sources of phosphate in some situations of anomalously high concentrations.

5.0 SUMMARY AND CONCLUSIONS

Streamwater chemistry is fairly variable among forested streams. Most forested streams have less than 0.15 mg N/L as nitrate, but some have more than ten times this level. Ammonium concentrations are commonly less than 0.01 mg N/L, but again some streams have ten times this median concentration. Some of the variation in streamwater chemistry can be explained by rates of atmospheric N deposition; the northeastern US has the highest rates of both N deposition and streamwater concentrations of nitrate. The Northeast also has the highest concentrations of inorganic phosphate in forested streams, indicating that regional differences in other factors (such as geology or vegetation type) play a role. Concentrations of phosphate tend to be low in streams draining igneous bedrock areas, and much higher in areas draining areas with volcanic bedrock or glacial till parent materials. Type of vegetation appears to be important across regions; hardwood forests have two to three times the concentrations of nitrate, ammonium, and inorganic phosphate as in streams draining conifer forests. Conifer forest streams, in contrast, have three to eight times the concentrations of organic N found in hardwood streams. Whereas nitrate-N accounts for about 60% of all dissolved N in streams in hardwood forests, organic N comprises about 80% of the dissolved N in streams in coniferous forests. These synoptic patterns of variation in water chemistry cannot be attributed (in most cases) to single factors; hardwood forests are found more commonly on richer soils, and under the climatic conditions of the northeast, where N deposition is highest. All three of these factors would be expected to contribute to higher concentrations of nitrate in streamwater.

The frequency of chemical concentrations in these streams in small forested watersheds appears to differ substantially from the frequencies found in national monitoring programs of larger, mostly forested watersheds (USGS Hydrologic Benchmark Network and National Water Quality Assessment Program). At the national level, the streams in small watersheds have a lower frequency of low concentration and a higher frequency of high concentration streams. The selection of streams for research and monitoring has not been based on a random or systematic sampling scheme, so it is difficult to assess whether the patterns in available data represent the true frequencies that would be found for all forested streams in the country. A few comparisons have been made of the streamwater concentrations in low order headwater streams and larger (third- to fifth-order) streams in the same basins, and these generally show either no trend with stream order, or declining concentrations in higher order streams (unless land use changes). At Hubbard Brook, no change in nitrate concentrations were found as watershed area increased up to 30 km^2 (with no change in land use within the basin). For the Canajoharie Creek in the Mohawk River drainage, nitrate concentrations in summer declined with increasing stream order because of increasing algal biomass and uptake of nitrogen. Similarly, nitrate concentrations were lower in watersheds >100 km^2 in Oregon, probably as a result of increasing biotic uptake of N. The consistency between patterns in local areas and the synoptic averages lends support to the conclusion that low order headwater streams may have higher frequencies of higher average nutrient concentrations than higher order reaches downstream. The likely mechanism for lower rates in higher order streams appears to derive from fundamental changes in stream ecology with increasing order (the river continuum concept) (Vannote et al. 1980). The trophic dynamics shift from processing detritus in low order headwaters to in-stream photosynthesis by algae in higher order streams, and the declines in nitrate in higher order streams do relate to increasing algal biomass (Wall, Phillips, and Riva-Murray 1998; Wigington et al. 1998). This inference is consistent with conventional expectations for stream ecosystems, but some additional surveys that examine the covariation between nutrient concentrations and algal biomass with stream order may be useful.

At a more local scale, the flow and chemistry of small streams are very dynamic over all scales of time. For example, the within-day sampling of streamflow at the Fraser, Colorado, and Calumet, Michigan, sites showed coefficients of variation of 100%. Within single days, it would be very common to observe a twofold range in streamflow. The variability in nitrate concentrations was similarly high at Fraser, but was much lower at Calumet. Repeated sampling within individual months again found very high variation (coefficients of variation >100%). The timescale of greatest variation across the eight streams that were intensively examined occurred between months within years. All eight streams showed more variation among months than across any other time scale. Variability was also high across years, where average concentrations for one year would commonly differ by 50 to 80% from another year. This intensive characterization of variations within streams over scales of time illustrates a fundamental challenge in detecting any significant difference in water quality between streams or within a single stream over time. Routine monitoring programs that sample at monthly intervals may miss a real spike in nutrient concentration that resulted from a short-term disturbance, or a normal-variation spike in concentration in one month might be interpreted as a disturbance when it really fell within the normal range of variation. The interpretability of less-intensive sampling schemes would be even more restricted. In situations where average concentrations differ by tenfold or more (such as the low nitrogen streams in the H.J. Andrews Experimental Forest in Oregon and the high nitrogen streams in the Hubbard Brook Experimental Forest), sampling with low to moderate intensity can clearly identify the general differences between streams. Where concentrations differ by only twofold, only intensive sampling schemes could discern differences between streams or trends over time within streams.

USEPA (2000b) suggested that states and tribes might use the idea of ecoregions to establish standards and criteria for water quality. At the broadest level, this assessment showed that some regions do differ substantially in nutrient concentrations. The differences in regional averages tended to be on the order of twofold, whereas the ranges found within regions typically spanned a fivefold (or greater) range. The high variability within regions means that the smaller variations observed between regions may not be useful in establishing water quality standards. For example, streams in the West generally had lower concentrations of nitrate than streams in the Northeast. Within the local area of the Oregon Coast Range, stream concentrations of nitrate are commonly >0.2 mg N/L and <1.0 mg N/L (Figure 4.2). This broad local range in chemistry appears to have little if any implication for designated uses of these waterways, especially as the concentrations decline downstream as a result of normal changes in biotic processes in streams (such as increasing algal uptake of nutrients). Changes in land use (to agricultural or urban use) appear to be necessary to substantially increase nutrient concentrations in higher order streams.

An additional issue of scale arises when examining the effects of forest practices on water quality and the implications for designated uses of streams. The flow of water increases dramatically in higher order streams, diluting the downstream legacy of streamwater changes in low order headwater streams. Consider the runoff of nitrogen following fertilization of a 1000 ha forest with 200 kg N/ha. A high estimate of 5% of the added fertilizer could leach into the stream over a period of year. If runoff equals 500 mm/yr, the added fertilizer would increase streamwater nitrogen concentrations by 2 mg N/L. If the basin that contains the fertilized forest has an area of 100,000 ha, the dilution of the leached fertilizer would reduce the increase in concentration for the whole basin to just 0.02 mg N/L, which would probably be too low to have much impact on the aquatic ecosystem or to detect amidst normal fluctuations in concentrations and flow rates.

What is the ecological significance of the variations in streamwater chemistry around local areas and across the country? The intensive studies of small watersheds generally did not address within-stream consequences of changes in nutrient concentrations over time, or differences among streams. As noted in the introduction, a report by the Ecological Society of America (Carpenter et al. 1998) on nonpoint sources of N and P pollution did not mention forest streams, and none of the studies reviewed for this report indicated any negative effects of the observed concentrations of nitrogen and phosphorus. Differences in streamwater chemistry over time within streams and among streams are expected to have impacts on biotic processes in streams, but these differences are probably small relative to the dynamics associated with light, temperature, sediment load, and other factors.

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APPENDIX A

WATER QUALITY SUMMARY FOR SMALL WATERSHED STUDIES IN THE UNITED STATES

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammonium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
Adirondacks	NY	Conifer and hardwood	80	glacial till	Outlet from Arbutus Pond	10	0.1					Mitchell et al. 1996; Driscoll and Vandreason 1993
Alsea	OR	Conifer/alder	4	sandstone	Needlebranch, harvest	5	0.4					Fredriksen et al. 1975; Brown et al. 1973; Brown and Krygier 1970
			70	sandstone	Flynn Creek,	5	1.2					
			3	sandstone	Deer Creek, 25% harvest	5	1.2					
Bear Brook	ME	Mixed hardwood	40	glacial till	Fertilized 75 kg N/ha	5	0.7	0.02				Norton et al. 1994
			40		Prefertilization	5	0.3	0.03				Norton et al. 1994
Beaver Creek	AZ	Ponderosa pine	8	basalt	Logged	8	0.022					M. Ryan, pers. comm.
			120									
			8			8	0.01					
			8		Logged	8	0.05					
Benner Run	PA	Mixed hardwood	100	sandstone		1.5	0.15					Dow and DeWalle 1997
Bens Creek	PA	Mixed hardwood				8	0.56	0.022				Aulenbach et al. 1996
Biscuit Brook	NY	Mixed hardwood		glacial till		8	0.5					
Bitterroot NF site 1	MT	Mixed conifer	120		Spruce Creek, control Lodgepole creek	1	0.11					Bateridge 1974
Bitterroot NF site 1	MT	Mixed conifer	3		Lodgepole Creek, 3rd yr post harvest	1	0.19					
Bitterroot NF site 2	MT	Mixed conifer	1		Mink Creek, first year post harvest	1	0.13					
Bitterroot NF site 2	MT	Mixed conifer	120		Springer Creek, Control for Mink Creek	1	0.17					

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
Bitterroot NF site 3	MT	Mixed conifer	120		Little Mink preharvest	1	0.17					
Bitterroot NF site 3	MT	Mixed conifer	1		Little Mink Creek, first year post harvest	1	0.4					
Bowl Nat. area upper	NH	Mixed hardwood	250	glacial till	Old growth	3	0.2086					
Bowl Nat. area upper	NH	Mixed hardwood	250	glacial till	Old growth	2	0.609					
Bowl Nat. area east	NH	Mixed hardwood	250	glacial till	Old growth	3	0.2212					
Bowl Nat. area east	NH	Mixed hardwood	250	glacial till	Old growth	2	0.644					
Bowl Nat. area lower	NH	Mixed hardwood	250	glacial till	Old growth	3	0.2814					
Bowl Nat. area lower	NH	Mixed hardwood	250	glacial till	Old growth	2	0.6216					
Bowl Nat. area west	NH	Mixed hardwood	250	glacial till	Old growth	3	0.1456					
Bowl Nat. area west	NH	Mixed hardwood	250	glacial till	Old growth	2	0.5712					
Bradford Co.	FL	Slash pine/LongP	naturally regenerating"	sand over clay		3	0.03	0.13		0.02	0.02	Riekirk 1983
Bradford Co.	FL	Slash pine/Loblolly pine	3	sand over clay	Logged low impact	3	0.04	.06 to .15		0 to 0.03	.02 to 0.05	Riekirk 1983
		Slash pine/Loblolly pine	3	sand over clay	Logged high impact	3	0.05	.08 to 0.09		0 to 0.01	.01 to 0.02	Riekirk 1983
Bull Run	OR	Mixed conifer	7	basalt	25% harvested Fox Creek	7	0.08			<0.004	.014 to .028	Fredriksen et al. 1975; Harr and Fredriksen 1988
		Mixed conifer	500	basalt	Control Fox Creek	10	0.01			<0.003	.014 to .025	

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
		Mixed conifer	9	basalt	25 % harvested and burned, Fox Creek	9				<0.003	.014 to .024	
Calumet	MI	Mixed hardwood	80	glacial till/old beach deposits		10	0.094	0.025				raw data
Caribou-Poker C2	AK	Conifer and hardwood	200	loess or alluvium over mica shist	3% permafrost	1	0.14	0.01	0.68			MacLean et al. 1999
Caribou-Poker C3	AK	Conifer and hardwood	200	loess or alluvium over mica shist	53% permafrost	1	0.12	0.01	0.71			
Carteret Co.	NC	Loblolly pine	15	coastal plain	Drained by ditches	3					0.07	Hughes et al. 1990
Cascade Mountains	WA	Douglas-fir	40		Fertilized 225 kg N/ha	0.5	0.8	0.08	1			Bisson et al. 1992
			40				.1 to .2	0.02	0.9			
Caspar Creek	CA	Mixed conifer	80									R. Dahlgren, pers. comm.
			2	Sandstone, shale	Logged	5	0.09	0.00		0.003		
			80	Sandstone, shale		5	0.01	0.00		0.001		
Castle Creek	AZ				Burned	1	<0.003					Gottfried and DeBano 1990
Catoctin, Bear Brch	MD	Mixed hardwood	80	quartzite			0.29					raw data from Rice; Aulenbach et al. 1996; Rice and Bricker 1995
Catoctin, Fishing Creek	MD	Mixed hardwood	80	quartzite			0.11					
Catoctin, Hauver Brch	MD	Mixed hardwood	80	Metabasalt, metarhyolite		8	0.14					
Catoctin, Hunting Cr	MD	Mixed hardwood	80	Metabasalt, metarhyolite		8	0.06					
Catskill Montains	NY	Mixed hardwood	100	glacial till		3	0.32		0.04			Lovett et al. 2000
						3	0.50		0.07			
						3	0.50		0.04			

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
						3	0.31		0.08			
						3	0.31		0.06			
						3	0.29		0.04			
						3	0.29		0.05			
						3	0.35		0.08			
						3	0.46		0.09			
						3	0.34		0.08			
						3	0.32		0.05			
						3	0.14		0.08			
						3	0.27		0.09			
						3	0.28		0.10			
						3	0.39		0.06			
						3	0.31		0.05			
						3	0.32		0.11			
						3	0.24		0.09			
						3	0.35		0.07			
						3	0.06		0.08			
						3	0.29		0.09			
						3	0.03		0.08			
						3	0.04		0.10			
						3	0.50		0.05			
						3	0.31		0.08			
						3	0.48		0.04			

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
						3	0.45		0.08			
						3	0.31		0.05			
						3	0.42		0.06			
						3	0.45		0.06			
						3	0.22		0.06			
						3	0.28		0.04			
						3	0.24		0.05			
						3	0.38		0.07			
						3	0.31		0.09			
						3	0.18		0.08			
						3	0.39		0.04			
						3	0.39		0.07			
						3	0.43		0.08			
Central	OR	Douglas-fir	35		Fertilized 225 kg N/ha		0.02	<0.01				Stay et al. 1979
			35				0.007	<0.01				
Cherokee	TX	Pine	3	sandstone	Harvested,chopped, burned	5	0.0102	0.034		0.0026	0.037	Blackburn et al. 1986; Blackburn and Wood 1990
			60	sandstone	Preharvested calibratrion	1	0.003	0.067		0.0003	0.068	
			60	sandstone	Control	6	0.011	0.131		0.0026	0.064	
			60	sandstone	Preharvest calibration	1	0.003	0.06		0.0026	0.06	
			3	sandstone	Harvested, sheared, windrowed, burned	5	0.0184	0.045		0.0032	0.083	
Chicken Creek	UT	Aspen			Harvested, beaver present		0.025					Johnston 1984

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
					Beaver present		0.008					
Coast Range	OR	Conifer/alder	40		Brush Creek pretreatment	2	.7 to 2.1					Miller and Newton 1983
			40		Brush Creek Harvested+ Herbicide	2	.7 to 2.1					
			2		Drift Creek, harvested, burned, herbicided	2	1.5 to 2					
			2		Siletz Creek harvested, herbicided	2	0.6					
			60		Siletz Creek pretreatment	2	0.6					
			60		Drift Creek, pretreatment	2	1.5 to 2					
Coast Range	WA	Douglas-fir	40				0.6	0.03	0.2			Bisson et al. 1992
			40		Fertilized 225 kg N/ha	0.25	1.5	0.07	1			
Cone Pond	NH	Conifer and hardwood	180	glacial till		2	0	0.04	0.12			Campbell et al. 2000
Coweeta ws1	NC	White pine	40	saprolite		10	0.02	0.003		0.008		Swank and Crossley 1988
Coweeta ws17	NC	White pine	40	saprolite		10	0.13	0.04		0.002		
Coweeta ws18	NC	Mixed hardwood	70	quartz diorite/ metasandstone/biotite schists		20	0.0085	0.003		0.001		
Coweeta ws2	NC	Mixed hardwood	70	saprolite		10	0.003	0.002		0.002		
Coweeta ws27	NC	Mixed hardwood	70	saprolite		10	0.018	0.004		0.001		
Coweeta ws37	NC	Mixed hardwoods	5	saprolite	Harvested		0.18	0.004		0.001		
Coweeta ws40	NC	Mixed hardwood	70	saprolite		1	0.005	0.004		0.003		
Coweeta ws6	NC	Mixed hardwood	70	saprolite		10	0.67	0.005		0.007		

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
Coweeta ws7	NC	Mixed hardwoods	5	saprolite	Harvested		0.01					
Coyote Creek	OR	Mixed conifer	200	andesite/basalt	Control for Coyote Creek harvesting		.015 to 0.04	0.005				Fredriksen et al. 1975; Harr et al. 1979; Adams and Stack 1989
			<5	andesite/basalt	Shelterwood		<0.015					
			<5	andesite/basalt	Patchcuts		.015 to 0.04					
			<5	andesite/basalt	Clearcut		0.1					
			200	andesite/basalt	Control for Coyote Creek fertilization		0.002	0.005				Fredriksen et al. 1975
			200	andesite/basalt	Fertilized 225 kg N/ha							
Dollar Creek	OR	Douglas-fir	20		Fertilized 225 kg N/ha							
			20				0.06	0.03				
Entiat Exp. For.	WA	Mixed conifer	300	volcanic ash	Preburn	0.5	0.002	<detection	0.06			Tiedemann et al. 1978
			300	volcanic ash	Lake Creek, unburned	4	0.002			0.007	0.012	
			5	volcanic ash	Fox Creek, wildfire	5			0.07	0.02	0.033	
			300	volcanic ash	Burns Creek, burned, fertilized 57 kg N/ha	5			0.06	0.015	0.025	
			2	volcanic ash	McCree Creek, burned, fertilized 54 kg N/ha	5			0.09	0.015	0.02	
Fernow	WV	Mixed hardwood	12	acidic shale/ sandstone	Fertilized 260 kg N/ha	3	4.86	0.13				Aubertin et al. 1973
Fernow	WV	Mixed hardwood	50	acidic shale/ sandstone	Control 1984-1988	5	0.75	<0.001				Adams et al. 1997
			55	acidic shale/ sandstone	Control 1989-1993	5	0.78 to 1.11	<0.001				Adams et al. 1997
			12	acidic shale/ sandstone	Upstream of harvest	3	0.1	0.19				Aubertin et al. 1973

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
			3	acidic shale/ sandstone	Harvested	3	0.2	0.2		0.04		Aubertin and Patric 1974
			50	acidic shale/ sandstone	Control for harvesting	3	0.2	0.2		0.04		Aubertin and Patric 1974; Patric 1980
			50	acidic shale/ sandstone	Fertilized 175 kg N/ha	5	0.78 to 1.71	<0.001				Adams et al. 1997
			50	acidic shale/ sandstone	Fertilized 335 kg N/ha; 45 kg P/ha	3	1.5			0.01 to 0.03		Helvey et al. 1989; Edwards et al. 1991
			50	acidic shale/ sandstone	Control 1984-1988	5	0.57	<0.001				Adams et al. 1997
			12	acidic shale/ sandstone	Prefertilziation	3	0.76	0.23				Aubertin et al. 1973
			50	shale/ sandstone	Control	3	0.6 to 0.8			0.02		Helvey et al. 1989; Edwards et al. 1991
			50	shale/ sandstone	Fertilized 335 kg N/ha; 45 kg P/ha	3	2			0.01 to 0.04		Helvey et al. 1989; Edwards et al. 1991
			50	shale/ sandstone	Control	3	0.8 to 1.1			0.01 to 0.02		Helvey et al. 1989; Edwards et al. 1991
Flathead NF; Coal Creek	MT	Mixed conifer	120	glacial till/volcanic ash	Harvested 8 % of watershed	5	0.03	0.005		0.003	0.015	Hauer and Spencer 1998
Flathead NF; Red Bench Cr.	MT	Mixed conifer	120	glacial till/volcanic ash	Burned 16%, Harvested 26%	5						
Flathead NF; Red Meadow Cr.	MT	Mixed conifer	120	glacial till/volcanic ash	Burned 96%, Harvested 16%	5		0.005			0.015	
Flathead NF; Wally Cr.	MT	Mixed conifer	120	glacial till/volcanic ash	Harvested 12 %	5		0.002		0.01	0.02	
Florida	FL	Slash pine	3	coastal plain				0.2		<0.1		Riekirk 1989
			3	coastal plain	Fertilized 225 kg N/ha; 90 kg P/ha			0.2		<0.1		

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Florida	FL	Slash pine	20	coastal plain	Fertilized 40 kg N/ha; 50 kg P/ha							Fisher 1981
			20	coastal plain			<0.1	<0.1	0.9			
Fraser	CO	Mixed conifer	30	gneiss/schist	Fool Creek, Harvested	1	0.002	0.014		0.0024		Alexander et al. 1985; Stottlemyer 1987
			12	gneiss/schist	Deadhorse Creek, Harvested	1	0.06	0.0042				
			350	gneiss/schist	Lexen Creek, short term comparisons with harvests	1	0.006	0.028				
			350	gneiss/schist	Lexen Creek, long-term							
George's Gorge	NH	Mixed hardwood	95	stony glacial till		1	0.28		0.868			Goodale 1999
Georgetown	SC	Loblolly pine	2			2	0.2	0.026			<0.01	Askew and Williams 1986
		Mixed pine and hardwood	40			2	0.47	0.047			<0.01	
		Loblolly pine	40			2	0.05	0.022			<0.01	
		Mixed pine and hardwood	2		Drained	2	0.94	0.074			<0.01	
		Loblolly pine	40			2	0.48	0.041			<0.01	
		Mixed pine and hardwood	2		Harvested	2	0.11	0.057			<0.01	
Giant Sequoia NP	CA	Mixed conifer	1000	granite	Log Creek; postburn	3	0.007	0		0.000462		Chorover et al. 1994
			1000	granite	Log creek; preburn	3	0.00504	0.014		0.0014		
			1000	granite	Tharps Creek; postburn	3	0.35	0.0266		0.000462		
			1000	granite	Tharps creek; preburn	3	0.0007	0.0224		0		
			250	stony glacial till	Old growth	1	0.56		0.98			Goodale 1999

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammonium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
Gibbs Brook hardwood	NH	Mixed hardwood	250	stony glacial till	Old growth	1	2.66		0.98			
Glacier National Park;.	MT	Akokola Creek, Mixed conifer	200	glacial till/volcanic ash	Burned 9% of watershed	5						Hauer and Spencer 1998
		Bowman Creek, Mixed conifer	200	glacial till/volcanic ash	Burned 11%	5						
		Logging Creek, Mixed conifer	200	glacial till/volcanic ash	Control	5	0.015	0.005		0.003	0.01	
		Quartz Crrek, Mixed conifer	200	glacial till/volcanic ash	Burned 29 %	5						
Glen Boulder	NH	Mixed conifer	250	stony glacial till	Old growth	1	2.1		0.98			Goodale 1999
Grant Forest	GA	Loblolly and shortleaf pine	30	piedmont	Preharvest calibration	1	0.043				0.23	Hewlett et al. 1984; Hewlett and Fortson 1982
			2	piedmont	Harvested 2yr post	2	0.027				0.32	
			5	piedmont	Harvested 3-5yr post	3	0.045				0.55	
			30	piedmont		5	0.116 to 0.156				.23 to .61	
Hansel Creek	WA	Mixed conifer	3	sandstone/serpentine/schist/granite		3	0.15					Fowler et al. 1988
				sandstone/serpentine/schist/granite			0.15					
High Ridge	OR	WS-1, Mixed conifer	300	basalt/volcanic ash	clearcut; pretreatment;		0.092			0.025		Tiedemann et al. 1988
			3	basalt/volcanic ash	clearcut; posttreatment	3	0.162			0.033		
		WS-2, Mixed conifer	3	basalt/volcanic ash	selection harvest; posttreatment	3	0.006			0.013		

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			300	basalt/volcanic ash	selection harvest; pretreatment		0.003			0.014		
		WS-3, Mixed conifer	300	basalt/volcanic ash	control; pretreatment		0.001			0.009		
			3	basalt/volcanic ash	control: post treatment	3	0.004			0.008		
		WS-4, Mixed conifer	300	basalt/volcanic ash	patchcuts; pretreatment		0.004			0.003		
			3	basalt/volcanic ash	patchcuts; posttreatment	3	0.008			0.013		
HJ Andrews	OR	WS-1, Mixed conifer	1	volcanic ash/andesite	Harvested, burned					.008 to .013		Fredriksen et al. 1975
		WS-10, Mixed conifer	4	volcanic ash/andesite	Post clearcut	4	0.031	0.022				Sollins and McCorrison 1981; Sollins et al. 1980
			400	volcanic ash/andesite	calibration	1	0.001				0.054	
		WS-2 Mixed conifer	400	volcanic ash/andesite			0.01			.005 to 0.01		Fredriksen et al. 1975
		WS-6 Mixed conifer	9	volcanic ash/andesite	clearcut treatment	9	0.02			0.014		Martin and Harr 1989
			400	volcanic ash/andesite	pretreatment; eventually clearcut treatment	3	0.001			0.016		
		WS-7 Mixed conifer	4	volcanic ash/andesite	shelterwood treatment	9	0.006			0.022		
			400	volcanic ash/andesite	pretreatment; eventually shelterwood treatment	3	0.001			0.022		
		WS-8 Mixed conifer	400	volcanic ash/andesite	pretreatment years for WS7 and WS6	3	0.001			0.021		

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			400	volcanic ash/andesite	post-treatment WS7 and WS6	9	0.003			0.022		
		WS-9, Mixed conifer	400	volcanic ash/andesite		5	0.003	0.014				Sollins and McCorrison 1981; Sollins et al. 1980
Hubbard Brook	NH	Mixed hardwood	65	glacial till	long term data for undisturbed watershed	25						WS#9 data from Andrews web site
			65	glacial till	control watershed for	25	0.2	.02 to .09				Likens et al. 1970; Hornbeck et al. 1987; Lawrence and Driscoll 1988
			1	glacial till	stripcut	3	1.4	0.028				
			1	glacial till	whole tree harvest	3	3.6					
			1	glacial till	blockcut	3	3.9	0.014				
Humbolt Co.	CA	Mixed conifer					0.03			0.001		Triska et al. 1989
Isle Royale, NP	MI	Mixed hardwood		basalt/sandstone/ glacial till		10	0.062	0.039				WS#6 data from Hubbard Brook Web site
Jimmy-Come-Lately Creek	OR	Douglas-fir	10		Fertilized 225 kg N/ha							Fredriksen et al. 1975
			10				0.05	0				
Jordan Creek	NC			coastal plain		8	0.03	0.035				Aulenbach et al. 1996
Lafayette Brook	NH	Mixed hardwood	250	stony glacial till	Old growth	1	2.8		1.54			
Leading Ridge	PA	Mixed hardwood	3	shale/sandstone/quartzite	Devegetated	3	2.5					Lynch et al. 1975; Lynch and Corbett 1990; Lynch et al. 1985
			3	shale/sandstone/quartzite	Harvested	3	0.08					
			80	shale/sandstone/quartzite		3	0.03					

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammonium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
Lewis Creek	OR	Mixed conifer		sandstone/siltstone		1					0.078	Norris et al. 1978 in Salminen and Beschta 1991
Little Valley	CA	Mixed conifer		granite colluvium		1						Johnson 1995
Little Wildcat	NH	Mixed hardwood	110	stony glacial till	Harvested	1	0.21		0.84			Goodale 1999
Lost Pond	NH	Mixed hardwood	110	stony glacial till	Harvested	1	0.49		1.4			
Lye Brook	NH	WS-6, Conifer and hardwood	85	glacial till		1	0.41					Campbell et al. 2000
		WS-8, Conifer and hardwood	85	glacial till		1	0.1	0.01	0.38			
Marcell Exp. For.	MN	Aspen	50	glacial till		2	0.3	0.41		0.039		Verry 1972
		Aspen	2	glacial till	Harvested	2	0.015	0.55		0.055		
Massanutten Mtn 1	VA	Mtn. 1, Mixed hardwood				8	0.028	0.011				Aulenbach et al. 1996
		Mtn. 2, Mixed hardwood				8	0.018					
Metolious River	OR	Mixed conifer		basalt		12					0.09	Salminen and Beschta (1991)
Mitkof Island	AK	Mixed conifer	200		Harvested, fertilized 210 kg N/ha		0.3	0.08				Meehan et al. 1975
			200		Harvested, fertilized 210 kg N/ha		0.5	0.1				
			200		Harvested		0.1	0.05				
			200		Harvested		0.1	0.05				
Mokelumne River	CA	Oak savanna		granite/diorite		1.5	0.028					Holloway et al. 1998

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
				metasedimentary/ metavolcanic		1.5	0.8					Holloway et al. 1998
Mt. Bickford	NH	Mixed hardwood	95	stony glacial till		1	0.07		0.98			Goodale 1999
Mt. Hood NF	OR	WS-15, all waterheds mixed conifer	500		Harvested	15				0.008		USDA unpublished cited in Salminen and Beschta 1991
		WS-18	500		Harvested	15				0.0036		
		WS-22	500		Harvested	16				0.0038		
		WS-24	500		Harvested	11				0.0036		
		WS-25	500		Harvested	5				0.0031		
		WS-35	500		Harvested	15				0.0034		
		WS-44	500			15				0.004		
		WS-79	500			1				0.0032		
		WS-9	500		Harvested	14				0.0032		
		WS-91	500		Harvested	1				0.0031		
		WS-92	500		Harvested	1				0.0034		
		WS-D17	500			6				0.0031		
		WS-D18	500		Harvested	6				0.003		
		WS-EO5	500			3				0.003		
Mt. Washington	NH	Mixed conifer	87	stony glacial till	Harvested	1	0.14		0.84			Goodale 1999
Nancy Brook	NH	Mixed conifer	250	stony glacial till	Old growth	1	1.05		0.98			
NC State	NC	Loblolly pine	35	piedmont		1	0.1	0.1				Sanderford 1975

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				piedmont	Fertilized 110 kg N/ha;13 kg P/ha	1						
Near Albany	OR	Douglas-fir	35		control is upstream reach							Malueg et al. 1972
					Fertilized 225 kg N/ha							
Nelson Creek	OR	Douglas-fir	20		Fertilized 225 kg N/ha							Fredriksen et al. 1975
							0.29	0.01				
North-Central	WA	Ponderosa pine			Burned, fertilized 54 kg N/ha		0.2	0				Klock 1971
					Burned		0	0				
					Burned		0	0				
					Burned, fertilized 56 kg N/ha		0.1	0				
Northern	ID	Mixed conifer	30		control is upstream reach	0.5						Loewenstein et al. 1973
			65			0.1						
			30		Fertilized 225 kg N/ha	0.5						
			65		Fertilized 225 kg N/ha	0.1						
Old Rag	VA	Mixed hardwood				8	0.008					Aulenbach et al. 1996
Olympic Nat. Park	WA	Mixed conifer	600	marine origen		10	0.084			0.042	0.17	Edmonds and Blew 1997
Pancake Creek	NY	Mixed hardwood	70	glacial till	Above beaver poind	1	0.392	0.013				Driscoll et al. 1987
				glacial till	Below beaver pond	1	0.322	0.057				
Panola Mtn	GA					8	0.04	0.003				Aulenbach et al. 1996
Pat Creek	OR	Douglas-fir	35				0.07	0.007				Fredriksen et al. 1975

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
					Fertilized 225 kg N/ha							
Pinelands	NJ	Pine	60	coastal plain		11	<.1	<.1			<.02	Zampella 1994
Priest River	ID	All mixed conifer; Site 1	100	metamorphic rock/ volcanic ash	above cut unit, Benton Creek	1	0.17					Snyder et al. 1975
			1		within cut unit, Benton Creek	1	1.5					
			1		below cut unit, Benton Creek	1	0.2					
		Site 2	1		within cut unit, Ida Creek	1	0.15					
					above cut unit, Ida Creek	1	0.15					
			1		below cut unit, Ida Creek	1	0.15					
		Site 3	100		above cut unit, Canyon creek	1	0.015					
			1		within cut unit, Canyon Creek	1	0.18					
			1		below cut unit, Canyon Creek	1	0.015					
Quaker Run	PA	Mixed hardwood	80		upstream reach	1	0.13					Lynch and Corbett 1990
			80		downstream reach	1	0.32					
Quartz Creek	OR	Mixed conifer		red breccia/ basalt		1					0.05	Norris et al. 1978 in Salminen and Beschta 1991
Robinson Forest	KY	Mixed hardwood	4	sandstone, siltstone, shale	Harvested, poor practices	8	0.38			0.04		Arthur et al. 1998
			4	sandstone, siltstone, shale	Harvested, with BMPs	8	0.35			0.03		

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
			40	sandstone, siltstone, shale		8	0.135			0.03		
Rocky Branch	NH	Mixed hardwood	85	Stony glacial till		1	0.07		0.63			Goodale et al. 2000
Sagehen Creek	CA	Mixed conifer	160	andesitic tuff		1						Johnson et al. 1997
Santee	SC	WS-77, Mixed pine and hardwood	120	coastal plain	Prehurricane, prelogging	6	0.016	0.07		0.02		Richter et al. 1982
			120	coastal plain	Post hurricane, post logging	6	0.019	0.05		0.02		
		WS-80, Mixed pine and hardwood	120	coastal plain	Burned	10	0.004	0.035		0.009		
			120	coastal plain	Burned	6	0.017	0.04		0.03		
Shenandoah National Park	VA	Mixed hardwood	70	phyllite, quartzite, metasandstone		3	0.04					Eshleman et al. 1998
					Defoliated	5	0.42					
						2	0.04					
					Defoliated	6	0.42					
					Defoliated	5	0.56					
					Defoliated	5	0.14					
						10	0.04					
						10	0.04					
Silver Creek	ID	Mixed conifer	5	granite	Harvested	4	0.018					Clayton and Kennedy 1985
			100	granite		6	0.01					
Sleepers River	VT	Conifer and hardwood	65	glacial till/ calcareous bedrock		2	0.2	0.025	0.1			Campbell et al. 2000
Smoky Mountains National Park	NC and TN	Mixed hardwood, some conifer	200	sandstone	Not harvest (75% at least) before park establishment 45 years prior	1	0.83					Silsbee and Larson 1982

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
			55	slate		1	0.85					
			55	sandstone		1	0.67					
			55	sandstone	Stands harvest prior to park establishment	1	0.36					
Tohetie Creek	OR	Mixed conifer		sandstone/ siltstone		1					0.035	Norris et al. 1978 in Salminen and Beschta 1991
Trapper Creek	OR	Douglas-fir	40		Fertilized 225 kg N/ha							Fredriksen et al. 1975
			40				0.034	0				
Upper Big Run	MD	Mixed hardwood		sandstone, siltstone, shale	Defoliated	8	0.28					Eshleman et al. 1998
Various	NewEng.	Mixed hardwood	various	glacial till		2	0.5					Martin et al. 1984
		Mixed conifer	various	glacial till		2	0.2					
		Mixed hardwood	various	glacial till		2	0.1					
Walker Branch	TN	Mixed hardwood	45	dolomite/ saprolite		6	0.02					Mulholland and Hill 1997
		1989 to 1995										
		Before 1989	35	dolomite/ saprolite		3	0.057	0.022		0.001		
Weyerhaeuser	NC	Loblolly pine	15	coastal plain	Fertilized 145 kg N/ha:45 kg P/ha		0.14	0.04	0.8	0.03		Fromm and Herrmann 1996
			6	coastal plain	Fertilized 210 kg N/ha;40 kg P/ha	1	0.03	0.51	1.59	0.17		Herrmann and White 1996
			15	coastal plain	Fertilized 170 kg N/ha;28 kg P/ha	0.2						Campbell 1989
			6	coastal plain		2	0.02	0.12	0.68	0.015		Herrmann and White 1996
			15	coastal plain		2	0.6	0.1	0.9			Campbell 1989

Site name	State	Forest type	Forest age (yr; approx. in some cases)	Parent material	Notes	Length of Record (yr)	Nitrate (mg N/L)	Ammon-ium (mg N/L)	Organic-N (mg N/L)	Inorganic phosphate (mg P/L)	Total phosphate (mg P/L)	Reference
			15	coastal plain			0.7	0.04	0.7	0.07		Fromm and Herrmann 1996
White Mountains	NH	Mixed conifer	70	glacial till	1973-1974 from graph fig. 8	1	0.112	< 0.014				Vitousek 1977
		Mixed hardwood	70	glacial till	1973-1974 from graph fig 6	1	0.56	< 0.014				
		Mixed conifer	90	glacial till	1996-1997		0.056					Goodale 1999
		Mixed conifer	200	glacial till	1973-1974	1	0.77	< 0.014				Vitousek 1977
		Mixed conifer	220	glacial till	1996-1997		0.28					Goodale 1999
White Oak Creek 1992 to 1995	TN	Mixed hardwood		dolomite/ saprolite	from graph;	4	0.05					Mulholland and Hill 1997
Woods Lake Outlet	NY	Mixed hardwood		glacial till	outlet from woods lake	2	0.364	0.1				Burns 1996
Zealand Valley	NH	Mixed hardwood	110	stony glacial till		1	0.56		0.56			Goodale 1999

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APPENDIX B

PATTERNS IN CONCENTRATION AT INTENSIVELY STUDIED SITES

1.0 H.J. ANDREWS EXPERIMENTAL FOREST, OREGON

The H.J. Andrews Experimental forest is in the western-central Cascade Mountains of Oregon, within the drainage of the McKenzie River. The experimental forest was established in the l940s, and the landscapes were dominated by old-growth (>400 year old) forests of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco), western hemlock (*Tsuga heterophylla* (Raf.) Sarg.), and western red cedar (*Thuja plicata* Donn ex D. Don), with younger forests that established after fires in the 1800s. Watershed #9 is a reference, old-growth forest, similar to Watershed #10 that was the site of intensive ecosystem studies (Sollins, Grier, et al. 1980; Sollins, Cromack, et al. 1981). Elevations of these watersheds range from about 430 m to 670 m, with an average slope of 25°. Soils are gravelly silty clay loam Typic Disrochrepts, formed in andesitic tuffs and breccias. Annual precipitation is concentrated in fall through spring, and averages 2500 mm/yr with mean air temperatures of 8°C. Streamwater chemistry was analyzed for Watershed #9 from 1968 through 1998, with data provided by D. Henshaw, USDA Forest Service. The information presented here is a modified version and not the original data or documentation distributed by the Andrews Long-Term Ecological Research group. The Andrews LTER is not liable for damages resulting from any use or misinterpretation of data sets. Data sets were provided by the Forest Science Data Bank, a partnership between the Department of Forest Science, Oregon State University, and the USDA Forest Service Pacific Northwest Research Station, Corvallis, Oregon. Significant funding for these data was provided by the National Science Foundation Long-Term Ecological Research Program (NSF Grant number BSR-90-11663 and DEB-96-32921).

1.1 Patterns in Streamwater Nitrate Concentrations

Concentrations of nitrate averaged 0.003 mg N/L, with a median near detection limits of 0.001 mg N/L (Figure B1.1). Few observations exceeded 0.01 mg N/L, and the maximum level reached was about 0.05 mg/L. Streamflow did not influence nitrate concentrations (Figure B1.2). Nitrate concentrations were lowest in mid-summer, and variability within months across years tended to be higher (with coefficients of variation of 200% or more) in months with higher average concentrations. No trend was apparent over the period of record, but a notable increase in concentrations (threefold) occurred in the mid- to late 1980s, followed by a return to very low levels.

1.2 Patterns in Streamwater Ammonium Concentrations

Concentrations of ammonium were somewhat higher than those of nitrate, with a mean of 0.005 mg N/L and a median of 0.008 mg N/L (Figure B1.3). Most observations were less than 0.02 mg N/L, and the maximum observed was 0.12 mg N/L. The relationship between streamflow and ammonium concentrations was very noisy ($r^2 = 0.01$), but ammonium concentrations did increase significantly with increasing flows (Figure B1.4). Concentrations of ammonium showed no monthly trend in either average values or variability, and no trend was apparent over the period of record.

1.3 Patterns in Streamwater Concentrations of Dissolved Organic Nitrogen

Concentrations of dissolved organic nitrogen (DON) rivaled those of inorganic forms, with a mean of 0.043 mg N/L, and a median of 0.036 mg N/L (Figure B1.5). Concentrations of DON declines slightly ($P = 0.05$) with increasing streamflow (Figure B1.6). Autumn and early winter showed about

50% higher concentrations than late winter through spring. Concentrations of DON declined significantly, by about 0.0008 mg N/L annually, from 1976 through 1998.

1.4 Patterns in Streamwater Concentrations of Particulate Nitrogen

Particulate nitrogen concentrations were also similar to those of DON and inorganic N, averaging 0.025 mg N/L with a median of 0.015 mg N/L (Figure B1.7). Concentrations of particulate N showed no relationship with streamflow. No seasonal pattern was evident in means or variations, but some months averaged more than twice the level of other months (Figure B1.8). Concentrations differed by up to threefold among years, but no trend was evident over time.

1.5 Patterns in Streamwater Concentrations of Inorganic Phosphate

Concentrations of phosphate averaged 20 µg P/L, very close to the median value of 18 µg P/L (Figure B1.9). Most observations fell below 25 µg P/L, with a maximum concentration of 50 µg P/L (Figure B1.10). Phosphate concentrations did not relate to streamflow and seasonal variation was very slight, with all months averaging between 18 and 21 µg P/L. Summer months appeared to be more variable across years (coefficients of variation >40%) than in winter (coefficients of variation 30%). Concentrations of phosphate appeared to decline over the years ($r^2 = 0.09$), but the trend was not significant ($P = 0.14$; data are missing for the mid 1980s).

1.6 Patterns in Streamwater Concentrations of Dissolved Organic Phosphate

Concentrations of dissolved organic phosphate (DOP) were similar to those of inorganic phosphate, averaging 23 g P/L with a median of 14 µg P/L (Figure B1.11). Most observations were less than 25 µg P/L, with maximum values reaching up to 100 µg P/L. Concentrations of DOP declined significantly ($P < 0.01$) with increasing stremflow (Figure B1.12), but the trend was weak ($r^2 = 0.03$). Peak concentrations (and highest variation) occurred in summertime, with values about 30% higher than in winter. Concentrations declined significantly over the period of record, dropping from about 25 µg P/L in the late 1970s to 10 to 15 µg P/L in the 1990s (a decline of about 0.6 µg P/L annually).

1.7 Patterns in Streamwater Concentrations of Particulate Phosphate

Particulate P concentrations were about half those of inorganic phosphate or DOP, averaging 9 µg P/L, with a median of 5 µg P/L (Figure B1.13). Most observations were below 20 µg P/L, with a single maximum value of 200 µg P/L. Particulate phosphate showed no relationship with streamflow, and no clear seasonal pattern (Figure B1.14). Concentrations in winter were most variable across years, with coefficients of variation exceeding 200% compared with 100% for the summer months. Over the period of record, concentrations of particulate phosphate also declined; concentrations declined from about 15 µg P/L in the late 1970s to 5 µg P/L in the 1990s (annual decline of 0.5 µg P/L).

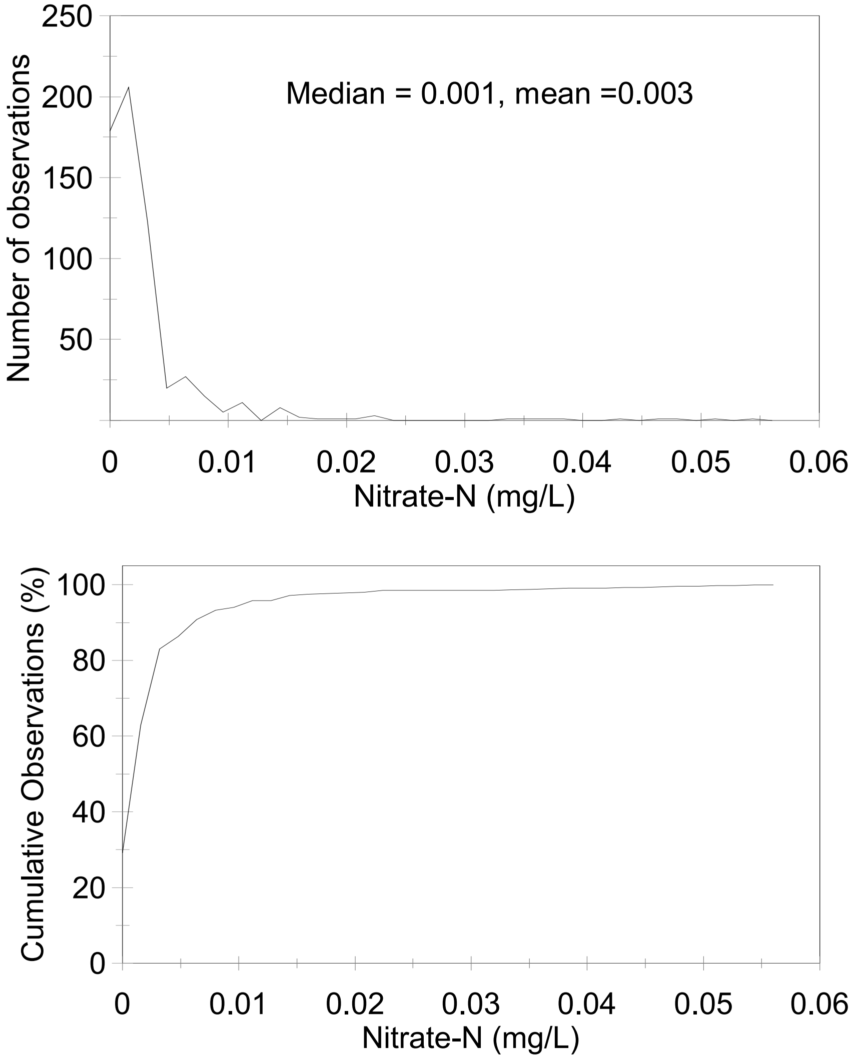


Figure B1.1. Frequency Distributions for Streamwater Nitrate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon

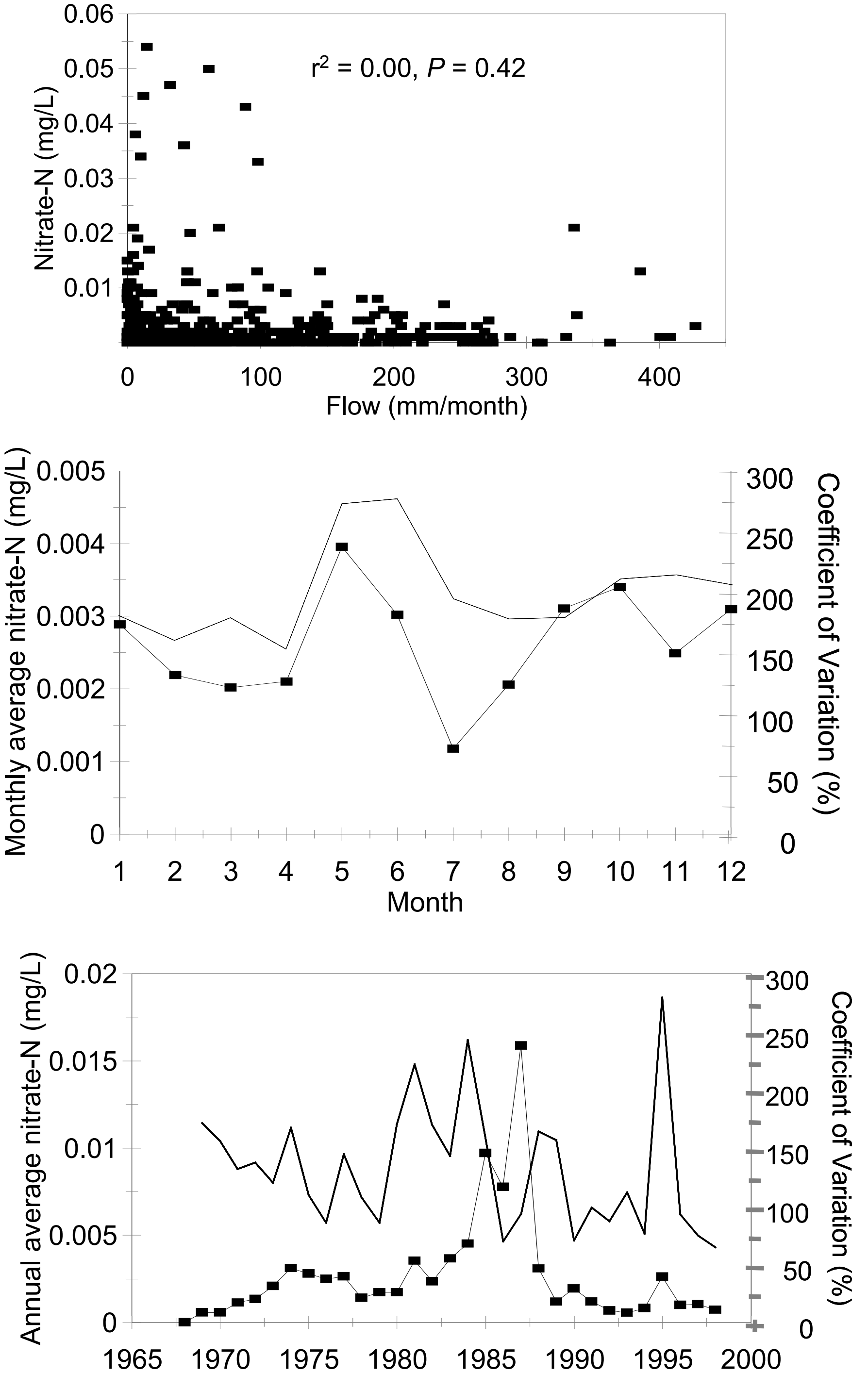


Figure B1.2. Variations in Nitrate Concentrations of Nitrate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon; lines with squares are nitrate concentrations, other lines are coefficients of variation

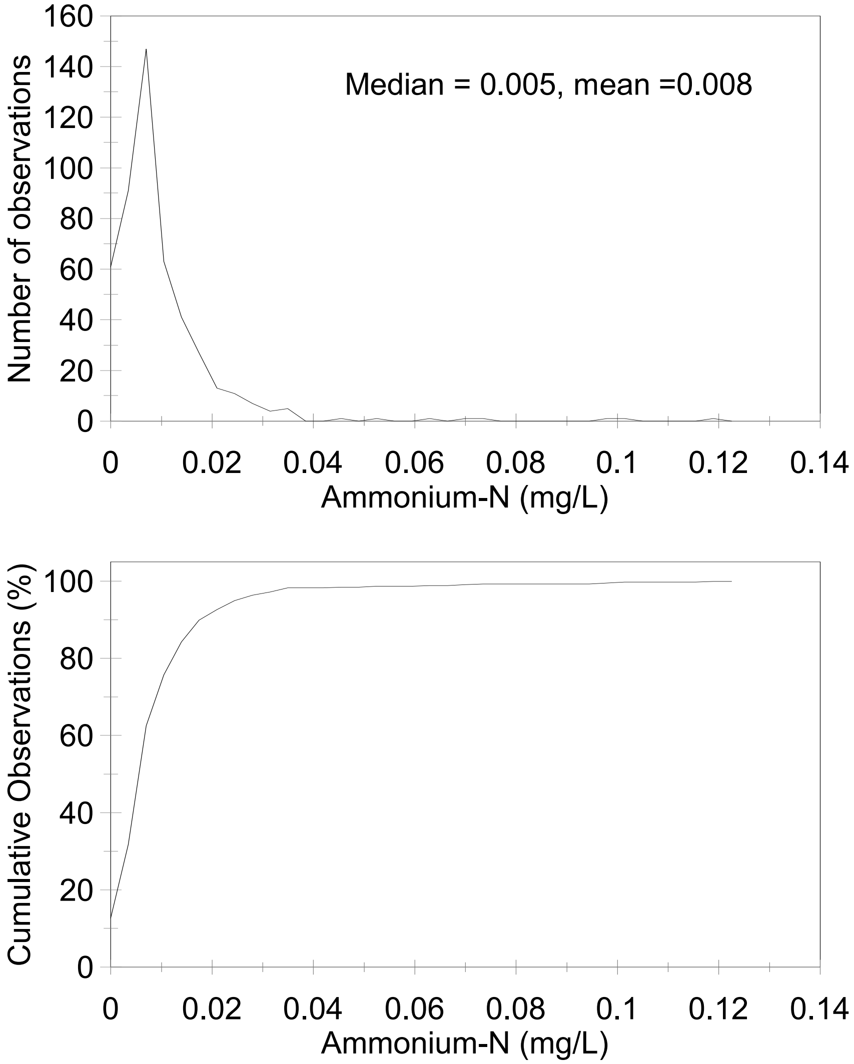


Figure B1.3. Frequency Distributions for Streamwater Ammonium in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon

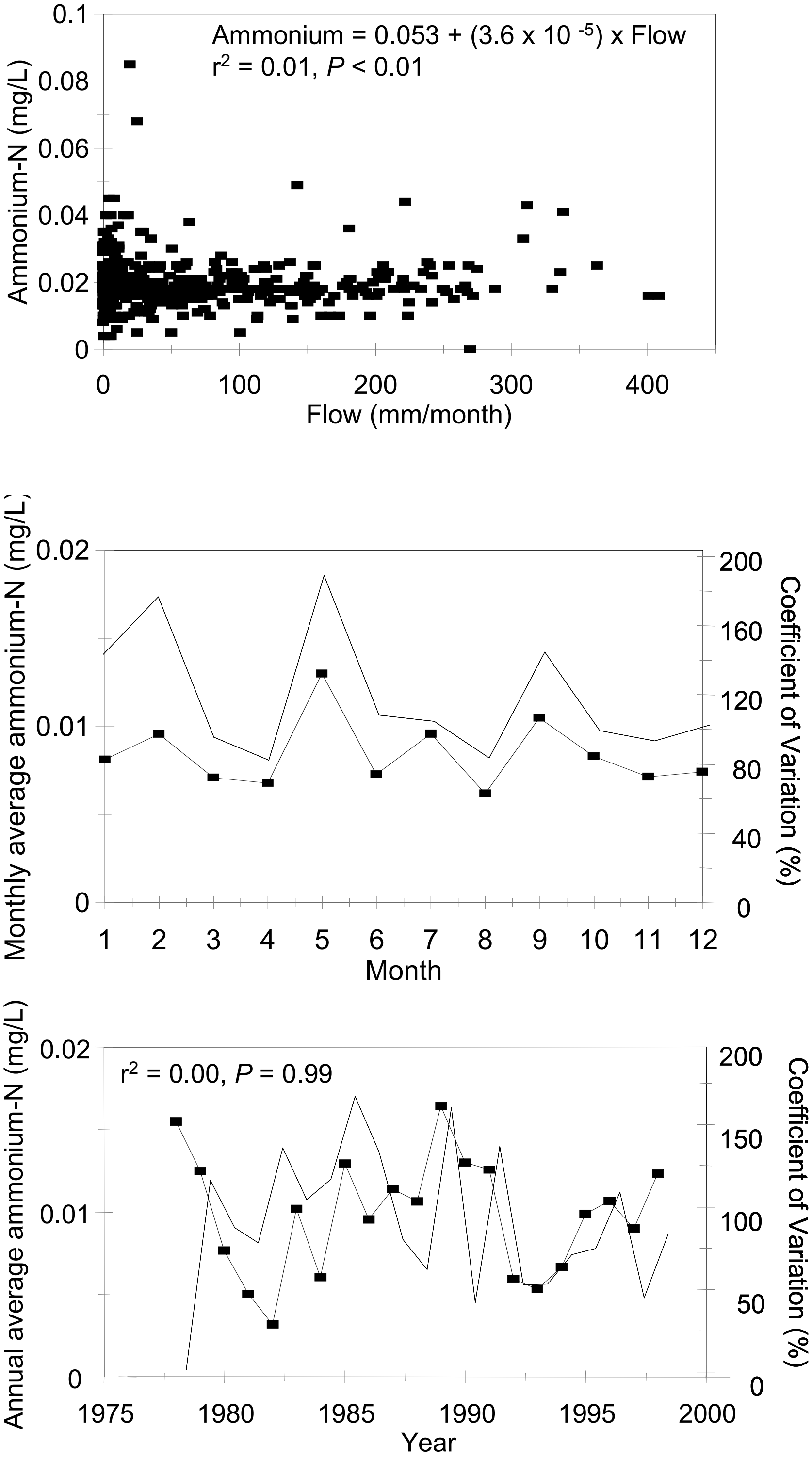


Figure B1.4. Variations in Concentrations of Ammonium in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon; lines with squares are ammonium concentrations, other lines are coefficients of variation

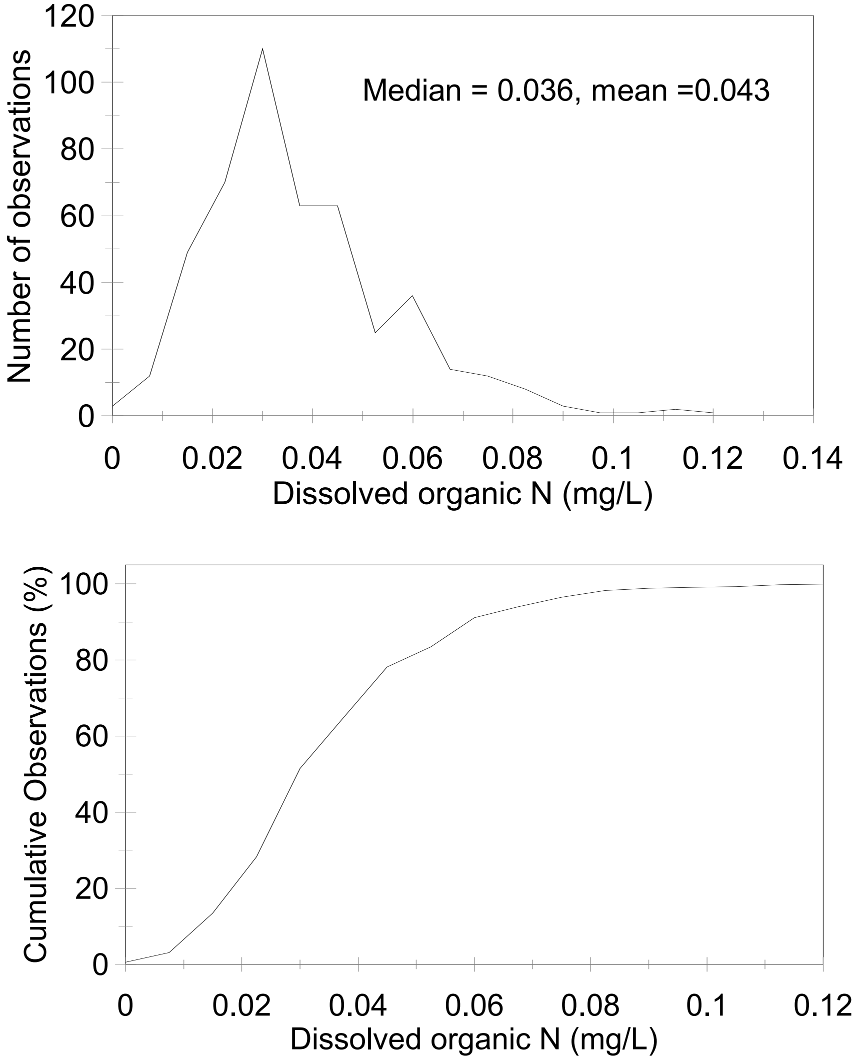


Figure B1.5. Frequency Distribution for Streamwater Dissolved Organic Nitrogen in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon

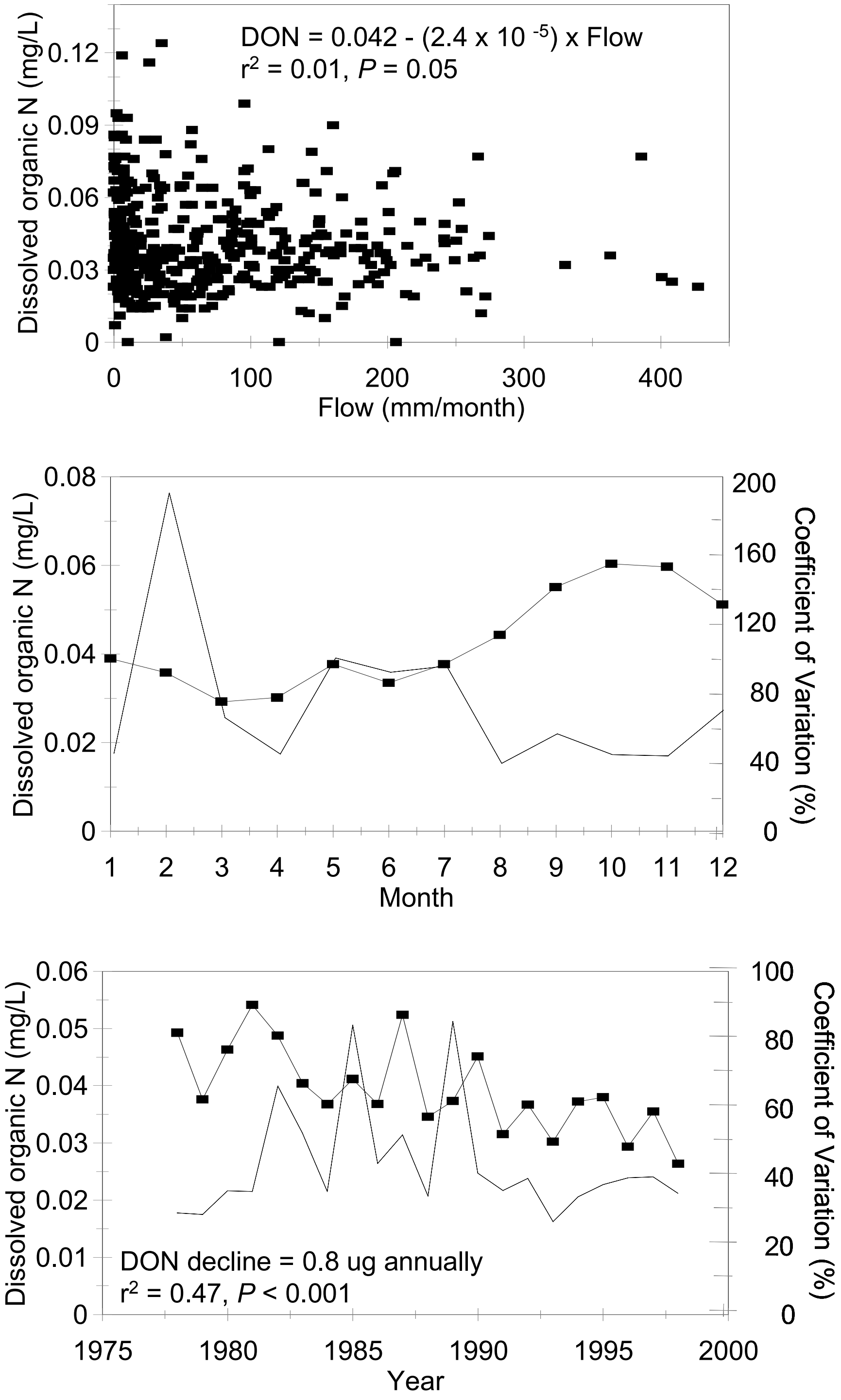


Figure B1.6. Variations in Concentrations of Ammonium in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon; lines with squares are nitrogen concentrations, other lines are coefficients of variation

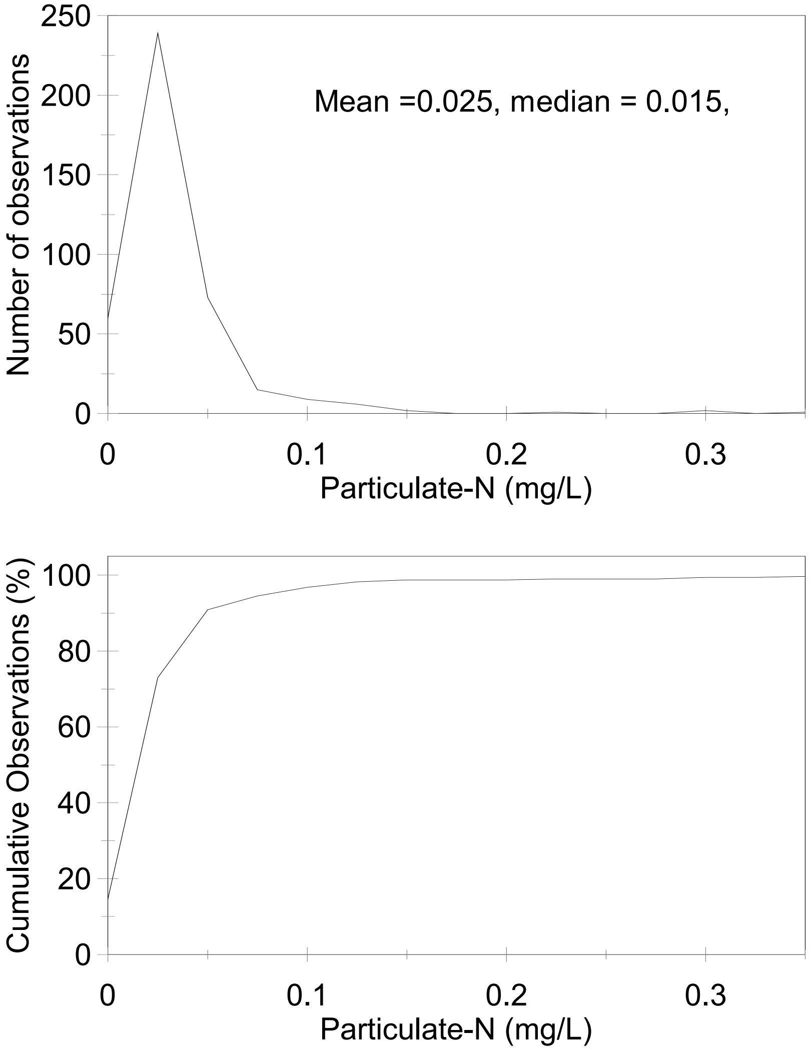


Figure B1.7. Frequency Distributions for Streamwater Particulate Nitrogen in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon

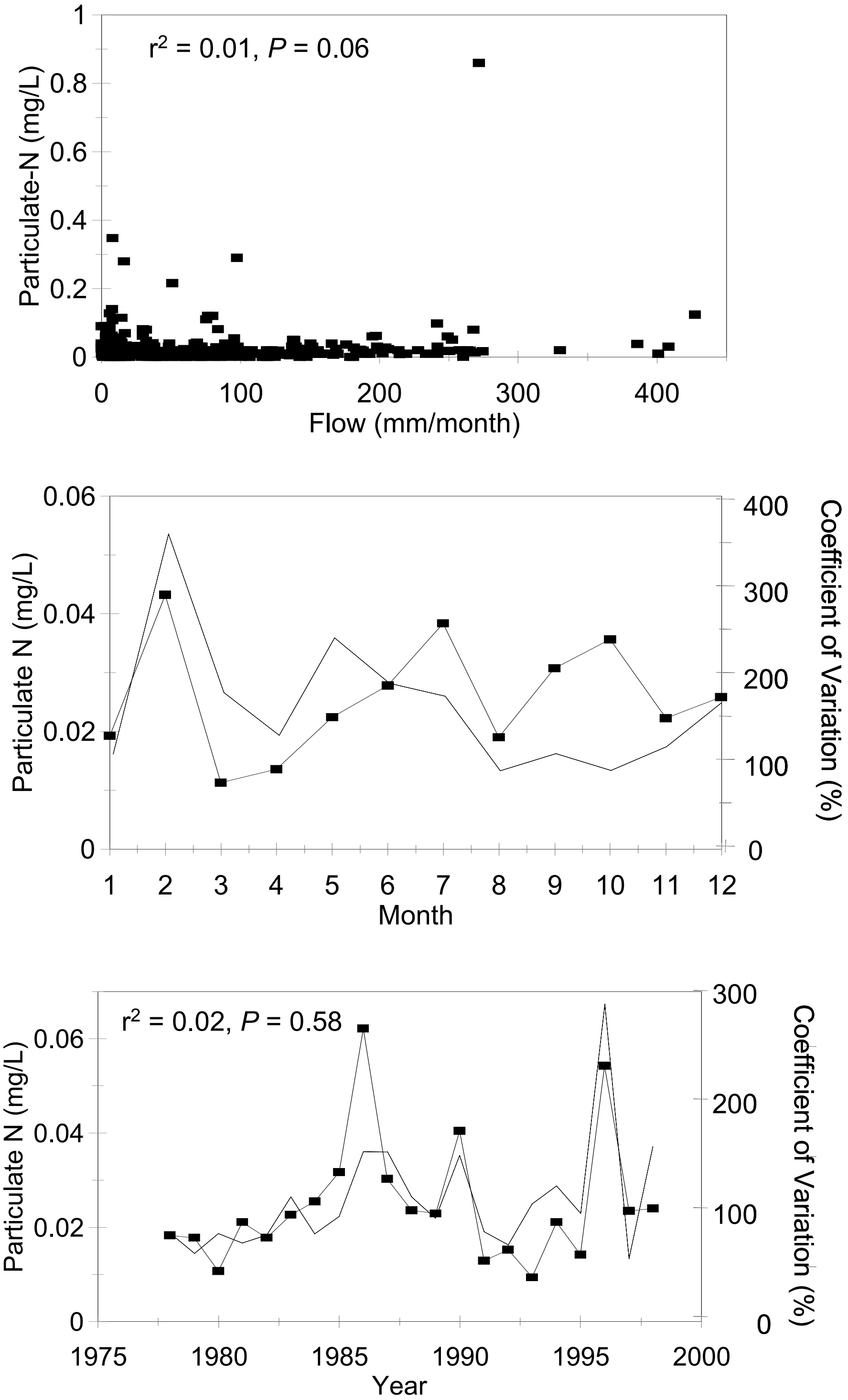


Figure B1.8. Variations in Concentrations of Particulate Nitrogen in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon; lines with squares are nitrogen concentrations, other lines are coefficients of variation

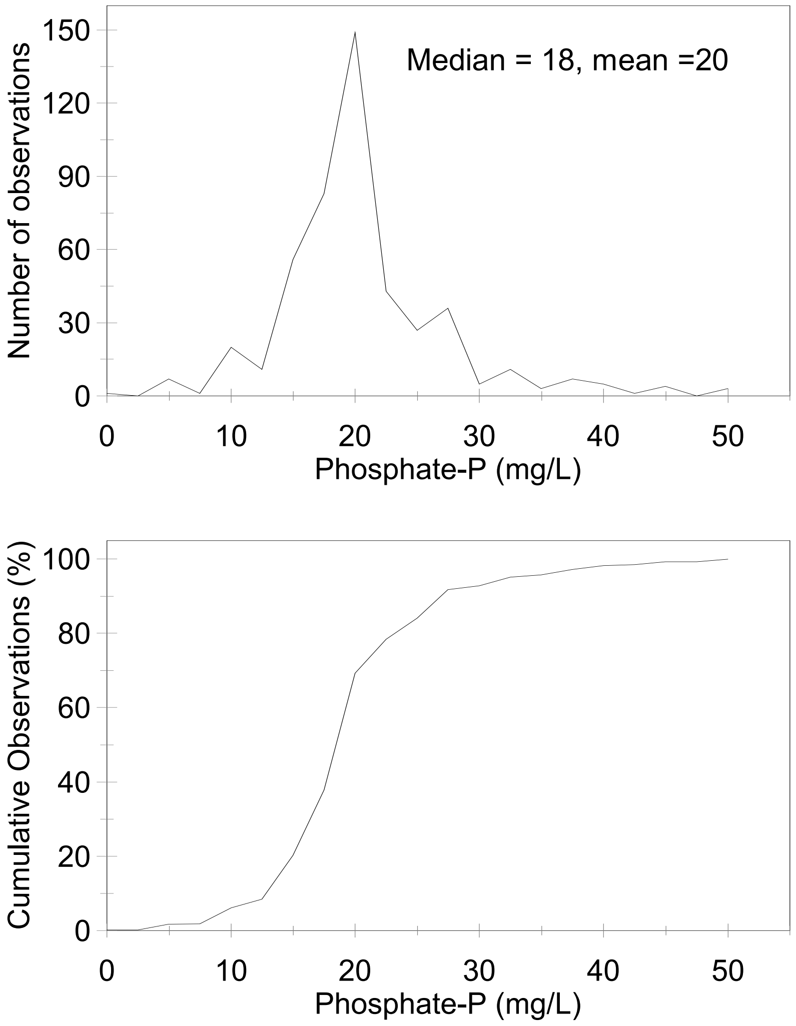


Figure B1.9. Frequency Distributions for Streamwater Inorganic Phosphate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon

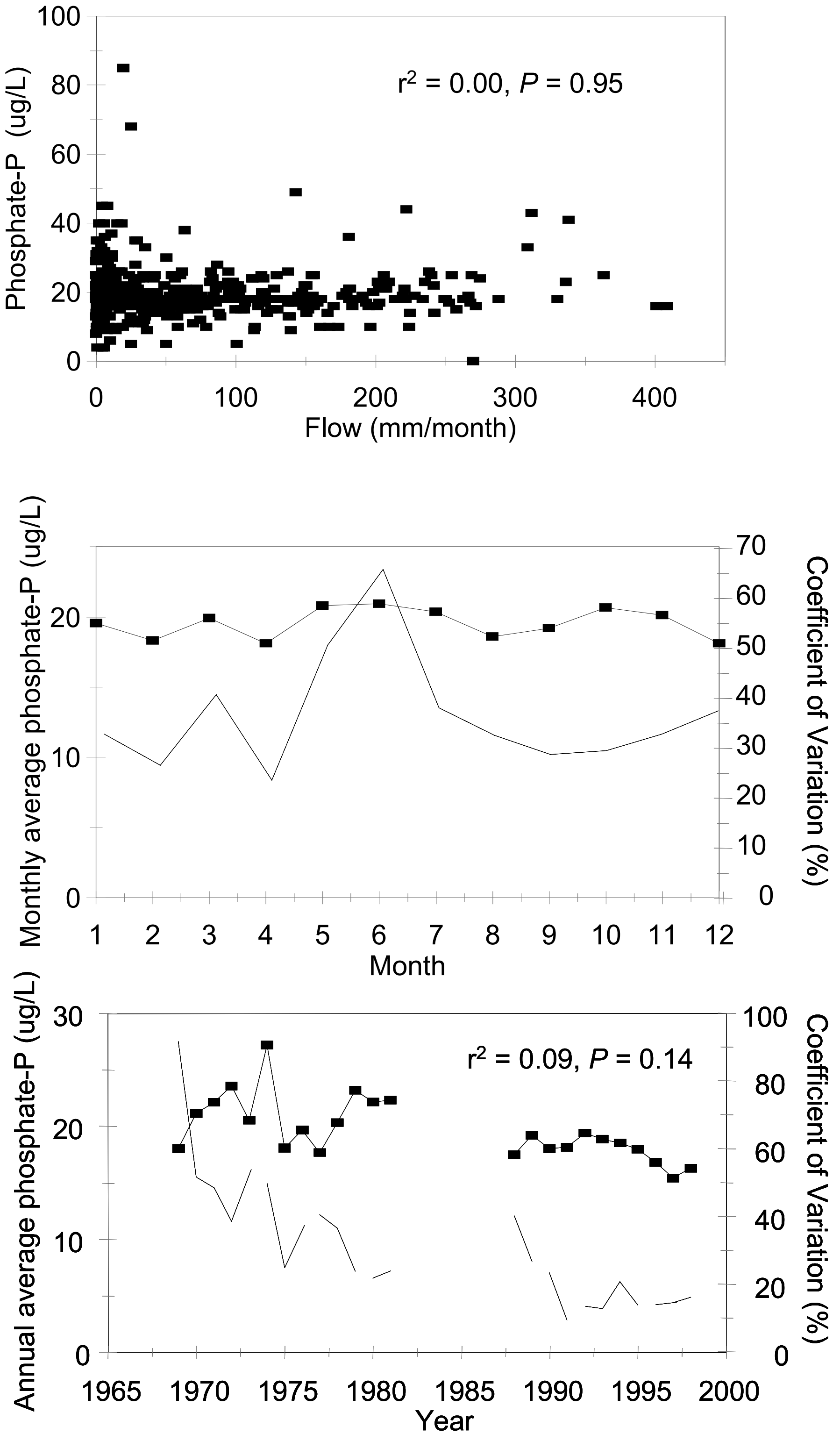


Figure B1.10. Variations in Concentrations of Inorganic Phosphate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon; lines with squares are nitrogen concentrations, other lines are coefficients of variation

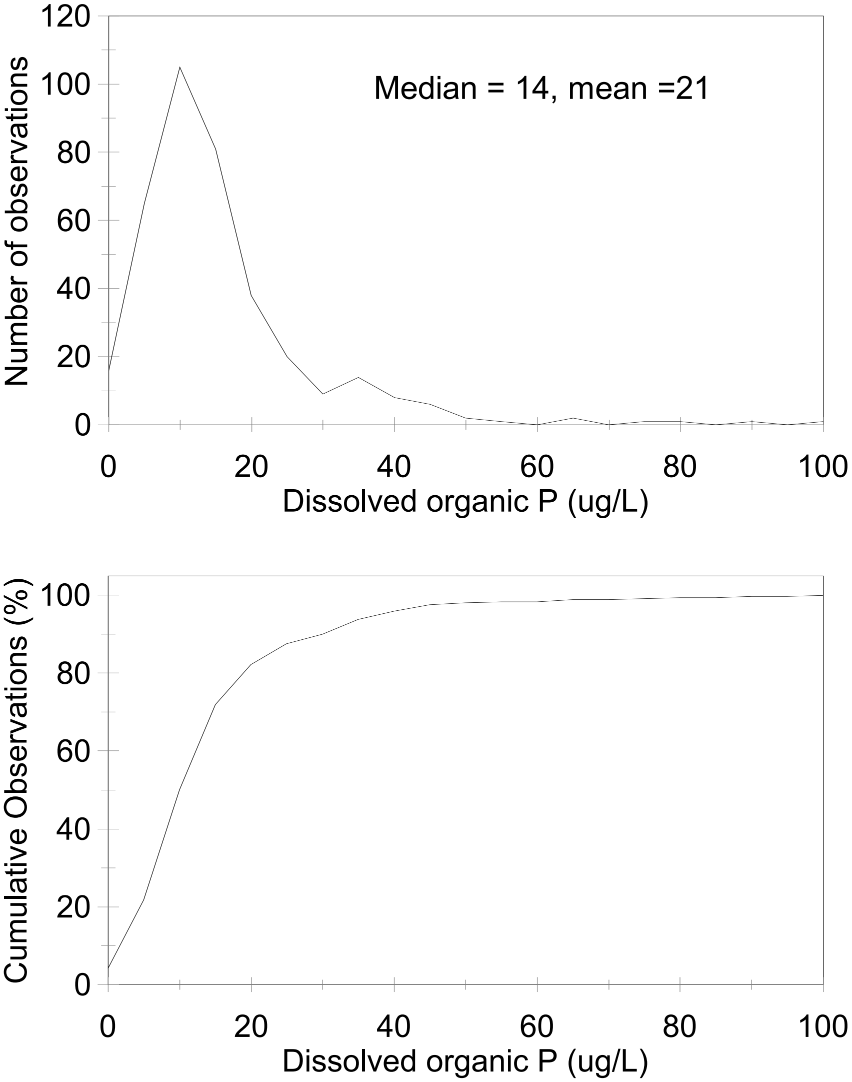


Figure B1.11. Frequency Distributions for Streamwater Dissolved Organic Phosphate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon

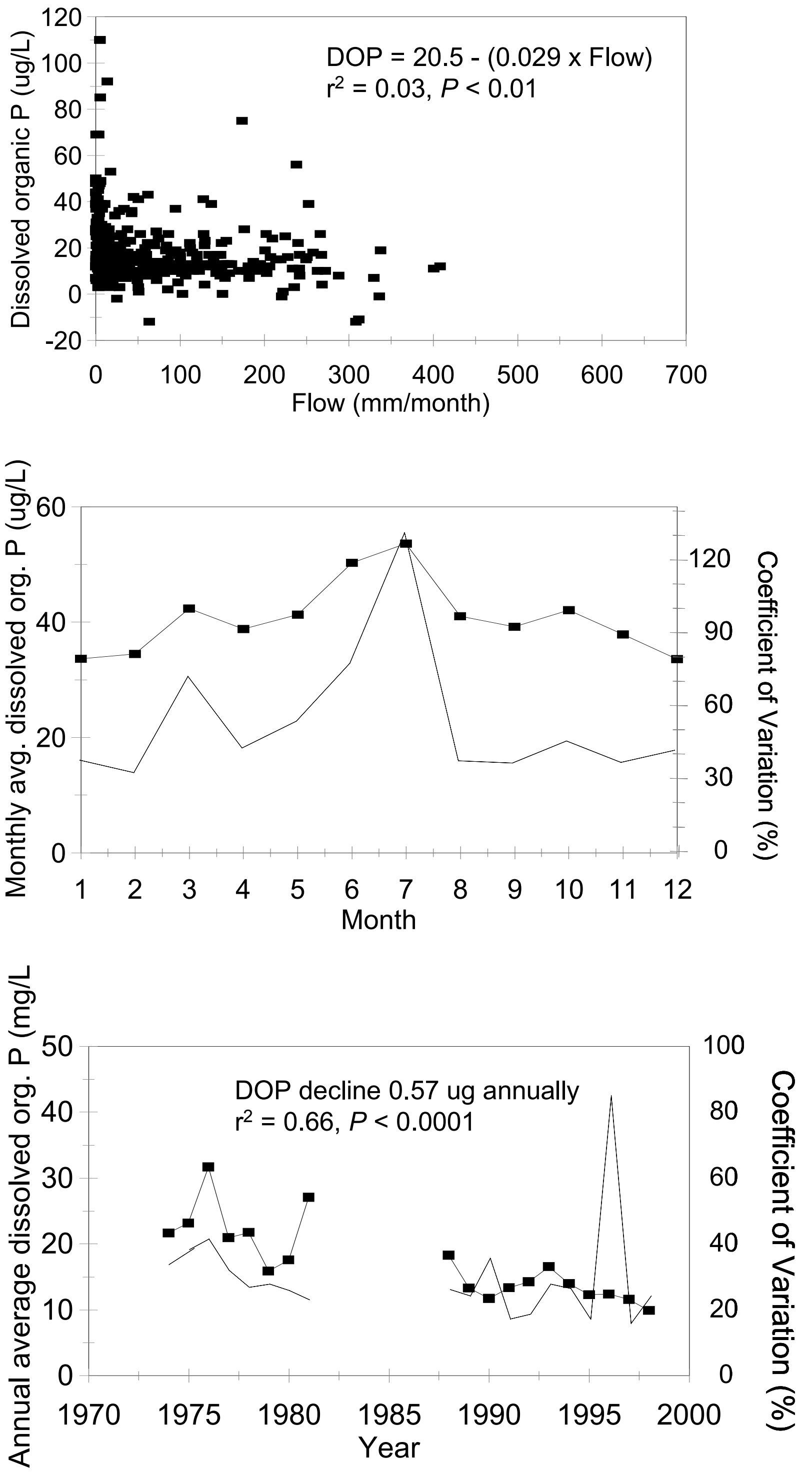


Figure B1.12. Variations in Concentrations of Dissolved Organic Phosphate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon; lines with squares are nitrogen concentrations, other lines are coefficients of variation

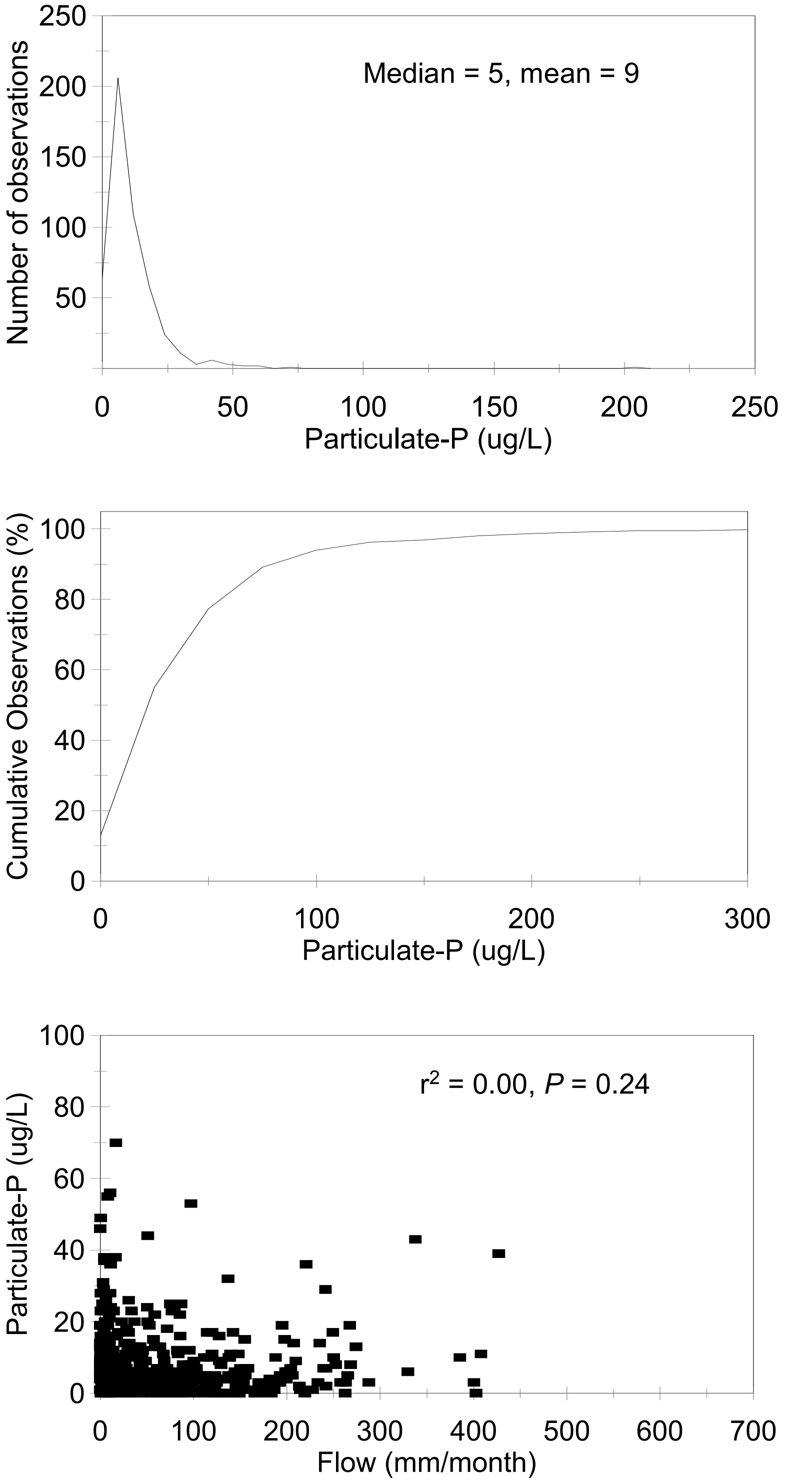


Figure B1.13. Frequency Distributions for Streamwater Particulate Phosphate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon

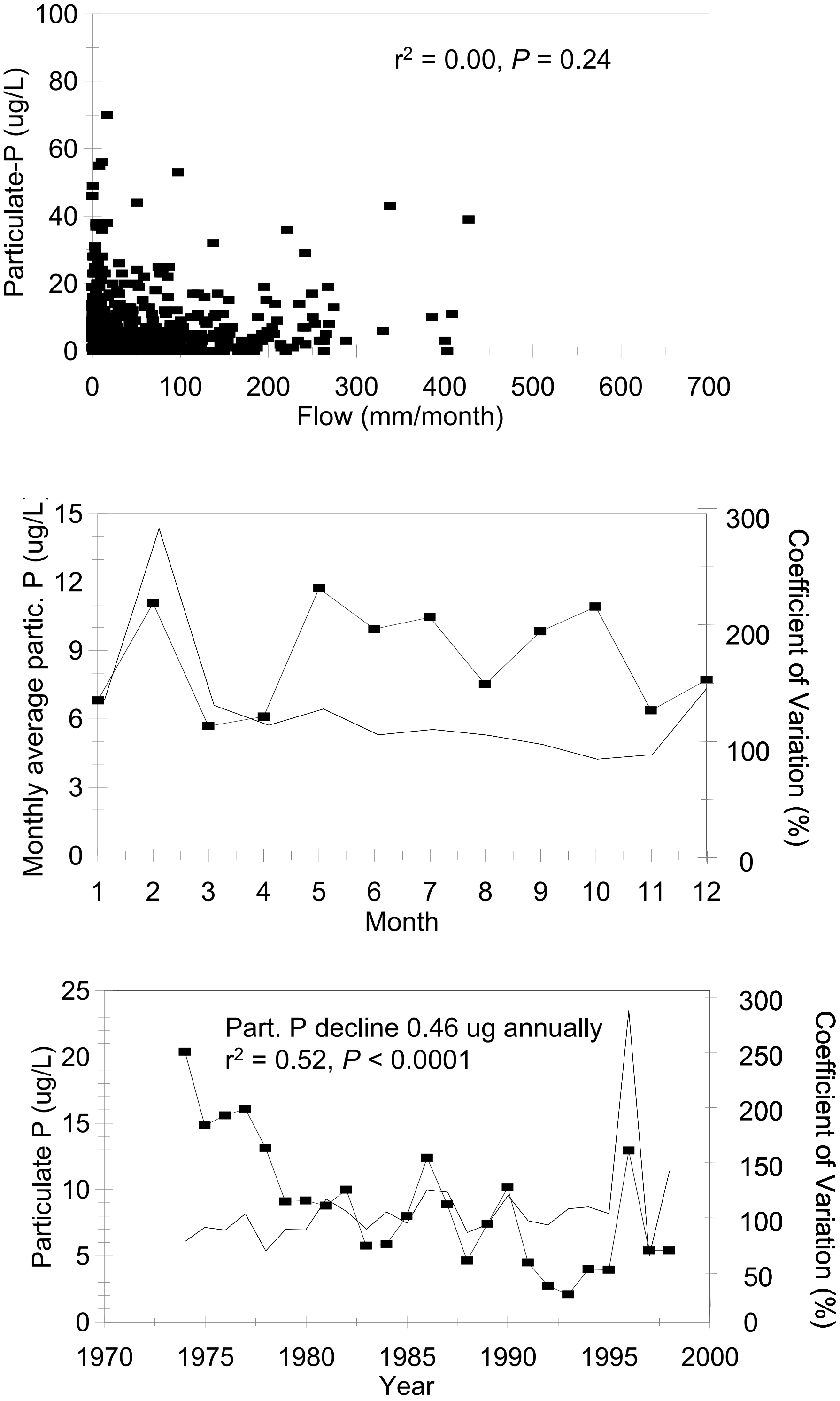


Figure B1.14. Variations in Concentrations of Particulate Phosphate in Watershed 9 at the H.J. Andrews Experimental Forest, Oregon; lines with squares are nitrogen concentrations, other lines are coefficients of variation

2.0 FRASER EXPERIMENTAL FOREST, COLORADO

The Fraser Experimental Forest was established by the USDA Forest Service in 1937 (Stottlemyer and Troendle 1987). The Forest is about 140 km west of Denver, Colorado, and includes subalpine and alpine ecosystems on gneiss and shist bedrocks, with some overlying sandstone at the upper elevations (Stottlemyer, Troendle, and Markowitz 1997; Stottlemyer and Troendle 1999). Lexen Creek is an east-facing, 124 ha watershed that drains into West St. Louis Creek. The top of the watershed is the 3515 m summit of Bottle Mountain, and the stream gauging station is at 2984 m. The soils of the Lexen Creek watershed are gravelly sandy loam lnceptisols. The lower and mid-elevation portions of the watershed are dominated by old-growth (>200-yr) forests of lodgepole pine (*Pinus contorta* Dougi.), and upper elevations by mixed forests of Engelmann spruce (*Picea engelmannii* Parry ex Engelm.) and subalpine fir (*Abies lasiocarpa* (Hook.) Nutt.). The mean annual temperature for the watershed is near 0°C, ranging from -11°C in December to 10°C in July. Precipitation averages about 600 mm/yr, increasing about 20% per 300 m rise in elevation. The peak snowpack averages about 400 mm of water content, and hydrology is dominated by snowmelt, which passes primarily through subsurface flow to the stream. Stream flow typically peaks between 50 and 200 L/sec. Patterns in streamwater chemistry in original data provided by R. Stottlemyer (USGS Biological Resources Division) were analyzed for the period of June 1982 to June 1998. Major funding for these investigations came from the Rocky Mountain Research Station, USDA Forest Service, Ft. Collins, Colorado.

2.1 Patterns in Streamwater Nitrate Concentrations

Nitrate concentrations averaged 0.016 mg N/L from 1982 through 1998 (Figure B2.1), with a median value of <0.001 mg N/L (detection limit). Almost 60% of the observations fell below detection limits, and all observations were below 0.08 mg N/L. Concentrations of nitrate decreased exponentially as flow increased (Figure B2.2), and were lower during the growing season months. This diverges somewhat from the pattern reported previously by Stottlemyer and Troendle (1992) for two nearby streams at the Fraser Experimental forest. They closely monitored changes in nitrate concentrations in 1987 and 1988 in relation to streamflow, and concluded that there was no association. The variation for individual months across years was highest in summer, where the coefficient of variation for nitrate concentrations in July reached 500% for the 16 year period. Average annual concentrations of nitrate showed no trend over time, and the coefficient of variation among months within years varied from a low of about 100% for 1986 to a high of 270% in 1997.

2.2 Patterns in Streamwater Ammonium Concentrations

Ammonium concentrations averaged 0.001 mg N/L, with the median falling below detection limits (Figure B2.3). About 90% of the observations were less than 0.05 mg N/L, and the maximum observed concentrations were <0.15 mg N/L. Concentrations of ammonium tended to decline with increasing streamflow (Figure B2.4), but the trend was weak ($P < 0.06$) and accounted for little of the variation among observations ($r^2 = 0.01$); this lack of relationship was mirrored in the 1987 and 1988 data summarized by Stottlemyer and Troendle (1992). Variations in average concentrations across months were relatively small, with no pronounced seasonality. Late autumn months showed the highest coefficient of variation across years. Ammonium concentrations varied substantially across years (with no trend over time), ranging from near 0 mg N/L in 1995 to 0.05 mg N/L in 1982 and 1992. The highest variations among months within years also occurred in 1995, when the annual average concentration was the lowest. No trend in ammonium concentrations was apparent across the years.

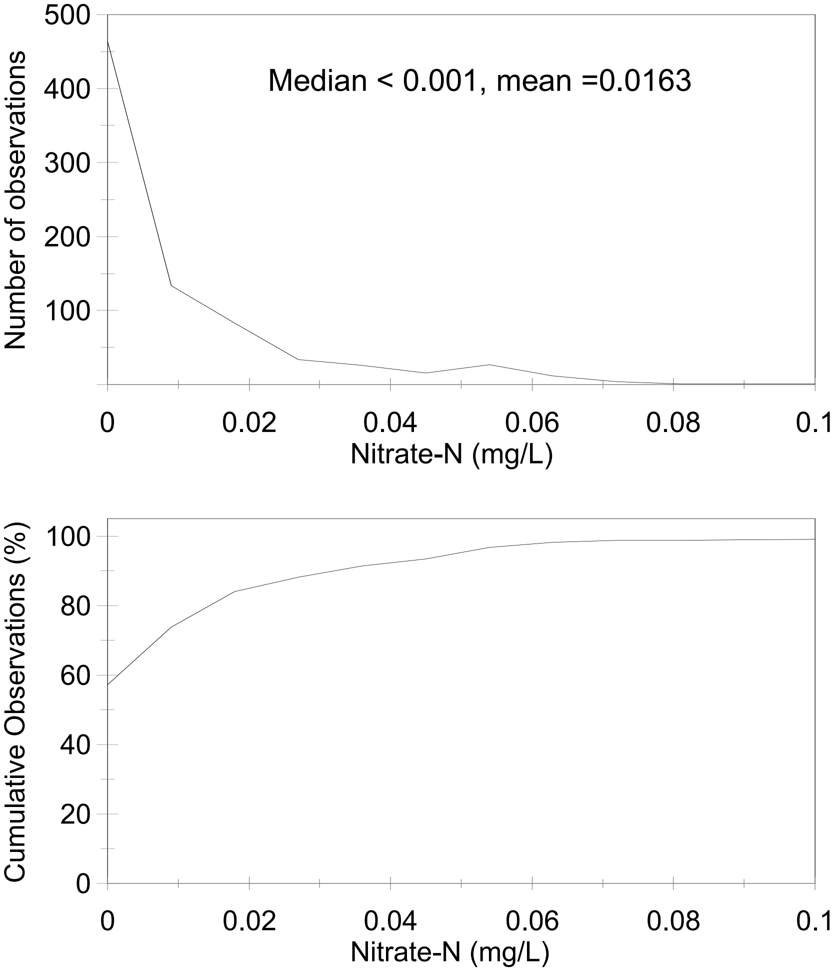


Figure B2.1. Frequency Distributions for Streamwater Nitrate for Lexen Creek, Fraser Experimental Forest, Colorado

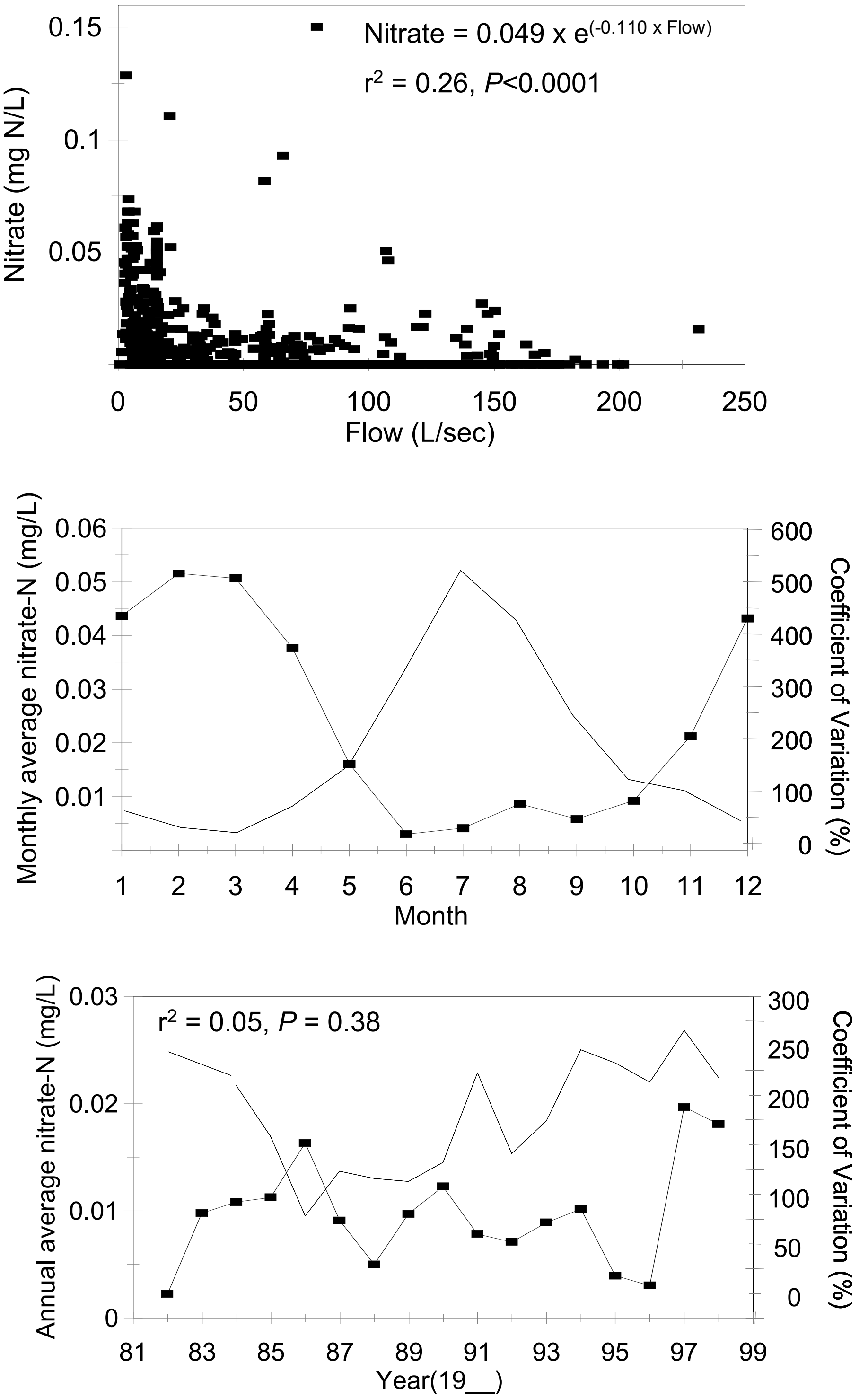


Figure B2.2. Variations in Concentrations of Nitrate in Lexen Creek, Fraser Experimental Forest, Colorado; lines with squares are nitrate concentrations, other lines are coefficients of variation

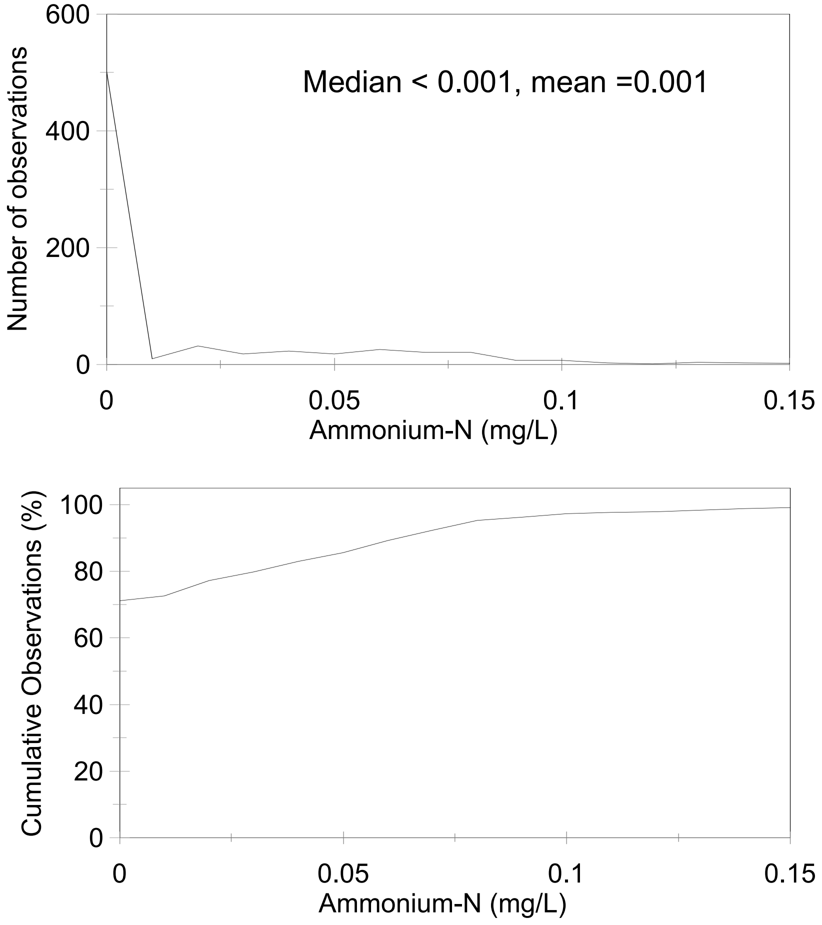


Figure B2.3. Frequency Distributions for Streamwater Ammonium for Lexen Creek, Fraser Experimental Forest, Colorado

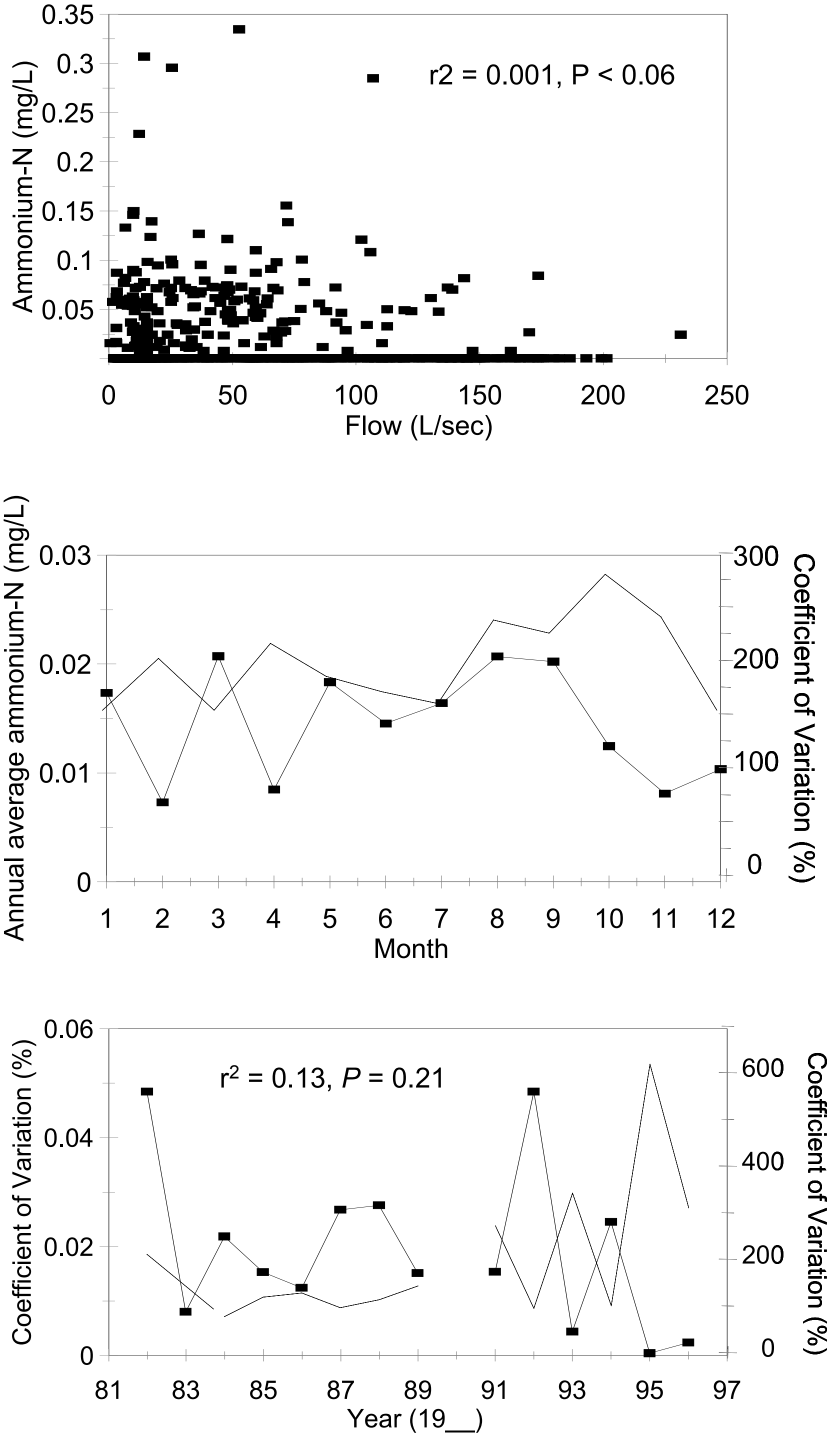


Figure B2.4. Variations in Concentrations of Ammonium in Lexen Creek, Fraser Experimental Forest, Colorado; lines with squares are ammonium concentrations, other lines are coefficients of variation

3.0 BEAVER CREEK WATERSHED, ARIZONA

A series of experiments was initiated along the Mogollon Rim in Central Arizona in the late 1950s and early 1960s to examine changes in water yield when ecosystems dominated by trees and shrubs were converted into grasslands. Deforestation was advocated as a means to increase water yield in the Salt and Verde River systems, and the USDA Forest Service and the University of Arizona examined the relationships between the density of trees and shrubs and water yield and other resources (Baker 1999). Watershed #13 was a control, untreated area of 368 ha, dominated by multiple age-class stands of ponderosa pine *(Pinus ponderosa* Dougl. Ex Laws.) with a bunchgrass understory, at an elevation of about 2200 m. The soils are rocky and variable in depth, formed on basalt parent material. Precipitation averages about 600 mm/yr, with a bimodal distribution of winter snow and rain and mid-summer thunderstorms. The stream draining Watershed #13 is not perennial, and flows commonly occur only from January through May. Sampling for water quality analyses reflected the variable flows among years. Original data for this analysis were supplied for 1974 to 1981 by M. Baker, USDA Forest Service. The data used here were obtained by scientists of the Beaver Creek Watershed Project and have not been reviewed by those scientists. The Beaver Creek Experimental Watershed is operated and maintained by the Rocky Mountain Research Station, USDA Forest Service, Ft. Collins, Colorado.

3.1 Patterns in Streamwater Nitrate Concentrations

Streamwater concentrations of nitrate averaged 0.004 mg N/L, with a median of 0.001 mg N/L. Only a few observations exceeded the median, and the highest concentration recorded was less than 0.07 mg N/L (Figure B3.1). Nitrate concentrations did not relate to streamflow ($r^2 = 0.00$, $P = 0.97$), but all three of the observations that exceeded 0.02 mg N/L occurred during periods of low flow.

3.2 Patterns in Streamwater Ammonium Concentrations

Ammonium concentrations exceeded those of nitrate, averaging 0.023 mg N/L with a median of 0.020 mg N/L (Figure B3.2). Ammonium showed the same maximum concentration as nitrate, 0.07 mg N/L. No relationship existed between streamflow and ammonium concentration.

3.3 Patterns in Streamwater Concentrations of Inorganic Phosphate

Phosphate concentrations averaged 27 μg P/L, with a median of 24 μg P/L (Figure B3.3). Few observations fell below 15 μg P/L or above 25 μg P/L, giving a steep cumulative frequency diagram. Streamflow again showed no relationship with concentrations of phosphate.

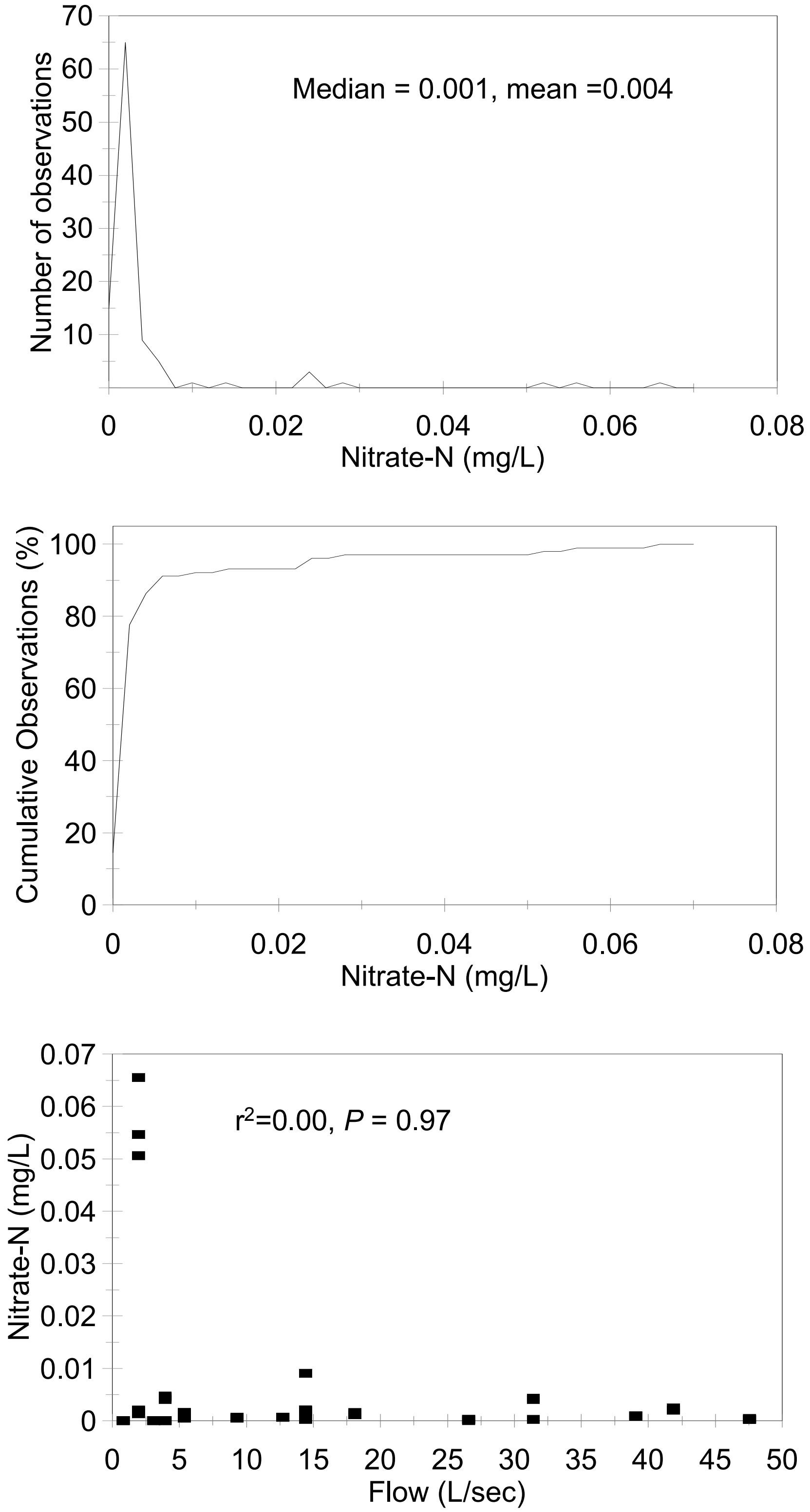


Figure B3.1. Frequency Distributions and Variation with Stream Flow for Nitrate in Beaver Creek Watershed, Arizona

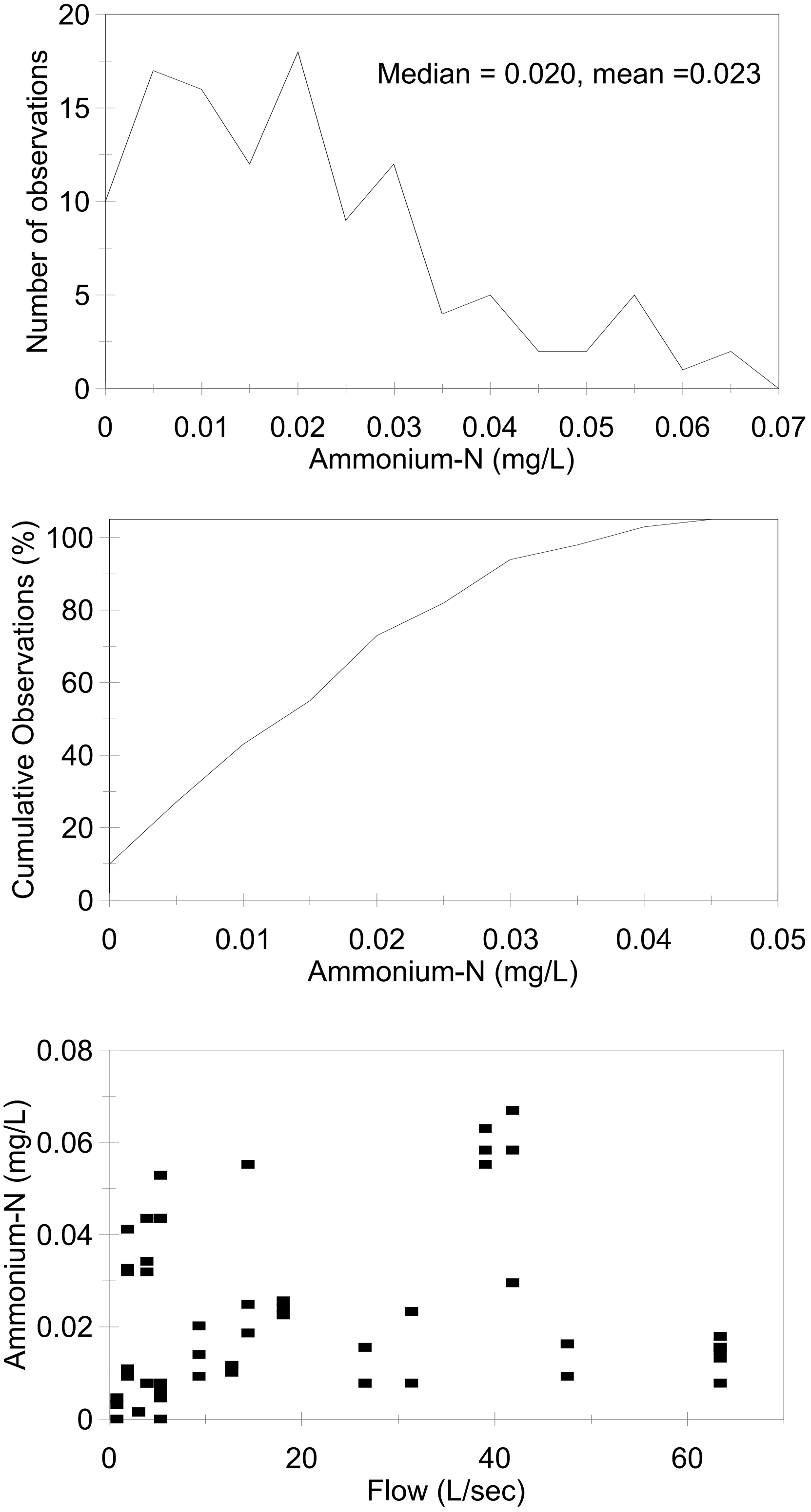


Figure B3.2. Frequency Distributions and Variation with Stream Flow for Ammonium in Beaver Creek Watershed, Arizona

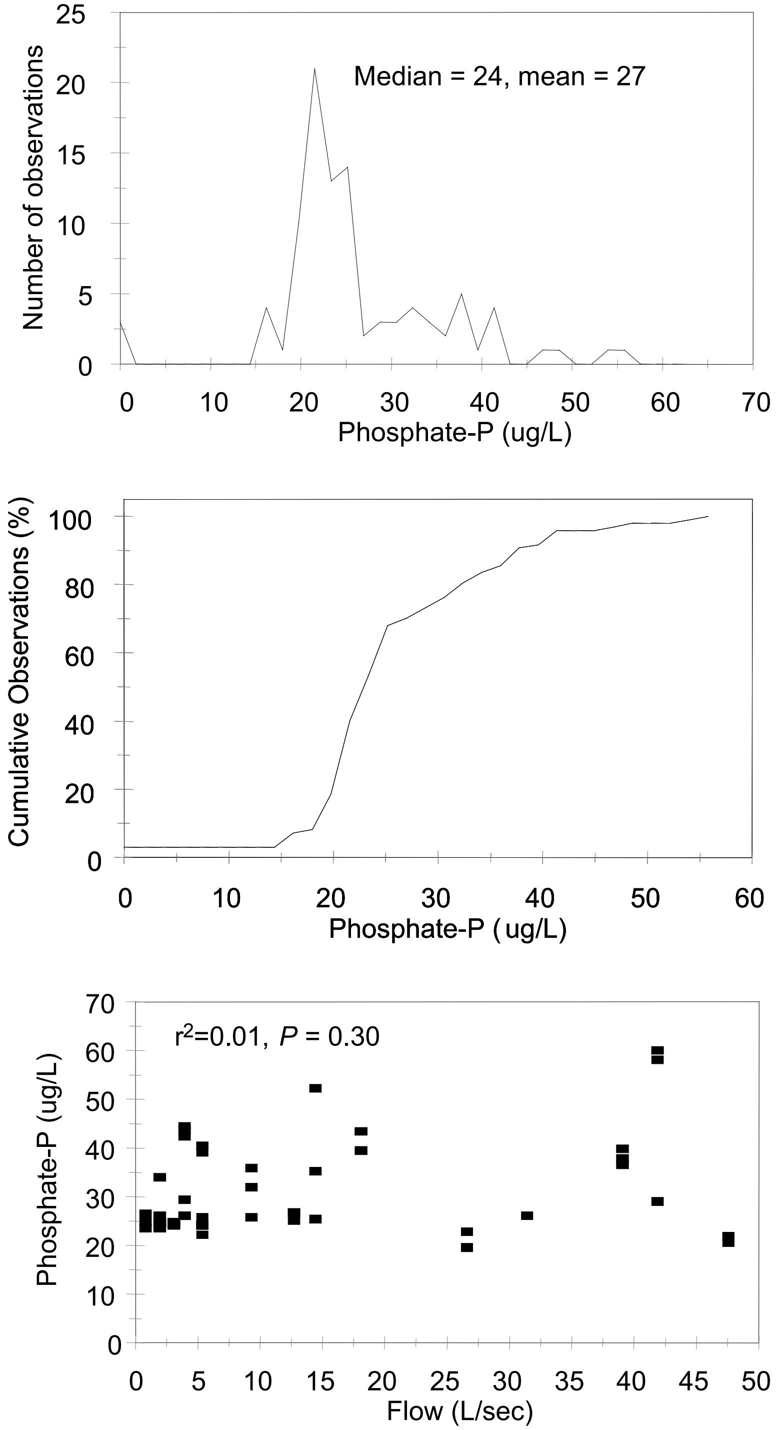


Figure B3.3. Frequency Distributions and Variation with Stream Flow for Inorganic Phosphate in Beaver Creek Watershed, Arizona

4.0 WALLACE LAKE WATERSHED, ISLE ROYALE NATIONAL PARK, MICHIGAN

The National Park Service established a watershed research program in 1982 to quantify ecosystem structure and function and to determine the responses of watersheds to atmospheric inputs and climate change (Stottlemyer, Toczydlowski, and Herrmann 1998). Isle Royale National Park was chosen as a research site because of its remote location (in Lake Superior, about 130 km north of Houghton, Michigan), minimal impact of direct human activities, and relatively high inputs of nitrogen (0.3 to 0.4 g N g m^{-2} yr^{-1}) and sulfur (0.4 g S m^{-2} yr^{-1}) in precipitation. The Wallace Lake watershed comprises 115 ha in the northeastern third of Isle Royale National Park, ranging in elevation from 195 m to 275 m. The watershed is relatively flat, with small ridges (<5 m high). Soils are sandy to mixed loamy Alfic Haplorthods, from 0.3 to 0.9 m in depth, formed in metamorphosed volcanic parent materials. Annual precipiation averages 750 mm/yr, with about 40% failing as snow. Mean monthly temperatures range from -9°C in January to 16°C in July. The four major tree species in the watershed were aspen *(Populus tremuloides* Michx.), paper birch *(Betula papyrifera* Marsh.), balsam fir *(Abies balsamea* (L.) Mill.), and white spruce *(Picea glauca* (Moench.) Voss). About 10% of the watershed burned in 1936, and the rest of the forest was at least 125 years old. Wallace Lake is about 5 ha in size, and streamwater chemistry was sampled by R. Stottlemyer and colleages above and below the lake. The original data presented here were supplied by R. Stottlemyer, USGS Biological Resources Division, and are from the outlet of the watershed below the lake from June 1982 through 1996. Major funding for these investigations came from the USDI National Park Service's Watershed Research Program and the USGS Biological Resources Division.

4.1 Patterns in Streamwater Nitrate Concentrations

Nitrate concentrations averaged 0.07 mg N/L, with a median of 0.04 mg N/L and a maximum of less than 6 mg N/L (Figure B4.1). Concentrations did not relate to streamflow (P = 0.19), but showed a clear peak in April with peak flows after snowmelt (Figure B4.2). The coefficient of variation within individual months across the years tended to be high (>120%) in late fall when nitrate concentrations were low, and low (<60%) in winter when nitrate concentrations were moderate to high. No trend in annual average concentrations was found over the period of the monitoring, but concentrations commonly differed by twofold between years. Nitrate concentrations where the stream entered Wallace Lake were about 50% higher than in the stream exiting the lake.

4.2 Patterns in Streamwater Ammonium Concentrations

Ammonium concentrations in the Wallace Lake Watershed were very low, averaging less than 0.04 mg N/L, with a median below detection limits of 0.001 (Figure B4.3). Ammonium showed no trend with streamflow, although peak ammonium concentrations tended to occur in April at the time of peak streamflow (Figure B4.4). Coefficients of variation were high (>200%) during the periods of low ammonium concentration in late summer and early fall, but lower (<100%) for the winter and spring. Ammonium concentrations showed no trend over the years of record, but twofold differences among years were common. Some years showed very small variation among months, such as the early 1990s where the coefficient of variation among months within each year were less than 75%. Other years showed great variations among months, such as the late 1980s with coefficients of variation of >200%.

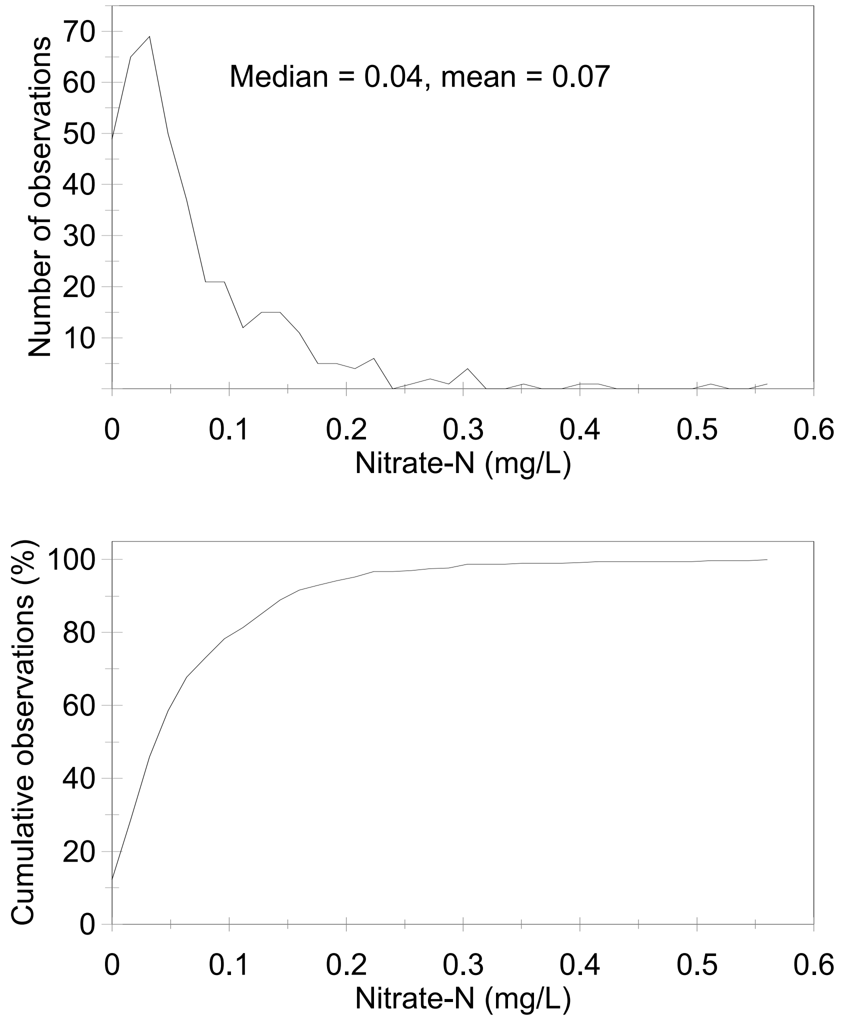


Figure B4.1. Frequency Distributions for Streamwater Nitrate for WallaceLake Watershed, Isle Royale National Park, Michigan

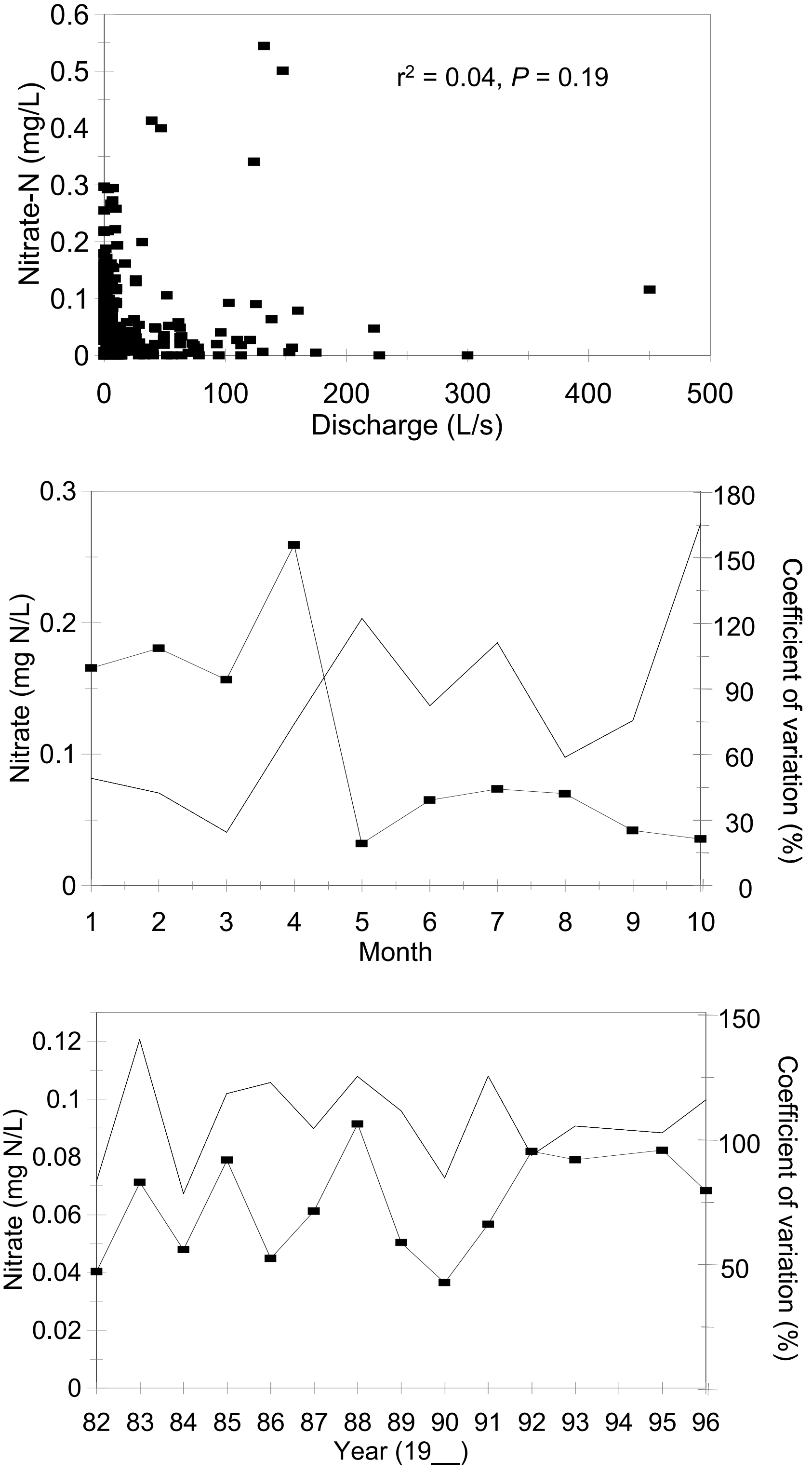


Figure B4.2. Variations Concentrations of Nitrate for WallaceLake Watershed, Isle Royale National Park, Michigan; lines with squares are nitrate concentrations, other lines are coefficients of variation

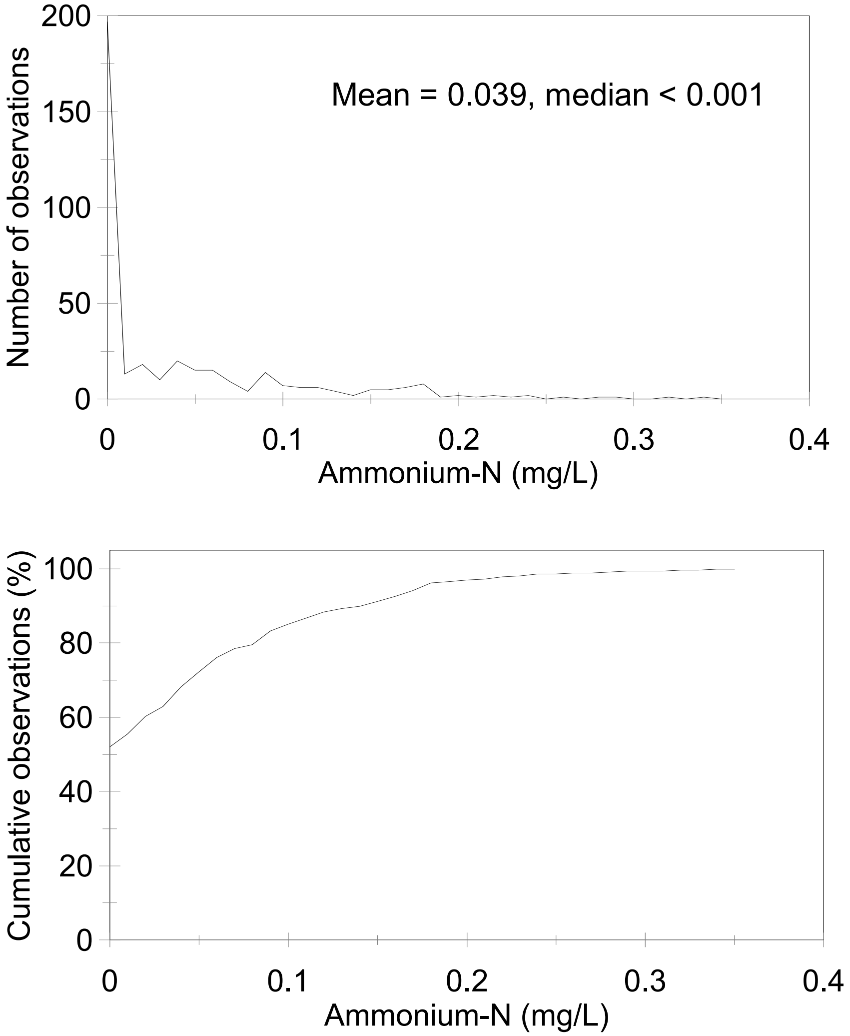


Figure B4.3. Frequency Distributions for Streamwater Ammonium for WallaceLake Watershed, Isle Royale National Park, Michigan

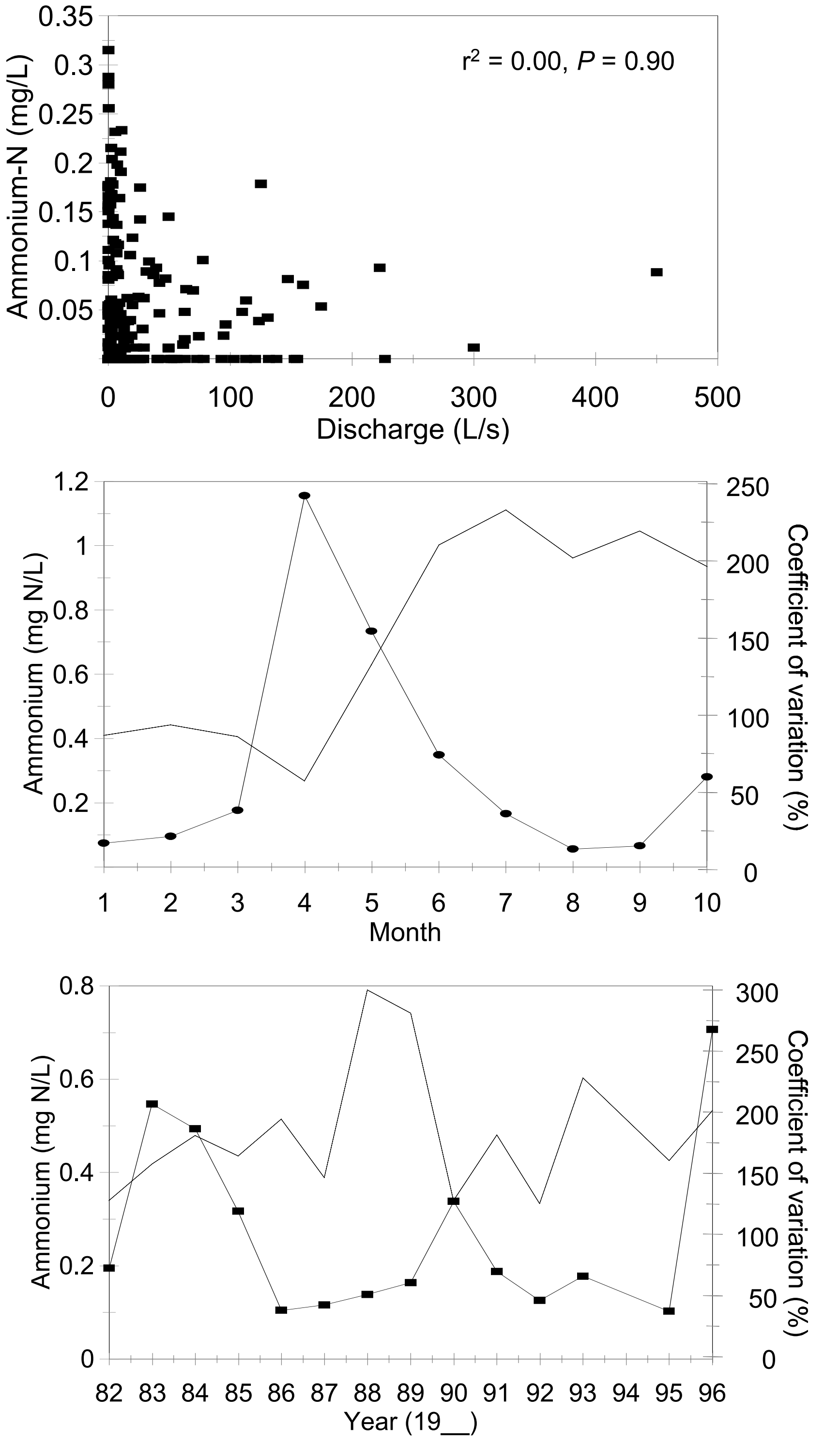


Figure B4.4. Variations in Ammonium Concentrations of Nitrate for Wallace Lake Watershed, Isle Royale National Park, Michigan; lines with squares are ammonium concentrations, other lines are coefficients of variation

5.0 CALUMET WATERSHED, MICHIGAN

The Calumet Watershed is adjacent to Lake Superior at the north end of the lower peninsula of Michigan (Stottlemyer and Toczydlowski 1996, 1999). The 176 ha watershed has a northwesterly aspect with moderate topographic relief. The soils are 1.5 to 2.0 m deep (underlain by an ortstein layer and bedrock of metamorphosed voicanics), classified as Typic Haplorthods. The upper end of the watershed has an elevation of 385 m, and the lower end reaches the shoreline of Lake Superior at 183 m. Precipitation averages about 800 mm/yr, with streamflow of about 300 mm/yr. Lake Superior does not freeze in winter, keeping the soils warmer than more inland sites. About one-third of the snowpack melts throughout the winter, unlike inland areas where snowmelt occurs only in the spring. The vegetation is dominated by 60 to 80 year old sugar maple *(Acer saccharum* Marsh.) and paper birch *(Betula papyrifera)*. The original data used here were provided for the period of June 1983 through 1996 by R. Stottlemyer, USGS Biological Resources Division. Major funding for these investigations came from the USDI National Park Service's Watershed Research Program and the USGS Biological Resources Division.

5.1 Patterns in Streamwater Nitrate Concentrations

Nitrate concentrations averaged 0.09 mg N/L, with median values of 0.08 mg N/L (Figure B5.1). The highest observed concentration was about 0.5 mg N/L. Streamflow had no significant influence on nitrate concentrations (P = 0.83) (Figure B5.2). Concentrations of nitrate were several-fold greater in October than in other months, corresponding with dry weather. The winter months were most variable across years in nitrate concentrations, with coefficients of variation of more than 500%. No trend in nitrate concentrations was apparent across years, and coefficients of variations across the months within years ranged from 50% to 150% with no trend over the years.

5.2 Patterns in Streamwater Ammonium Concentrations

Ammonium concentrations were substantially lower than nitrate concentrations for the Calumet Watershed, averaging 0.025 mg N/L with a median below detection limits of 0.001 mg N/L (Figure B5.3). A few observations were as high as 0.2 mg N/L. Ammonium concentrations showed a weak decline with increasing streamflow ($P = 0.09$) (Figure B5.4) and a trend toward higher values from January through to December. The coefficient of variation for months across the years tended to be low during the late summer and early autumn (about 200%), and higher and more variable at other times (250% to 350%). No trend in ammonium concentration was apparent over the 13 year period, but the values jumped by an order of magnitude from year to year.

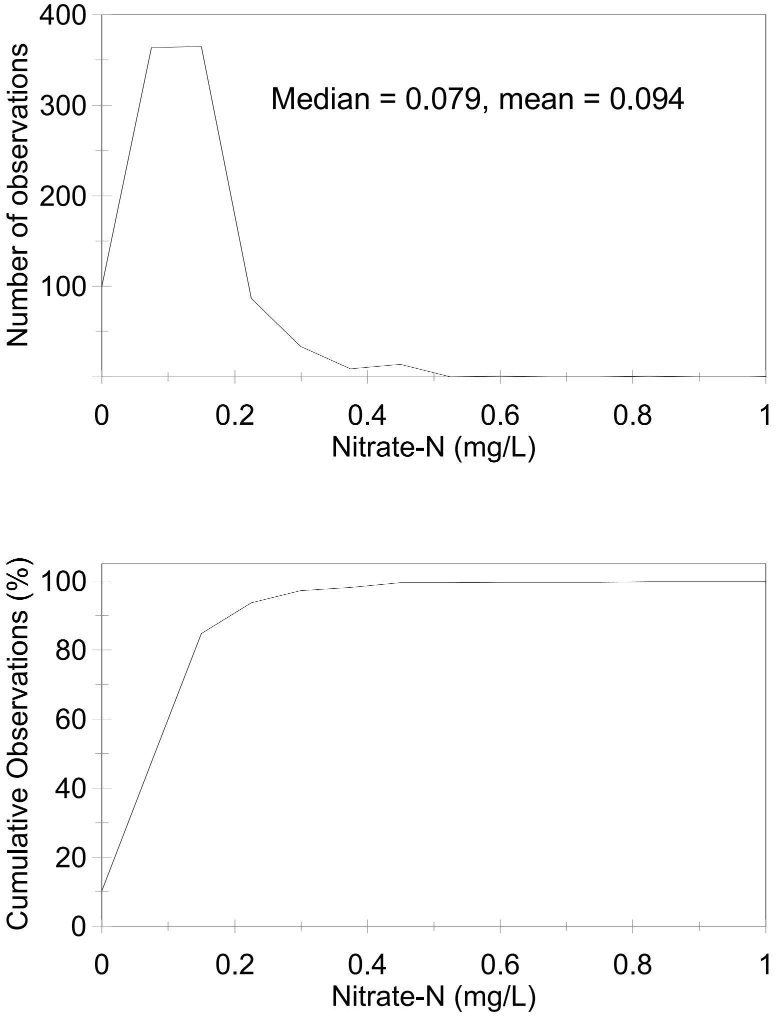


Figure B5.1. Frequency Distributions for Streamwater Nitrate for Station 319, Calumet Watershed, Michigan

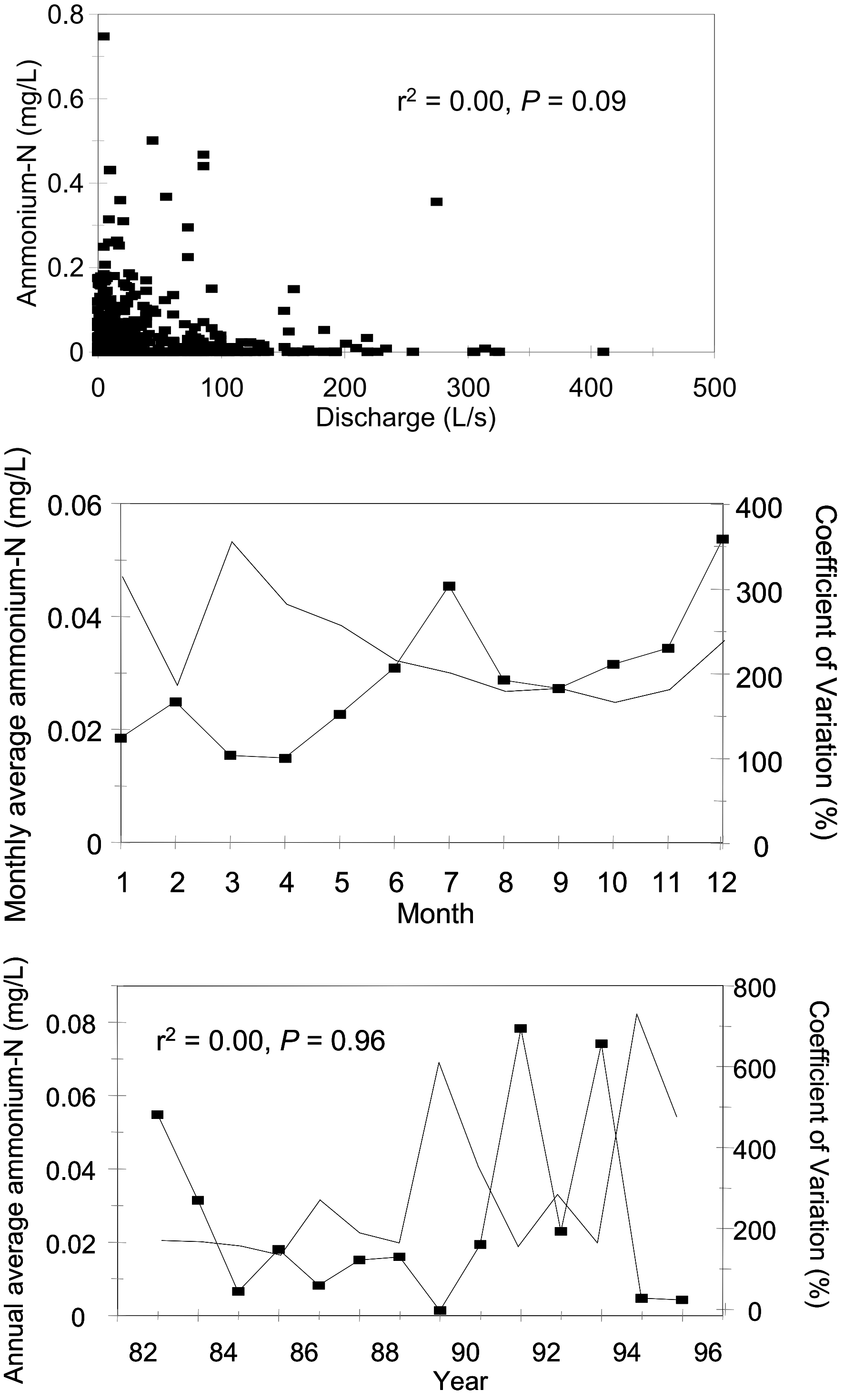


Figure B5.2. Variations in Nitrate Concentrations at Station 319, Calumet Watershed, Michigan; lines with squares are nitrate concentrations, other lines are coefficients of variation

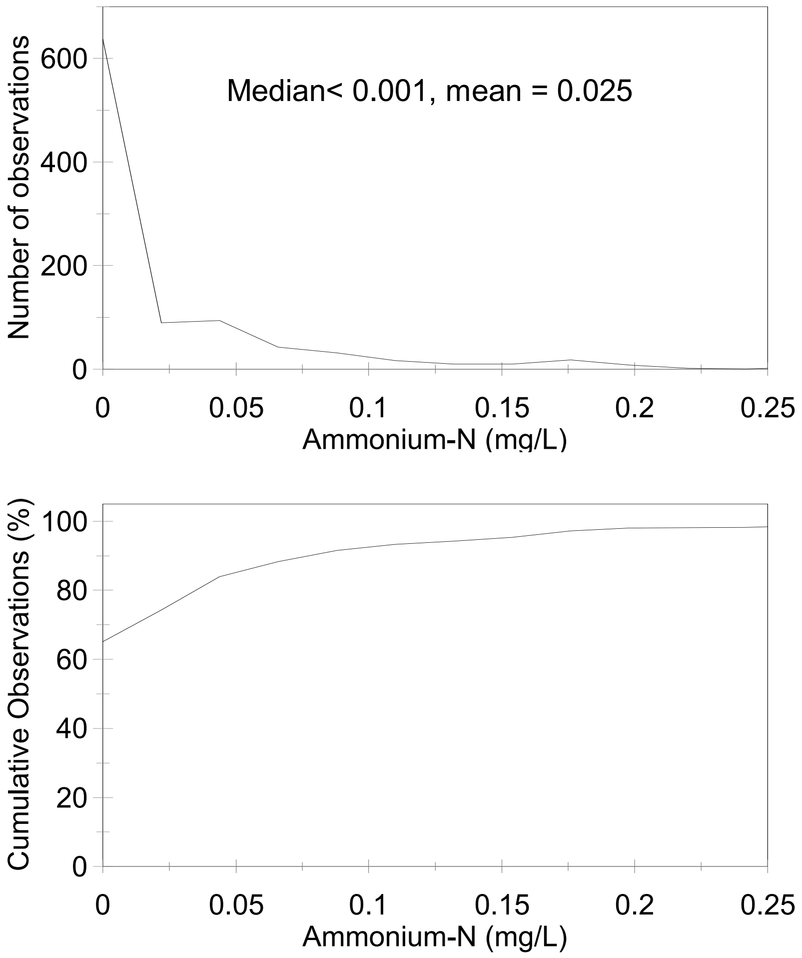


Figure B5.3. Frequency Distribution for Streamwater Ammonium for Station 319, Calumet Watershed, Michigan

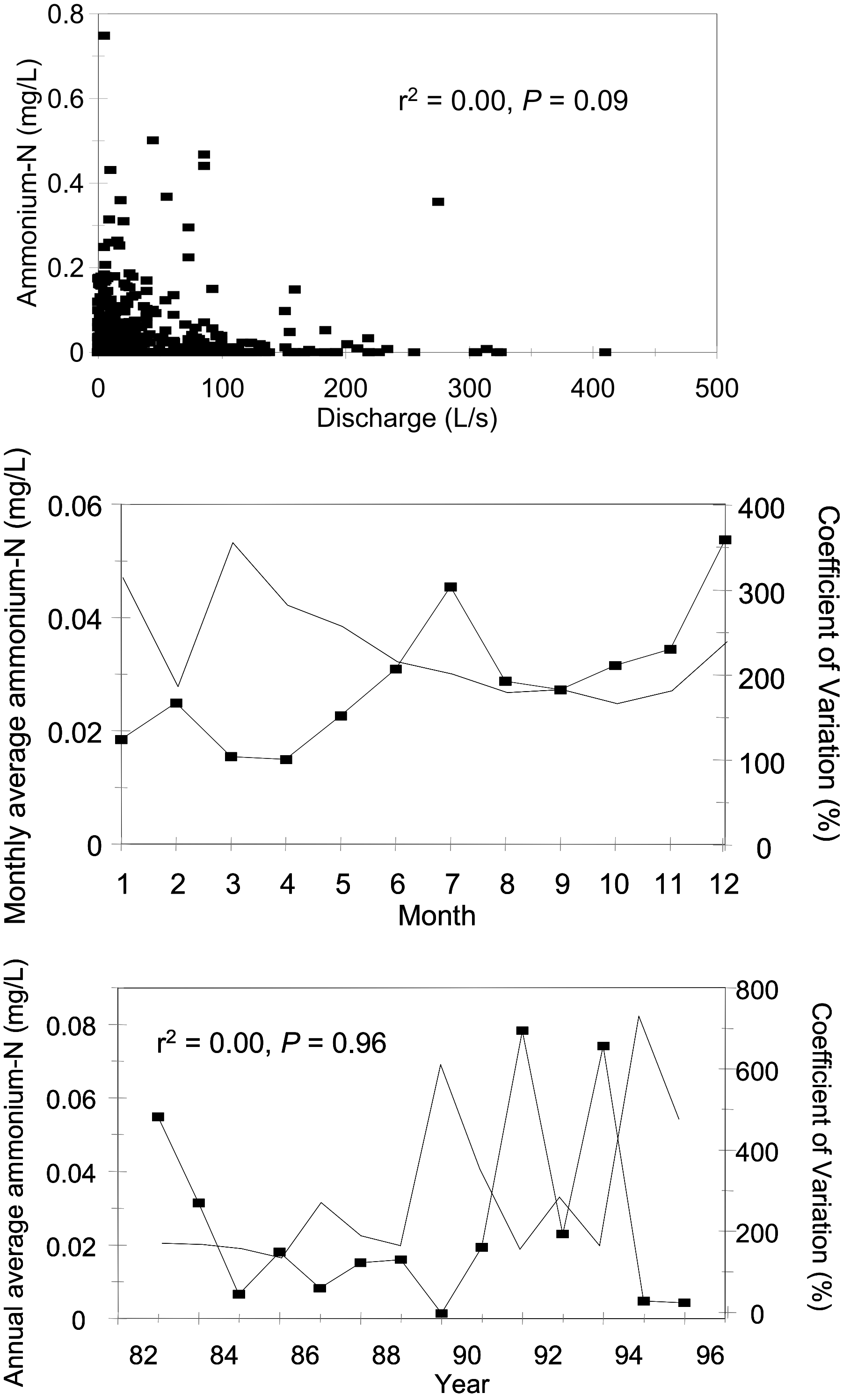


Figure B5.4. Variations in Ammonium Concentrations at Station 319, Calumet Watershed, Michigan; lines with squares are ammonium concentrations, other lines are coefficients of variation

6.0 COWEETA HYDROLOGIC LABORATORY, NORTH CAROLINA

The Coweeta Experimental Forest was established in the Appalachian Mountains of western North Carolina in 1933 to examine the effects of land use (including livestock grazing) on forest hydrology (Swank and Crossley 1988). Precipitation averages 1900 mm/yr, with streamflow of 1000 mm/yr. Watershed #18 (data summary: http:/landscape.ecology.uga.edu/cwqis/map/ws/wsl8.html) is a northeast-facing control area of 13 ha, with an average slope of 52° (elevation from 726 m to 993 m), with Typic Hapludult soils formed in metasandstone parent materials. The vegetation in Watershed #18 is dominated by oaks *(Quercus prinus* L., *Q. coccinea* Muenchh., *Q. rubra* L., and Q. *velutina* Lam.), red maple *(Acer rubrum* L.), and other hardwoods. Extensive logging occurred in the Coweeta basin in the early 1900s, but Watershed #18 has remained undisturbed since 1924. Original data for 1972 through 1992 were provided by J. Vose and J. Moore, USDA Forest Service. Coweeta and the principal investigators who provided the data disclaim any responsibility for errors that may or may not exist within the online data used for this report. Significant funding for these data was provided by the National Science Foundation Long-Term Ecological Research Program.

6.1 Patterns in Streamwater Nitrate Concentrations

Nitrate concentrations averaged 0.008 mg N/L, with a median of 0.003 mg N/L (Figure B6.1). Most observations were less than 0.01 mg N/L, with maximum values of 0.07 mg N/L. Nitrate concentrations declined strongly with increasing streamflow ($r^2 = 0.31$, $P < 0.001$); flows exceeding 50 L/sec always had concentrations less than 0.02 mg N/L (Figure B6.2). The seasonal pattern in nitrate concentrations was very pronounced, with summer months showing five times higher concentrations. The coefficients within months across the years tended to be lower in summer when the concentrations were high. Nitrate concentrations increased significantly ($r^2 = 0.33$, $P < 0.01$) over the period of record, at a rate of 0.0004 mg N/L annually.

6.2 Patterns in Streamwater Ammonium Concentrations

Ammonium concentrations were even lower than nitrate concentrations, averaging 0.003 mg N/L with a median of 0.002 mg N/L (Figure B6.3). Most observations fell below 0.004 mg N/L, with a maximum values of 0.015 mg N/L. Ammonium concentrations increased slightly with increasing streamflow ($r^2 = 0.04$, $P < 0.01$) (Figure B6.4). Seasonal trends showed increasing concentrations of ammonium from March through September, followed by a decline. Whereas nitrate concentrations increased over the period of record, ammonium concentrations declined slightly ($r^2 = 0.36$, $P < 0.02$).

6.3 Patterns in Streamwater Concentrations of Inorganic Phosphate

Phosphate concentrations were quite low, averaging just 1.1 μg P/L with a median of 0.9 μg P/L (Figure B6.5). Most observations were below 2 μg P/L, and the highest values observed were near 5 μg P/L. Phosphate concentrations were unrelated to streamflow (Figure B6.6), and no seasonal pattern was evident. Concentrations declined significantly ($r^2 = 0.32$, $P < 0.01$) through the period of record.

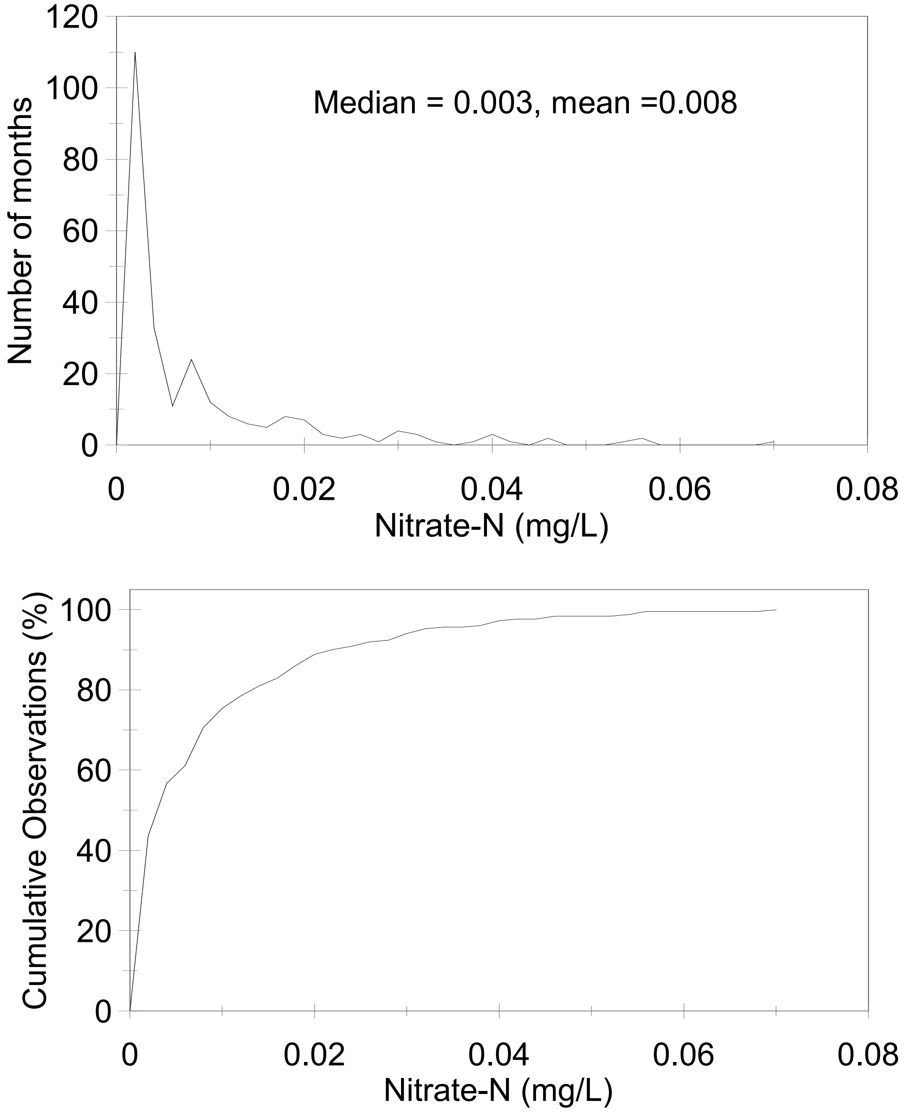


Figure B6.1. Frequency Distributions for Streamwater Nitrate in Watershed 18 at Coweeta Hydrologic Laboratory, North Carolina

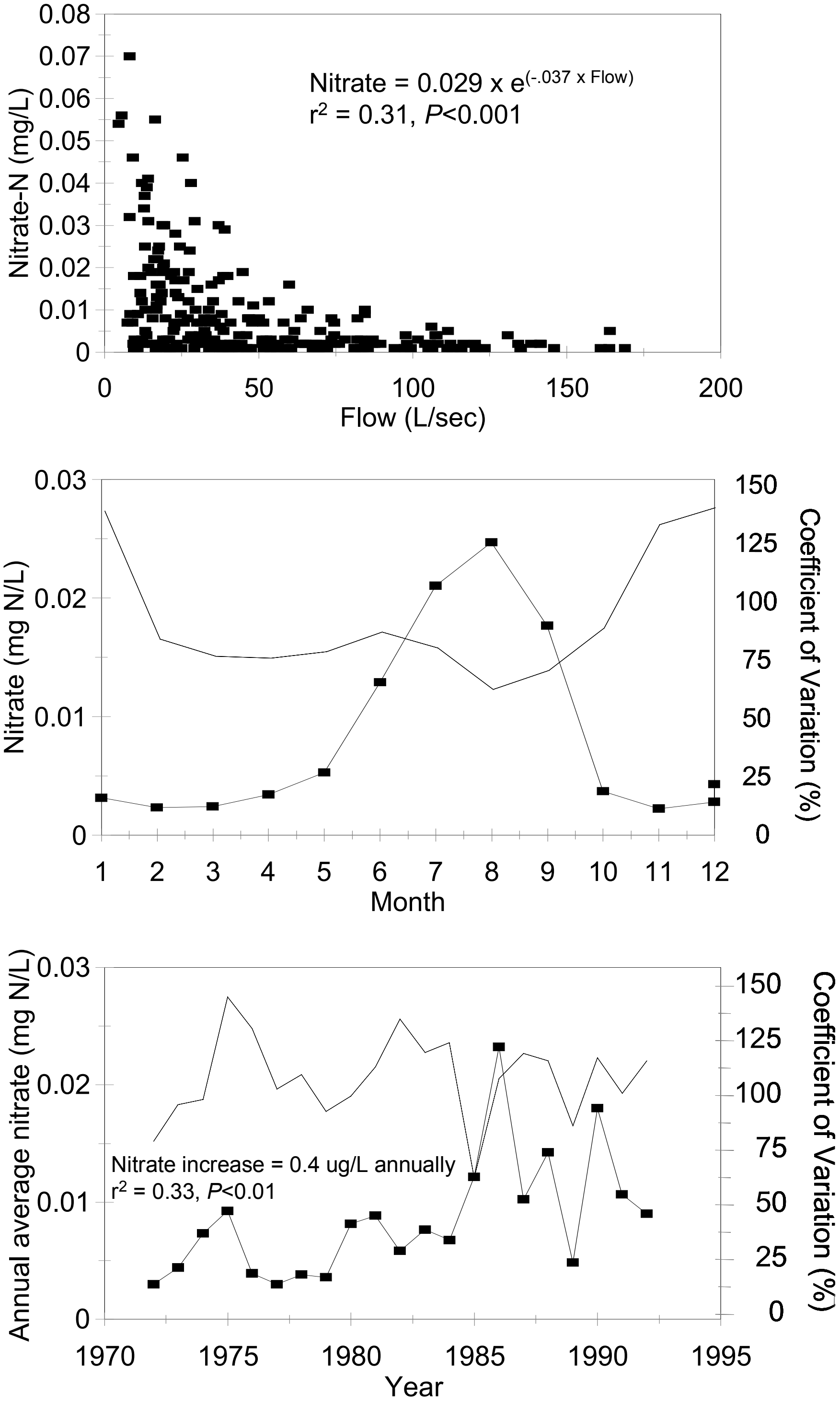


Figure B6.2. Variations in Nitrate Concentrations at Coweeta Watershed #18 in Response to Flow, Month, and Year; lines with squares are nitrate concentrations, other lines are coefficients of variation

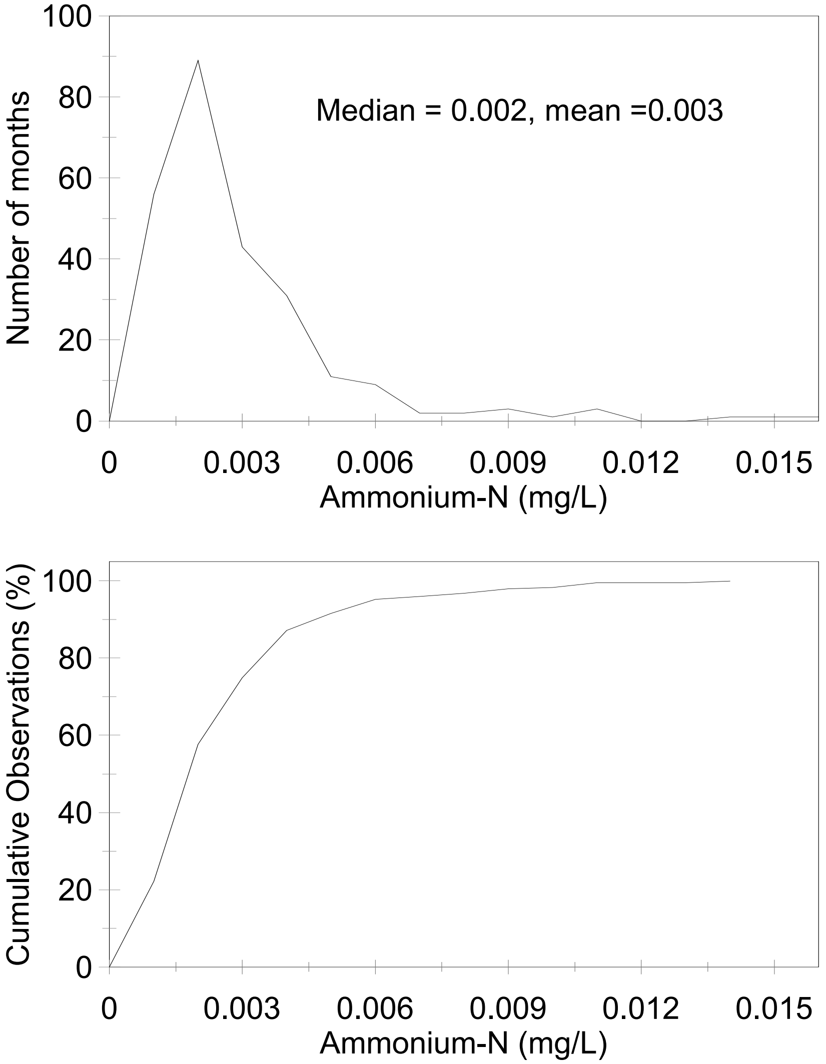


Figure B6.3. Frequency Distributions for Streamwater Ammonium in Watershed 18 at Coweeta Hydrologic Laboratory, North Carolina

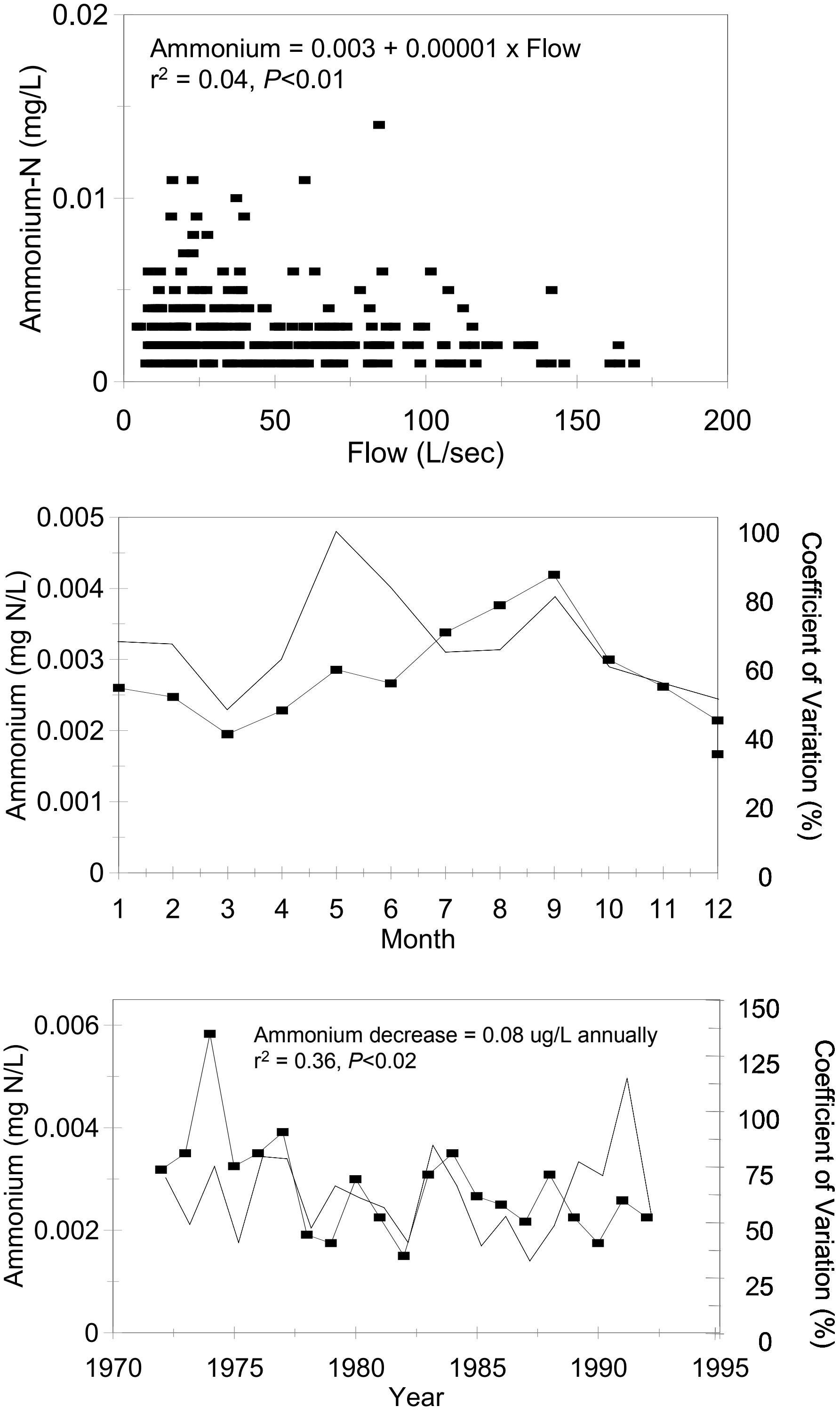


Figure B6.4. Variations in Ammonium Concentrations at Coweeta Watershed #18 in Response to Flow, Month, and Year; lines with squares are nitrate concentrations, other lines are coefficients of variation

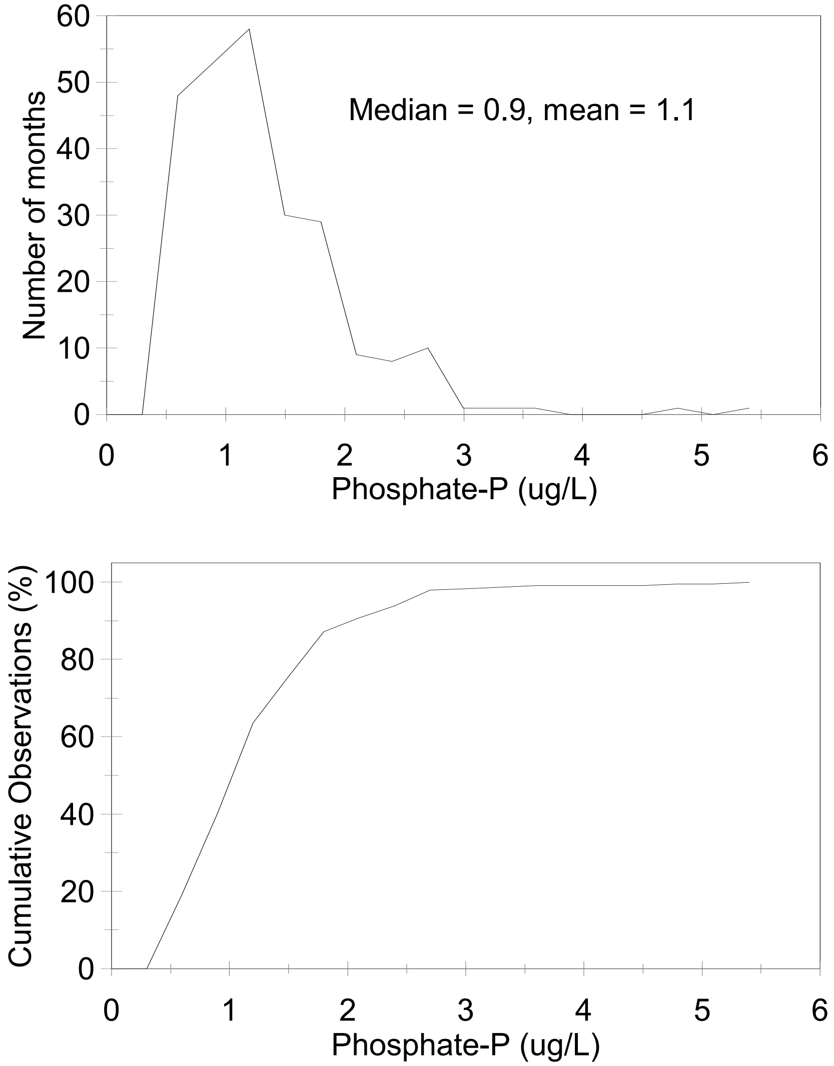


Figure B6.5. Frequency Distributions for Streamwater Inorganic Phosphate Nitrate in Watershed 18 at Coweeta Hydrologic Laboratory, North Carolina

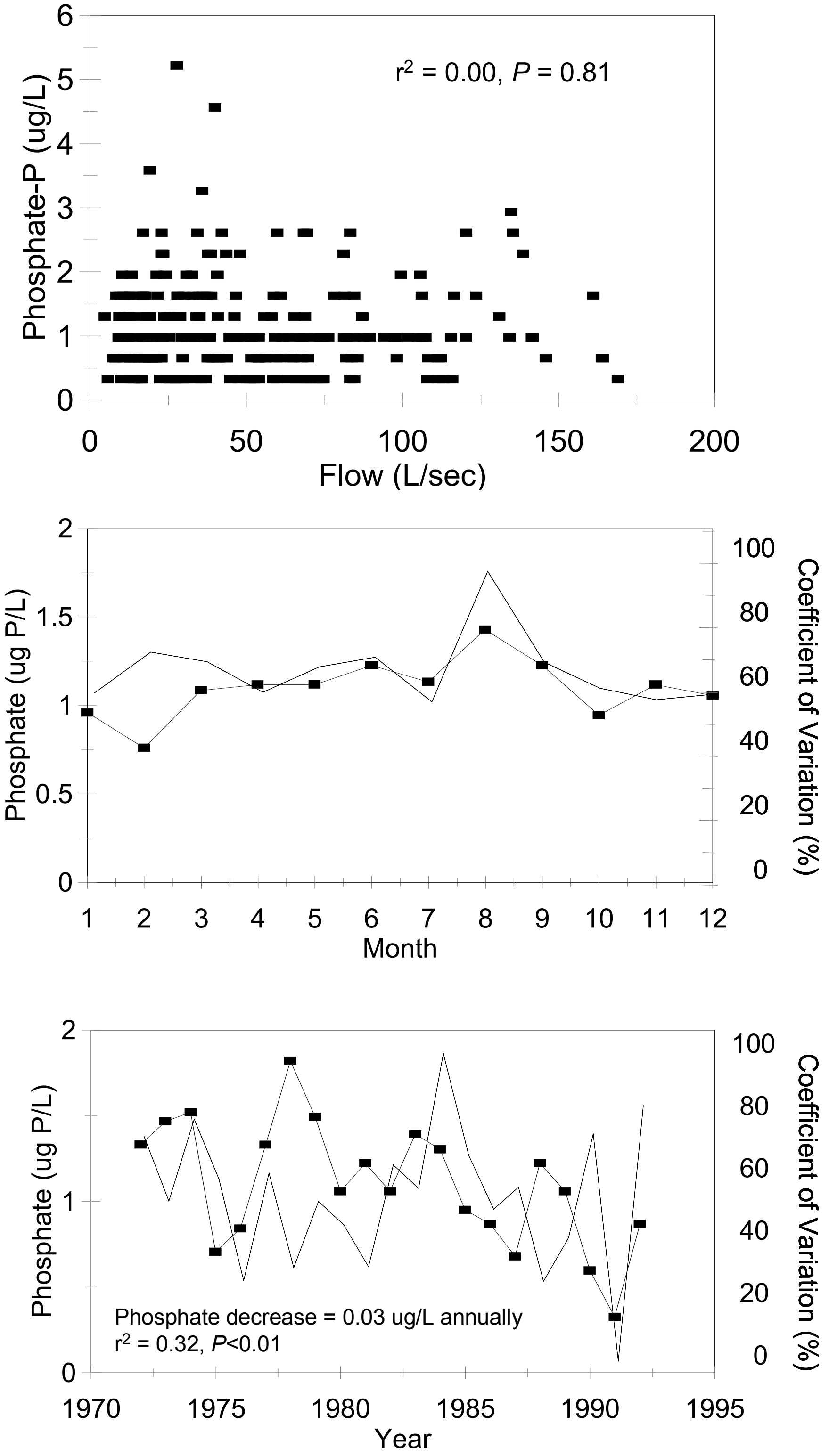


Figure B6.6. Variations in Concentrations of Inorganic Phosphate at Coweeta Watershed #18 in Response to Flow, Month, and Year; lines with squares are nitrate concentrations, other lines are coefficients of variation

7.0 HUBBARD BROOK EXPERIMENTAL FOREST, NEW HAMPSHIRE

The Hubbard Brook Experimental Forest in the White Mountains of New Hampshire includes about 3000 ha and ranges in elevation from 200 to 1000 m (Bormann and Likens 1979; Johnson et al. 2000). The sandy loam Haplorthod soils average 0.6 m in depth (ranging from 0 on ridges to several meters downslope), and are developed in glacial till comprised of medium- to coarse-grained schist. Annual precipitation averages 1400 mm/yr with an even distribution through the year, and streamflow averages 870 mm/yr. Watershed #3 is a 42 ha reference watershed for the Forest, with vegetation that developed following intensive logging in 1909 and 1917. The overstory is dominated by sugar maple *(Acer saccharum),* American beech *(Fagus grandifolia* Ehrh.), and yellow birch *(Betula alleghaniensis* Britt.), with a variety of other species. Variations in original datasets covering June of 1972 through June of 1992 were examined (data provided by G. Likens, Institute for Ecosystem Studies). Significant funding for these data was provided by the National Science Foundation Long-Term Ecological Research Program.

7.1 Patterns in Streamwater Nitrate Concentrations

Nitrate concentrations averaged 0.21 mg N/L over the 20 year period, with a median concentration of 0.13 mg N/L (Figure B7.1). Maximum observed concentrations were about 1.5 mg N/L. Streamflow accounted for little of the variation in streamwater concentrations of nitrate in Watershed #3 ($r^2 = 0.07$), but the data did show a significant trend ($p < 0.0001$) of increasing nitrate concentrations with increasing flow (Figure B7.2). The average monthly concentrations showed strong peaks in winter and low values through summer and early autumn. The coefficient of variation of monthly averages across the years showed little variation among months; the coefficient of variation for the highest month (May) was 160%, compared with 100% for the lowest months. Across the 20 year period, average nitrate concentrations declined by 0.019 mg N/L annually; concentrations in the late 1980s were 75% lower than those of the mid-1970s. The causes of this decline remain unconfirmed. Over the same period, the rate of N deposition from the atmosphere remained relatively constant and the vigor of the forest seemed to decline (Johnson et al. 2000), which might be expected to lead to increased nitrate concentrations in streamwater. The decline in nitrate concentrations appears to be widespread through New England, and possible mechanisms are discussed in the main body of this report. The decline in nitrate concentrations in Watershed #3 was not associated with any change in the relative variability of concentrations among months within years; the coefficient of variations for months within years ranged from about 40 to 130%.

7.2 Patterns in Streamwater Ammonium Concentrations

Ammonium concentrations averaged 0.014 mg N/L, which matched the median concentration of 0.013 mg N/L (Figure B7.3). Maximum concentrations approached 0.04 mg N/L, more than an order of magnitude lower than nitrate concentrations. Unlike the frequency distributions of many other streams, ammonium showed a broad spread of observed concentrations. Streamflow had no apparent effect on streamwater concentrations of ammonium (Figure B7.4), and these concentrations were remarkably consistent across months. The variations within months across the years were also remarkably consistent, ranging between 30% and 45% for all months. Ammonium showed a weak ($r^2 = 0.15$) increasing trend of 0.003 mg N/L over the 20 year period; concentrations in the late 1980s were about double those of the mid-1970s. The early 1970s also showed high concentrations, so this temporal trend may not be directional. As concentrations of ammonium increased over the years, the coefficient of variation among months within years appears to have declined from about 40% to 25%.

7.3 Patterns in streamwater concentrations of inorganic phosphate

Inorganic phosphate concentrations averaged 1.3 µg P/L, with a median of 1.1 µg P/L and a maximum value of almost 4 µg P/L (Figure B7.5). The frequency distribution of observations was broad, similar to that for ammonium. Streamflow did not account for a significant amount of the variation in concentrations of inorganic phosphate (Figure B7.6). Summer months showed slightly elevated concentrations of phosphate, and the coefficients of variations for months (across the years) was uniformly 50 to 70%. Phosphate concentrations increased by about 0.05 µg P/L annually, giving a 50% increase in 10 to 15 years. The increasing concentrations over the years was not accompanied by any trend in the coefficient of variation among months within the years.

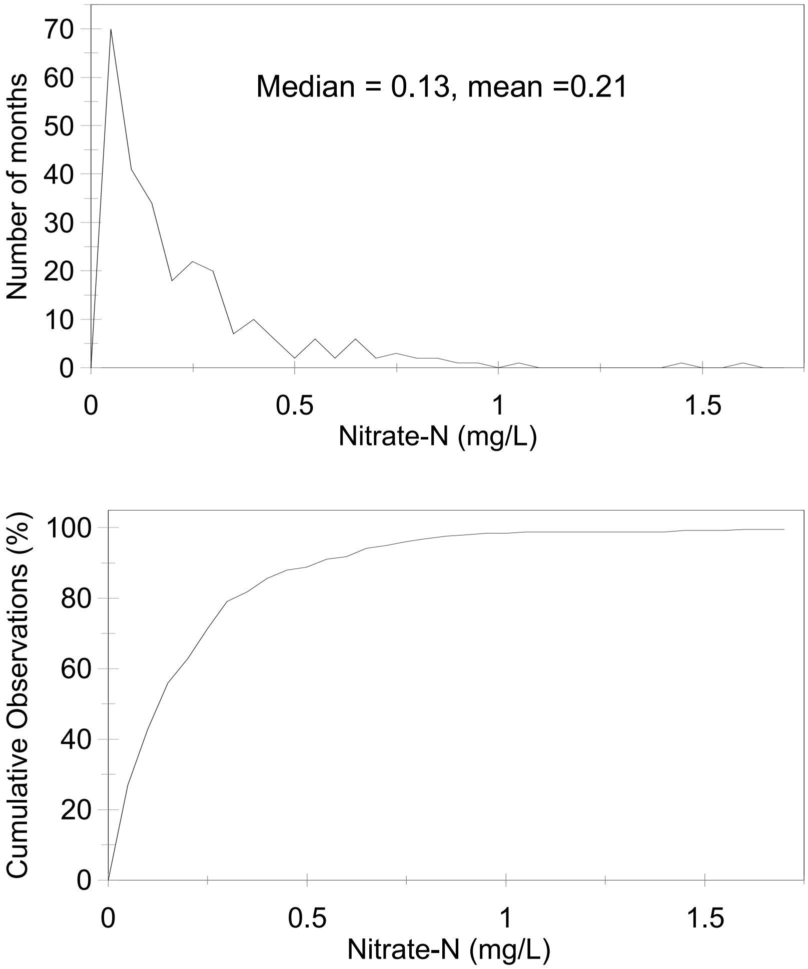


Figure B7.1. Frequency Distributions for Streamwater Nitrate for Watershed #3, Hubbard Brook, New Hampshire

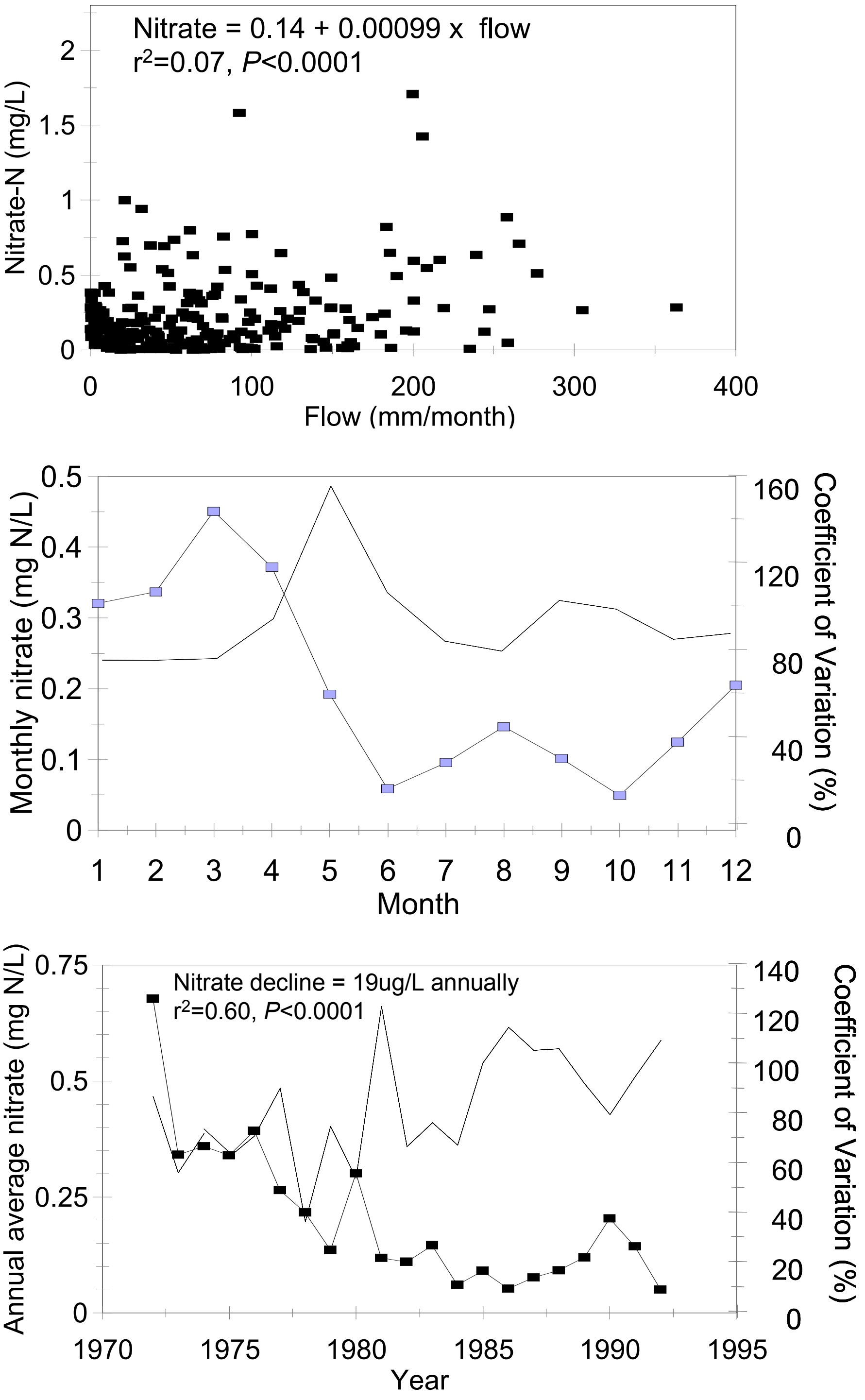
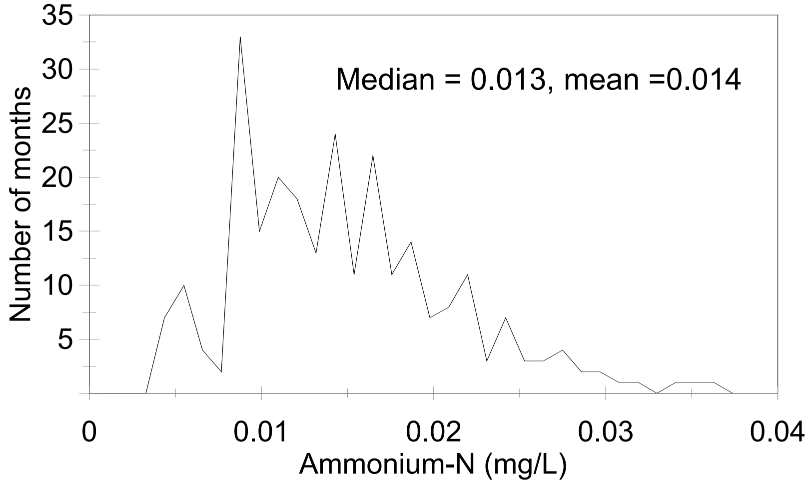


Figure B7.2. Variations in Nitrate Concentrations for Watershed #3, Hubbard Brook, New Hampshire; lines with squares are nitrate concentrations, other lines are coefficients of variation



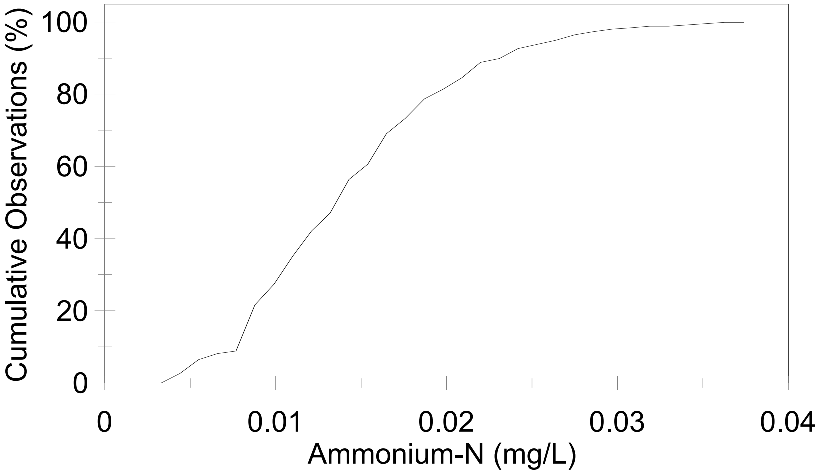


Figure B7.3. Frequency Distributions for Streamwater Ammonium for Watershed #3, Hubbard Brook, New Hampshire

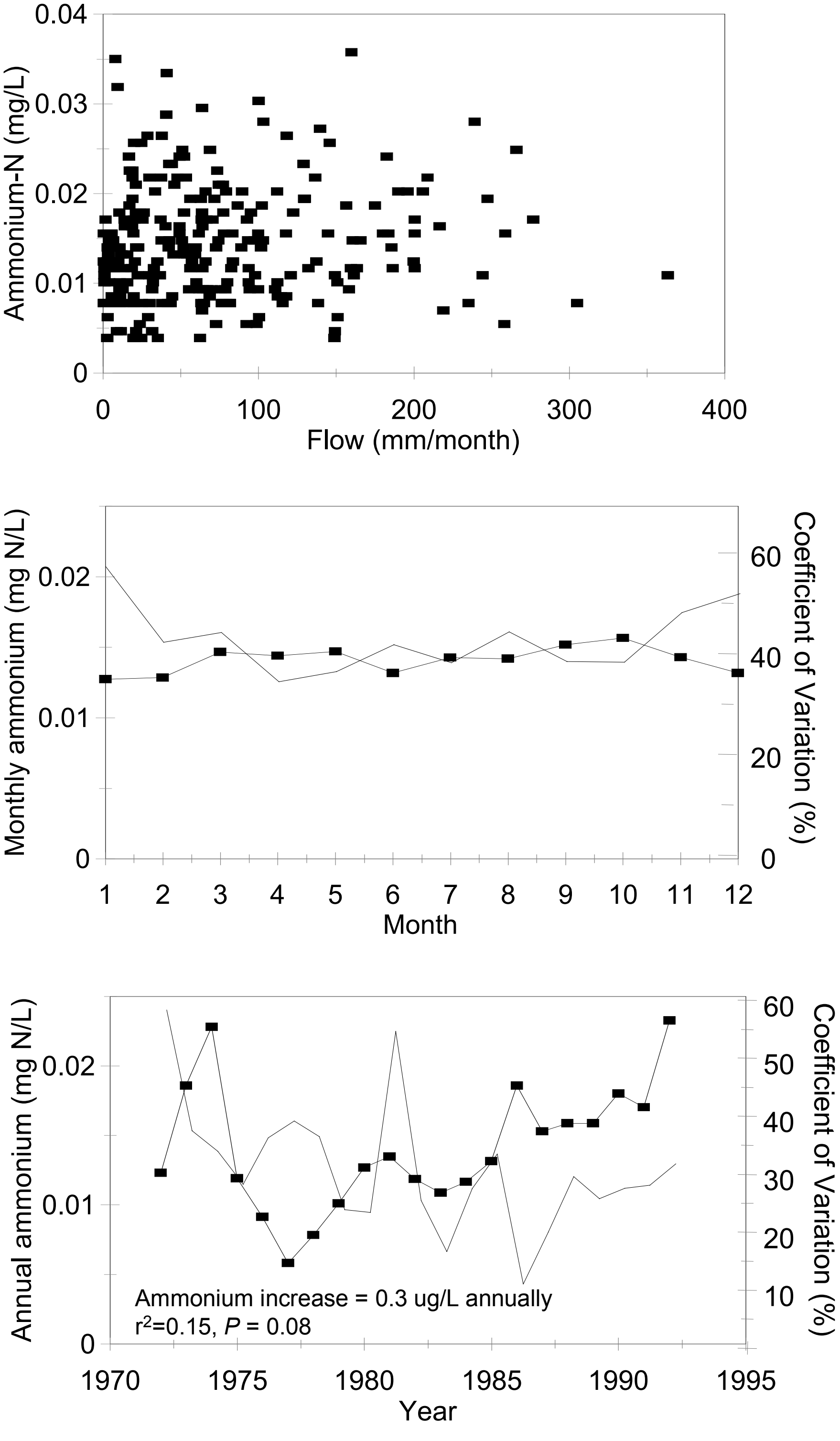


Figure B7.4. Variations in Ammonium Concentrations for Watershed #3, Hubbard Brook, New Hampshire; Lines with squares are ammonium concentrations, other lines are coefficients of variation

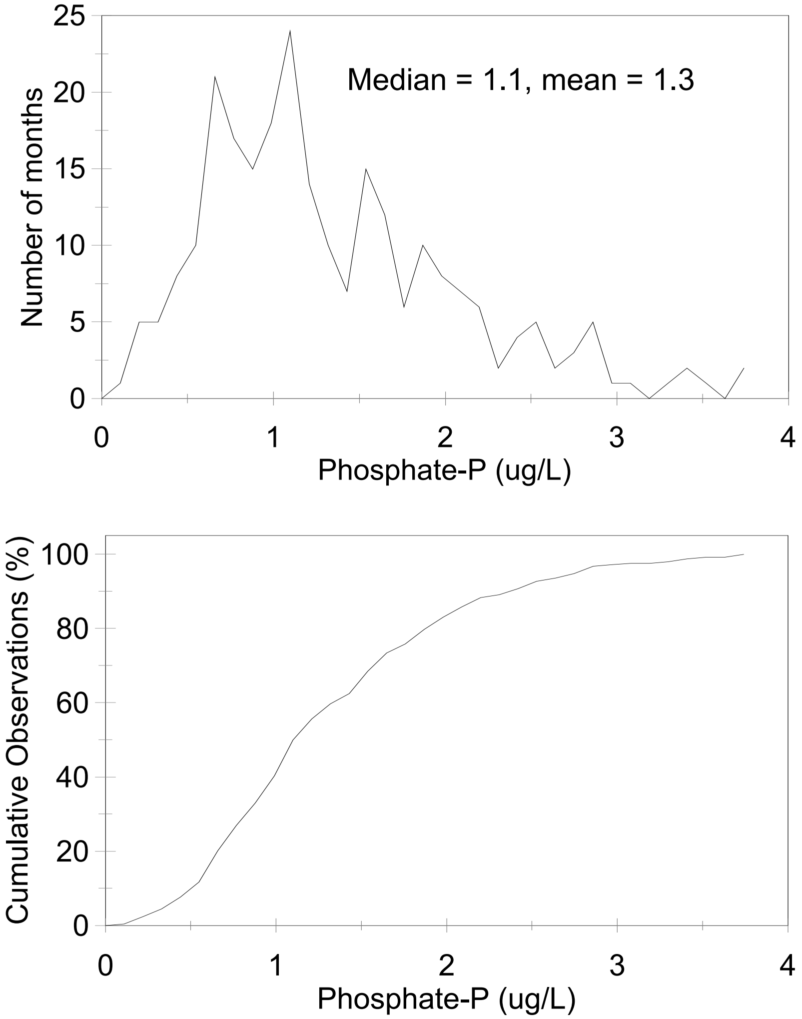


Figure B7.5. Frequency Distributions for Streamwater Inorganic Phosphate for Watershed #3, Hubbard Brook, New Hampshire

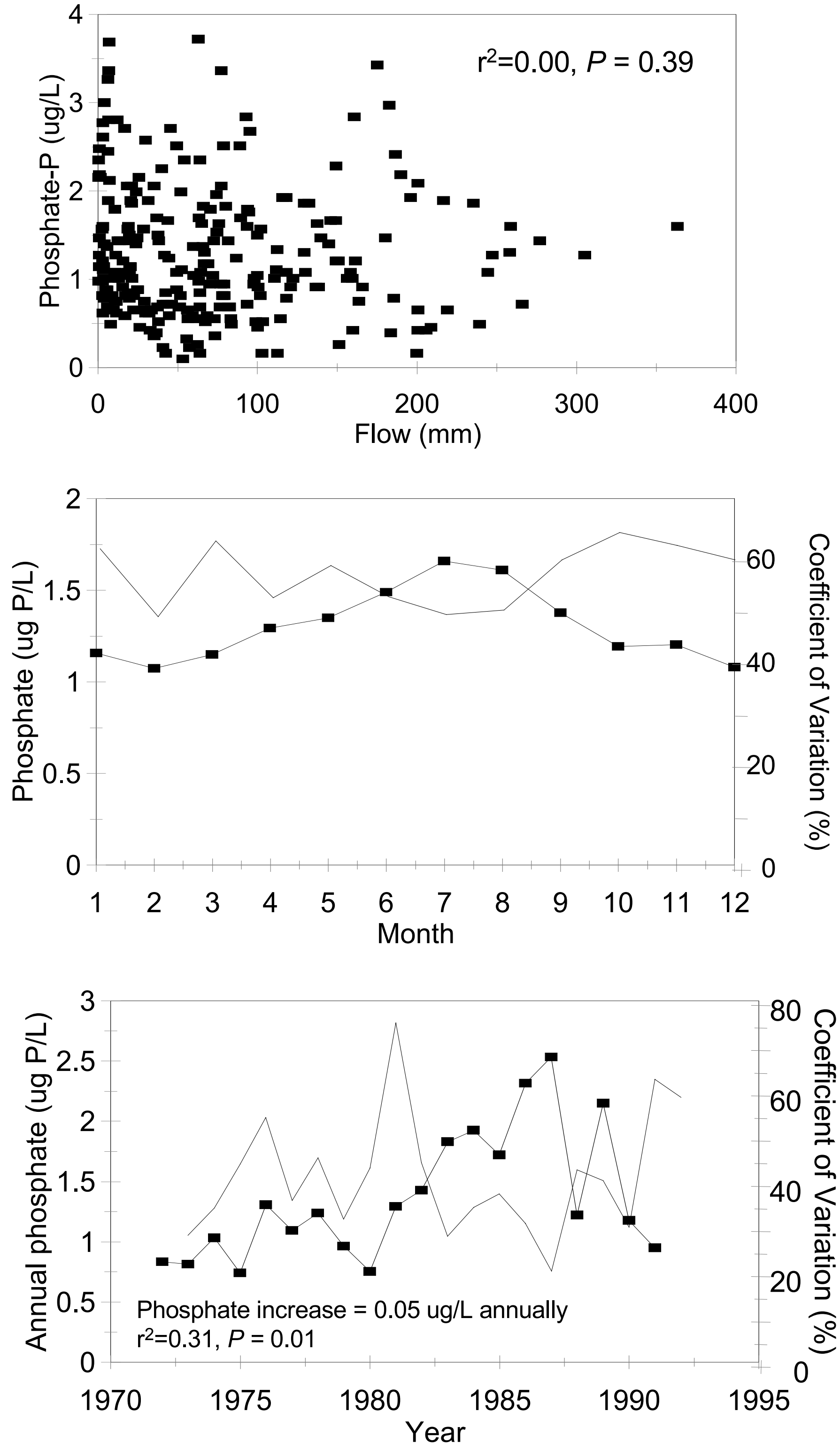


Figure B7.6. Variations in Nitrate Concentrations of Inorganic Phosphate for Watershed #3, Hubbard Brook, New Hampshire; lines with squares are phosphate concentrations, other lines are coefficients of variation

8.0 SANTEE EXPERIMENTAL FOREST, SOUTH CAROLINA

The Santee Experimental Forest is in the coastal flatwoods of the Francis Marion National Forest, about 25 km from the coast and 50 km north-northeast of Charleston (Richter, Ralston, and Harms 1982, 1983). The climate is mild and wet, with a mean annual temperature of 18°C and annual rainfall of 1200 mm. The soils of the control Watershed #80 are primarily strongly acidic, infertile Aquults with seasonally high water tables. Some calcareous soils are present along the stream. Relief in the 200 ha Watershed #80 is less than 5 m, and water tables are near the surface in winter. Before Hurricane Hugo in 1989, the vegetation on Watershed #80 was mostly old (>80 year) loblolly pine *(Pinus taeda* L.). The hurricane destroyed over 80% of the overstory trees, and forest recovery has been dominated by newly established seedlings of loblolly pine and resprouting hardwoods. Streamwater monitoring stopped in 1982, but resumed in 1989 after the hurricane. The original data analyzed here were provided by C. Trettin, USDA Forest Service. These investigations were supported by the USDA Forest Service.

8.1 Patterns in Streamwater Nitrate Concentrations

Nitrate concentrations were very low, averaging 0.017 mg N/L, with a median of 0.009 mg N/L (Figure B8.1). Most observations were less than 0.04 mg N/L, with a maximum value of 0.1 mg N/L. Streamflow did not affect nitrate concentrations (Figure B8.2), but higher values tended to occur in winter and early spring than in summer. No effect of the massive hurricane disturbance was apparent; annual average concentrations before the hurricane ranged from 0.08 to 0.24 mg N/L, compared with 0.05 to 0.045 mg N/L after the hurricane.

8.2 Patterns in Streamwater Ammonium Concentrations

Concentrations of ammonium were more than double those of nitrate, averaging 0.045 mg N/L with a median of 0.030 mg N/L (Figure B8.3). Most ammonium concentrations were below 0.07 mg N/L, but some values ranged from 0.2 to 0.4 mg N/L. Ammonium concentrations declined significant ($P < 0.0001$) with increasing streamflow (Figure B8.4), though the trend was weak ($r^2 = 0.04$). Flows exceeding 10 L/sec always had <0.1 mg N/L. In the summer, ammonium concentrations tended to be about double those of late autumn and early winter. The hurricane disturbance had little if any effect on ammonium concentrations.

8.3 Patterns in Streamwater Concentrations of Dissolved Organic Nitrogen

Streamwater nitrogen loads were dominated by dissolved organic nitrogen (DON), with concentrations about an order of magnitude greater than dissolved inorganic forms. Dissolved organic nitrogen averaged about 1 mg N/L, with a median of 0.8 mg N/L (Figure B8.5). Most observations fell below 2 mg N/L, with a maximum of 4 mg N/L. Concentrations showed a very weak relationship with streamflow ($r^2 = 0.01$, $P = 0.09$); concentrations of more than 1.5 mg N/L occurred only at flows less than 5 L/sec (Figure B8.6). Winter concentrations of DON averaged about half of those of summer months, and no effects of the hurricane disturbance were apparent.

8.4 Patterns in Streamwater Inorganic Phosphate Concentrations

Phosphate concentrations averaged 28 μg P/L, with a median of 17 μg P/L and a maximum of 225 μg P/L (Figure B8.7). Increasing streamflow showed a weak decline in phosphate concentrations ($r^2 = 0.01$, $P < 0.06$) (Figure B8.8). Little seasonal variation was apparent; peak concentrations and variability were observed in July, where concentrations were double those of most other months. The hurricane had no effect on streamwater phosphate concentrations.

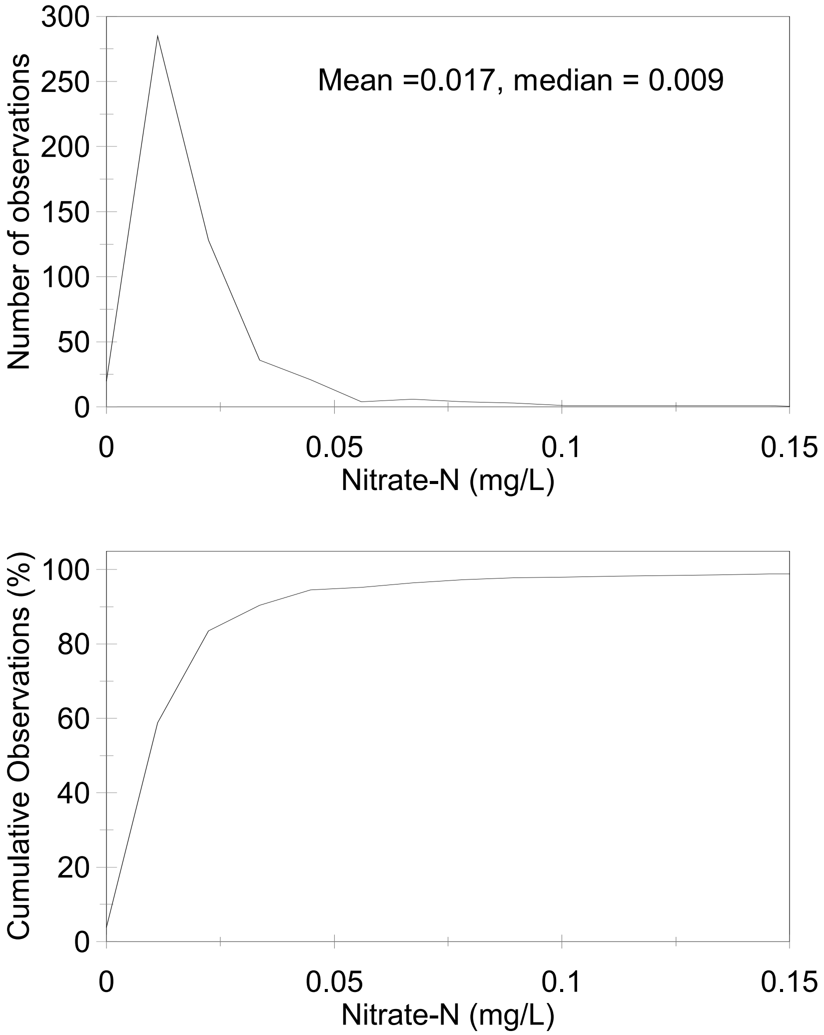


Figure B8.1. Frequency Distributions for Streamwater Nitrate for Watershed #80, Santee, South Carolina

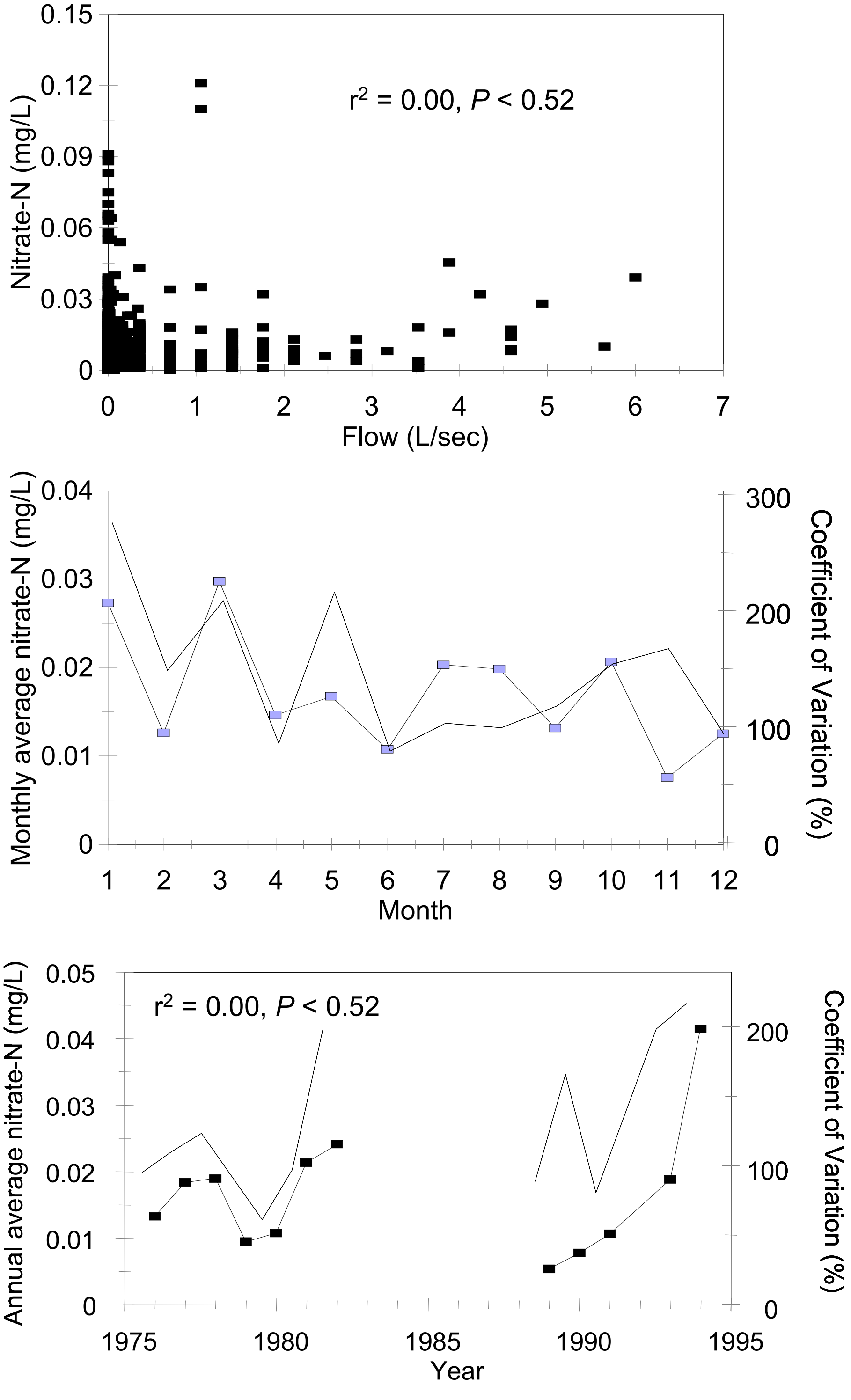


Figure B8.2. Variations in Nitrate Concentrations for Watershed #80, Santee, South Carolina; lines with squares are nitrate concentrations, other lines are coefficients of variation

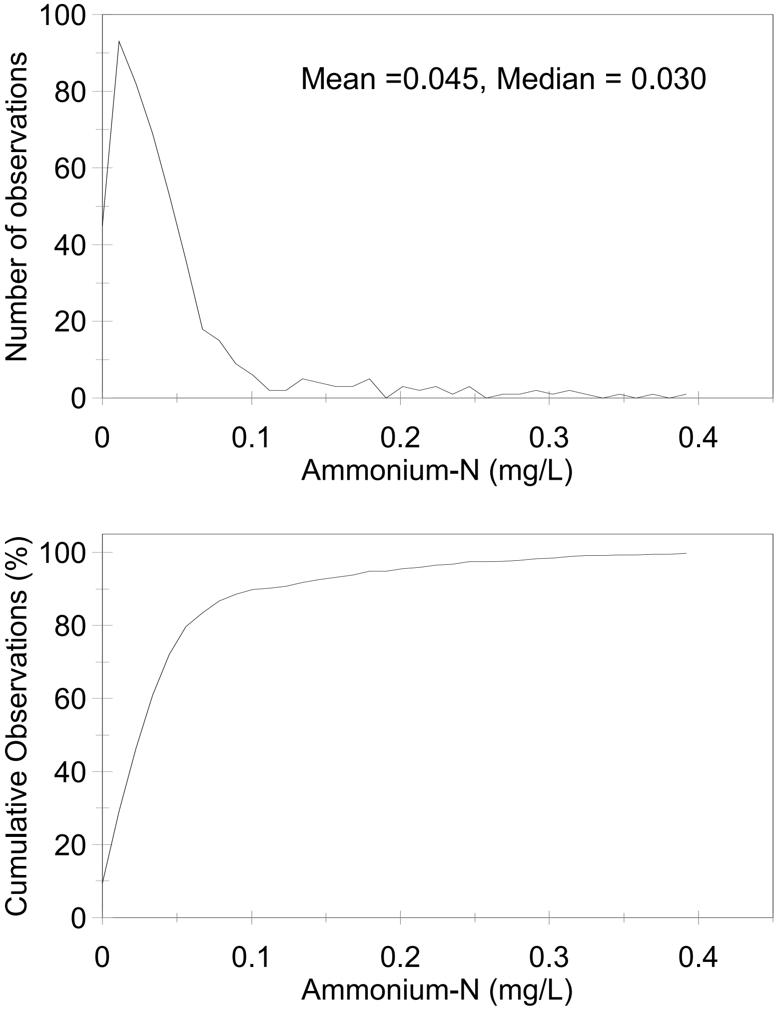


Figure B8.3. Frequency Distributions for Streamwater Ammonium for Watershed #80, Santee, South Carolina

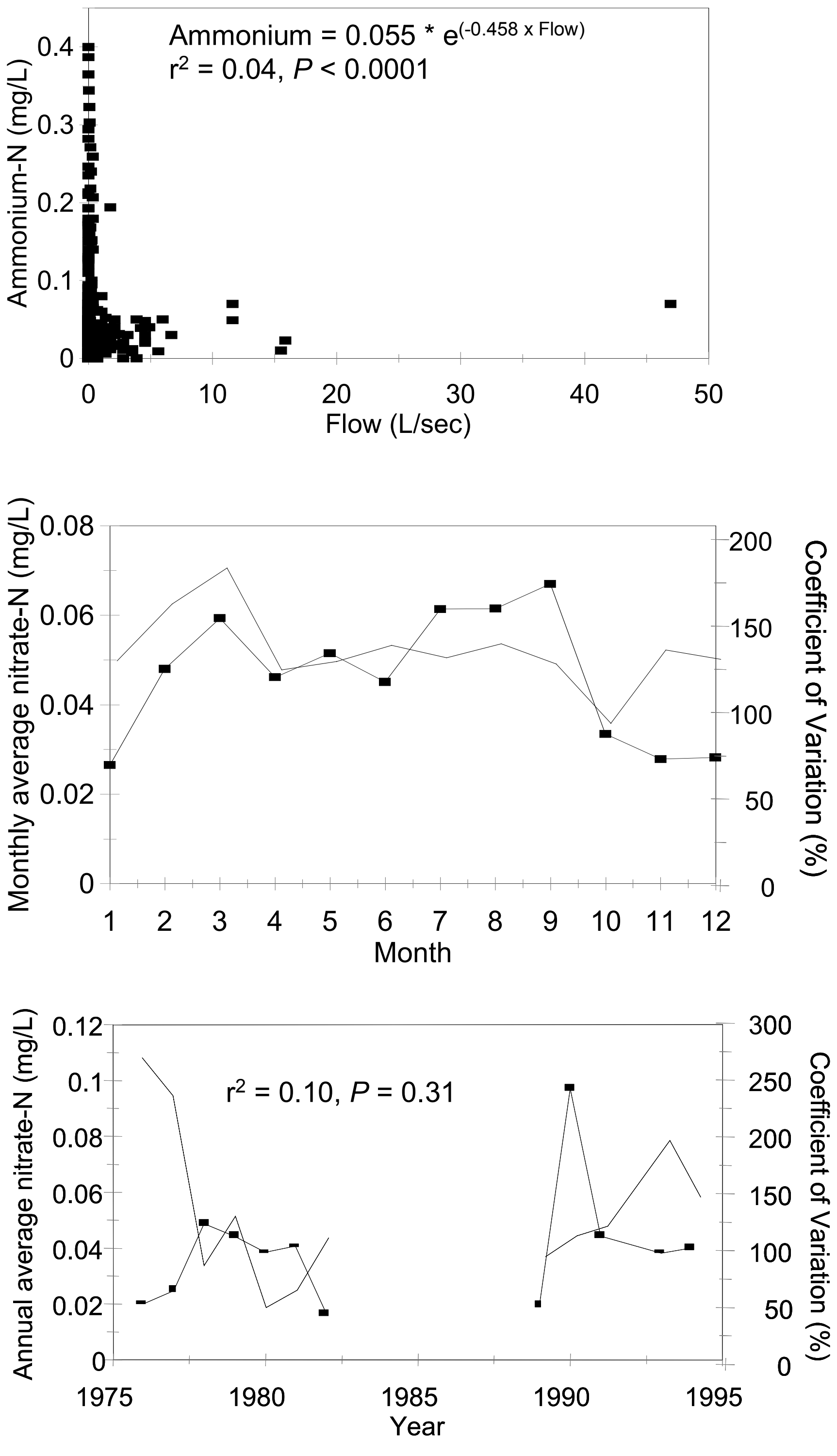


Figure B8.4. Variations in Ammonium Concentrations for Watershed #80, Santee, South Carolina; lines with squares are ammonium concentrations, other lines are coefficients of variation

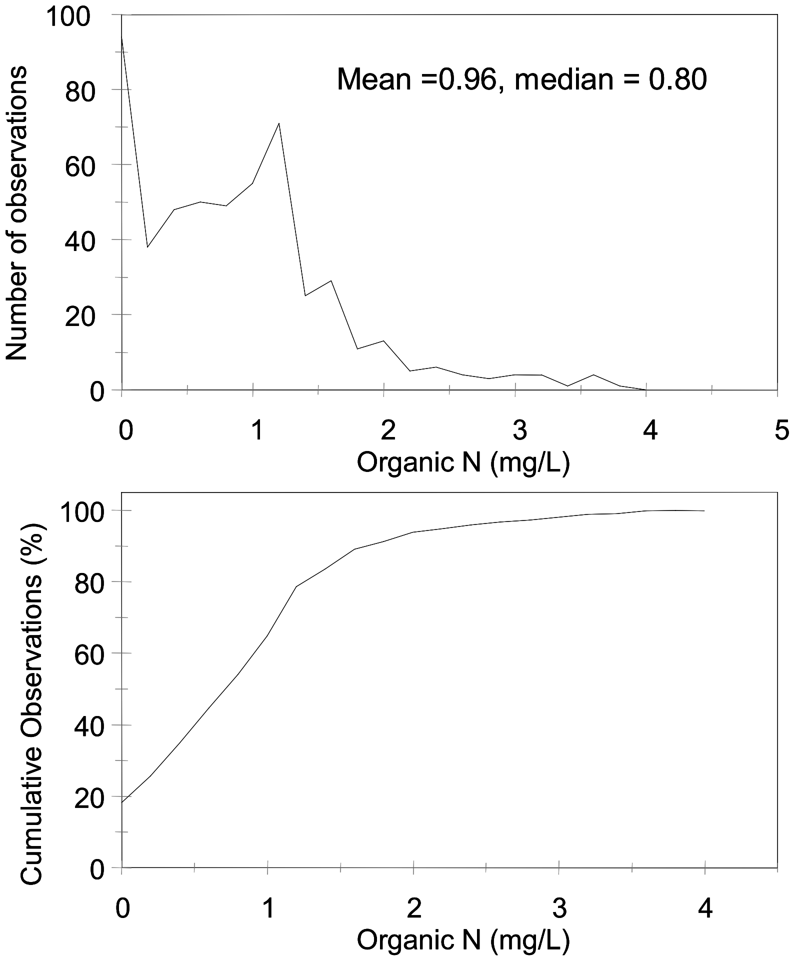


Figure B8.5. Frequency Distributions for Streamwater Organic Nitrogen for Watershed #80, Santee, South Carolina

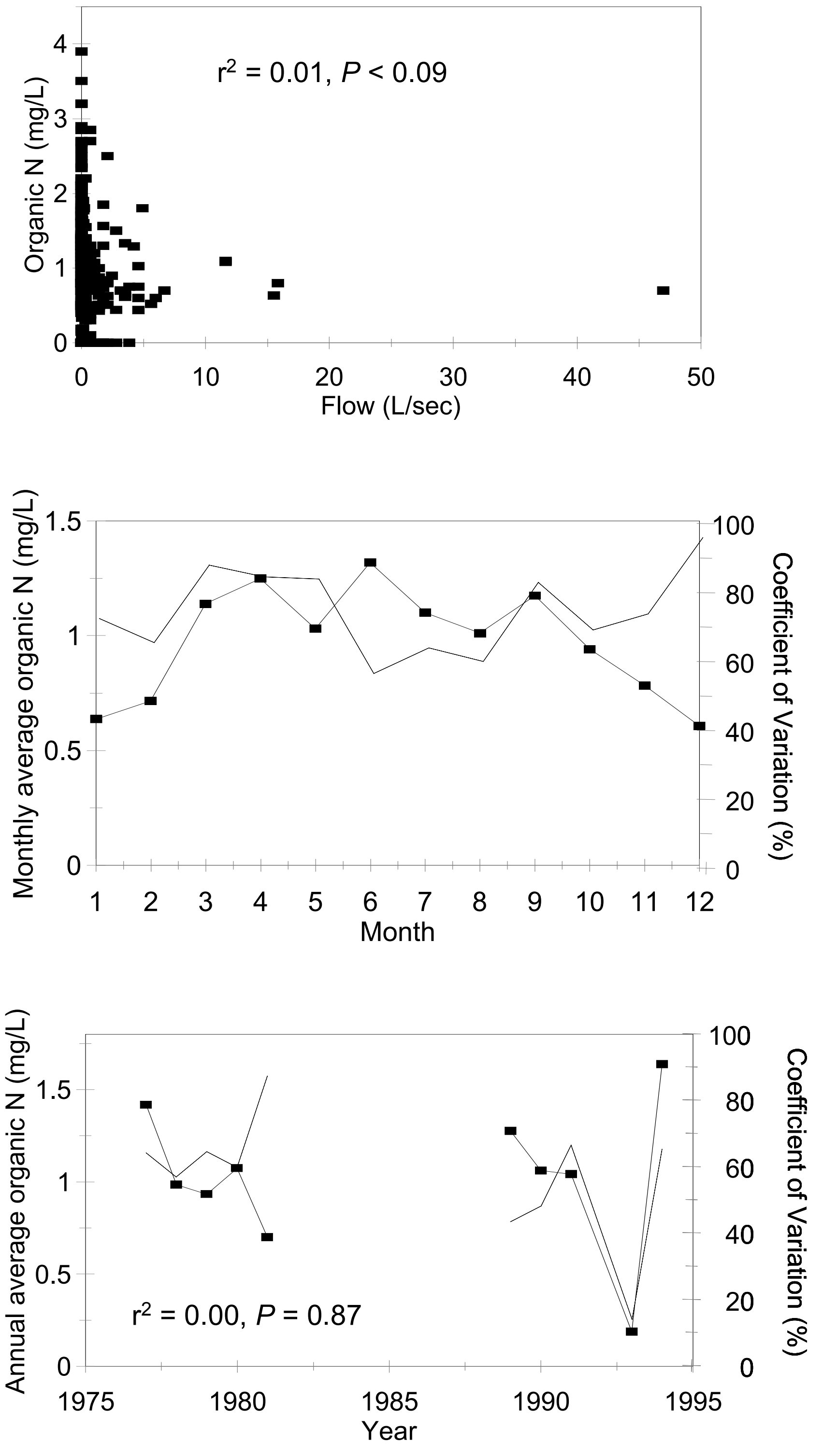
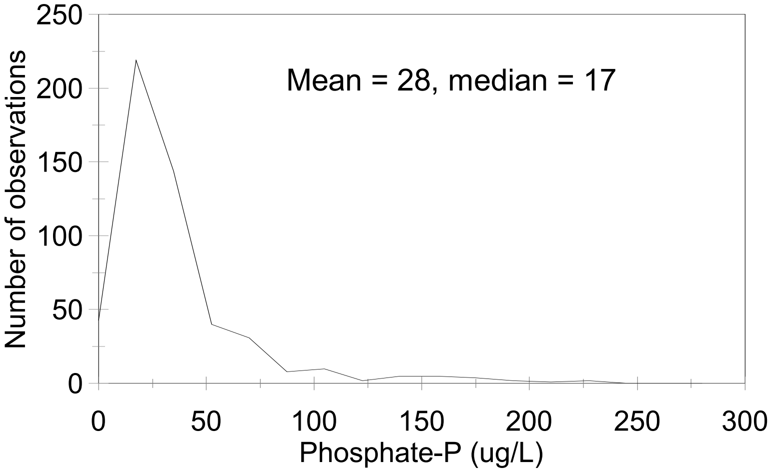


Figure B8.6. Variations in Organic Nitrogen Concentrations for Watershed #80, Santee, South Carolina; lines with squares are nitrogen concentrations, other lines are coefficients of variation



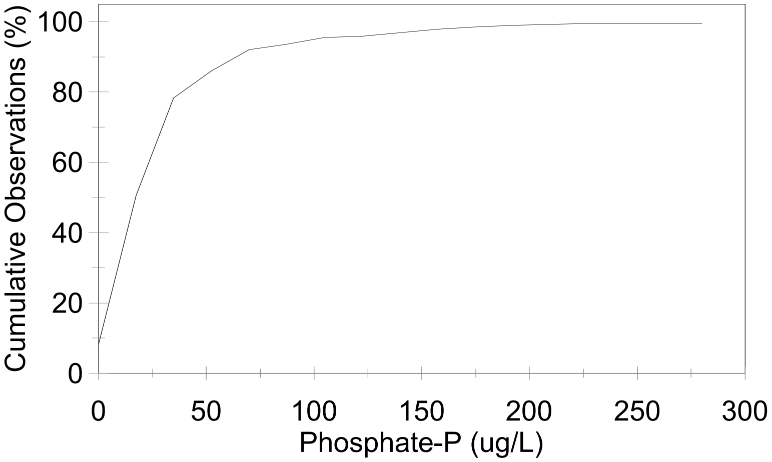


Figure B8.7. Frequency Distributions for Streamwater Inorganic Phosphate for Watershed #80, Santee, South Carolina

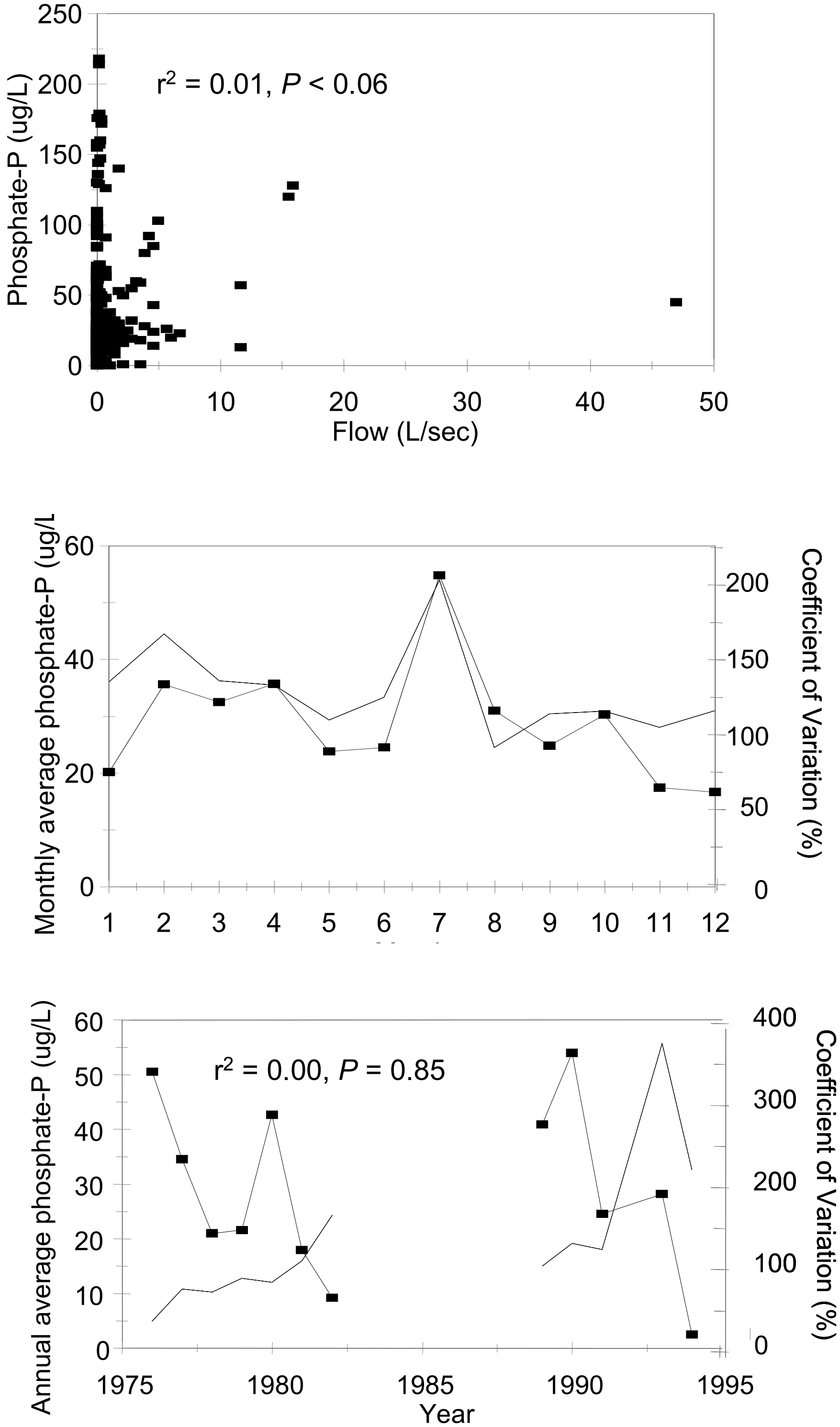


Figure B8.8. Variations in Inorganic Phosphate Concentrations for Watershed #80, Santee, South Carolina; lines with squares are phosphate concentrations, other lines are coefficients of variation

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