

NITROGEN AND PHOSPHORUS CONCENTRATIONS IN FOREST STREAMS OF THE UNITED STATES¹

Dan Binkley, George G. Ice, Jason Kaye, and Christopher A. Williams²

ABSTRACT: Seventy to eighty percent of the water flowing in rivers in the United States originates as precipitation in forests. This project developed a synoptic picture of the patterns in water chemistry for over 300 streams in small, forested watersheds across the United States. Nitrate (NO_3^-) concentrations averaged 0.31 mg N/L, with some streams averaging ten times this level. Nitrate concentrations tended to be higher in the northeastern United States 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) were similar to those of NO_3^- , whereas ammonium (NH_4^+) concentrations were much lower (mean 0.05 mg N/L). Nitrate dominated the N loads of streams draining hardwood forests, whereas dissolved organic N dominated the streams in coniferous forests. Concentrations of inorganic phosphate were typically much lower (mean 12 mg P/L) than dissolved organic phosphate (mean 84 mg P/L). The frequencies of chemical concentrations in streams in small, forested watersheds showed more streams with higher NO_3^- concentrations than the streams used in national monitoring programs of larger, mostly forested watersheds. At a local scale, no trend in nitrate concentration with stream order or basin size was consistent across studies. (KEY TERMS: forest hydrology; stream water quality; watershed management; nonpoint source pollution; synopsis.)

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INTRODUCTION

Water is one of the most fundamental and important renewable resources. Between 70 and 80 percent of the water flowing in rivers in the United States

originates as precipitation falling on forests (USEPA, 2000; Sedell *et al.*, 2000). The quality of the water that flows from forests is generally among the best in the nation (Dissmeyer, 2000). Nutrient concentrations in forested streams usually are less than 15 percent of the levels found in streams that run through agricultural or urban areas (Omernik, 1976, 1977). In the Chesapeake Basin of the eastern U.S., concentrations of nitrate (NO_3^-) declined linearly with increasing forest cover in basins from a high of 11.7 mg N/L with no forest in the watersheds to less than 1 mg N/L in completely forested basins (Lindsey *et al.*, 2001). The quality of water from forested streams is generally so high that a report by the Ecological Society of America on nonpoint pollution of surface waters with phosphorus (P) and nitrogen (N) did not even mention forests or forest practices as areas of concern (Carpenter *et al.*, 1998).

Typical concentrations and forms of N differ by geographic regions (Omernik, 1977; Rohm *et al.*, 2002) and dominant tree species. No single region or forest type can represent the spectrum of forest streams in the country. For example, Likens *et al.* (1970) found that NO_3^- was the dominant N form in the streams of the Hubbard Brook ecosystem in New Hampshire. About the same time, Henderson and Harris (1975) described a stream in the hardwood forests of Walker Branch in Tennessee with more than twice the N load of Hubbard Brook, but with concentration of dissolved organic N (DON) that were three times higher than the NO_3^- concentration.

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Existing summaries of stream water chemistry in forests have tended to focus on relatively large basins, such as the U.S. Geological Survey's Hydrologic Benchmark Network, and National Water Quality Assessment Program (Clark *et al.*, 2000). Forest hydrologists and ecosystem ecologists have developed a great deal of information on water quality in smaller, upland watersheds in the past four decades (Binkley and Brown 1993), but no synoptic analysis of this wealth of information has been available. This paper synthesizes published data on stream water concentrations of N and P compounds from more than 300 forest streams (within watersheds of 1 to 1,000 ha) to provide a synoptic view of average conditions, and causes of variation around those averages. The full details of this synthesis (including data tables) are presented in National Council for Air and Stream Improvement (2001). This survey used only published data for sites with more than one year of monitoring. The pattern among these sites may provide a biased view of forest stream water chemistry, as the sites were not chosen at random by the original investigators, and most forest types are underrepresented. Nevertheless, this synthesis of available information provides the best baseline for gauging general expectations of forest stream water and for identifying unusual cases that merit more investigation.

NITROGEN FORMS

Nitrate

Across the United States, forested streams average 0.31 mg N/L as NO_3^- , with a median value of 0.15 mg N/L (Figure 1) (for original data and site information, see tables in NCASI (2001). 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). Concentrations of more than 1 mg N/L were reported for some forests in the Northeast, and forests containing N-fixing alders in the West.

The regional pattern of NO_3^- concentrations relates well to the concentrations of NO_3^- in precipitation across the country, with high rates of deposition in the Northeast (National Atmospheric Deposition Program, 2001). Concentrations in precipitation across the Northeast average about 1.5 mg NO_3^- /L (0.33 mg N/L), about double the concentrations for the Southeast and West.

The regional pattern is also confounded by patterns in vegetation. Hardwood species dominate the Northeastern forests, whereas conifers are more common in the Southeast and West. Across all hardwood forests, NO_3^- 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. This trend was consistent even when broken down by vegetation types within regions; NO_3^- concentrations in streams draining hardwood forests exceeded those for streams draining coniferous forests in each region.

Only one watershed scale experiment provides information on the effect of hardwoods and a conifer species on water quality without confounding major differences in geography. Two watersheds at the Coweeta Hydrologic Laboratory in North Carolina were intentionally converted to white pine (*Pinus strobus*) to compare water use and streamflow with hardwood dominated watersheds. Pine watersheds had lower streamflow (740 mm/yr versus 1,050 mm/yr for hardwoods), and contrary to national averages, higher NO_3^- concentrations (0.084 mg N/L pine, 0.005 mg N/L hardwood) (Swank and Vose, 1997). More experimentation is needed to identify the effects on water quality of conifers versus hardwoods.

The influence of tree species on stream water chemistry also may differ among hardwood species. Lovett *et al.* (2000) found a broad range of NO_3^- concentrations in 39 streams in the Catskill Mountains of New York. They concluded that species composition of the forests probably influenced NO_3^- concentration. The three watersheds with the lowest concentrations of NO_3^- were dominated by red oak (*Quercus rubra*), and the five watersheds with the highest concentrations of NO_3^- had no oaks. Both oaks and beech (*Fagus grandifolia*) have poorer quality litter than maples, and stream water concentrations of NO_3^- may be influenced by the relative influences of these species (Lovett and Rueth, 1999; Lovett *et al.*, 2000). Lewis and Likens (2000) also examined stream water NO_3^- concentrations in relation to species composition of 20 forests in the Allegheny National Forest of northwestern Pennsylvania. Watersheds with at least 10 to 20 percent cover of red oak averaged about 0.15 mg N/L as NO_3^- , compared with 0.4 mg N/L for comparable watersheds without red oak.

The maximum reported concentrations of NO_3^- were higher for sites with high annual average concentrations (Figure 2). Across all sites, the maximum NO_3^- concentrations reported for individual streams tended to be about 80 percent higher than the annual average.

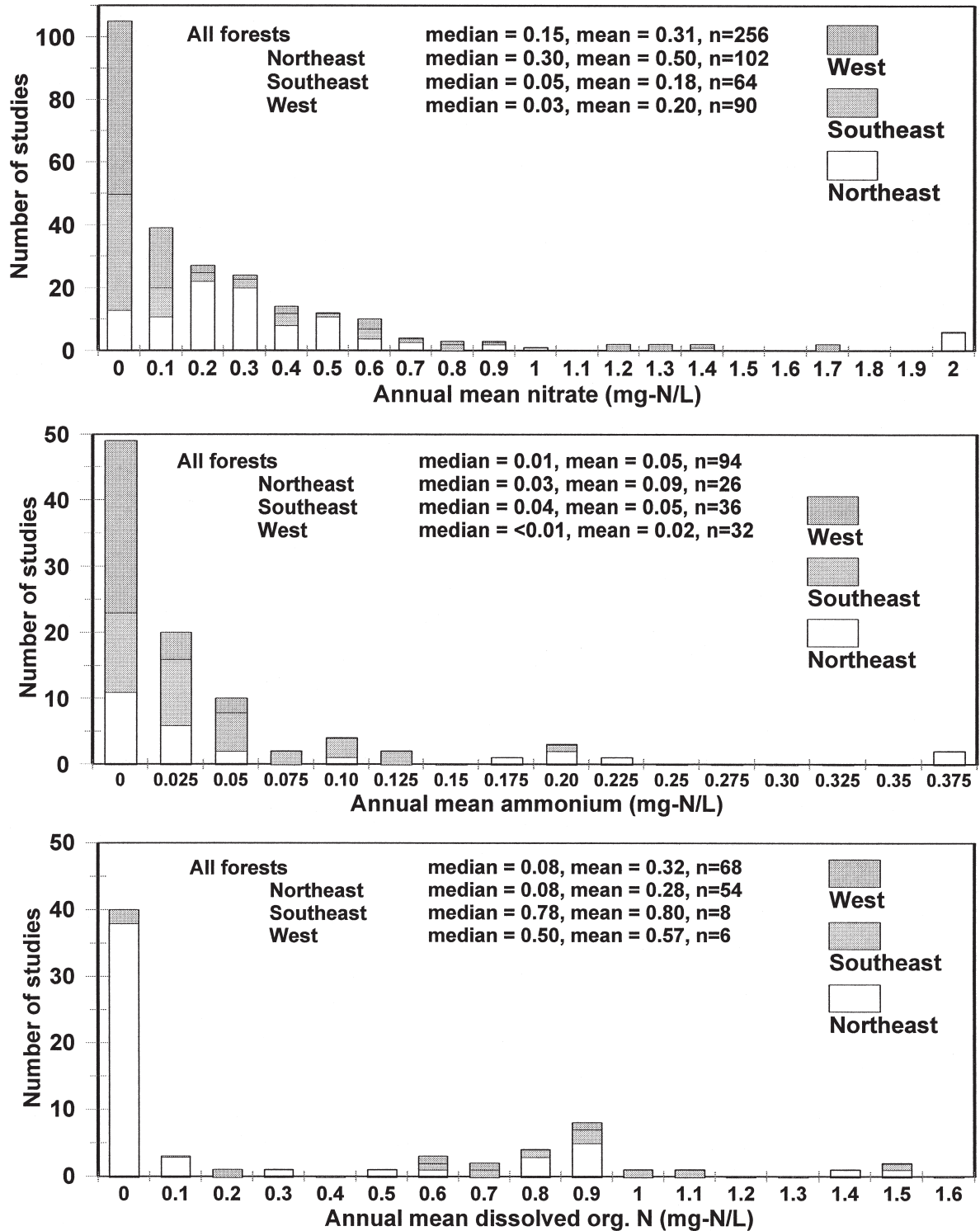


Figure 1. Average Annual Concentrations of Nitrogen Compounds.

Ammonium

Across the United States, concentrations of NH_4^+ in stream water are much lower than NO_3^- concentrations (Figure 1). 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 in the Southeast (mean 0.05 mg N/L, median 0.04 mg N/L).

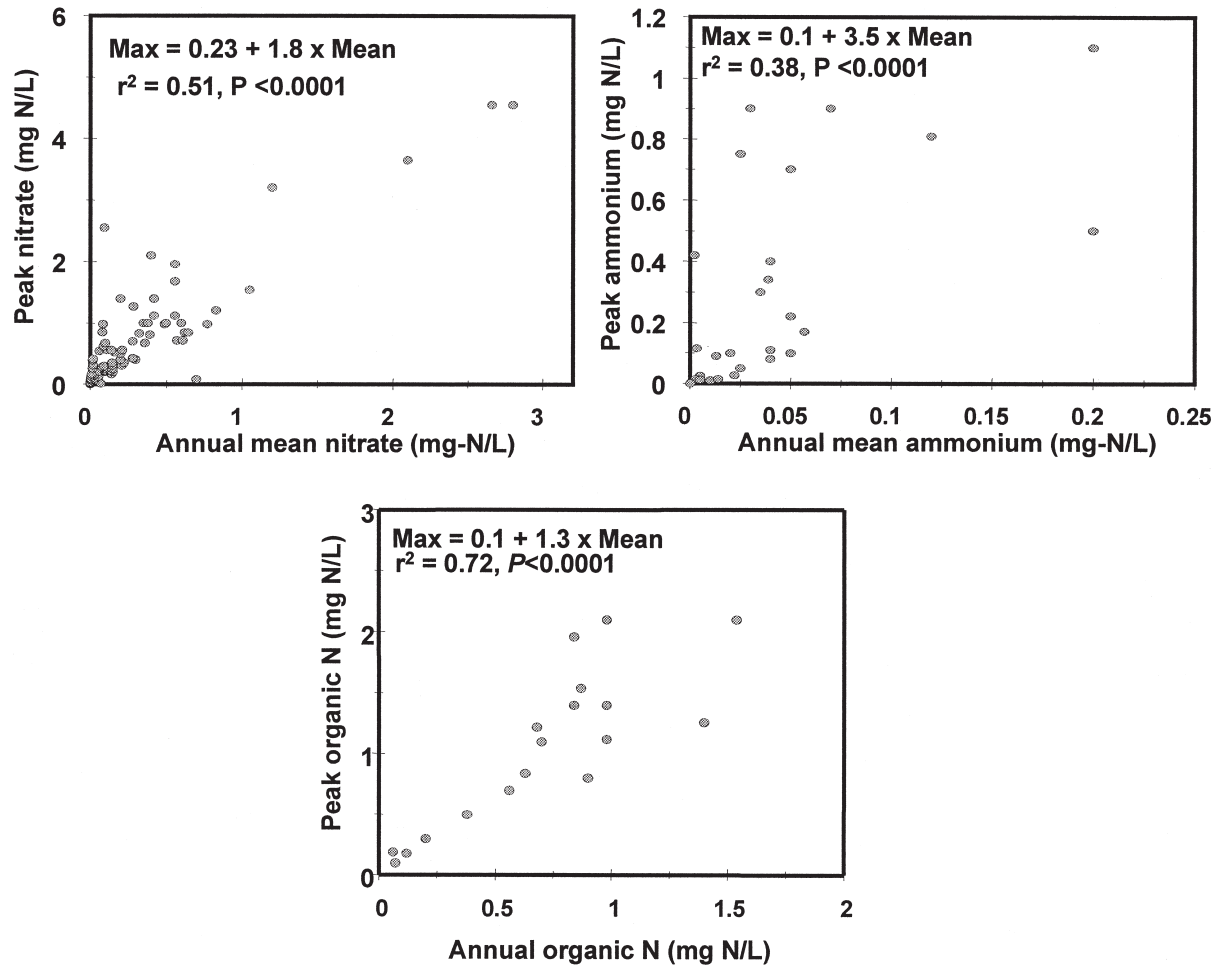


Figure 2. Maximum Observed Concentration of NO_3^- , NH_4^+ , and Organic N as a Function of the Reported Annual Average Concentrations.

Unlike NO_3^- , the pattern of NH_4^+ concentrations does not relate to the pattern of NH_4^+ concentrations in precipitation.

Forest type had less effect on stream water concentrations of NH_4^+ than NO_3^- . 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. The maximum observed concentrations of NH_4^+ were higher in streams with higher annual average concentration (Figure 2), and the slope of the relationship (maximum is more than three times average) was much steeper than for NO_3^- .

Organic Nitrogen

Across the country, the concentrations of dissolved organic N (DON) were similar to the concentrations of NO_3^- , averaging 0.32 mg N/L (median 0.08 mg N/L)

(Figure 1). 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 N forms in streams in the Northeast are about 45 percent NO_3^- , 10 percent NH_4^+ , and 45 percent DON. In the Southeast and West, NO_3^- comprises about 30 percent of the stream water N, NH_4^+ 10 percent, and DON about 60 percent. For comparison, Lewis *et al.* (1999) characterized stream water NO_3^- concentrations from tropical streams in the Americas and found that DON comprised about 50 percent of the dissolved N load, with NO_3^- contributing 40 percent and NH_4^+ just 10 percent.

Coniferous forests showed much higher concentrations of DON (mean and median 0.7 mg N/L) than hardwood forests (mean 0.2 mg N/L, median 0.1 mg N/L). Overall, stream water N in hardwood forests was dominated by NO_3^- (60 percent of all dissolved N forms), followed by DON (30 percent) and NH_4^+ (10

percent). In conifer forests, DON accounted for 80 percent of all dissolved N forms, followed by NO_3^- at 17 percent, and NH_4^+ at 3 percent.

The maximum observed concentration of DON was about 30 percent greater than the annual average DON, which is notably less than the differences between maximums and means for NO_3^- and NH_4^+ (Figure 2). Streams that had high annual average NO_3^- concentrations also showed high annual average concentrations of DON. No pattern was apparent between DON concentrations and stand age or geology (data not shown).

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 stream waters. For example, the total stream load of N in the control Watershed No. 9 at the H.J. Andrews Experimental Forest was comprised of 30 percent particulate N, 60 percent dissolved organic

N, and $\text{NH}_4^+ + \text{NO}_3^-$ contributed just 10 percent (NCASI, 2001).

PHOSPHATE FORMS

Inorganic Phosphate

Across the United States, the average concentration of inorganic P in forested streams was 12 $\mu\text{g P/L}$, with a median of 4 $\mu\text{g P/L}$ (Figure 3). Concentrations were higher in streams from the Northeast (mean 35 $\mu\text{g P/L}$, median 15 $\mu\text{g P/L}$) than for the Southeast (mean 14 $\mu\text{g P/L}$, median 7 $\mu\text{g P/L}$), or the West (mean 8 $\mu\text{g P/L}$, median 3 $\mu\text{g P/L}$).

Phosphate concentrations appeared to be two to four times higher for streams in hardwood forests (mean 20 $\mu\text{g P/L}$, median 15 $\mu\text{g P/L}$) than in coniferous forests (mean 10 $\mu\text{g P/L}$, median 4 $\mu\text{g P/L}$), but the number of hardwood streams was too small ($n = 16$) for high confidence in the effects of forest

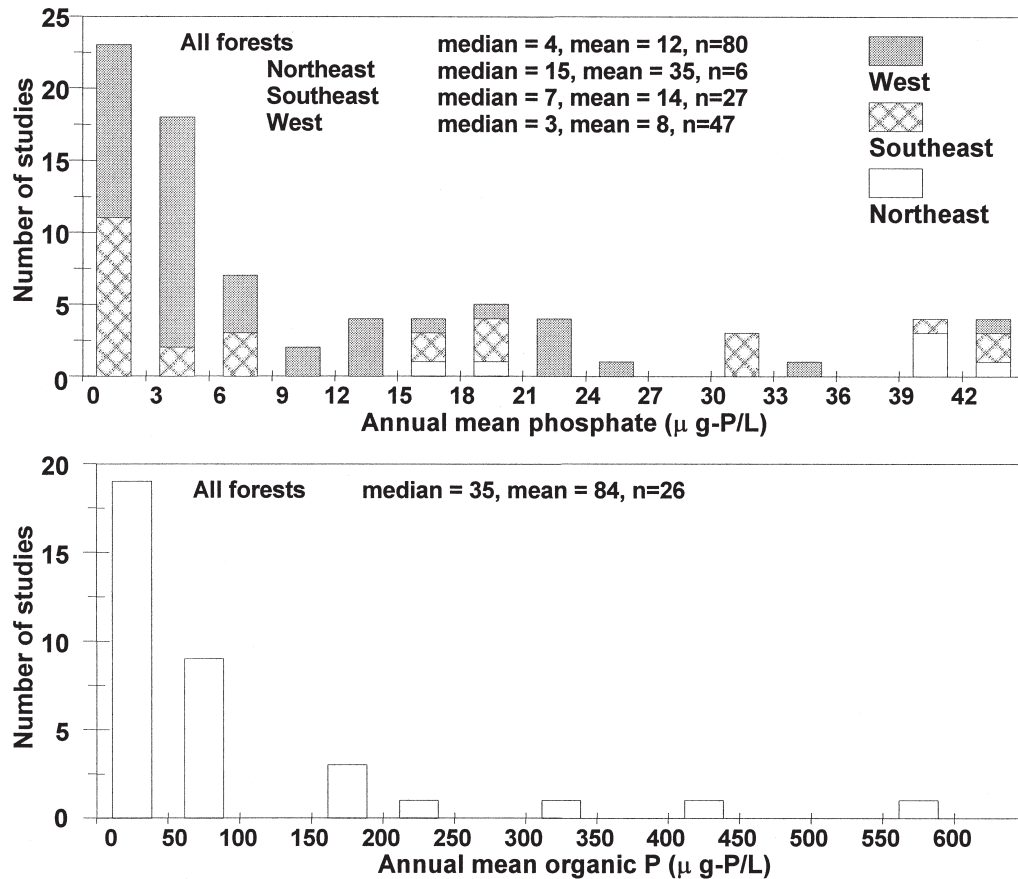


Figure 3. Average Annual Concentrations of Phosphorus Compounds.

type. Concentrations of phosphate tended to be twice as high in younger forests than in forests over 100 years of age. This pattern could result from more frequent timber harvesting on more productive (higher P) soils. In contrast to the patterns for N compounds, the maximum observed concentrations of inorganic phosphate did not relate to the annual average concentrations ($r^2 = 0.04$).

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 4). Within individual streams, average concentrations of dissolved organic phosphate showed no correlation with annual average inorganic phosphate. Fifteen streams had data for the

concentrations of both dissolved inorganic and organic P, and in every case, the concentration of organic P equaled or exceeded the concentration of inorganic P. Information from more streams would be useful, but these data indicated that dissolved organic phosphate probably dominates the pool of dissolved phosphate in forested streams (Martin and Harr, 1989).

Particulate Phosphate

Few studies have measured concentrations of suspended particulate phosphate in forested streams. In the control Watershed No. 9 at the H.J. Andrews Experimental Forest in Oregon, particulate P accounted for about 20 percent of the stream water P, compared with 40 percent for dissolved inorganic phosphate and 40 percent for dissolved organic phosphate (NCASI, 2001).

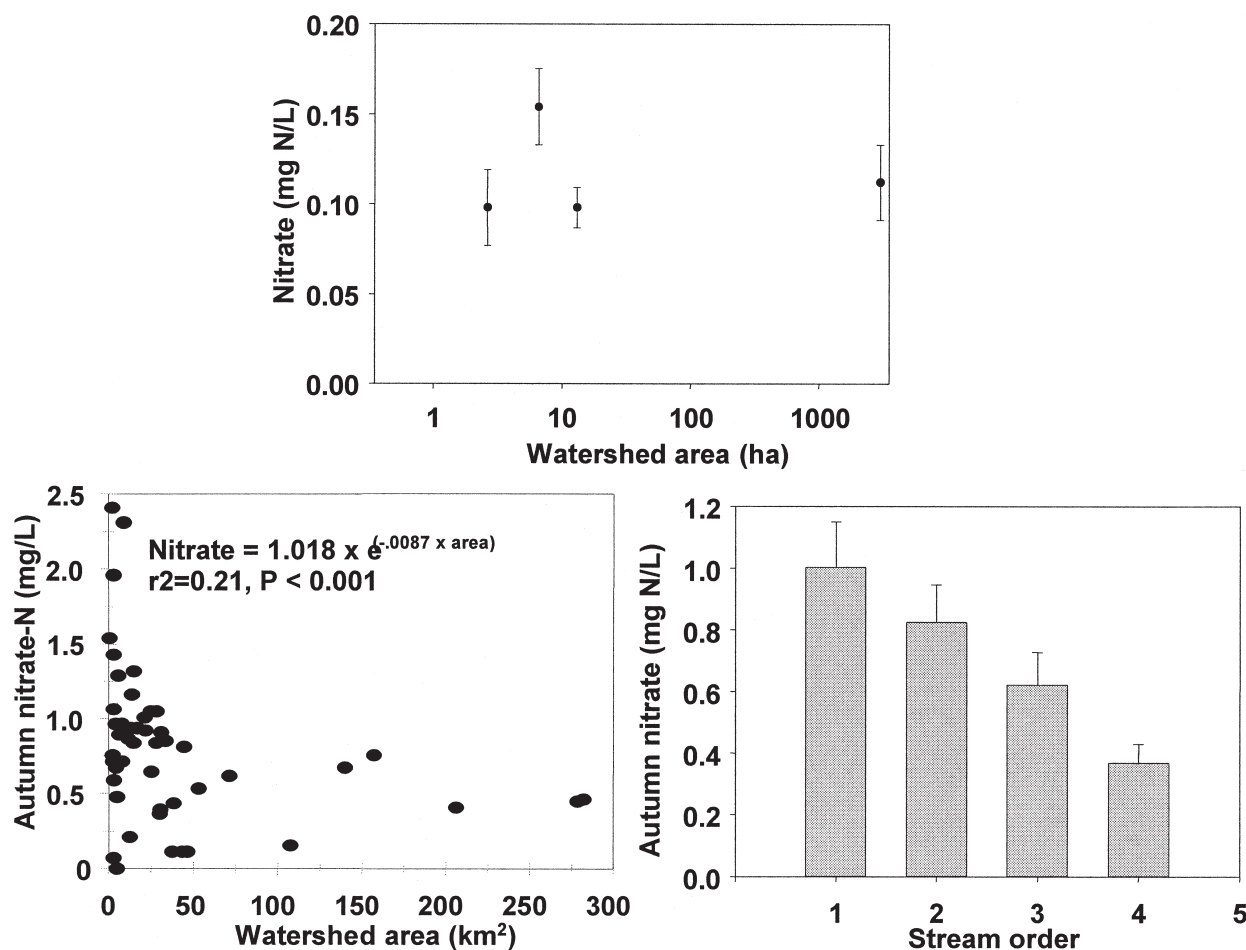


Figure 4. Longitudinal Patterns of Variation in NO_3^- Concentrations. Top: WS No. 6 and the Hubbard Brook Valley, New Hampshire, USA, based on data from Johnson *et al.* (2000). Bottom: Forest streams in the Oregon Coast Range, USA, by watershed area (left) and stream order classes (right), from data in Wigington *et al.* (1998). Bars are standard errors.

FACTORS ACCOUNTING FOR VARIATION IN STREAM WATER CHEMISTRY PATTERNS

Some of the variation in the broad scale, synoptic patterns relate to differences in vegetation type (higher concentrations of NO_3^- in hardwood watersheds), age (higher concentrations of some elements in streams draining younger forests), or from differences associated with geology, stream order, and basin size. 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, in relation to forest management treatments, and in relation to watershed size within basins. The state of knowledge does not allow a full accounting for the importance of each of these features, though some case studies illustrate likely influences of these factors.

Variations in Stream Water Chemistry Within Local Watersheds

Patterns of variation in stream water chemistry among small watersheds in a local (10 to 100 km) area may not resemble patterns from across the U.S., or from large basins in the same region. Lovett *et al.* (2000) monitored 39 first-order 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. Fewer than 20 percent of the streams had NO_3^- concentrations less than 0.2 mg N/L. This 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 NO_3^- , with 85 percent of the streams falling below 0.1 mg N/L.

Watershed elevation may account for some differences among local watersheds. Stream water concentrations of NO_3^- declined from 0.75 mg N/L at 1,600 m elevation in the Great Smoky Mountains National Park to 0.2 mg N/L below 800 m elevation (Flum and Nodvin, 1995). 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 to that found for national trends. Streams draining old, unlogged forests averaged about twice the NO_3^- concentrations

of streams in watersheds with more than 75 percent of the forest in post-harvest, regrowing forests (Silbee and Larson, 1982). Flum and Nodvin (1995) considered the upper elevation forests to be saturated with N, 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 1,000 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 saturated with N.

Intriguingly, Lawrence *et al.* (2000) reported an opposite trend in NO_3^- concentrations with elevation in the Catskill Mountains of New York. They examined the trend with elevation within a single watershed, and found that winter NO_3^- concentrations increased from 0.22 mg N/L at 1,060 m elevation to about 0.35 mg N/L at 800 m elevation (summer concentrations showed no pattern with elevation). This pattern of lower NO_3^- concentration in winter at the higher elevation was the reverse of the pattern in annual NO_3^- deposition in precipitation: 20 kg N/ha/yr at the higher elevation, 14 kg N/ha/yr at the lower elevation. Lawrence *et al.* (2000) concluded that stream water NO_3^- concentrations probably increased with decreasing elevation as a result of a shift from high elevation conifer forests to low elevation hardwood forests, along with an associated decrease in forest floor mass. This pattern is consistent with the national pattern of increased N for hardwood dominated watersheds compared to watersheds dominated by conifers.

Stottlemeyer *et al.* (1997) followed changes in NO_3^- concentrations from the upper reaches of Lexen Creek in the Fraser Experimental Forest in Colorado. Annual average concentrations of stream water NO_3^- declined ($P < 0.05$) from 0.11 mg N/L at 3,415 m elevation to 0.04 mg N/L at 2,985 m elevation. Stottlemeyer *et al.* (1997) attributed the decline to uptake within the soil system in the watershed, rather than to retention within the aquatic ecosystem.

Effects of Local Differences in Parent Material

Although N is a minor constituent of most parent materials, exceptional situations have been reported where geologic substrates provide large amounts of NO_3^- to streams. For example, Holloway and Dahlgren (1999) found that some rocks in the Mokelumne watershed of California contained 250 to 1,000 mg N/kg of rock, and 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 2,500 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) attributed high concentrations of NO_3^- in lower reaches of the Mokelumne River to sources in metasedimentary and metavolcanic rocks.

Rock type influences stream water NO_3^- concentrations in the Fernow Experimental Forest in West Virginia. Streams in the Fernow area generally have high concentrations of NO_3^- , and are N saturated (inputs equal outputs) (Gilliam *et al.*, 1996, 2001; Williard *et al.*, 1999); concentrations of NO_3^- were higher in streams draining limestone bedrock than sandstone bedrock (Wooten *et al.*, 1999).

Bedrock and subsoil can also provide substantial quantities of phosphate to streams in some situations. Kelly *et al.* (1999) intensively characterized the mass balance of water and P for the Tualatin River in Western Oregon. During low flow periods, much of the river water is derived from ground water sources that are in contact with P-bearing minerals (particularly vivianite and iron phosphate). Their mass balance showed that ground water source of mineral derived phosphate contributed about 25 percent 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 (particularly during critical periods of low flow when eutrophication may be a problem).

Longitudinal Trends in Stream Chemistry Within Basins

Stream water chemistry may or may not be affected by increasing basin and stream size in downstream reaches. Johnson *et al.* (2000) examined stream water chemistry from the headwaters of Hubbard Brook Watershed No. 6 (a 13 ha watershed) to the main stream draining the 30 km² watershed. Despite changes in vegetation and basin area, NO_3^- concentrations were between 0.10 and 0.15 mg N/L for all stream segments (Figure 5). Lindsey *et al.* (2001) evaluated the effect of basin area (from 0.2 to 115 km²) on NO_3^- concentrations in streams draining from the Ridge and Valley Province into Chesapeake Bay and also found no relationship between basin area and NO_3^- concentration ($r^2 = 0.01$, $P = 0.51$).

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 NO_3^- showed a strong,

exponential decline in relation to watershed area, and a linear decline in relation to stream order (Figure 5). The authors hypothesized that vegetation was responsible for most of the variation in stream water chemistry, with higher values for smaller streams draining watersheds with substantial influences of N-fixing red alder. However, they found little association between NO_3^- 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.

This pattern of declining NO_3^- 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 km² Willamette Basin, and found that watersheds that were entirely in forest land use had median NO_3^- and total N concentrations of 0.36 and 0.45 mg N/L, respectively. These N values for forested streams were about one-third of the median value for other watersheds in the Willamette Basin (NO_3^- 1.0 mg N/L, total N 1.5 mg N/L). Phosphorus concentrations for forested watersheds (both inorganic phosphate and total phosphate were less than the minimum reporting limit of 10 $\mu\text{g P/L}$) were also far lower than the basin wide median concentration of 60 $\mu\text{g P/L}$ of inorganic P and 100 $\mu\text{g P/L}$ of total P. Higher concentrations in nonforested 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. They concluded that the areal distribution of N-fixing red alder trees was less important in losses of NO_3^- than where the alder occurred. Subbasins with abundant alder in the riparian area or a contribution zone had greater NO_3^- concentrations and fluxes. However, Compton *et al.* (2003) examined patterns of N loss from 26 small watersheds and concluded that the total cover of broadleaved trees (largely red alder) predicted the stream water concentrations of N better than the dominance of broadleaves within the riparian zone.

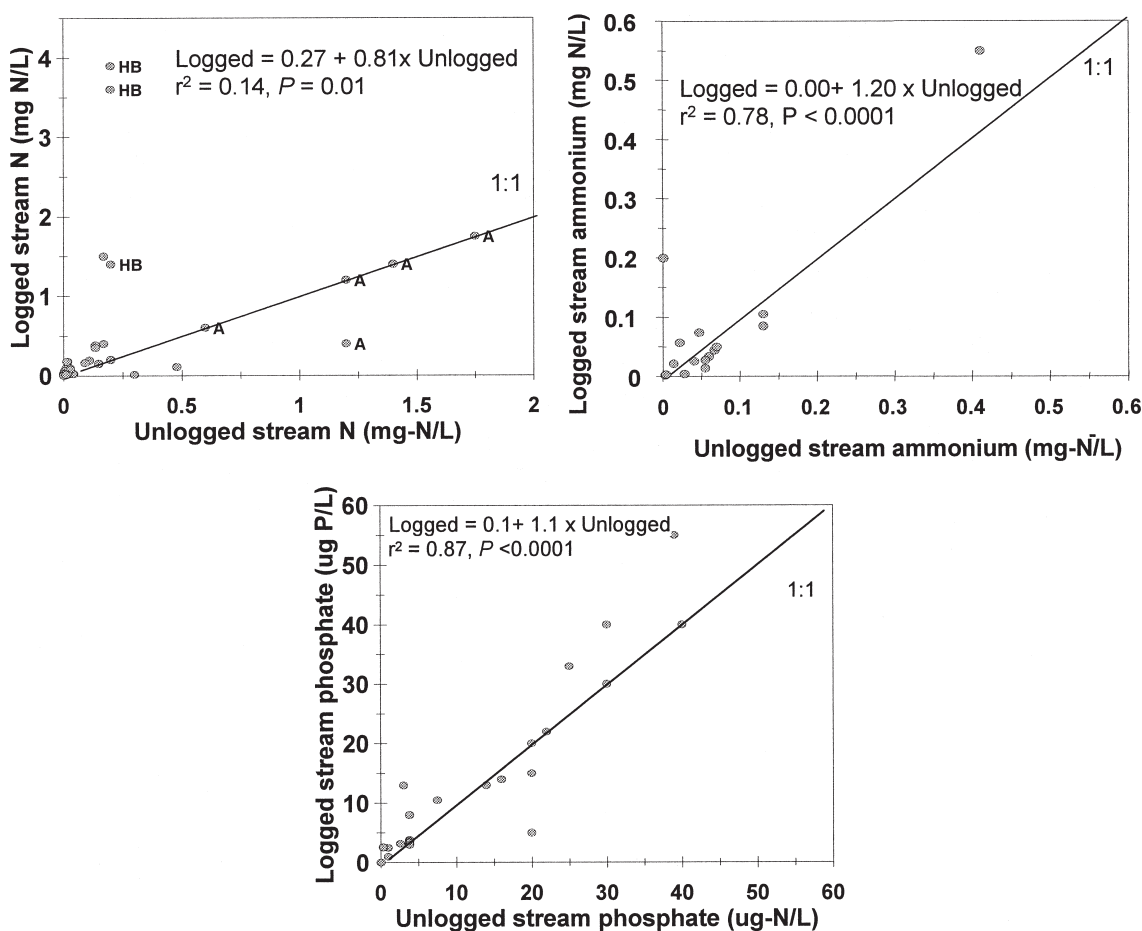


Figure 5. Annual Average Concentrations of NO_3^- (left), NH_4^+ (right), and Inorganic Phosphate (bottom) in Logged Watersheds in Relation to Prelogging (or control) Watershed Concentrations (HB = Hubbard Brook, A = Alder).

Recent Time Trends in Stream Water Chemistry Within Local Watersheds

Decadal scale trends in stream water have been characterized for a number of forests. No general time trends have been noted across the United States, but many streams in New England have shown strong declines in NO_3^- concentration over the past two decades. Goodale (1999) and Goodale *et al.* (2000) resampled 28 streams in the White Mountains that had been sampled earlier by Vitousek (1977). After 23 years of forest aging, NO_3^- concentrations in streams declined by 68 percent in both younger (<100 years) and older forests. Martin *et al.* (2000) resampled the streams in the old growth Bowl Natural Area of the White Mountains of New Hampshire, and found declines of more than 50 percent in NO_3^- concentrations over 20 years. Nitrate concentrations in reference Watershed No. 6 at Hubbard Brook declined from about 0.35 mg N/L in the mid 1970s to about

0.10 mg N/L in the late 1980s to early 1990s. Atmospheric deposition of N was relatively uniform across this local area, and no time trend in deposition occurred over this period (Goodale *et al.*, 2000, 2003).

The region wide pattern remains unexplained, but two possibilities are climatic trends and trends in vegetation composition. Mitchell *et al.* (1996) found that peak NO_3^- concentrations in watersheds in New York and New England were about 30 percent higher following an unusually cold period. Fitzhugh *et al.* (2003) examined the relationship between several indexes of frost severity and stream water chemistry. Between 1970 and 1987, the frost indexes accounted for about 25 percent of the variation ($P < 0.05$) in the three-year running mean concentration of NO_3^- . When the same trends were examined for the longer period of 1970 to 1997, the associations between frost severity and stream water NO_3^- were weaker and largely nonsignificant. Major frost impacts in the early 1990s (the most severe three years in the period of record) showed particularly low concentrations of

NO_3^- in stream water (Fitzhugh *et al.*, 2003). Groffman *et al.* (2001) manipulated the snowpack in stands of sugar maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*) and found that reduced snowpack lowered soil temperatures and found increases in soil NO_3^- concentrations under sugar maple but not yellow birch. If soil freezing played a substantial role in the patterns of stream water NO_3^- concentrations across the Northeast, interactions with other factors were also important (see also Park *et al.*, 2003).

Other climatic factors could influence long term trends in stream water NO_3^- concentrations. Aber and Driscoll (1997) used a model to suggest that drought in the 1960s could have led to high NO_3^- concentrations in the 1970s through a legacy of effects on N mineralization and plant uptake and storage of N. However, the model failed to account for the very low concentrations of NO_3^- 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 and beech, and major recruitment of understory beech seedlings (T. Siccama, Yale University, October 2002, personal communication). Such changes in the forests may influence rates of both N mineralization in soils (e.g., Lovett and Rueth, 1999) and N increment in biomass, and patterns in net N mineralization appear to relate well with stream water NO_3^- concentrations in this region (Goodale *et al.*, 2000).

Variations in Stream Water Chemistry From Forest Disturbances

Disturbances are a normal part of forest landscapes, and disturbances may strongly alter stream water chemistry. Some disturbances affect tree vigor or growth without major mortality of trees. For example, insect defoliation may increase stream water NO_3^- 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.*, 1998).

The effects of forest harvesting on stream water chemistry have been investigated in a wide range of small watersheds. Most of these have documented increases in stream water NO_3^- concentrations, but others have found no effect or even a decline in concentrations (Figure 5). In 43 harvesting experiments, control or unlogged watersheds averaged 0.21 mg N/L as NO_3^- , compared with 0.44 mg N/L for one to five years after logging. Thirty studies showed increases in NO_3^- concentrations (although only four increased

to more than 0.5 mg N/L), nine showed no change, and five declined by 24 to 95 percent. The overall effect of logging was not significant when analyzed by analysis of variance ($P = 0.12$). The post-harvest NO_3^- concentrations correlated with the control values ($r^2 = 0.14$, $P = 0.01$); streams with high NO_3^- concentrations after logging either had high NO_3^- concentrations before logging (site with N-fixing alders), or were from the Hubbard Brook Experimental Forest. The only other exception of NO_3^- increasing by greater than 1 mg N/L after logging resulted from logging a 100-year-old mixed conifer forest along Benton Creek near Priest River, Idaho (Snyder *et al.*, 1975). Confounding factors such as burning and site-preparation may also be important (see discussion on fire below).

Forest harvesting appeared to have little effect on concentrations of NH_4^+ in stream water, 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 ($r^2 = 0.78$, $P < 0.0001$). The pattern was similar for phosphate, with average concentrations for unlogged watersheds of 12 $\mu\text{g P/L}$ compared with 13 $\mu\text{g P/L}$ for logged watersheds ($P = 0.77$). Phosphate concentrations in unlogged and logged watersheds correlated highly ($r^2 = 0.87$, $P < 0.0001$).

Forest harvesting may alter stream water chemistry, but the effects should not be expected to be consistent across forest types and regions. Any initial increase in NO_3^- 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 *et al.*, 1995).

Fire is a major factor in most forests of the United States, including both wildfires and prescribed management fires (DeBano *et al.*, 1998). Burning typically increases stream water nutrient concentrations, but these increases are usually too small and too short in duration to substantially impair water quality. Richter *et al.* (1982) found no differences in concentrations of NO_3^- (0.02 mg N/L), NH_4^+ (0.03 mg N/L), or inorganic phosphate (30 $\mu\text{g P/L}$) in streams draining control or burned watersheds dominated by old loblolly pines. Williams and Melack (1997) found significant increases in stream water NO_3^- concentrations following prescribed fires in mixed conifer forests of the Sierra Nevada in California. Nitrate concentrations in stream water increased dramatically in the first two years after fire, rising from near zero before the fire to annual averages of about 0.5 mg N/L. The concentrations declined in the third year after burning, returning to background levels in the fourth year. Concentrations of NH_4^+ rose from near zero to 0.3 mg

N/L shortly after the burn, but returned to background levels within several months.

Fire intensity appears to be an important factor in watershed nutrient response. A severe windstorm in the Experimental Lakes Area of Ontario preceded a very intense fire that consumed all understory vegetation less than 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 stream water nutrient concentrations after the fire rose by about five-fold to nine-fold. Before the fire, NO_3^- 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 NH_4^+ 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 fire, NH_4^+ 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 $\mu\text{g P/L}$, compared with 12 to 20 $\mu\text{g P/L}$ for two streams in burned watersheds. The highest observed concentration of 91 $\mu\text{g P/L}$ was in a stream in a burned watershed. A severe wildfire in eastern Washington increased stream water concentrations of NO_3^- from background levels of about 0.02 mg N/L to about 0.5 mg N/L for three years (Tiedemann *et al.*, 1978). Concentrations of inorganic phosphate increased from 7 $\mu\text{g P/L}$ to 20 $\mu\text{g P/L}$, and total P increased from 12 $\mu\text{g P/L}$ to 33 $\mu\text{g P/L}$. 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), and this interaction remains largely unexplored in the literature.

The effects of forest fertilization have been examined in several dozen case studies in North America (reviewed by Binkley *et al.*, 1999). Forest fertilization commonly leads to moderate, short term increases in

stream water nutrient concentrations. Average annual NO_3^- concentrations of fertilized forests remained below 0.5 mg N/L for most cases. About 15 percent of the studies showed NO_3^- concentrations above 0.5 mg N/L after fertilization. The peak observed concentrations of NO_3^- were much higher in fertilized forest streams; about half of the studies found peak NO_3^- 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 NH_4^+ concentrations, 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 $\mu\text{g P/L}$, and fertilization either had no effect on the annual average concentration or increased the concentrations up to about 20 $\mu\text{g P/L}$. Short term peak concentrations of phosphate rose to 25 to 150 $\mu\text{g P/L}$ for short periods in about half of the cases.

Insect outbreaks were mentioned above as influencing N loss from forest watersheds (Eshleman *et al.*, 1998, 2000). In some cases, heavy N discharge has been linked to gypsy moth caterpillar droppings. At the peak of an infestation in the Chesapeake Bay as much as 12 percent of the forest was defoliated, which may have also contributed to the increased N losses.

Patterns in Stream Water Chemistry in Small and Large Watersheds

As noted above, stream water chemistry may relate to basin size or stream order as a result of integrating larger areas and changing physical and ecological characteristics of higher stream orders (Vannote *et al.*, 1980). The patterns for the small watersheds in this summary were compared to the systematic networks of sites maintained by the U.S. Geological Survey (USGS). 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 2,500 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 *et al.* (2000) summarized patterns in stream water 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 . Ten of the 43 HBN basins and 2 of the 22 NAWQA basins used by Clark *et al.* (2000) were primarily dominated by grasslands or shrublands (G.M. Clark, USGS, January 2001, personal communication) and were omitted from this comparison.

SUMMARY AND CONCLUSIONS

All data sets showed roughly similar distribution frequencies for stream water concentrations of NO_3^- , NH_4^+ , and phosphate (Figure 6). The HBN sites had the highest frequency of streams with less than 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 NO_3^- concentrations less than 0.5 mg N/L, compared with 94 percent of the NAWQA and RW sites and 82 percent of the small watershed sites. The higher frequency of streams with higher NO_3^- concentrations in the small watersheds were from three types of sites with NO_3^- 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 N-fixing red alder in Oregon. These high NO_3^- systems did not fall within any of the HBN or NAWQA sites (and the RW group included only one high NO_3^- stream at Hubbard Brook, New Hampshire), so the lack of high NO_3^- 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. Wightington *et al.* (1998) suggested that even if high nitrate streams are present in the region being monitored it is likely that small streams will display greater extremes while larger watersheds will integrate watershed conditions.

The patterns for concentrations of NH_4^+ and inorganic phosphate were similar across the three types of sites (data not shown) and the overall distribution of concentrations of these compounds appears to be largely consistent in small and larger basins.

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 stream water N concentrations. For example, Alexander *et al.* (2000) examined the rate of loss of stream water N as a function of stream size. As water flows downstream, N compounds may be removed through biotic uptake, movement into sediments, or conversion to gas. Small streams with flows of less than $28 \text{ m}^3/\text{s}$ tended to lose about half of their N load daily, while larger streams lost about 5 to 10 percent of their N load daily, and rivers lost less than 1 percent daily.

Stream water chemistry is variable among forested streams. Most forested streams have less than 0.15 mg N/L as NO_3^- , 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 stream water chemistry can be explained by rates of atmospheric N deposition. The northeastern U.S. has the highest rates of both N deposition and stream water concentrations of NO_3^- . 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.

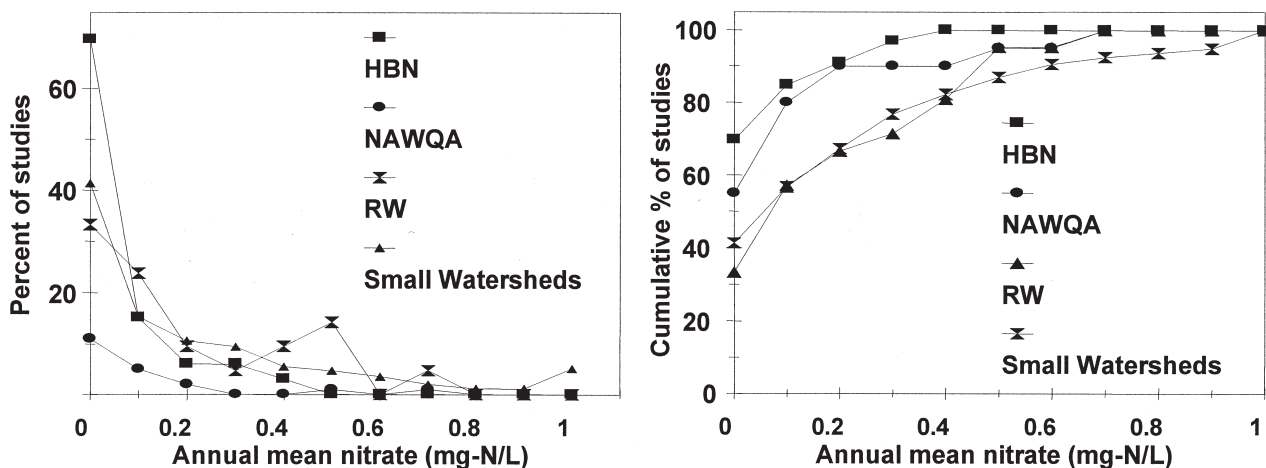


Figure 6. Frequency Diagrams for Concentrations of NO_3^- for Three Sets of Forested Streams. HBN is the USGS Hydrologic Benchmark basins, NAWQA is the USGS National Water Quality Assessment basins, RW is the set of research watersheds from Clark *et al.* (2000), and Small Watersheds is the group of streams described in this paper.

Hardwood forests have two to three times the concentrations of NO_3^- , NH_4^+ , 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 NO_3^- N accounts for about 60 percent of all dissolved N in streams in hardwood forests, organic N comprises about 80 percent of the dissolved N in streams in coniferous forests. Process based understanding of the biogeochemistry of dissolved organic N will require substantially more investigation (Neff *et al.*, 2003). These synoptic patterns of variation in water chemistry cannot be attributed (in most cases) to single factors. Hardwood forests are found more commonly in the northeast, where the combination of temperate climate and high N deposition may contribute to higher concentrations of NO_3^- in stream water.

The frequency of chemical concentrations in streams draining small, forested watersheds appears to differ substantially from the frequencies found in national monitoring programs of larger, mostly forested watersheds. 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 stream water concentrations in low order headwater streams and larger (third-order 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). 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 concentrations in higher order streams appears to derive from fundamental changes in stream ecology with increasing order (the river continuum concept) (Vannote *et al.*, 1980). Trophic dynamics shift from processing detritus in low order headwaters to in-stream photosynthesis by algae in higher order streams. Declines in NO_3^- in higher order streams relate to increasing algal biomass (Wall *et al.*, 1998; Wigington *et al.*, 1998). This inference is consistent with conventional expectations for stream ecosystems, but some additional surveys that examined the covariation between nutrient concentrations and algal biomass with stream order may be useful.

The USEPA (2000) 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 two-fold, whereas the ranges found within regions typically spanned a five-fold (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 NO_3^- than streams in the Northeast. Within the local area of the Oregon Coast Range, stream concentrations of NO_3^- are commonly less than 0.2 mg N/L and greater than 1.0 mg N/L. 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.

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 previously, the Ecological Society of America (Carpenter *et al.*, 1998) did not mention forest streams as nonpoint sources of N and P pollution, and none of the studies reviewed for this report indicated any negative effects of the observed concentrations of N and P. Differences in stream water 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.

The synopsis contained herein analyzed published data on forest streams, and the diverse array of original studies was not designed as an integrated network with common protocols or randomly selected streams that would ensure consistency among studies or balanced sampling of forest types, management practices, and regions. Such a designed network is not likely to develop soon, though statistically designed sampling programs, such as USEPA's Environmental Monitoring and Assessment Program, may provide a major step forward (Rohm *et al.*, 2002). Some general trends from the literature are robust, such as the major contribution of dissolved organic N to the stream water load of N in conifer streams, and the consistent relationship between annual average and peak concentrations for nitrate and for ammonium, but not for phosphate. This overview may be most

useful in providing a baseline against which individual cases may be compared, and concentrations that differ substantially from this compilation of published results would warrant further investigation.

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