The Spatial and Temporal Variability of Nitrate in Streams of the Bull Run Watershed, Oregon

by

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An 18-year record of nitrate (NO₃), orthophosphate, total nitrogen and total phosphorus in four streams of the Bull Run watershed, Oregon, was examined to determine its precision and time resolution. Of these four species, only NO₃ was found to be known to a sufficient level of detail for modeling and inference purposes. The precision of precipitation NO₃ and total nitrogen measurements at the Bull Run was found to be inadequately determined and much poorer than the precision of corresponding stream chemistry data.

An autoregressive time-series multiple-regression model was developed to predict stream NO₃ load (kg/ha/day) based on 14-day cumulative stream discharge, the current day's, previous day's and cumulative 7-day precipitation, the 14-day average maximum air temperature and a storm hysteresis factor. Coefficients of determination ranged from 0.66 to 0.75. The model was found to be of limited use in inference about watershed processes due to the coarse time resolution of the data (1 to 3 week sampling intervals). Although the 47 independent variables considered were known at much finer time scales (30 minutes to 1 day), this was insufficient to offset the problem of long sampling intervals and strengthen the inference capability. Complete description of the nutrient record would require sampling intervals of less than one day during periods of rapid change.

Peak NO₃ concentration and load events were found to be unrelated to suspended sediment concentration or the magnitude of snow melt. Stream NO₃ showed a weak inverse relationship with precipitation NO₃ or total nitrogen content. Where light and other non-nutrient factors are present in abundance, streams of the Bull Run watershed were found to be predominantly phosphorus limited, although nitrogen-limited conditions occur in 1 to 37 percent of the days sampled, depending on sub-basin.

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THE SPATIAL AND TEMPORAL VARIABILITY OF NITRATE IN STREAMS OF THE BULL RUN WATERSHED, OREGON

I. INTRODUCTION

As the principal municipal water source for the city of Portland, Oregon, the Bull Run Watershed has been widely recognized as possessing water of the highest quality (Aumen et al., 1989). As such, the watershed has often been the focus of public debate over how it should be managed and what activities can occur on its soil without significantly impairing that water quality. Public concern has been voiced in a series of congressional rulings to clarify the roles, rights and responsibilities of the two governmental bodies most directly concerned with the fate of the watershed: the city of Portland, which has extracted water from the basin since 1895, and the U.S. Forest Service (USFS), which manages the land as part of the Mt. Hood National Forest.

This clarification process, which makes an interesting story in itself (see City of Portland (1983) for a detailed historical account), culminated in the passage of Public Law (PL) 95-200 in 1977. PL 95-200 created the 38,601-ha (95,382-acre) Bull Run Watershed Management Unit and affirmed that the primary objective within the unit would be the continued production of pure, clear, raw, potable water for the city of Portland (USFS, 1979). A secondary management objective would be to administer the renewable resources within the unit in accordance with the laws, rules, and regulations applicable to National Forest System lands except to the extent that any practice is found to adversely affect the water quality.

To this end, the law mandated the establishment of a water quality monitoring system and a set of water quality standards. The standards were to be based on data collected during the period from 1967 to 1975 or the first three years of record thereafter if no data for the parameter in question existed during this baseline period (USFS, 1979). Current standards, it should be noted, were developed using a non-parametric time series method which required more data than three years (six years minimum) and provided better estimates of background variability (Robbins, 1986).

Even before the passage of PL 95-200, the USFS and the city had been cooperating to systematically collect water quality data. Five key monitoring stations had been established (see Figure 1), and a water quality laboratory, operated by the city, had been situated at the Headworks. The key stations correspond to five major sub-basins within the drainage: Headworks (Station No. 2), Fir Creek (Station No. 44), North Fork (Station No. 15), South Fork (Station No. 35) and the Main Stem (Station No. 18). Monitoring at these stations for nutrients began with nitrate (NO₃) and orthophosphate (PO₄) in July, 1974. In April, 1985, monitoring was extended to include total nitrogen and total phosphorus. Data was collected on a weekly basis for the first four years, then at two-week intervals between June, 1978 and June, 1979. A three-week collection interval was used between June, 1979 and September, 1985. Since September, 1985, data has again been collected every two weeks.

Although this data has been used frequently for assessing compliance with the set of water quality standards which has been selected for the Bull Run, it has never been systematically examined *in toto* with scientific objectives in mind. Thus, a somewhat unique research opportunity exists to investigate the dynamics of water quality parameters and to model the relationship between these parameters and other environmental factors in a system having only modest influence by management and a relatively long period of record. The time span is significant in that water quality parameters frequently exhibit large variabilities which may go undetected in short-term studies, and which may mask the trends present in studies of intermediate length. Furthermore, no other data set of comparable



Figure 1. Map of the Bull Run watershed, Oregon (adapted from Rinella, 1987).

duration, accuracy and consistency exists for stream nutrients in Western Oregon, which makes this data significant as a document of long-term trends, if any, for the region.

The original intention of this study was to focus on four nutrients (NO₃, PO₄, total nitrogen and total phosphorus) at each of the four monitoring stations which lie upstream from the reservoirs (thus excluding the Headworks site) to create predictive models and make conclusions about watershed processes controlling nutrient levels. However, considerations of data resolution, to be described below, dictated that efforts be concentrated on NO₃ and to a lesser extent total nitrogen. Furthermore, a greater portion of the effort has been directed at the issue of data resolution, its measurement, and its effect on study conclusions.

Specifically, the objectives of this study are: 1. to conduct an assessment of the resolution of the Bull Run NO₃ data to evaluate the scope of inference possible given that data and to contrast it with data available for other nutrients; 2. to devise a mathematical model to predict the NO₃ loads¹ and concentrations at the key monitoring stations, given the values of other, more easily-measured environmental variables, and; 3. to investigate, within the scope of possible inference, watershed processes which act to influence the NO₃ levels in streams of the Bull Run system.

 $^{1}NO_{3}$ load is the product of concentration and stream discharge, converted to units of Kg/ha/day.

II. DESCRIPTION OF THE AREA

The Bull Run River Basin lies about 25 miles east of urban Portland, Oregon in a zone of transition between the Western Cascades and High Cascades physiographic provinces (Schultz, 1981). Two manmade storage reservoirs dominate the lower elevations of the watershed. Total basin area at the lower dam (Reservoir No. 2) is 26,417 ha (102 mi²). The portion of the basin upstream from the reservoirs is partitioned into four sub-basins as indicated in Table 1. These sub-basins directly correspond to four of the key monitoring stations (the Headworks monitoring station, which lies downstream of the reservoirs, was not included in this study).

Sub-basin	Area, ha (mi ²)	Mean elevation, m (ft)	Percent of area above 792 m	Mean azimuth, degrees	Mean slope, m/km (ft/mi)
Fir Creek	1,414 (5.46)	920 (3,020)	68.4	102	295 (1,560)
North Fork	2,155 (8.32)	860 (2,820)	68.5	31	252 (1,330)
South Fork	3,989 (15.4)	823 (2,700)	48.6	93	252 (1,330)
Main Stem	12,410 (47.9)	939 (3,080)	73.0	107	316 (1,670)

Table 1. Physical characteristics of the Bull Run sub-basins (from Rinella, 1987). See text for definitions.

In addition to sub-basin areas and mean elevation, Table 1 shows the percent of basin area above 792 m (2,600 ft) elevation, mean subbasin azimuth, and mean sub-basin slope. Mean azimuth is defined as the compass bearing of a line connecting the points delimiting 10 and 85 percent of the distance between the gage site and basin divide (Rinella, 1987). Mean basin slope was obtained from a U.S. Geological

Survey (USGS) topographic map by multiplying the contour interval by the total length of contours within the sub-basin, then dividing by the sub-basin area (Rinella, 1987).

Streams of the watershed are deeply incised, producing the steep canyon walls characteristic of the Western Cascades. Elevations in the watershed range from 262 m (860 ft) and 319 m (1,045 ft) at the lower and upper reservoirs (Reservoir No. 2 and Reservoir No. 1), respectively, to 1,400 m (4,600 ft) at Hiyu Mountain in the eastern end of the Main Stem sub-basin.

Four geological formations dominate the landscape (Schultz, 1981). The oldest rocks are part of the Grande Rhonde and Wanapum Basalt Formations of the Columbia River Basalts (middle Miocene age). Next oldest is a layer of weak pyroclasic material, the Rhododendron Formation (late Miocene to early Pliocene age). Slump and earthflow type mass failures in the basin tend to concentrate in the Rhododendron Formation, which has been highly altered to smectite clays and other secondary minerals, making it the source of occasional large pulses of suspended sediment in adjacent streams. On top of the Rhododendron Formation lies a somewhat complex assemblage of Pliocene and Quaternary volcanic rocks. Finally, Quaternary landslide deposits cover the bedrock in parts of the North Fork sub-basin, while glacial moraine and outwash occur in the Main Stem drainage (see Table 2).

	Percent of	sub-basin area	occupied by:	
Sub-basin	Columbia River Basalts	Rhododendron Formation	Pliocene and Quaternary Volcanics	Quaternary Landslide and Glacial Deposits
Fir Creek	0.1	7.1	92.8	0.0
North Fork	5.5	8.5	84.7	1.3
South Fork	0.2	3.3	96.5	0.0
Main Stem	15.6	2.3	80.6	1.5

Table 2. Sub-basin surface geology (from Rinella, 1987; Schultz, 1981).

Soil parent material, then, consists mainly of andesitic, pyroclastic and basaltic rocks with some deposits of loess and volcanic ash (Green, 1983). Soils are mostly deep (greater than 1 m) and well drained. Organic matter content of the upper 30 cm typically ranges from 3 to 32 percent, with the greatest accumulations at low elevations. Total nitrogen content ranges from 0.06 to 0.64 percent, and carbon/nitrogen ratios vary between 18 and 44 percent (USFS, undat.). Specific information on cation and anion exchange capacities of these soils is not available, although both may be substantial due to the amorphous silicate clays and aluminum-humus complexes typically present in fine-textured andic (volcanic-derived) soils (Brady, 1990).

Vegetation on the Bull Run watershed is typical of that found in the western Oregon Cascades. The western hemlock (<u>Tsuga heterophylla</u>) climax forest zone occupies much of the area, particularly below elevations of 1,070 m (3,500 ft) (USFS, 1979). This zone consists of a predominantly closed canopy of Douglas-fir (<u>Pseudotsuga menziesii</u>) and western hemlock, with western redcedar (<u>Thuja plicata</u>), red alder (<u>Alnus rubra</u>) and bigleaf maple (<u>Acer macrophyllum</u>) commonly forming the overstory in riparian zones and other wet areas. The occurrence of red alder is noteworthy, given that species' reputation as a nitrogen fixer. However, the exact coverage and spatial distribution of red alder throughout the watershed has not been quantified.

Above 1,070 m (3,500 ft), plant assemblages belonging to the Pacific silver fir (<u>Abies amabilis</u>) zone are found, with the mountain hemlock (<u>Tsuga mertensiana</u>) zone represented at the highest elevations and in cooler, shadier micro-climates. Extensive areas of talus occur in some parts of the watershed, particularly the upper reaches of the Main Stem sub-basin. These talus slopes are sparsely vegetated, but support growth of red alder and Sitka alder (<u>Alnus sinuata</u>), another nitrogen fixer, around their fringes.

Commonly occurring shrub species include huckleberries (Vaccinium spp.), vine maple (Acer circinatum), salal (Gaultheria shallon), rhododendron (Rhododendron macrophyllum), Oregon grape (Berberis nervosa), devil's club (Oplopanax horridum), trailing blackberry (Rubus ursinus) and salmonberry (Rubus spectabilis). Common elements of the forb component are sword fern (Polystichum munitum), oxalis (oxalis troliifolium), bunchberry (Cornus canadensis), beargrass (Xerophyllum tenax) and twinflower (Linnea borealis) (USFS, 1979).

About 33 percent of the watershed, overall, consists of old growth forest (USFS, 1979). The rest is at various seral stages from 0 to 200 years of age. Timber harvest first became a significant activity in the 1950's. Between the years 1958 and 1991, total harvest on the North Fork, South Fork and Main Stem sub-basins amounted to 24.6, 24.9 and 18.6 percent of the areas of those subbasins, respectively. Most of that occurred prior to 1981. Between 1982 and 1991, harvest was mainly restricted to areas affected by blowdown from a severe wind storm occurring in December of 1983, which affected approximately 2,335 ha (5,770 acres) of old growth forest. During this ten-year period, total harvest as a percentage of subbasin area amounted to 0.8, 7.0 and 4.6 percent on the North Fork,

South Fork and Main Stem drainages, respectively. The Fir Creek subbasin has experienced no harvest since 1967 when 5.7 ha (14 acres, or 0.4 percent of the sub-basin area) was clearcut.

Natural disturbances in the form of catastrophic (i.e. basinwide) fire are estimated to occur on the average about once every 500 years (USFS, 1979).

Average annual precipitation at the Headworks is 218 cm (85.7 inches) (USFS, 1979). Precipitation increases with increasing elevation and in a general north-northeast direction, reaching maximum values of 432 to 457 cm (170 to 180 inches) in the upper end of the North Fork drainage and on the high point of the divide between Fir Creek and the South Fork (USFS, 1979). Unit runoff values (cm/year see Table 3) are high even for the Pacific Northwest (Aumen et al., 1989). Variation in runoff values between sub-basins is large due to differences in aspect and elevation. Evapotranspiration losses are estimated to be roughly 76 cm (30 inches) per year (Aumen et al., 1979). Fog drip has been identified as a potentially large moisture input (perhaps as much as 30 percent of gross annual precipitation) on some parts of the Bull Run watershed, particularly during the summer months (Harr, 1982). However, the overall importance of this hydrologic input, which goes unmeasured by standard precipitation gages, its areal extent, and its response to timber harvest is a subject of ongoing debate (Ingwerson, 1985).

	Average runoff	
Sub-basin	cm/yr (in/yr)	m ³ /s (CFS)
Fir Creek	233 (91.9)	1.05 (37)
North Fork	321 (126.4)	2.18 (77)
South Fork	252 (99.2)	3.17 (112)
Main Stem	300 (118.1)	11.7 (416)

Table 3. Hydrological characteristics of the sub-basins for the period 1960-1987 (from Aumen et al., 1989)

III. GENERAL LITERATURE REVIEW:

NITROGEN IN STREAMS OF THE PACIFIC NORTHWEST

A. <u>Overview</u>

Simplified textbook depictions of the nitrogen cycle belie the complexity of the processes and interactions governing the movement of that element through stream ecosystems. Occurring as dissolved organic nitrogen (DON), nitrate (NO₃), and ammonium (NH₄), dissolved nitrogen exhibits not only a diversity of chemical species but also an extreme spatial variability, both on reach (Aumen, 1987; Triska et al., 1989) and regional scales (Aumen et al., 1990; Brown et al., 1973; Clayton and Kennedy, 1985; Feller and Kimmins, 1979 and 1984; Meyer et al., 1988), and confusing patterns of temporal variability (Hill, 1986; Triska et al., 1982 and 1989).

Understanding the dynamics of dissolved nitrogen in streams of the northwest is desirable because it is often the limiting element in reaches not limited by low light intensity (Gregory, 1980; Aumen, 1987). This is in contrast to lakes and to rivers in other regions where phosphorus is usually limiting (Wetzel, 1983; Welch, 1980). The presence of nitrogen and phosphorus in a ratio (N:P, by weight) of 7 has been shown to be optimum for aquatic systems (Wetzel, 1983). Where N:P < 7, the growth of organisms is limited by nitrogen availability. Thus, changing the stream dissolved nitrogen levels could potentially have large effects on the populations and species composition of aquatic communities at all trophic levels. Excessive dissolved nitrogen concentrations could result in algal blooms followed by periods of algal decomposition which could deplete stream oxygen levels. Although extreme dissolved nitrogen levels are unlikely to result directly from common forest practices, any increase in dissolved nitrogen could potentially exacerbate problems occurring downstream from the forest boundary. In contrast to the regional

norm, streams of the Bull Run seem to be phosphorus rather than nitrogen limited (Aumen, undat., 1987 and 1990), at least in some areas and over most parts of the year.

Along with dissolved nitrogen concentration, the temporal variability of dissolved nitrogen represents a significant component of the stream physical environment, just as does the variability of stream flow over the course of a year or a single storm. These patterns of variability, like the absolute concentrations, may be subject to change by management activities.

Furthermore, at high concentrations, dissolved nitrogen can be toxic to humans, or can promote the growth of pathogenic organisms. The maximum recommended NO_3 concentration in drinking water, for example, has been set at 45 mg/l (or 10 mg-N/l) by the U.S. Environmental Protection Agency (USEPA, 1976).

An understanding of dissolved nitrogen levels and variability in natural systems is necessary before models of NO₃ dynamics can be proposed or tested. What follows is a review of the current state of knowledge regarding dissolved nitrogen in forested streams of the Pacific Northwest.

B. <u>Processes Governing Dissolved Nitrogen in Streams</u>

In general, dissolved nitrogen originates as direct input from precipitation or as input from biological fixation or decay of organic matter. Weathering of minerals, a dominant source of many dissolved ions, plays almost no part in the nitrogen cycle (Brady, 1990). In undisturbed systems, average levels of certain forms of dissolved nitrogen, particularly NO₃, can be remarkably low compared to concentrations found in precipitation (see Table 4). NO₃ carried in precipitation enters a complex system with many interacting processes and compartments, and may undergo numerous transformations before finally appearing at the gaging site of a stream.

Vitousek and Mellilo (1979) identify twelve mechanisms affecting nitrogen loss and retention in forest ecosystems: mineralization, uptake by decomposers, uptake by plants, chemical fixation of NH₄ by clays, NH₄ volatilization, adsorption to colloids, nitrification, biological nitrogen fixation (both in-stream (Meyer et al., 1988; Triska et al., 1984) and in the riparian zone (Brown et al., 1973; Coates et al., 1976; Tiedemann et al., 1988)), leaching to groundwater, denitrification (Kaushik and Johnson, 1976; Swank and Caskey, 1982; Triska and Oremland, 1981), nonassimilatory NO₃ reduction to NH₄, and soil retention due to insufficient leaching water. Other processes include hydraulic detention in the hyporheic zone (i.e. the saturated streambed sediment) (Triska et al., 1989 and 1990).

Table 4. Comparison of average annual concentrations of NO₃ in precipitation and stream water for selected systems. References: [1] Feller and Kimmins, 1979. [2] Tiedemann et al., 1988. [3] Martin and Harr, 1988.

Location	NO3 Concentrati	on, mg-N/l	Ref.
	Precipitation	Streamwater	
Streams A, B, & C, Haney, B.C.	0.700	0.266	[1]
High Ridge Streams, Blue Mtns., OR	0.040	0.025	[2]
WS8, H.J. Andrews Ex. For., OR	0.031	0.003	[3]
WS9, H.J. Andrews Ex. For., OR	0.017	0.003	[3]
WS10, H.J. Andrews Ex. For., OR	0.015	0.001	[3]

C. Dissolved Nitrogen Background Levels and Variability

Table 5 is a summary of annual mean concentrations of two dissolved nitrogen parameters, NO₃-nitrogen and total dissolved Kjeldahl nitrogen (TDKN)², for undisturbed streams throughout the Pacific Northwest. It is instructive to notice the wide geographic variability of dissolved nitrogen levels, even from adjacent watersheds, and the wide temporal variability, which can range from the limits of detectability to more than five times the annual mean for a particular stream.

It is also important to note, however, that most of the studies described in this discussion are based on integrated composite samples collected over a period of one to three weeks duration. Estimates of data precision were not given, and seldom is there any information provided which would allow the reviewer to assess whether the integrated samples were known to be stable over their accumulation time in the field. These issues are discussed more fully with regard to the Bull Run data in section IV, parts B and C. Without precision estimates, any statements about nutrient patterns, average values or variability must be treated with caution.

Aumen (1987) studied the spatial variability of NO₃ and TDKN during a single day (August 18, 1987) on four small headwater streams in the Bull Run Watershed. NO₃ concentrations in grab samples were found to decrease dramatically in a downstream direction, ranging from 0.284 mg-N/l at the headwaters of one stream (Big Bend Creek) to 0.080 mg-N/l at its confluence with the Bull Run River, a total channel distance of about 3 km (1.9 mi). Likewise, TDKN ranged from 0.063 to 0.041 mg-N/l over the same interval. No information on stream discharge was included. These changes could be attributed to dilution by low-NO₃ groundwater or to in-stream biotic uptake. Some

²TDKN includes ammonium ions plus the broad assemblage of compounds known collectively as dissolved organic nitrogen.

Background dissolved nitrogen levels in undisturbed Pacific Northwest streams. Notes: [1] Total dissolved Kjeldahl nitrogen, which includes ammonium and amino organic Table 5.

- nitrogen.

 - Estimated from a graph. Median value given.
 - References: 1. 3.2. 5.4. 9.9. 9.9. [4]
- Rinella, 1987
- Harr and Fredricksen, 1988 Martin and Harr, 1988 Sollins and McCorison, 1981 Brown et al., 1973 Adams and Stack, 1989

- Feller and Kimmins, 1979 Clayton and Kennedy, 1985 Tiedemann et al., 1988

Location	Concentrati	on, mg-N/l			Ref.
	NO3		TDKN [1]		[4]
	Mean	Range	Mean	Range	
Fir Creek, Bull Run Watershed, OR	0.040 [3]	<0.010-0.190	-	-	1
Fox Creek, Bull Run Watershed, OR	0.010 [2]	0-0.060 [2]	0.042		2
WS8, H.J. Andrews Exp. Forest, OR	0.003		0.042		3
WS9, H.J. Andrews Exp. Forest, OR	0.003		0.066		3
WS10, H.J. Andrews Exp. Forest, OR	0.001	0-0.003	0.047	0.029-0.065	4
Needle Branch, Coast Ranges, OR	0.155	0.100-0.700 [2]	1	-	5
Flynn Creek, Coast Ranges, OR	1.185	0-3.190 [2]			5
Deer Creek. Coast Ranges, OR	1.050	0.700-3.170 [2]	ł	8	ß

Table 5. (Continued)

NO3 TDKN [1] Aean Range Mean TDKN [1] Coyote Creek, Umpqua N.F., OR 0.011 [2] 0-0.050 [2] 0 Stream A, Haney, B.C. 0.400 0-1.200 - Stream B, Haney, B.C. 0.200 0-1.200 - - Stream B, Haney, B.C. 0.200 0-1.000 - - - Stream B, Haney, B.C. 0.200 0-1.000 - </th <th>Location</th> <th>Concentrati</th> <th>.on, mg-N/l</th> <th></th> <th></th> <th>Ref.</th>	Location	Concentrati	.on, mg-N/l			Ref.
Mean Mean Range Mean Hean Coyote Creek, Umpqua N.F., OR 0.011 [2] 0-0.050 [2] 0.072 [2] 0 Stream A, Haney, B.C. 0.400 0-1.200 - - Stream B, Haney, B.C. 0.200 0-1.000 - - Stream C, Haney, B.C. 0.200 0-1.000 - - - Stream C, Haney, B.C. 0.200 0-0.800 0-1.000 - </td <td></td> <td>NO₃</td> <td></td> <td>TDKN [1]</td> <td></td> <td>[4]</td>		NO ₃		TDKN [1]		[4]
Coyote Creek, Umpqua N.F., OR 0.011 [2] 0-0.050 [2] 0.072 [2] 0 Stream A, Haney, B.C. 0.400 0-1.200 - - Stream B, Haney, B.C. 0.200 0-1.200 - - Stream B, Haney, B.C. 0.200 0-1.000 - - - Stream C, Haney, B.C. 0.200 0-1.000 0-1.000 - <th></th> <th>Mean</th> <th>Range</th> <th>Mean</th> <th>Range</th> <th></th>		Mean	Range	Mean	Range	
Stream A, Haney, B.C. 0.400 0-1.200	Coyote Creek, Umpqua N.F., OR	0.011 [2]	0-0.050 [2]	0.072 [2]	0.010-0.180 [2]	6
Stream B, Haney, B.C. 0.200 0-1.000 Stream C, Haney, B.C. 0.200 0.2000 0-0.800 Stiver Creek, Idaho Batholith, ID 0.007 [2] 0.002-0.022 High Ridge No. 1, Blue Mtns., OR 0.003 0.002-0.004 0.0110 0 0	Stream A, Haney, B.C.	0.400	0-1.200	5	-	7
Stream C, Haney, B.C. 0.200 0-0.800 - Silver Creek, Idaho Batholith, ID 0.007 [2] 0.002-0.022 - High Ridge No. 1, Blue Mtns., OR 0.092 0.073-0.111 0.110 0 High Ridge No. 2, Blue Mtns., OR 0.003 0.002-0.004 0.060 0	Stream B, Haney, B.C.	0.200	0-1.000	-		7
Silver Creek, Idaho Batholith, ID 0.007 [2] 0.002-0.022 High Ridge No. 1, Blue Mtns., OR 0.092 0.073-0.111 0.110 0 High Ridge No. 2, Blue Mtns., OR 0.003 0.002-0.004 0.060 0	Stream C, Haney, B.C.	0.200	0-0.800			7
High Ridge No. 1, Blue Mtns., OR 0.092 0.073-0.111 0.110 0 High Ridge No. 2, Blue Mtns., OR 0.003 0.002-0.004 0.060 0	Silver Creek, Idaho Batholith, ID	0.007 [2]	0.002-0.022	8		8
High Ridge No. 2, Blue Mtns., OR 0.003 0.002-0.004 0.060 0	High Ridge No. 1, Blue Mtns., OR	0.092	0.073-0.111	0.110	0.090-0.130	6
	High Ridge No. 2, Blue Mtns., OR	0.003	0.002-0.004	0.060	0.051-0.069	6
	High Ridge No. 3, Blue Mtns., OR	0.001	0.0006-0.0014	0.020	0.010-0.030	6
High Ridge No. 4, Blue Mtns., OR 0.004 0.002-0.006 0.030 0	High Ridge No. 4, Blue Mtns., OR	0.004	0.002-0.006	0.030	0.020-0.040	6

speculation exists that many of these small headwater streams owe their unexpectedly high NO₃ levels to their origins beneath talus slopes vegetated around the edges by alders. The alders provide a source of high-nitrogen detritus in the absence of a well developed forest community to utilize that nitrogen before it leaches to the subsurface. How typical this stream system is of the Northwest as a whole is unknown, but it does cast doubt on claims that the nutrient status of a stream can be known from measurements taken at one point.

Current thinking in stream ecology supports the view that nutrient dynamics in rivers changes in some continuous fashion from being dominated by forest detritus and groundwater input in the headwaters to being driven by photosynthesizing organisms in lower reaches (the "River Continuum Concept" of Vannote et al. (1980)). Although this concept is a good framework for organized thinking about stream nutrients in general, it must be emphasized that any conclusions made about the nitrogen dynamics of a stream from grab samples taken at single locations on a single day are highly prone to error.

As indicated by the annual concentration ranges listed in Table 5, changes over time can be as dramatic as changes over space. Few authors have examined variability at the low end of the temporal scale. None of the existing studies which included short sampling time intervals extended beyond a day or two in duration, nor do they include enough diversity of stream size, season or hydrological conditions to truly characterize short-term temporal variability.

Aumen (1987), in the study mentioned above, found no regular diel trend in NO_3 concentrations during a mid-August day of intensive (every 4 hours) sampling at one location (Otter Creek in the Bull Run Watershed), but noted that NH_4 exhibited a night time minimum and a maximum in early afternoon. Triska et al. (1989) found a strong sinusoidal variation in NO_3 over the course of two mid-August days in

Little Lost Man Creek, a third-order Northern California stream, with low concentrations corresponding to mid-afternoon peaks in photosynthetic activity. Similar patterns were documented for streams of the H. J. Andrews Experimental Forest, Oregon, also during the summer (Triska et al., 1982).

On a seasonal scale, knowledge of temporal variability and its causes is sketchy. Many researchers in the northwest report that dissolved nitrogen species reach peak concentrations during the first flush of autumn storms (Brown et al., 1973; Feller and Kimmins, 1984; Feller, 1979; Rothacher et al.1967). This has been attributed to a dominance by terrestrial processes; nitrogen accumulates in the soil during the summer when the rates of mineralization, nitrification and nitrogen fixation are high but leaching rates are low, and then is washed out later. Similar patterns are seen in the Eastern U.S. (Meyer, et al., 1988; Likens, et al., 1977), where winter time maxima are observed.

Others report that concentrations reach their peak during low flow (summer) conditions, dropping during the high flow season (Harr and Fredriksen, 1988; Martin and Harr, 1988). This pattern indicates a dominance of in-stream and riparian zone processes, since leaching is insufficient during the dry season to allow soil processes in upland areas to influence stream water. In parts of the Northwest where winter snow accumulates, the peak in NO₃ is often seen during the spring thaw (Clayton and Kennedy, 1985; Coates et al., 1976; Tiedemann et al., 1988), which is a pattern observed in other regions as well (Foster et al., 1989; Hill, 1986; Likens et al., 1970 and 1977). Flushing of soil reserves during a time of low biological demand has usually been assumed. Caution is indicated, however, since winter time mineralization and nitrification may occur (Foster et al., 1989) and, presumably, mineralization may more be active in-stream than in the soil during the thaw. In at least one case (Zeman, 1975) it was

thought that the winter season maximum in NO_3 concentration merely reflected the content of rainwater without the transformations and net dissolved nitrogen decline due to summertime biological activity.

A 16-year study conducted in the H.J. Andrews Experimental Forest, Oregon, forms the upper end of the temporal scale in current northwestern literature (Martin and Harr, 1988). This duration is only marginally sufficient to discern long-term trends or to catch potentially major changes due to episodic disturbances such as large floods (Meyer et al., 1988).

Several studies do, however, track the change in dissolved nitrogen species occurring when a forest is harvested in some manner (Brown et al., 1973; Clayton and Kennedy, 1985; Feller and Kimmins, 1984; Feller, 1989; Harr and Fredriksen, 1988; Likens et al., 1970; Sollins and McCorison, 1981; Tiedemann et al., 1988; Adams and Stack, 1989; Gholz et al., 1985). Typically, dissolved nitrogen rises sharply within a year following the disturbance, then declines to predisturbance levels over 2-7 years. In the northwest, maximum NO_3 concentrations have been observed to increase by a factor ranging from 2.4 (Clayton and Kennedy, 1985) to 10 (Adams and Stack, 1989; Brown et al., 1973) after cutting. The study by Brown et al. (1973) reported the highest post-harvest NO3 levels appearing in the literature (2.100 mg-N/l in Needle Branch, which was clearcut and burned, and 2.700 mg-N/l in Deer Creek, which was 25-percent patch cut). Although concentrations in Needle Branch were considerably elevated from preharvest conditions, they were not outside the range exhibited by the pre-harvest control watershed (Flynn Creek - see Table 5). In fact, the high natural variability of dissolved nitrogen levels often makes it hard to prove statistical significance for such post-harvest changes (Brown et al., 1973; Feller and Kimmins, 1984; Tiedemann et al., 1988).

Post-harvest concentrations of NO_3 in the northwest have never been observed to exceed the 10 mg-N/l EPA limit for human health, although this level has been surmounted under certain conditions in other regions (eg. Hubbard Brook, New Hampshire (Likens et al., 1970)).

Reasons for this temporary dissolved nitrogen increase include (Gholz, 1985): reduced uptake by vegetation; input to the stream of fine organic debris from logging; a warmer and moister soil and stream microclimate, leading to increased rates of soil and in-stream mineralization; increased fine organic sediment input from soil erosion, and; increased soil water percolation rate.

In some cases, the variance of dissolved nitrogen concentration may increase after a disturbance. This phenomenon is apparent in the data presented by Brown et al. (1973) for the Oregon Coast Range, although their report makes no mention of it. Conversion of coniferous riparian vegetation to red alder may be the cause, since the presence of nitrogen-fixing alder in the riparian zone places a large reservoir of potentially transportable nitrogen within easy access of the stream.

While the biological effects of increased dissolved nitrogen variance are poorly known, the overall consequence of increased NO₃ levels is to increase stream productivity unless some other element (such as phosphorus) is still severely limiting. As is the case with their recovery from floods and landslides, stream systems are probably resilient to alterations in nutrient levels and temporal variability in the long term, provided that the system is not overwhelmed by basin-wide change and provided that a continuity exists with unaffected reaches that can become sources of recolonization and temporary refugia for those organisms whose limits of tolerance are exceeded (Resh, 1988).

IV. EVALUATION OF THE DATA

A. <u>Description of the Data</u>

A variety of environmental data from several sources was examined for the purposes of this study, as summarized in Table 6. All data was obtained in electronic form to facilitate computer-aided analysis and graphics.

Water used in analysis through 1990 was collected as a depthintegrated sample whenever streams were wadeable and as a grab sample otherwise. Currently, only grab samples are collected. Samples are placed in a cooler for transport to the City of Portland Water Quality Lab (PWQL), which is located at the Headworks (see Figure 1), only 8 to 16 km (5 to 10 mi) from the sampling stations. Water samples are thus less than a few hours old when analyzed, which is well within the prescribed Environmental Protection Agency (EPA) time limits (Sceierstad, 1992).

Unfiltered samples are analyzed for the nutrient species in question using the methods listed in Table 7. This table also provides information on detection limits. Details of these processes can be found in the standards literature (American Public Health Association (APHA), 1976 and 1985).

Use of the Brucine method for NO₃ analysis requires some explanation, as that method is not considered to be as accurate as newer techniques such as ion chromatography or cadmium reduction, and thus is not currently regarded as an acceptable procedure. The Brucine method has been used because of historical precedence. At the time water analysis in the Bull Run began, manual cadmium reduction was the best alternative technique. This test was very time consuming, and thus not attractive. The Brucine method can be unreliable if the process is not strictly temperature controlled, which led to its reputation for poor inter-laboratory accuracy.

Variable	Symbol	Units	Sampling Location [1]	Sampling Frequency	Dates of Record	Source [2]
NO ₃ -nitrogen	NO3	mg-N/l	44,15,35,18	2 weeks [3]	7/74-12/91	USFS
PO4 -phosphorus	P04	mg-P/1	44,15,35,18	2 weeks [3]	7/74-12/91	USFS
Total nitrogen	TOTN	mg-N/l	44,15,35,18	2 weeks	4/85-12/91	USFS
Total phosphorus	TOTP	mg-P/1	44,15,35,18	2 weeks	4/85-12/91	USFS
Suspended sediment	SS	mg/l	44,15,35,18	1 week	5/74-12/91	USFS
Time of sampling	RTIME	time	44,15,35,18	[4]	[4]	USFS
Air temperature at time of sampling (at each site)	AIRTEMP	° °	44,15,35,18	[4]	[4]	USFS
H ₂ O temperature at time of sampling (at each site)	H2OTEMP	ບຸ	44,15,35,18	[4]	[4]	USFS
Maximum H ₂ O temperature at each site	H2OMAX	ະ	44,18, 15,35	daily	10/77-12/91 10/78-12/91	USGS
Minimum H ₂ O temperature at each site	H20MIN	ບຸ	44,18, 15,35	daily	10/77-12/91 10/78-12/91	USGS
Mean H ₂ O temperature at each site	MTEMP	С °	44,18, 15,35	daily	10/77-12/91 10/78-12/91	USGS

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Variable	Symbol	Units	Sampling Location [1]	Sampling Frequency	Dates of Record	Source [2]
Stream discharge at each site	CFS	ft³/s	44, 15, 35, 18	30 minutes	10/75-12/91 7/74-12/91 11/74-12/91 7/74-12/91	USFS/ USGS
Daily mean stream discharge	MCFS	ft³/s	44,15,35,18	daily	7/74-12/91 [6]	USGS
Daily precipitation	PRECIPIN	in	Headworks	daily	7/74-12/91	STCLIM
Maximum daily air temperature	TMAX	0.1 °F	Headworks	daily	7/74-12/91	STCLIM
Minimum daily air temperature	NIMT	0.1 °F	Headworks	daily	7/74-12/91	STCLIM
Snowpack- NF SNOTEL site	SNOWNF	in	NF SNOTEL site [5]	daily	10/78-12/91	SCS
Snowpack- BA SNOTEL site	SNOWBA	in	BA SNOTEL site [5]	daily	10/81-12/91	SCS
Precipitation- NF SNOTEL site	PPNF	in	NF SNOTEL site [5]	daily	10/79-12/91	scs
Precipitation- BA SNOTEL site	PPBA	in	BA SNOTEL site [5]	daily	10/80-12/91	SCS
Max. Temp NF SNOTEL site	TXNF	C °	NF SNOTEL site [5]	daily	10/90-12/91	scs

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Table	

35 and 18 refer to the key monitoring stations Fir Creek, Notes: [1].

- [2].
- 44, 15, 35 and 18 refer to use and wain Stem, respectively.
 N. Fork, S. Fork and Main Stem, respectively.
 Sources: USFS U.S. Forest Service, Mt. Hood National Forest
 USGS U.S. Geological Survey
 STCLIM Oregon State Climatologist
 STCLIM Oregon State Climatologist
- SCS Soil Conservation Service NADP National Atmospheric Deposition Program/National Trends Network Sampling interval was 1 week from 7/74 to 6/78, and 3 weeks from 6/79-9/85.

 - [3]. [5].
- [9]
- Data was recorded whenever water samples were taken. NF (North Fork) SNOTEL site located at 3,120 ft. elevation, BA (Blazed Alder) SNOTEL site located at 3,650 ft. elevation. MCFS on Fir Creek and South Fork predicted by cubic regression with MCFS at North Fork for dates prior to installation of gaging stations on those streams.

Variable	Symbol	Units	Sampling Location [1]	Sampling Frequency	Dates of Record	Source [2]
Max. Temp BA SNOTEL site	TXBA	ວ.	BA SNOTEL site [5]	daily	8/84-12/91	SCS
Min. Temp NF SNOTEL site	TMNF	р	NF SNOTEL site [5]	daily	10/90-12/91	scs
Min. Temp BA SNOTEL site	TMBA	ບຸ	BA SNOTEL site [5]	daily	8/84-12/91	scs
Precip. NO ₃	AIRNO3	mg-NO ₃ /1	Dam No. 2	weekly	7/82-12/91	NADP
Precip. NH4	NH4	mg-NH ₄ /1	Dam No. 2	weekly	7/82-12/91	NADP
NADP site precip.	PP	uu	Dam No. 2	weekly	7/82-12/91	NADP
Table 7. Nutrient measurement techniques and detection limits (Sceierstad, 1992). TKN is total Kjeldahl nitrogen; TOTP is total phosphorus.

Nutrient:	Lab Technique:	Detection Limits:		
NO3	Brucine method	0.010 mg-N/L		
TKN	Kjeldahl digestion with electrode finish	0.010 mg-N/L		
PO ₄	Stannous chloride method	0.003 mg-P/L		
TOTP	Acid digestion-stannous chloride method	0.003 mg-P/L		

However, workers at the PWQL have long adhered to a strictlycontrolled routine for the procedure, which has resulted in very good accuracy and precision relative to national averages, and much better than would be expected from the water quality standards literature (APHA, 1976). Thus, in order to maintain data consistency, the use of this method was allowed to persist until January, 1993, when finally supplanted by an automated cadmium reduction process (Sceierstad, 1992).

Total nitrogen, as reported in the data set, is actually the sum of NO_3 and total Kjeldahl nitrogen (TKN), the latter being a measure of ammonia plus that organic nitrogen in the form of amino groups (APHA, 1985).

Precipitation chemistry data was obtained from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), which maintains a monitoring site on Dam No. 2, about 400 m (0.25 miles) from the Headworks where the official precipitation and air temperature measurement facilities are located. Sampling is performed automatically by an AeroChem Metrics model 301 wet/dry precipitation sampler, consisting of a 13-liter polyethylene pail set in a device which uncovers the pail only when precipitation is detected. The "wet side" pail is retrieved each Tuesday morning and mailed to the Central

Analytical Laboratory (CAL) of the Illinois State Water Survey, Champaign, Illinois, for water analysis (NADP/NTN, 1992). A Belfort Model 5-780 dual traverse recording precipitation gage is also located at the collector site. As there exists some discrepancy between this gage and the one at the Headworks, the NADP precipitation data is used in determining precipitation nutrient loads. The NADP gage, on the average, collects 9.1 percent less (median = 9.0, standard deviation = 34.8) than the Headworks gage, probably due to the more exposed location of the former.

Snowpack data comes from two SNOTEL sites maintained by the Soil Conservation Service. Data is transmitted by meteor burst telemetry, and instrumentation consists of a snow pillow, a thermometer and a precipitation gage capable of recording snow as well as rain. These are located in the upper North Fork and Blazed Alder Creek sub-basins, at elevations of 951 and 1,113 m (3,120 and 3,650 ft), respectively (see Figure 1). This places them within the transient snow zone.

B. Precision and Accuracy of the Stream Chemistry Data

The effective resolution of these data, which has profound bearing on the scope of inference possible in this study, has two independent but equally significant aspects which must be addressed. The first is the accuracy and precision of the measurement techniques used. Included in this category are all errors which originate from the sample collection procedure, the handling and transport of samples, and the laboratory analysis techniques. The second, and potentially more difficult problem, is the relatively long time interval between samples.

Accuracy is defined here as the difference between an average measurement and the real value of the quantity being measured. Accuracy thus refers to the amount of systematic bias, if any, in the measurement procedure. Precision, by contrast, refers to the random scatter or spread of a set of measurements about their average value. If the bias of a procedure is known, it can be algebraically added to each measurement. Uncertainty in the corrected measurement still exists, however, and is a function of the precision. The result is that the true value, even in a situation where measurement quality control is excellent, is only known to lie within a specified range with a certain probability. This is the concept of the confidence interval.

All measurements in science and engineering have finite accuracy and precision, although sometimes this measurement variability is masked by the resolution to which a measurement is read and reported. Here, resolution refers to the smallest difference in a quantity which is distinguished by a measuring devise or procedure. For example, if an unknown DC voltage is measured by a voltmeter that reads to the nearest .01 volt, the same result may be obtained even after hundreds of readings. If the voltmeter is known to be calibrated accurately according to some reference standard (i.e. no bias exists), then it is

often assumed that the measurement is "exact," that is, that no uncertainty exists. However, if the same DC voltage is applied to an equally accurate voltmeter which can resolve readings to .000001 volts, a slightly different number may be recorded at every reading, even though to the nearest .01 volts the readings may still be the The second meter thus has the resolving power to determine the same. finite precision or uncertainty of the measurement, and if the measurement were reported to the nearest .000001 volts, information on that uncertainty ought to be included. The alternative is to report the measurement only to the nearest .01 volts, which, although truthful, gives the reader no direct information about the uncertainty of the measurement other than that it is probably somewhat less than half of the last significant figure, or ±.005 volts. This type of reporting also can lead to the implicit (and erroneous) assumption that the measurement has no uncertainty.

Information on the uncertainty of stream nutrient measurements is thus vital to any interpretation of those measurements. The magnitude of any patterns seen in a record of stream nutrient concentration or load must be greater than the magnitude of the uncertainty if any conclusions about patterns are to be made. Yet, paradoxically, graphs of stream nutrients appearing in the literature seldom portray confidence intervals, and information on variability expected from sample handling and laboratory analysis is usually not included. The limits of detection, which often are included in such reports, do provide some indication of the precision near the lower end of the scale, but even there they are actually a measure of instrument resolution rather than precision. As such, the limits of detection usually overestimate the experimental variability at the low end of the scale and underestimate it at the high end. Likewise, blanket estimates of precision for various analysis procedure

appearing in the standards literature (such as APHA, 1976 and 1985) only provide nationwide averages and thus only a very gross picture of expected variability at a particular laboratory.

True precision can be estimated only by some form of replicate sampling of each desired measurement. In lieu of that, quality control data from the laboratory can be used to reconstruct the sample precision. Data provided by the Portland Water Quality lab (PWQL) on measured "precision and accuracy" of the tests is given in Table 8. "Sample replicate" tests involve running duplicate pairs of analyses on the same water sample. The resulting mean "relative standard deviation" or RSD (Thiess, 1992) is the average of the differences in measured concentration between paired replicates, expressed as a percent of the average of the two measurements, for 100 or more tests³ (APHA, 1985; American Society for Testing and Materials (ASTM), 1992). The standard deviation of the tests is also given (in units of "percent RSD"). For the quality control recovery tests, a water sample is "spiked" with a known amount of the nutrient in question, and an analysis performed on both this and the un-spiked sample. Mean recovery is the percentage of added nutrient recovered after subtracting the un-spiked nutrient content.

³Relative standard deviation as defined here is actually an incorrect usage of the term. For a pair of analyses A and B made on the same given water sample,

 $RSD_i = \frac{(A-B)x100}{(A+B)/2}$ and RSD is the average of all individual RSD_i's.

Likewise, S_{RSD} in Table 8 is the standard deviation of the set of RSD_i 's. The proper meaning of RSD, however, is the ratio of the standard deviation to the average value of a distribution.

	Sample rep	plicate tests	Quality control standard recovery tests		
Nutrient	Mean RSD	Standard deviation, S _{RSD}	Mean Recovery	Standard deviation, σ	
NO3	5.23%	5.08%	98.5%	5.9%	
TKN	13.1%	14.3%	102%	7.0%	
PO4	3.66%	3.22%	95.3%	8.2%	
TP	26.3%	23.9%	104%	13.0%	

Table 8. Quality control data for Portland Water Quality Lab nutrient measurements (Sceierstad, 1992). See text for details.

In general, quality control at the PWQL is excellent relative to other labs nationwide. It is significant that water chemistry analysis has been done at the same lab for the entire period of record. This fact alleviates fears that variability between labs (which may be substantial) could enter into the data analysis.

These quality control data can be used to reconstruct the standard deviation of the hypothetical population of replicate analyses of the same water sample. If $W = R/\sigma$ where R is the range of a pair of samples and σ is the standard deviation of the population (assumed to be normally distributed), statistical theory dictates that, for large numbers of pairs, W approaches an average value of 1.128 (Duncan, 1952). Thus, it is possible to recover the standard deviation of an individual measurement. Letting avg{R} be the average value of R and A be the population average (which is the true measurement value),

$$\sigma = \operatorname{avg}\{R\}/1.128 \text{ or, in terms of RSD,}$$
[1]

 $\sigma/A = RSD/1.128$ [2]

and thus $\sigma = (RSD)(A)/1.128.$ [3]

From the average RSD given in Table 8, 95-percent confidence intervals can then be computed for each measured value. One

implication of equation [3] is that precision decreases (i.e. σ becomes larger) as the value of the measurement increases. This is counter-intuitive; precision is expected to decrease as the limits of resolution of the test are approached. In actuality, a single mean RSD does not apply uniformly throughout the total range of the data. Mean RSD should increase for smaller measurements. However, the variation of RSD was found to be small enough over the range that only the single mean value was reported by the PWQL (Thiess, 1992).

Another assumption implicit in the use of equation [3] to compute a confidence interval is that there is no bias in the data. This is justified on the basis of the recovery tests shown in Table 8, which suggest that none of the procedures yield recoveries differing from 100 percent by more than fraction of a standard deviation.

Finally, it must be assumed that no significant change in the nutrient content of the water sample occurs during transport to the lab and that the samples consistently do represent a depth-integrated specimen of stream water. Based on stated compliance with EPA guidelines for sampling and sample transport, It is believed that any errors introduced by this phase of the measurement process are likely to be small relative to the precision of the laboratory analysis. However, good practice would dictate an occasional testing of these assumptions.

C. Precision and Accuracy of the Precipitation Chemistry Data

The foregoing assumption that samples remain stable between collection and analysis becomes an even greater issue with regard to the precipitation chemistry data. By the time a sample is analyzed, it could have aged for a week in the sampler pail, being alternately covered and exposed to the elements many times, and then further ripened during the many days it spends being packaged, sent through the U.S. mail, and waiting in the processing que at the Central Analytical Lab (CAL).

The effects of this delay in processing are difficult to quantify, and are, in fact, a matter of controversy. Intuitively, it is expected that microbial action would result in a steady and substantial uptake of NO3, while NH4 concentrations may approach some steady-state value that marks a balance between ammonification (decay) and volatilization. Harr and Fredriksen (1988) describe the results of a study of the effects of sample storage time on composite streamwater samples. Water stored for three weeks in the dark, cool environment beneath the gage house at the sampling site was found to average 17 percent less NO3 than the same water analyzed within two days after collection. In general, the Standard Methods literature recommends analysis within two days for NO3 and immediately for NH4 (APHA, 1985). The acidic pH of rainwater will tend to have some preservative effect, but even intentionally acidified samples which are stored cold (4°C) are only reliably stable for about seven days (Stednick, 1991).

This problem has not been adequately addressed by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) in any of its quality control literature (Lockard, 1987; Peden, 1988; James, 1988, 1989, 1990, 1991 and 1992; Bigelow, 1986; Schroder and Bricker, 1985; Brooks, et al., 1985 and 1987; Brooks and Schroder, 1988; See and Schroder, 1988; See, et al., 1989 and 1990; Willoughby,

et al., 1989, 1990 and 1991). Citing studies by Galloway and Likens (1976) and Peden and Skowron (1978), from which rain samples were judged to be chemically stable over long periods of time, the blind audit surveys used by the U.S. Geological Survey to assess bias and precision of NADP/NTN field operations were not designed to include any way to estimate sample maturation, even though to do so would have been straightforward, and would have removed a major apprehension about the validity of the NADP/NTN field protocol.

In the study by Galloway and Likens, a 12-liter sample of rainwater was divided into three parts which were stored at 21°C (on the laboratory shelf), 4°C (in a refrigerator) and -4°C. Aliquots of the three fractions were then analyzed for NH_4 and NO_3 over the course of seven months as shown in Table 9. In this particular experiment, the samples were stable over time, at least to the resolution of the laboratory analysis (which is not given, and appears not to have included replicate samples), and provided we assume that the sample did not already have a lengthy period of maturation to accumulate its 12 liter bulk before the experiment began.

Date	Sample Storage Temperature						
	21°C		4°C		-4°C		
	NH4	NO3	NH4	NO3	NH4	NO3	
Nov 1974	0.37	2.15	0.38	2.20	0.40	2.15	
Dec	0.43		0.43		0.46		
Jan 1975	0.42	2.20	0.43	2.20	0.42	2.10	
Feb							
Mar	0.42	2.05	0.38	2.05	0.40	2.30	
Apr	0.38		0.38		0.41		

Table 9. Effects of storage time on precipitation sample chemistry, from Galloway and Likens (1976). Values in mg/l.

However, in the same paper, another experiment is described in which rain water was gathered in two collectors, side by side; water from one collector was analyzed after each storm, while water in the other collector was allowed to accumulate for three storms (usually two or three weeks) before analysis. In all, five sets of three storms were analyzed, all in winter and early spring when wind-blown dust would be minimal and temperatures would be low. Comparison of total mass yields in the composite samples with the sum of yields from the three individual storms yielded discrepancies ranging from a factor of 0.93 to 2.8 and 0.93 to 1.2 for NH₄ and NO₃, respectively. Could this be the result of differential sample maturation rates in addition to laboratory error?

The statistically more well-designed study by Peden and Skowron (1978) casts further doubt on the sample stability assumption. This study compared the changes in ionic composition over time of rain water samples obtained from three types of collector (one of which was an automated wet-only collector very similar to those used by NADP/NTN), under five types of sample storage. The concentrations of some ionic species varied dramatically over time, particularly if the sample was allowed to mature unfiltered. Although the automatic lid of the wet-only collector improved matters by excluding dust during dry conditions, the authors note that particulate matter from some sources (such as cloud condensation nuclei, particulates removed by diffusion and electrostatic forces within the cloud, and particle scavenging by impaction on falling rain drops) can still be a source of interference, especially during periods of light rainfall or heavy aerosol dust loadings.

With the wet-only collector, the greatest changes in concentration over time (with no immediate sample filtration) were observed for potassium. By comparison, NO₃ and NH₄ appear relatively stable. This stability, however, is only relative, and is mainly an

illusion produced by the use of a logarithmic scale on the graph displaying the results (Figure 6-A, page 2348 of Peden and Skowron (1978)). Careful interpretation of this graph reveals that the NO₃ concentration increased 17 percent, from 1.23 to 1.44 mg/l between day 1 and day 5 after collection, and to 1.51 (a 23 percent increase) by day 47. Likewise, NH₄ decreased from 0.54 to 0.49 mg/l (an 8.8 percent change) between days 5 and 29, reaching 0.38 mg/l (a 29 percent change) at day 46. Even the most stable case for NO₃ (rainwater collected by a narrow mouth polyethylene bottle and funnel) showed a notable change (a 6.7 percent decrease over 40 days). These authors did not conclude, as the NADP/NTN investigators suggest (Bigelow et al., 1986), that samples are stable, but rather that a wet-only type collector with immediate sample filtration was the most effective means of retaining sample integrity over time.

USGS investigators examined the relative precision of the NADP/NTN field sampling protocol in a study by Niles, et al. (1992). Replicate wet deposition sampling equipment was collocated at each of eight official NADP/NTN sampling site (all of which were in the eastern or midwestern U.S.). Two samples, treated identically, were thus generated at each of the selected sites each week for a period of one year. A median relative precision (MRP) was computed for each sample pair using the equation

 $MRP = M\{(C1 - C2)/[(C1+C2)/2]\} \cdot 100$ [4] where C1 and C2 are the sample concentration (or deposition in kg/ha) from the original and collocated samplers, respectively, and M{ } denotes the median value. MRP for NO₃ concentration averaged 3.5 percent (range 1.8 to 5.9 percent), while MRP for NO₃ deposition averaged 6.9 percent (range 3.8 to 12.2 percent). Likewise, MRP averaged 17.0 (range 9.5 to 22.2) and 19.7 (range 9.9 to 33.3)

percent, respectively, for NH4 concentration and deposition. However, the nature of this study did not permit assessment of sample maturation changes.

Two other recent studies come close to examining sample maturation changes. Willoughby et al. (1990) compared the results of daily subsampling with weekly sampling of the same ten storms in Denver, Colorado to assess possible sample changes over a one week collection period. After capture of the storm precipitation in the sample pail, the lid-opening mechanism of the automated wet/dry sampler was disabled so that the lid covering the sample would remain closed. Subsamples were then withdrawn from the pail at one day intervals, filtered, preserved and refrigerated. NO₃ was found to increase in concentration with time at a statistically significant average rate of 2.6 μ g-N/l/day in each sample pail. This amounts to an average change of 4.9 percent over a seven day maturation period.

The same investigators (Willoughby et al., 1989) also explored the stability of NO3 ions in simulated precipitation samples which contained NO₃ at four different concentrations (0.5, 1.0, 2.0 and 3.0 mg/l NO₃, having pH values of 5.0, 4.6, 4.2 and 3.8, respectively) as well as calcium, magnesium, potassium, sodium, chloride and sulfate at levels assumed to represent natural deposition. A total of six replicate samples were measured at each of 10 time intervals ranging from 10 to 100 days. Samples were kept in 2-liter high density polyethylene bottles. No other information on storage conditions is provided, but room temperature is assumed. Sample NO3 concentrations were found to increase on the average by more than two standard deviations from the initial value, with most of the change occurring within the first 8 days. This increase was attributed to biological contamination, and this type of sample was judged insufficiently stable for use in quality control audits. It should be noted that although the samples were not sterilized, ultrapure filtered (0.2 μ m)

water was used to create them, and many of the nutrient elements present in normal rainfall (most notably phosphorus) were not added. Thus, biological activity under field conditions may have been underestimated.

When confronted with these concerns, workers at NADP/NTN admitted to being aware of the problem of sample maturation, but stated that the changes are only likely to be significant for NH4 and some of the cations (Bigelow, 1993). NO_3 and sulfate (SO₄) are believed to change by only 1 to 3 percent. Indeed, this level of stability has been demonstrated for the USGS standard water reference samples (SWRS), which were used to create some of the artificial precipitation samples deployed in the blind audit program between 1985 and 1989 (Janzer, 1983). However, these samples were highly filtered $(0.45 \ \mu\text{m})$ and then sterilized by exposure to UV light when they were created, which renders them unrepresentative of typical field conditions. No good explanation as to why the USGS blind audit program did not include a provision for quantifying sample maturation changes was given, other than that some changes will occur in the sample pail during the week that it is out in the field anyway and that this is unavoidable without going to a much more expensive daily sampling protocol. Yet, the basic concern remains that even if the changes are unavoidable, they ought to be quantified.

The best that can be done, then, in assessing the precision and bias of the precipitation chemistry data is to use the results of the USGS external blind audit program, acknowledging that these results account for only a portion of the experimental error. In the blind audit program, bottles containing artificially prepared "rain water" (usually 500 ml), having an ionic composition assumed to be similar to typical natural rain water samples, are sent to each individual site operator. At some undetermined time later, the site operator pours about two thirds of the audit sample into a clean polyethylene

sampling pail (after removing about 20 ml for pH and conductivity determination), caps the pail, then sends it to the Central Analytical Lab on Tuesday morning as if it were a real rainwater sample. A fictitious collection data form is included so that CAL personnel do not know that the sample is part of the audit program. The remaining one third of the audit sample is mailed to the USGS, which then mails it to the CAL to provide an independent check of the known constituent concentration (which was determined by a USGS lab when the sample was mixed) (Brooks, et al., 1987). Average differences between the known (i.e. original) audit-sample constituent concentration and the concentration measured in the samples shipped in buckets gives some measure of experimental accuracy; the standard deviation of replicate measurements gives a measure of precision.

Blind audit samples prepared for 1983 did not contain NO₃ or NH₄ (Schroder et al., 1985). Concentrations of NO₃ and NH₄ in blind audit samples processed during 1984 were observed to be unstable, and thus information on these constituents was omitted from the report (Brooks, et al., 1987). Estimates of precision and bias of NO₃ and NH₄ are given in Tables 10 and 11, respectively, for 1985 through 1989 (Brooks, et al., 1988; See, et al., 1988, 1989 and 1990; Willoughby, et al., 1991). Mean RSD (relative standard deviation), is used in its correct sense here, defined as the ratio of average standard deviation to average sample concentration, expressed as a percent. This RSD is based on a number of replicate measurements rather than differences (range) of individual pairs of measurements, and thus does not need to be corrected by the factor 1.128 as was done for the stream chemistry data.

For NO_3 in 1985, bias is given as defined above; for all other cases, bias is defined as the difference between concentrations in the bucket sample and concentrations measured in the bottle of audit fluid after it was returned to the CAL.

Table 10. Precision and bias for NO₃ measurements in precipitation. N = number samples used in computations; σ = standard deviation; RSD = relative standard deviation; * = number not given; ** = median rather than mean concentrations used.

Year	Mean	Bias		N	Precision		N
	Conc., mg/l	mg/l	Percent		σ, mg/l	RSD, Percent	
1985	0.51**	0.04	7.8	46	0.135	26.5	37
1986	0.66	-0.06	-9.1	71	0.360	54.5	*
1987	1.35	-0.02	-1.5	57	0.100	7.4	*
1988	1.21	0.00	0.0	71	0.180	14.9	*
1989	1.06**	0.02	1.9	107	0.020	1.9	*

Table 11. Precision and bias for NH_4 measurements in precipitation. N = number of samples used in computations; σ = standard deviation; RSD = relative standard deviation; * = number not given; ** = median rather than mean concentration used.

Year Mean		Bias		N	Precision		N
	Conc., mg/l	mg/l	Percent		σ, mg/l	RSD, Percent	
1985	0.23**	0.08	34.8	6	0.062	27.0	11
1986	0.04	0.01	25.0	71	0.040	100.0	*
1987	0.09	0.03	33.3	20	0.040	44.4	*
1988	0.15	0.04	26.7	18	0.140	93.3	*
1989	0.13**	0.00	0.0	107	0.010	7.7	*

As can be seen from the tables, the estimated bias was always smaller or of comparable magnitude to σ . Thus, bias was judged not to be significantly different from zero. The relative standard deviations are highly variable from year to year, and are in most cases are disconcertingly large both for NO₃ and for NH₄. This poor precision is evident on Figures 2 and 3, which depict a two-year window of the precipitation NO₃ and total nitrogen (NH₄ + NO₃) records along with 95-percent confidence intervals, computed as $\pm 1.96\sigma$ (where σ was determined by multiplying the measurement value by the RSD). The complete record is given in Figures 71 and 72 of Appendix C. For those years lacking precision estimates, the mean RSD values for the years 1985-1989 were used to compute the confidence intervals. These mean values were 21.0 and 54.5 percent for NO₃ and NH₄, respectively. From these figures it is clear that any conclusions made using this data must be interpreted lightly.



Figure 2. NO₃ concentrations in precipitation. Horizontal bars indicate 95-percent confidence intervals for each measurement. Only a two-year window of data is presented here (see Figure 65 in Appendix C for complete data set).



Figure 3. Total nitrogen $(NO_3 + NH_4)$ concentrations in precipitation. Horizontal bars indicate 95-percent confidence intervals for each measurement. Only a two-year window of data is presented here (see Figure 66 in Appendix C for complete data set).

D. Choice of Nitrate as the Subject of Analysis

Figures 4, 5, 6 and 7 present a two-year window of the data for NO_3 , total Kjeldahl nitrogen (TKN), PO_4 and total phosphorus (TOTP), respectively, for the Fir Creek sub-basin. Ninety-five percent confidence intervals are included on these figures. The confidence intervals represent ±1.96 σ , where σ , the estimated standard deviation, is computed as described in Part IV, Section B. For completeness, the total data set for these nutrients is depicted in Figures 67, 68, 69 and 70 of Appendix C.

From the figures, it is evident that of the four nutrient constituents, only NO_3 is known to a resolution sufficient to be modelled to any degree of detail. The others either display a wide band of uncertainty relative to their absolute magnitudes and apparent patterns of variability (TKN and TOTP) or remain at or below their minimum detection levels for most of the time (PO₄ in all sub-basins except the North Fork), thus obscuring any conclusions which might be made about temporal variability. For this reason, although the original intention of this work was to derive models and make inferences about all four nutrient species, the majority of the effort has been directed towards NO_3 .

It is recognized, of course, that the nitrogen cycle includes numerous chemical constituents which under the right conditions are readily transformed to and from NO₃, and that any study focusing exclusively on NO₃ will thus present an incomplete picture of watershed nutrient dynamics. This problem will be addressed in later sections where it will be shown that NO₃ and total nitrogen are directly correlated, and that conclusions made about NO₃ apply to total nitrogen as well without being complicated by the much lower resolution of the TKN data. Furthermore, NO₃ is certainly the most biologically available form of nitrogen in stream water, given that NH₄ concentrations are usually low by comparison (Aumen, 1987). Thus, changes in ecosystem productivity or species composition are more likely to correlate with NO3 than with total nitrogen per se (Meyer et al., 1988).

From figure 8, which shows a two-year window of the NO₃ load data for Fir Creek, it is evident that NO₃ load has a precision comparable to that of NO₃ concentration. The complete record of NO₃ load for the four key stream monitoring stations, converted to units of kg/ha/day⁴, is given in Figures 71, 72, 73 and 74 of Appendix C. Finally, Figures 75, 76 and 77 of Appendix C depict NO₃ concentrations for the North Fork, South Fork and Main Stem stations, respectively.

⁴The product of NO₃ concentration in mg-N/l and discharge in CFS must be multiplied by 2.4466 to yield kg-N/day, then divided by the sub-basin area (from Table 1) to arrive at kg-N/ha/day.



Figure 4. NO₃ concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement. Only a two-year window of data is presented here (see Figure 67 in Appendix C for complete data set).



Figure 5. Total Kjeldahl nitrogen concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement. Only a two-year window of data is presented here (see Figure 68 in Appendix C for complete data set).



Figure 6. PO₄ concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement. Only a two-year window of data is presented here (see Figure 69 in Appendix C for complete data set).



Figure 7. Total phosphorus concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement. Only a two-year window of data is presented here (see Figure 70 in Appendix C for complete data set).



Figure 8. NO₃ loads in Fir Creek. Horizontal bars indicate 95percent confidence intervals for each measurement. Only a two-year window of data is presented here (see Figure 71 in Appendix C for complete data set).

E. The Problem of Long Sampling Intervals

1. Perspective from the Literature

As mentioned previously, the time interval between samples presents a second data resolution problem. The two-week sampling interval does not correspond well with the scale at which changes in nutrient levels occur in streams. Several studies have shown significant changes on a daily cycle, even when the hydrograph is fairly constant.

Aumen (1987) collected samples at 4-hour intervals over a 24hour period (beginning on August 18, 1987) from Otter Creek, a small tributary of the Bull Run River in the Main Stem sub-basin. As shown in Figure 9, little variation of NO₃ was observed although NH₄ displayed a pronounced nighttime minimum.

Triska et al. (1982) describe a similar study done on the H.J. Andrews Experimental Forest, Oregon, during a summer day when the stream discharge was fairly constant. No significant change in NO₃ concentration was observed for a forested, first-order stream (Watershed 10). The open (clearcut) section of a third-order stream (Mack Creek) and a fifth-order stream (Lookout Creek) experienced pronounced midday reductions in NO₃, down to about 50 percent and 12 percent of their midnight values, respectively. These patterns were attributed to the daily cycle of biological activity where light was not a limiting factor.

Working in a 327-m reach of Little Lost Man Creek, a third-order stream in Northwestern California, Triska et al. (1989) observed significant diel variations in NO₃ concentrations at each of four stations sampled at 4-hour intervals over a 42-hour period on August 16 to 17, 1979. Sinusoidal patterns were observed, with minima at



Figure 9. NO₃ and NH₄ concentrations in Otter Creek (a small tributary of the Main Stem Bull Run River). Time is given in hours past 0:00 (midnight) on August 18, 1987.

about 15:00 and maxima at 06:00, the range being from 0.027 to 0.043 and from 0.034 to 0.051 mg $NO_3-N/1$ at the most upstream and most downstream stations, respectively.

Rapid changes in NO₃ concentrations which are linked to the hydrographic response of the stream are also expected to occur. Stream discharge during a storm varies widely on a time scale much shorter than two weeks. This phenomenon is illustrated by data taken at short time intervals over the early portions of storms which began on October 21 and December 5, 1991, at the North Fork and Fir Creek stations on the Bull Run watershed. As evident from Figures 10 through 13, concentrations varied rapidly over a short time span. NO₃ load was also highly variable.



Figure 10. NO₃ concentrations and loads in Fir Creek during a storm beginning October 21, 1991. Discharge is also shown for reference.



Figure 11. NO₃ concentrations and loads in the North Fork Bull Run River during a storm beginning October 21, 1991. Discharge is also shown for reference.





Figure 12. NO₃ concentrations and loads in Fir Creek during a storm beginning December 5, 1991. Discharge is also shown for reference.



Figure 13. NO₃ concentrations and loads in the North Fork Bull Run River during a storm beginning December 5, 1991. Discharge is also shown for reference.

2. Semivariogram study

Another technique useful for exploring how the temporal or spatial scale of observation affects the variability of a quantity is the semivariogram (Royle et al., 1980). To construct the semivariogram, the data set is scanned and the squared differences between all possible sets of readings separated by specific selected time intervals are computed. Then, the squared differences for each selected time interval are averaged and plotted as shown in Figure 14. This plot or semivariogram illustrates how the temporal variability of both the discharge and the NO₃ concentrations and loads from the Fir Creek station change with sampling interval.

For small separation times (lags) between readings, both the data and its first derivative will vary in a smooth or continuous fashion and the squared differences between readings will be a steep, nearly linear function of the time lag. This pattern indicates that the time lags between data points are short enough relative to the temporal scale on which major changes occur that the system is described completely by the data.

For larger time lags, the data no longer appears smooth. The first derivative changes abruptly at each point, and the squared differences become more a function of the overall variance of the total data set than the size of the time lag. Thus, the curve approaches an asymptote which describes the long-term seasonal variability of the data. In this region of the semivariogram, the time lags between data points are large relative to the scale on which changes occur, and the system is not completely described by the data points; missing information exists between those points.

Note the sharp inflection in the curve for discharge which occurs for reading separations (lags) of about one day. This indicates that one day is about the maximum time lag which can be used to completely and smoothly characterize the discharge versus time



Figure 14. Semivariograms of NO₃ concentration, NO₃ load and stream discharge for Fir Creek.

curve. The semivariograms for NO₃ concentrations and loads are much more irregular due to the much coarser time scale of the data, the much smaller size of the data set, and probably also to the lower precision of nutrient data compared to discharge data. However, it does show that the two-week sampling interval lies beyond the realm of smooth, continuous characterization. In fact, if NO₃ is at least partially driven by the discharge (although the nature of that relationship remains to be determined), then it can be expected to vary on the same time scale as does the discharge, that is, one day or less.

Yet another way of examining the problem is in terms of the persistence or duration time of discharge events having a given probability of being exceeded. Here, the instantaneous discharge data is sorted in descending order to produce a discharge "duration" table (an ordered listing of discharge and the corresponding probability of exceeding that discharge), as is done in routine flow duration analysis (McCuen, 1989). Then, the data is scanned to determine the mean and median times, in hours, that a discharge event exceeds each given magnitude (and thus exceedence probability).

Figure 15 depicts such an analysis for the Fir Creek sub-basin. From this figure it is evident that large flow events with low exceedence probabilities usually persist for only 24 hours or less, and are unlikely to be captured by a sampling scheme which is any less frequent. Again, the implications are that most major flow-driven changes in NO₃ or NO₃ load have probably been missed by the data collection scheme.



Figure 15. Mean and median duration times for stream discharge events having given probabilities of being exceeded.
3. Implications to Analysis and Modeling

Thus, interpretation of the NO₃ record from a two-week sampling interval presents a problem which is analogous to that of trying to reconstruct a sine wave from a scheme that recorded only one measurement for every one or two cycles. It may appear from this limitation that the prospects of developing any sort of predictive model or making conclusions about watershed processes is slim, good data precision and long record notwithstanding.

However, the problem is not quite so extreme since most of the environmental variables to be used in the modeling investigation are known from daily values, and the hydrograph is known from readings at 30minute intervals. Consequently, placement of each nutrient sample in an exact hydrological and climatic context is possible. It is possible that the more complete record of other predictor variables may at least partially compensate for the missing information in the nutrient record. Thus, model development remains feasible, particularly given the long record and the relatively good data precision, if antecedent conditions and climatic context are carefully incorporated into the model.

V. STATISTICAL MODELING

A. <u>Literature Review</u>

The literature contains few attempts to develop mathematical models, either statistically- or physically-based, to predict natural levels of stream nutrients (Salminen and Beschta, 1991). Even fewer of those attempts have met with success. This is due, at least in part, to an overly-simplistic approach to modelling, such as trying to derive a linear correlation between nutrient concentrations and discharge alone.

Rinella (1987), for example, attempted to fit NO₃ concentrations on the Bull Run watershed to seven different types of functional relationships to discharge (including the simple linear case). None proved to be significant. Tiedemann et al. (1988) attempted unsuccessfully to correlate NO₃ concentrations with stream discharge for streams in the Blue Mountains of Oregon.

Hill (1986) successfully correlated NO₃ concentrations with discharge (producing a concentration "rating curve") for the snowmelt-dominated East Duffin Creek in Ontario, Canada, but was unable to produce a workable rating curve for the nearby Nottawasaga River. Monthly average concentrations on the latter stream were successfully modeled using a sinusoidal function with time (month) as the independent variable.

Gall (1986) attempted to correlate nitrate plus nitrite (NO_3+NO_2) levels in three streams near Bellingham, Washington with stream discharge, 1-, 5- and 14-day rainfall totals, and instantaneous water temperature. Six separate multiple regressions were performed; one for each creek for each year of record (1983 and 1984), based on two-week sampling intervals. This represents the only case in the literature where some measure of antecedent conditions (the rainfall totals) was included in a correlation. Of the six multiple regressions, water temperature and 14-day rainfall were significantly

correlated (at the P = 0.10 level) to NO_3+NO_2 concentration in five of them, and discharge was significantly correlated in three. 1- and 5day rainfall was never significant. Coefficients of determination (R^2) ranged from 0.563 to 0.726. Although interesting, these results can only weakly suggest links between NO_3 and watershed processes due to the fact that only one year of data were used in each regression, and it is unknown whether the same relationships would persist under a longer period of record. The predictive value of these relationships is doubtful for the same reason. Since Gall's study was mainly exploratory and descriptive in nature, no discussion of watershed processes was included. No other published attempts to correlate dissolved nitrogen parameters with environmental variables exist for the Pacific Northwest.

Gall (1986) also attempted the same correlations with total phosphorus (TOTP) and soluble reactive phosphorus (SRP) levels. The results were even less enlightening; SRP correlated significantly (at the P = 0.10 level) with discharge and 14-day rainfall in two of the six regressions, with water temperature in one and with 5-day rainfall in one, while TOTP correlated with discharge in two of the six, and with each of the 14-day rainfall, 1-day rainfall and 5-day rainfall in one of the six. Two on the regressions for TOTP and one for SRP failed to be statistically significant. Coefficients of determination (R^2) ranged from 0.308 to 0.805. All told, there was no consistency in the relationships from one stream to another or from one year to the next, either with NO₃+NO₂ or with the phosphorus parameters.

Prairie and Kalff (1988a) attempted to correlate dissolved phosphorus levels with solar irradiance, time of year between March and August, and discharge for seven small streams in Quebec, Canada. Solar irradiance was found to be poorly correlated to dissolved phosphorus. dissolved phosphorus was positively correlated with discharge in some streams, negatively correlated in others and showed

no relationship with discharge in a third group. Time of year from March to August was positively correlated with dissolved phosphorus for six of the seven streams.

Salminen and Beschta (1991) found only a poor regression relationship between PO₄ and TOTP ($R^2 = 0.56$) for streams of the Bull Run Watershed (Fir Creek and the North Fork Bull Run River) during the period from 1985 to 1990. Concentrations of PO4 and TOTP were correlated with discharge (at significance levels of P = 0.10 or better), but the correlation was sometimes negative and sometimes positive depending on the stream and on whether the period considered was annual or the interval from May 1 to November 15. Furthermore, coefficients of determination were poor, ranging from 0.02 to 0.57. Daily PO_4 and TOTP loads ($lb/mi^2/day$) were more strongly correlated with discharge $(0.42 < R^2 < 0.80)$, but this is mainly an artifact of colinearity, since daily load includes discharge in its calculation. In their analysis, measurements recorded as below limits of detection, of which there are a substantial number in the Fir Creek record, were treated as missing values. This practice could obscure the regression results unless readings below detection limits always correspond to small discharges.

The studies done by Nuckols and Moore for the West Fork Walker Branch (Nuckols and Moore, 1982) and the Little Millseat (Moore and Nuckols, 1984) watersheds in Tennessee and Kentucky, respectively, represent perhaps the most thorough attempt to model stream nutrients and use the models as an inference tools. Integrated composite samples were analyzed weekly for NO_3 , NH_4 and organic nitrogen for a period of 217 and 230 days for the West Fork Walker Branch and Little Millseat, respectively. Data was segregated by season, and multiple regressions were then devised to relate the weekly concentrations and areal loadings of these three constituents to 31 different independent variables which were in categories related to atmospheric deposition

(precipitation and particulate dryfall), stream hydrology, blow-in and leaf fall, and throughfall (that portion of rainfall which penetrates the forest canopy). For the Little Millseat, NO₃ concentration was explained best by atmospheric deposition (dryfall and rainfall content) and throughfall amount in the spring, and by dryfall, canopy retention and stream baseflow in the summer, with no significant regression relationships in the autumn. NO₃ load was best explained in the spring by throughfall, storm flow, atmospheric deposition and precipitation amount, in the summer by precipitation amount and in the autumn by throughfall. These results are indicative of a seasonal shift in dominance of watershed processes from atmospheric input during the spring (wet season) to subsurface water influx during the drier summer season. However, the extremely short duration of this study renders its conclusions dubious and the regression equations themselves useless for long-term prediction purposes.

Thus, creation of a predictive model for any stream nutrient, particularly in the Pacific Northwest constitutes information new to the field. Figures 4 through 7 clearly indicate that of the four nutrient species in the record, only NO₃ is suitable for predictive modelling. Before describing the modelling process and the results, it is first necessary to discuss the reasons for the modelling effort, the significance of having a predictive model for NO₃, and the potential uses to which such a model might be put.

B. The Goals of Mathematical Modelling

Mathematical modelling, in general, has two purposes, both of which play a role in this study. First, creating a mathematical model is a way to test our understanding of natural processes. Those concerned with management of the Bull Run Watershed have repeatedly expressed their interest in gaining an improved understanding of watershed processes through the present study, and their hopes that a working model will provide such understanding, or, at least, suggest which processes ought to receive attention in future research (Tracy, 1992 and Smart, 1992). Secondly, models become useful tools for design and/or management.

The level of a chemical constituent of stream water, or of any environmental variable for that matter, is an integrated response to a great number of natural processes. Some processes act to increase the constituent's level while others act to decrease it, and each process acts with its own particular timing, magnitude, and response to antecedent conditions. Nevertheless, the system may be dominated by only a few of the many possible processes, and thus may be adequately described by a relatively simple model. Such a model may best be pictured as a set of compartments representing the various locations where the constituent can reside in the watershed. Connecting these compartments are flux pathways representing transport and transformation within the system as well as system inputs and outputs. If intuition or knowledge of physics can be used to devise equations which relate the rates of flux along the pathways to the volumes contained in the compartments or to other physical factors, then the model (which has been conceptual or diagrammatic up until now) can be stated as a set of algebraic or differential equations.

These equations may then be used directly to predict the level of the constituent via simple calculations or via numerical methods. Or, if the equations are not simple and if numerical programming is

beyond the scope of the study, the equations may at least suggest relationships between variables which can be used as indirect tests of the model's validity.

Johnson et al. (1969), for example, developed this kind of model in their study of water chemistry at the Hubbard Brook Experimental Forest in New Hampshire. Rain water in a volume proportional to stream discharge was assumed to mix with a fixed volume of soil water. This model (see Figure 16) is described mathematically by a simple hyperbolic relationship:

 $C = [1/(1 + bD)]C_d + C_a$

where C = concentration of constituent in stream water; D = stream discharge; C_d = difference between soil water and rain water constituent concentration; C_a = rain water constituent concentration, and; b = a constant, found to be 10⁻⁴ or 10⁻⁵. Mathematically, this constitutes a zero-order, lumped-parameter model. The model was shown to be valid for NO₃ as well as for sodium, silicate, magnesium, sulfate, aluminum, hydrogen ions and calcium. The validity of the relationship suggests that the investigators were correct in their assumptions. It would be unwise to generalize, however, since nutrient transformations, sources or storage compartments which could be important on other stream systems may be negligible or mutually counterbalanced on this particular watershed.

Unfortunately, this simple model does not accurately describe the Bull Run NO₃ data, probably because processes other than simple mixing are significant. It is also possible that the variability in NO₃ concentration in the soil water solution and in the rainfall render the model useless. No consistent functional relationship exists between NO₃ concentration and discharge alone for the Bull Run River system (see discussion regarding Figure 25 in Section VI, Part A, below). This finding is typical of many streams world-wide (Meyer et al., 1988).



Figure 16. Block diagram illustrating the model proposed by Johnson et al. (1967) to describe concentrations of stream water constituents.

In fact, no simple, internally-consistent, physically-based model for processes on the Bull Run has been forthcoming. To move even the first step beyond the zero-order model of Johnson et al. would seem to require much more intimate knowledge of processes than is currently in existence. Such knowledge is difficult to obtain even for a small watershed (see, for example, Sollins and McCorison, 1981) and thus may never be available for the Bull Run system. As it stands, knowledge is limited to stream nutrient export and precipitation nutrient import, leaving the system open-ended, with no knowledge about the rates of other imports, such as nitrogen fixation, other exports such as denitrification, or internal transformations and storages.

Thus, modeling research has focused on the next best approach, which is to identify, intuitively, those variables which are believed to be the best surrogates for the driving processes and use them to create a statistically-based model via multiple regression techniques. Since correlation does not prove causation, this method can only suggest that groups of related processes which are influenced by each surrogate variable are significant. The method cannot identify the physical model which underlies the system. However, regression can be a tool to gain insight into the behavior of the watershed, and as such it can help in the creation of a physically-based model. Regression can uncover the existence of functional relationships even if the complete form of those relationships remain unknown. It can support inferences about which watershed processes are significant and the time scale over which the effects of those processes are integrated, and can allow one to do this in a way that is more systematic and objective than the strictly graphical methods often employed for such purposes (see, for example, Minor and Scott, 1992). When dealing with independent variables which are not measurements of significant processes but merely surrogates for groups of processes, regression

may offer an easier means to test hypotheses about processes than physical models which all to often involve unknown bulk parameters (such as "b" in the model of Johnson et al. cited above) or variables which have not been (or cannot be) directly measured.

Finally, it should be recognized that even in the most exact of the physical sciences, where workers are accustomed to taking a measurement only once, the empirical relationships and hypothesis testing are still, ultimately, statistical regressions by nature. The difference is only in the degree of precision present.

Whether its origin is physical or statistical, a working model can become a management tool. There are two scenarios for how this might be the case for the Bull Run. The first involves refinement of the water quality standards which are currently in use. The second scenario involves the use of the model to simulate watershed response to environmental extremes and/or management effects.

Currently, the operational water quality standards for the Bull Run watershed are based on a ninety-ninth percentile for each 28-day interval of the year, established from a baseline period (which was 1975-1982 for the North Fork, South Fork and Main Stem stations and 1976-1982 for Fir Creek). This ninety-ninth percentile is computed by means of a non-parametric method which incorporates both the standard deviation for the 28-day period and a pooled estimate of total baseline-period variability (Robbins, 1986).

When the two NO₃ measurements for the current 28-day period are obtained, they are averaged and the average compared with the ninetyninth percentile standard for that period. If the current average for one of the managed sub-basins exceeds the standard, the next step is to compare the Fir Creek (unmanaged or "control") NO₃ levels with the corresponding standard for Fir Creek. If those levels are also high, no action is taken. However, if the control NO₃ levels are low, the measurements are declared to be a deviation from the standards and the

"source search" process is initiated (Aumen et al., 1989; USFS, 1979). The "source search" process involves an evaluation of ambient watershed conditions and/or management activities which could be a possible source causing the deviation. Interpretation of data from other less-frequently sampled monitoring sites (the "source search stations), if available, can be used to determine upper watershed conditions or to isolate the source. If the deviation is determined to be a "violation" (caused by management activities), then actions on the ground are taken to prevent the deviation from continuing.

Thus, the water quality standards are driven by concern over the effects of management, and presuppose that a way exists to sort out these effects from natural variability. The idea is that any significant change in stream nutrient status away from levels present during the baseline period is unacceptable, or, at least, is worthy of immediate attention.

There is some theoretical justification for this degree of caution. Small permanent increases in the level of a limiting nutrient (even if far below levels considered directly toxic to humans) could degrade water quality overall by increasing stream or reservoir algal biomass or altering community composition, which may affect the type and availability of food to higher trophic levels and the availability of oxygen during crucial parts of the year. This could initiate changes in the overall structure of the aquatic ecosystem. Such changes and cascading trophic interactions have been documented but are poorly understood (Meyer et al., 1988; Carpenter et al., 1985) and are difficult to predict.

For example, the Blue River Reservoir near Eugene, Oregon, which is an oligitrophic system, has recently developed an annual pattern of blue green algal blooms. These blooms, which may originally have been triggered by subtle changes in reservoir nutrient loading, can become self perpetuating once algal propagules are a part of the lake

sediment (Gregory, 1992). Blue green algae are considered a nuisance in public water supplies because they produce objectionable tastes and odors, exacerbate nitrogen loading with their nitrogen-fixing habits, and, in sufficient quantities, are toxic to mammals and fish (Welch, 1980).

In general, lakes and reservoirs are long-term integrators of nutrient loading from their watersheds. As such, they respond to changes in average nutrient input even if the magnitude of that change is small compared to short-term variability (Wetzel, 1983). Although the streams of the Bull Run system are beleived to be phosphorus limited, the reservoirs, at least during significant parts of the year, are nitrogen limited (Eilers and Bernert, 1991). This emphasizes the need to watch NO₃ concentrations and the factors which cause NO₃ to vary, even if the absolute values of those concentrations are usually small.

The important point here is that comparison of a measurement with a prediction from a working model would have a much better potential for sorting out changes which are chronic in nature from those which are due to a temporary combination of environmental extremes. A model could do this better than the current standards by taking into account factors other than just the particular 28-day period in which a measurement is placed. Since the wet season in the Pacific Northwest does not begin on a fixed date each year, placement of a particular NO₃ concentration regime consistently within a given fixed 28-day period is problematic.

Along this line of reasoning, a working model can allow managers to investigate hypothetical future scenarios. What are the worst possible NO₃ levels which can be expected, for example, based on possible extreme values of the significant environmental variables? If the model could be designed to incorporate road building or harvest acreage as an independent variable, then it could be used to test the

effects of various management scenarios on the NO₃ levels or loading. Whether management effects can be discerned from the Bull Run data using multiple regression techniques, however, remains questionable since only a small fraction of the watershed was harvested in any given year and since rigorous procedural monitoring has greatly reduced the occurrence on logging practices which have the potential to adversely affect water quality. Other techniques, such as a double mass curve comparing cumulative NO₃ load in the harvested sub-basins with Fir Creek could be more fruitful in this regard. Examination of the data set for trends of that nature are beyond the scope of this study.

In summary, development of a working regression model of NO₃ loads and levels for streams of the Bull Run watershed can be a useful inference tool as long as one is cautious about recognizing the limits of the statistical process and its inherent assumptions. Strictly speaking, the statistical model is only valid for the time interval which includes the data used in its development. However, it is not unreasonable to expect its validity to extend into the future provided that changes have not occurred which would greatly alter the watershed processes, and that none of the independent variables lie outside the ranges present in the original data.

From an academic point of view, any successful effort to model NO₃ constitutes new information and provides important clues as to how NO₃ levels and loads are driven not simply by discharge but by other factors and antecedent conditions. Such a model can suggest functional relationships, and can allow inferences to be made about the relative significance and integration time of physical processes. Although frowned upon by theoreticians, such inferences, as well as the extrapolations in time mentioned above, are congruent with the principles of inductive reasoning as applied to the environmental sciences where controlled experimentation is usually impractical.

Finally, a working model can become a useful tool for predicting natural extremes and the effects of management if the type and scale of management activity is large enough to produce changes discernable from background variability.

C. <u>Description of the Modeling Process</u>

The choice of independent variables to use in the statistical modeling process was driven by the need to include both instantaneous and antecedent conditions, and the need for simplicity. Dependent variables were NO₃ concentration and NO₃ load (discharge times concentration, converted to consistent units of kg/ha/day as described on page 45) at each of the four stream key monitoring stations. In all, some 47 independent variables were considered, which fell into several natural groupings depending on their descriptive function. These groups were chosen based on knowledge and experience of watershed function, and judgements about which factors, theoretically, ought to drive NO₃ in streams and how best to describe those factors, either directly or in surrogate form. Some variables were available directly and others, which acted as indices of antecedent conditions, were calculated from the data.

The functional groups considered were: temperature variables, hydrograph positioning variables, precipitation variables, discharge variables, time variables, and solar variables. Within these groups, similar variables differed mainly in the time scale over which each variable was integrated. A complete list of the variables considered in the modelling process, along with detailed definitions, is given in Appendix A.

Statistical modeling consisted of multiple regression analysis and time series analysis. All analyses and computer graphics were performed using the Statistical Analysis System (SAS) software package (SAS, 1988a, 1988b, 1988c, 1988d and 1988e). Use of this system greatly facilitated the numerous file merging and computation operations needed to compile the working data files which contained all the desired variables, and promoted compatibility with USFS data files, which were also in SAS format.

The validity of multiple regression analysis depends on the following four basic assumptions (Neter et al., 1989):

 <u>Specification</u>: the mathematical form of the model must be correctly specified;

 <u>Constant variance</u>: the variance of the dependent variable must be constant with respect to any one independent variable;

3. <u>Normality</u>: at a given value of an independent variable, the dependent variable must be normally distributed; and,

4. <u>Independence</u>: measurements of the dependent variable must be independent of each other (i.e. no autocorrelation is present).

Correct specification of the model depends on the skill and judgement of the investigator. The rationale behind choices of independent variables and their form (sometimes the independent variables must be transformed to meet the constant variance criterion) will be discussed in later sections.

In order to satisfy the normality criterion, all modeling was performed using the base 10 logarithms of NO₃ and NO₃ load. This transformation was necessary to adjust for skewness in the NO₃ concentrations and loads. This skewness was indicated by the large size of the standard deviation of the data relative to its mean (see Table 12) and, more explicitly, by the smoother appearance of the "valleys" on the graph of NO₃ versus time relative to the "peaks" (see Figure 67 in Appendix C).

Station	No. Obs- ervations	Minimum	Maximum	Mean	Standard Deviation
Fir Creek	489	0.010	0.570	0.0516	0.0476
North Fork	491	0.010	0.260	0.0306	0.0198
South Fork	488	0.010	0.177	0.0285	0.0171
Main Stem	472	0.010	0.232	0.0421	0.0254
Precipitation	381	0.00452	1.52	0.163	0.223

Table 12. Statistical summary of the NO_3 data. All values are in mg-N/1.

Preliminary screening of variables was done using graphical displays of $Log(NO_3)$ or $Log(NO_3$ load) versus the variable in question to identify functional relationships (if any), and to check for equal variance across the range of each independent variable to see if a transformation of that variable would be necessary. This process resulted in a much smaller and more manageable number of independent variables.

Next, stepwise multiple regression was used to identify highly significant functional relationships (using a minimum "F to enter" corresponding to a P = 0.15 probability of a Type I error (Neter et al., 1989), and to eliminate redundancies due to variable interaction and cross-correlation. This resulted in further simplification of the developing model. At this point, models for each sub-basin were compared. The models were generally similar in that one or two variables from each functional grouping would be highly significant in each model. However, the exact variable which was chosen by the stepwise regression algorithm was not always the same. For example, the three-day precipitation total (PREC3) was selected for Fir Creek and the Main Stem, while the seven-day precipitation (PREC7) came out of the stepwise procedure for the South Fork in modeling for Log(NO₃ load). In such cases, where subtle disagreement over the time scale of the variable occurred, best judgement was exercised to select one variable to apply to all sub-basin models, unless both variables could be included in all models and still remain highly significant (at the P = 0.05 level). This process resulted in only minor (less than 2 percent) changes in the adjusted coefficient of determination (adj. R^2), and resulted in a more universally-applicable model.

Some variables were eliminated from consideration not for lack of correlation or physical reasons, but because an inordinate number of missing values threatened to damage the resolution of the model if they were included. For example, the variable MTEMP14, the 14-day mean stream temperature, was highly significant in three of the four sub-basins models for Log(NO₃ load), but caused the degrees of freedom to drop from about 490 to 360, and in the process, eliminated most of the peak NO₃ load values from the analysis.

In order to incorporate non-linear functional relationships, an attempt was made to include quadratic terms of each of the significant variables. However, the improvement in coefficient of determination was minimal. The variables LSTPRCP (previous day's precipitation) and SUM14 (14-day cumulative discharge) were the only two independent variables which had functional relationships with NO₃ or NO₃ load which were clearly better represented by anything more complex than a linear function; a base-10 logarithm of these parameters was used.

Finally, the presence of serial correlation (a violation of the fourth assumption listed above) necessitated the use of time series analysis to account for the autocorrelated residuals. A method suggested by Ramsey (1992) was used.

First, the time series of Log(NO₃ load) values was interpolated linearly to produce a new time series with values equally spaced in time (at two week intervals, beginning and ending on Tuesday). Although this process altered the form of the series somewhat by reducing the magnitude of some of the larger peaks, the amount of

interpolation necessary was small since most of the stream nutrient samples were already at one- or two-week intervals, and since 42 to 55 percent (depending on sub-basin) of the data was collected on Mondays, with 92 to 94 percent of the collection days falling on the interval from Saturday to Tuesday. Independent variables were transformed in the same fashion. Note that this transformation was only a mathematical technique used to accommodate the time series analysis and was not meant to suggest that the data set can be meaningfully interpolated in this way to extract values corresponding to noncollection days.

Next, the equally-spaced time series was analyzed with a time series autoregression procedure to obtain the lag-1 autocorrelation coefficient, α_1 , which quantifies the correlation between adjacent values in the time series. Partial autocorrelation coefficients corresponding to separations greater than one time interval (lag-2, lag-3, etc.) were then checked to make sure that a lag-1 autocorrelation model was sufficient to eliminate the serial correlation. If it had not been, then a procedure more complex than that described below would have been required.

In general, it can be shown that for the case of lag-1 serial correlation, the transformed multiple regression function,

 $V_{t} = \Gamma_{o} + \beta_{1}U_{1,t} + \beta_{2}U_{2,t} + \ldots + \beta_{k}U_{k,t}$ (5) where $\Gamma_{o} = \beta_{o}(1-\alpha_{1})$; $V_{t} = Y_{t} - \alpha_{1}Y_{t-1}$; $U_{1,t} = X_{1,t} - \alpha_{1}X_{1,t-1}$;

 $U_{2,t} = X_{2,t} - \alpha_1 X_{2,t-1}$, etc.,

will be an ordinary multiple regression with independent residuals (Ramsey, 1992). Here, Y_1 is the original dependent variable at time t; $X_{1,1}$ and $X_{2,1}$, etc. are independent variables at time t, and the original untransformed multiple regression relationship was

$$Y_{1} = \beta_{0} + \beta_{1}X_{1,1} + \beta_{2}X_{2,1} + \dots + \beta_{k}X_{k,l}.$$
 [6]

Thus, after transforming the variables according to equation [5], an ordinary multiple regression can be performed to obtain the regression coefficients β_1 , β_2 , etc. without the problems associated with bias introduced by serial correlation.

D. Rationale for Choices of Independent Variables

Initial modeling efforts were based on a conceptual hypothesis, consistent with the literature, about factors controlling stream NO_3 concentration. This conceptual hypothesis is useful as a framework for discussion of the role of the six independent variable groups.

NO₃ was thought to build up in the soil and litter layers during periods when leaching was low, the rate of accumulation being especially great during the early autumn when leaf fall is occurring but temperatures are still relatively warm and terrestrial biological uptake is on the decline. This accumulation period would then be followed by a flushing period during late autumn and early winter. As accumulated reserves were reduced, the flushing effect from each successive storm would decline. Superimposed on this scheme would be the biological uptake from in-stream organisms and from terrestrial plants with roots intercepting groundwater inputs, and mineralization or release from decay organisms.

The function of the time variables, then, were twofold. First, RTIME (time of day) was included to account for any potential diel variations. Secondly, an index of season was needed, which suggested the use of WYDATE (Julian day of the water year) and the related factors SEASON1 ($\cos(WYDATE \cdot 2\pi/365)$) and SEASON2 ($\sin(WYDATE \cdot 2\pi/365)$), both of which were suggested by Hirsch (1988).

The discharge variables were needed to account for dilution, supply depletion, and hysteresis. If the overall amount of mobile (i.e. dissolved) NO₃ available on the watershed at a given instant is finite, then the immediate effect of increasing the amount of water moving through the system would be to dilute the NO₃ already present. This implies that NO₃ load tends to be relatively constant, at least during times when new NO₃ sources are not becoming active or old

sources becoming expended. This implies an inverse correlation of NO_3 concentration to discharge (CFS). CFS cannot be used to predict NO_3 load, however, due to colinearity.

As discharge increases in the autumn, new sources are encountered and progressively flushed out. In general, it was expected that this pattern of flushing, depletion and recharge would cause NO_3 concentrations and loads to show a hysteresis pattern similar to that described for suspended sediment. Beschta (1987) observed that when plotted against stream discharge in order of sample collection time, suspended sediment concentrations are higher on the rising limb of the hydrograph than they are at a corresponding discharge on the falling limb. He theorized that as the discharge increases, new sources of suspended sediment are progressively encountered by the stream. Once a source comes on line, it becomes depleted exponentially over time, providing less material to the stream during the falling limb than it did earlier on in the storm. Graphically, this pattern manifests itself as a classic hysteresis loop. Once a source is depleted, it can begin to recharge. However, the time between storms in the wet season is too small to allow much recharge to occur. Thus, successive storms during the wet season have smaller hysteresis loops.

HSLOPE (hydrograph slope), HCURVE (hydrograph curvature) and their sister variables were included to allow placement of the sample on the proper limb of the hydrograph, and thus account for the hysteresis effect. Another approach was to create the hysteresis indices HYST6, HYST8 (which was the form suggested by Hirsch (1988), computed as 0.8^{R} where R is the number of days since the hydrograph was rising), and HYST95. The progressive flushing during the season (shrinking of hysteresis curves) would be a function of SUMCFS

(cumulative stream discharge for the water year), and the degree of recharge between storms a function of SUM7 and/or SUM14 (the 7- and 14-day cumulative stream discharges, respectively).

If (or when) leaching of soil reserves of NO₃ dominate the process, the precipitation variables would be important predictors of NO₃. This would also be true if NO₃ concentration is occasionally driven by precipitation NO₃ levels. The fact that precipitation often carries higher average concentrations of NO₃ than stream water (see Table 12) suggests that this may sometimes be the case. This direct control by precipitation would be more likely to occur during midwinter, after the easily-flushed soil reserves are gone but while the activity of intervening biological processes is still low.

Temperature variables are indices of current and recent antecedent biological activity. Likewise, solar variables are surrogates for biological activity in particular and season in general. Inclusion of these variables in the model was designed to help explain the seasonal trends evident in the data.

E. <u>Modeling Results</u>

Modeling success, as measured by the adjusted coefficient of determination (adj. R^2), was significantly greater for NO₃ load than for NO₃ concentration. This was due to the much greater variability present in the NO₃ concentration data relative to the NO₃ load data. Thus, although results are reported here for a regression model involving NO₃ concentration as the dependent variable (actually Log(NO₃)), use of this model is not recommended for predictive purposes. A better approach is to compute NO₃ concentration from the predicted NO₃ load.

Table 13 shows the time series regression results for NO_3 load, LNLD. For example, to compute NO_3 load for the Main Stem, equation [5] (page 80) would translate into the following procedure:

 $LNLD_{t} = LNLD_{t-1} \alpha_{1} + \Gamma_{o} + \beta_{1} (LSUM14_{t} - \alpha_{1}LSUM14_{t-1})$

+ $\beta_2(PRECIPIN_t - \alpha_1PRECIPIN_{t-1})$ + $\beta_3(LLSTPCP_t - \alpha_1LLSTPCP_{t-1})$

+ $\beta_4(PREC7_1 - \alpha_1PREC7_{11})$ + $\beta_5(HYST8_1 - \alpha_1HYST8_{11})$

$$+ \beta_6(TX14, - \alpha_1TX14_{t,1})$$
^[7]

where $\Gamma_o = -3.09095$, $\alpha_1 = 0.35850$, $\beta_1 = 0.624176$, $\beta_2 = 0.0.197724$, $\beta_3 = 0.128852$, $\beta_4 = 0.020889$, $\beta_5 = 0.352737$, and $\beta_6 = -0.000382$. Here, LSUM14 is base-10 logarithm of the sum of the previous fourteen mean daily discharge values (in ft³/s), PRECIPIN is the current day's precipitation in inches, LLSTPRCP is the base-10 logarithm of the previous day's precipitation in inches, PREC7 is the total inches of precipitation for the previous seven days (not counting the current day), HYST8 is 0.8^R , where R is the number of days since the hydrograph was rising, TX14 is the average of the maximum Headworks air temperatures for the fourteen-day period ending on the previous day, and where the subscripts t and t-1 denote values at the current time and at two weeks prior to the current time, respectively. Then,

 NO_3 load, = NLD_1 = 10^{LNLD_1}

[8]

(in kg-N/ha/day) and NO₃ concentration (in mg-N/l) will be

 $NO3_t = NLD_t AREA/CFS_t/2.4466.$

where AREA = 12,410 ha for the Main Stem sub-basin.

Table 13. Time series regression results for $Log(NO_3 \ load)$, LNLD. Root MSE is the root mean square for error. Total DF is the total degrees of freedom. NS means the variable is not statistically significant at the P = 0.05 level (P level is given in parentheses). All models are significant at the P = 0.0001 level.

Variable/	Sub-basin				
Parameter	Fir Creek	N. Fork	S. Fork	Main Stem	
Intercept, F.	-2.175524	-2.711879	-2.928297	-3.090950	
Lag-1 corr. coef., α_1	0.38840	0.35544	0.36052	0.35850	
LSUM14, B ₁	0.374108	0.449932	0.557589	0.624176	
PRECIPIN, B ₂	0.321736	0.340894	0.260795	0.197724	
LLSTPCP, B ₃	0.080363	0.101484	0.098382	0.128852	
PREC7, β_4	0.033068	0.023468	0.054533	0.020889	
HYST8, B ₅	0.324928	0.210639	0.200115	0.352737	
TX14, B ₆	-0.000622	NS (P=0.59)	-0.000302	-0.000382	
Total DF	455	455	455	447	
Root MSE	0.212025	0.184760	0.188497	0.222942	
Adjusted R ²	0.6864	0.6648	0.7464	0.6978	

Figures 17 through 20 show the performance of the time series model for predicting NO₃ load. In these figures, 95-percent confidence intervals were estimated using a width of ± 1.96 (root MSE), as suggested by Ramsey (1992). The time series technique does not lend itself to some of the better approaches for assessment of the validity of an ordinary multiple regression model, such as dividing the data randomly into two sets and attempting to predict one set from regressions derived from the other set. However, some idea of model

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[9]

correctness can be gained from a plot of the each residual (predicted value minus actual value) against the previous (lag-l) residual (Ramsey, 1992). As can be seen in Figures 21 through 24, the pattern is random, with no large outliers and no trends which would indicate the persistence of serial correlation at higher orders.

Table 14 shows the results of an ordinary multiple regression analysis for NO₃ load. As explained above, serial autocorrelation renders such a model less accurate than the time series model (and virtually worthless for estimating coefficients of determination or confidence intervals). However, it is included here for completeness and for estimation purposes in the event that missing data or data collection at intervals other than two weeks makes the time series model inapplicable.

Table 14. Ordinary multiple regression results for Log(NO₃ load), LNLD. Root MSE is the root mean square for error. Total DF is the total degrees of freedom. NS means the variable is not significant at the P = 0.05 level (P level is given in parentheses). Both Root MSE and Adjusted R² are inaccurate (see text).

Variable/ Parameter	Sub-basin				
	Fir Creek	N. Fork	S. Fork	Main Stem	
Intercept, B _o	-3.214406	-4.080230	-4.312628	-4.506336	
LSUM14, B ₁	0.272642	0.376421	0.464755	0.536333	
PRECIPIN, B ₂	0.375565	0.366786	0.267736	0.241087	
LLSTPCP, β_3	0.100808	0.071132	0.090463	0.100893	
PREC7, ß ₄	0.037782	0.037094	0.063227	0.024797	
HYST8, B ₅	0.307635	0.248903	0.246242	0.390707	
TX14, β ₆	-0.000730	NS (P=0.94)	-0.000339	-0.000494	
Total DF	488	487	482	470	
Root MSE	0.27730	0.23445	0.23618	0.28349	
Adjusted R ²	0.7568	0.7182	0.7750	0.7258	

Table 15 shows the results of an ordinary multiple regression analysis for NO₃ concentration. These results are intended only to provide insight into the possible relationships between variables driving NO₃ concentrations, and not as a predictive tool (for which the recommended procedure is to first compute NO₃ load and then obtain concentration from load as shown above). In Table 15, SUMCFS is the sum of the daily mean discharge values (in ft³/s) for the water year (including the current day), LANG14 is the sum of the previous fourteen day's solar input values in Langleys, LCFS is the base-10 logarithm of the current mean daily discharge, and the other variables are as defined above.

Table 15. Ordinary multiple regression results for Log(NO₃ concentration), LNO3. Root MSE is the root mean square for error. Total DF is the total degrees of freedom. NS means the variable is not significant at the P = 0.05 level (P level is given in parentheses). Both Root MSE and Adjusted R² are inaccurate (see text).

Variable/ Parameter	Sub-basin				
	Fir Creek	N. Fork	S. Fork	Main Stem	
Intercept, B _o	-1.634019	-1.936573	-1.991948	-1.305405	
SUMCFS, B ₁	-1.6675E-5	-3.237E-6	-1.982E-6	-1.327E-6	
PRECIPIN, β_2	0.177338	0.151180	0.101066	NS (P=0.30)	
LANG14, B_3	-7.6717E-5	-6.7230E-5	-6.7030E-5	-2.2398E-5	
TX14, B ₄	0.001164	0.001183	0.000940	NS (P=0.34)	
HYST8, B ₅	0.138229	0.123113	0.084634	0.158879	
LCFS, B ₆	-0.141503	-0.119396	NS (P=0.98)	NS (P=0.92)	
Total DF	323	330	356	354	
Root MSE	0.17210	0.16274	0.16880	0.18238	
Adjusted R ²	0.4846	0.3136	0.2376	0.3336	



Figure 17. Model predictions for NO₃ loads in Fir Creek. Stars represent predicted values, and solid lines delimit the 95-percent confidence intervals. Actual values and associated 95-percent confidence intervals are shown as triple bars. Note that the dates of predicted and actual values are not necessarily congruent.











Figure 18. Model predictions for NO₃ loads in the North Fork Bull Run River. Stars represent predicted values, and solid lines delimit the 95-percent confidence intervals. Actual values and associated 95-percent confidence intervals are shown as triple bars. Note that the dates of predicted and actual values are not necessarily congruent.







Figure 18. (Continued)



Figure 19. Model predictions for NO₃ loads in the South Fork Bull Run River. Stars represent predicted values, and solid lines delimit the 95-percent confidence intervals. Actual values and associated 95-percent confidence intervals are shown as triple bars. Note that the dates of predicted and actual values are not necessarily congruent.










Figure 20. Model predictions for NO₃ loads in the Main Stem Bull Run River. Stars represent predicted values, and solid lines delimit the 95-percent confidence intervals. Actual values and associated 95-percent confidence intervals are shown as triple bars. Note that the dates of predicted and actual values are not necessarily congruent.



Figure 20. (Continued)



Figure 20. (Continued)



Figure 21. Current model residuals (predicted value - actual value) plotted against the previous residual for Fir Creek.



Figure 22. Current model residuals (predicted value - actual value) plotted against the previous residual for the North Fork Bull Run River.



Figure 23. Current model residuals (predicted value - actual value) plotted against the previous residual for the South Fork Bull Run River.



Figure 24. Current model residuals (predicted value - actual value) plotted against the previous residual for the Main Stem Bull Run River.

VI. INVESTIGATION OF WATERSHED PROCESSES

A. Interpretation of the Model

The collection of variables comprising the best case model for NO₃ load suggests that the system is heavily driven by current and antecedent precipitation. The current day's, and to some degree the previous day's precipitation, are strong determinants of discharge for these relatively small, rain-dominated watersheds. This linkage is moderated somewhat by antecedent soil moisture, which is represented in the model by PREC7 (7-day total precipitation). This precipitation-driven character, combined with the observation that peaks in NO₃ load generally occur in the winter and early spring rather than in early autumn (when flushing of soil reserves and sediments would peak) suggests that rainwater itself, or perhaps snow melt, may drive peak loads.

However, one would then expect NO₃ load to correlate well with precipitation NO₃ or total nitrogen loads, which is not the case, as can be seen from Figures 55 and 58 in Appendix B. It is possible that these correlations exist but are obscured by inaccurate precipitation chemistry data (due to inappropriate collection and storage methods for the precipitation samples), or by intrinsic differences in the sampling techniques used (grab samples for stream data versus 1-week integrated samples for the precipitation data). Another likely explanation for the linkage is that the precipitation variables are driving discharge, and discharge, in turn, is well correlated to NO₃ load both because of coliniarity (i.e. discharge is a factor in calculation of NO₃ load) and because of a possible flushing effect.

The positive sign on the coefficients of SUM14 (14-day cumulative stream discharge) indicate that this variable probably does not play the function intended, that is, to act as an index of source recharge. It may be functioning here as a seasonal index, since NO₃

load is higher during the wet season when SUM14 will tend to be large. TX14 (14-day average of daily maximum air temperatures) also functions as a seasonal index, as evidenced by its negative coefficients in the model. In fact, TX14 and LANG14 (14-day total solar input) can be interchanged in the model; the choice of TX14 over LANG14 was made because the former shows significantly fewer missing values in the record. These variables are also indices of biological activity, and negative coefficients would also be expected for this role.

That the variable HYST8 (the hysteresis index 0.8^R, where R is the number of days since the hydrograph was rising) is highly significant in the model lends credence to the conceptual hysteresis theory described above. This interpretation is strengthened by the fact that when HYST8 is absent from the list of variables in the stepwise regression procedure, it becomes replaced in the model by the variable MHSLOPE (mean daily hydrograph slope). However, the latter was not included in the final model because of its peculiar cuspate form, seen in Figure 48 of Appendix B, which violates the assumption of equal variance across its range.

Both graphical interpretation and stepwise regression favored the selection of HYST8 over HYST6 (0.6^R) and HYST95 (0.95^R) . This provides some understanding of the correct time scale for the hysteresis effect. HYST8 decays from 1 to 0.1 in about 10 days, as opposed to 5 days and 44 days for HYST6 and HYST95, respectively. This 10-day period is, as expected, about the frequency of winter frontal storms in the Pacific Northwest (Aumen et al., 1989).

Likewise, although the variables proved of little use for modeling, hydrograph slope computed on a mean daily time scale was shown to be favorable to the other scales examined (0.5, 4 and 6 hours). Only MHSLOPE correlated well with NO₃ load. HSLOPE (slope computed over 0.5 hour intervals) proved to be highly erratic except during periods when rapid changes in discharge was occurring. This

would indicate that except during those rapidly changing events, discharge measurements were more frequent than necessary to completely characterize the hydrograph, and thus calculations made from adjacent readings (0.5 hours apart) in the record were responding more to the precision of the measurement than to the true hydrograph slope. The same conclusions apply to hydrograph curvature.

Similar, albeit weaker, sets of inferences can be made from the NO_3 concentration model. The variable LCFS (Log(CFS) where CFS is stream discharge in ft³/s) was highly significant with negative coefficients in the Fir Creek and North Fork sub-basins. This would seem to be consistent with an anticipated dilution effect, whereby a relatively constant (at least in the short term) groundwater concentration is diluted by incoming precipitation. If dilution is a dominant process, there should be a period of the year (probably winter), after the flushing and depletion of new sources has occurred but before the onset of soil desaturation and NO3 buildup, when an inverse correlation exists between NO₃ concentration and discharge. However, separate graphs of NO₃ concentration versus Fir Creek discharge for each month of the year do not show any correlation, even during the winter (Figure 25). The same conclusion also applies to the other three sub-basins, indicating that the data does not support the hypothesized dilution effect.

The season indices SEASON1 and SEASON2 ($\cos(WYDATE \cdot 2\pi/365)$) and sin(WYDATE $\cdot 2\pi/365$), respectively, where WYDATE is the Julian day of the water year) can replace the variable LANG14 (14-day total solar input) to produce a very similar model with similar adjusted coefficients of determination, having positive coefficients for SEASON1 and SEASON2. This is further confirmation that LANG14 is a surrogate for season-dependent processes, such as mineralization, decomposition or biological uptake. Levels of NO₃ in stream water are



Figure 25. Relationship between NO₃ concentration and discharge in Fir Creek for each month of the year.







expected to fall when the system is dryer and more biologically active (high LANG14), thus tending to retain NO_3 in the soil, duff, canopy, vegetation, and periphyton.

TX14 was expected to be an index of biological activity as well, as it apparently was in the NO₃ load model. However, here the coefficients are positive rather than negative, which is puzzling. Although higher temperatures during autumn litter fall may expedite rapid mineralization and nitrification may be favored by warmer periods, peak NO₃ concentrations generally do not correspond to peak temperatures an annual basis.

The positive coefficients for the variable PRECIPIN (daily precipitation) seems to suggest a dominant role for the flushing process, a role which could not be clearly distinguished in the NO₃ load model due to confounding with discharge (which is collinear with NO₃ load). The two opposing hypothetical roles for PRECIPIN, both as a driver of the flushing of new sources and as an index of discharge and corresponding dilution, may account for the fact that precipin is significant in only three of the four sub-basins.

It should be noted, in light of the unexplained effects of some of the variables in the NO₃ concentration model, that this model had disconcertingly low estimated coefficients of determination $(0.23 < R^2 < 0.48)$. With only 23 to 48 percent of the variability of NO₃ concentration explained by this model, any linkages between it and objective reality were tenuous to begin with, and it is not surprising that greater confirmation of watershed process theory was not forthcoming.

These models can suggest combinations of conditions which produce peaks in NO_3 load or, more weakly, concentration. In particular, NO_3 load is expected to be highest under conditions of

high current and antecedent precipitation, on the rising limb of a hydrograph when the average discharge over the previous two weeks has been high, and during the season when maximum temperatures are down.

Partly in order to test these ideas further, but also to look for other possible driving factors not included in the model, four other investigations were conducted to elucidate watershed processes which influence NO₃. First, the NO₃ load and concentration peaks were examined individually to look for patterns in the simultaneous response of the independent variables. Then, the correlation of NO₃ load with snow melt was scrutinized to see if NO₃ peaks corresponded to rapid snow melt events. Next, a potential link between high NO₃ levels and high suspended sediment concentration was investigated. Finally, the relationship of stream to rain chemistry was elaborated. The following four sections contain the details of these efforts.

B. Graphical Examination of Peak Events

Since the two-week sampling interval gave no real clues as to NO₃ loads (NLD) or levels (NO3) on days immediately before or after an observed peak, it was possible that potential correlations with the environmental variables were missed by the multiple regression procedure because the true peak event did not fall on the hour of sampling. It was also possible that since large NO₃ peaks are relatively infrequent in the record (occurring only two or three times per year), the important drivers of those peaks may only be significantly correlated to NO₃ during that small portion of the year, and thus may not be picked up by the multiple regression process.

For example, if the observed peak were actually the falling limb of a peak NO₃ load or concentration event which reached its maximum two days earlier, the significant observable changes in the environmental variables may have happened early on in the event, and may no longer be discernable at the time the sample was taken. This is less likely to be true for those variables integrated over many days to reflect antecedent conditions, but is still nevertheless possible.

Thus, a window in time larger than the point sample was desired. The approach taken was isolate a number of known NO₃ load and concentration peaks and then to graph each independent variable against time for a period straddling the peak and the two adjacent NO₃ readings (approximately 28 days in all). The environmental variables were plotted using daily values to give as fine a time resolution as possible.

In all, six peak NO₃ load events (selected from the 24 total events having NLD > 0.0087 kg-N/ha/day) and six peak NO₃ concentration events (having NO3 > 0.100 mg-N/l) were chosen from the record for Fir Creek (see Table 16). For each of these twelve events, graphs were produced to display the behavior of each of 15 environmental variables (PRECIPIN, PREC3, PREC7, MCFS, SUM7, SUM14, MHSLOPE, MHCURVE, MTEMP, MTEMP14, TMAX, TMIN, LANGLEYS, LANG7, LANG14 - see Appendix A for definitions) during the 28-day window straddling the peak event. Figures 26 and 27 are two examples.

Date:	NO3 conc., Mg-N/l	NO_3 load, kg-N/ha/day
A. Peak concentration events (NO ₃ conc. > 0.100 mg-N/l):		
10/23/89	0.130	0.00158
10/27/86	0.123	0.00324
11/13/87	0.422	0.01505
11/03/88	0.224	0.01250
10/12/90	0.340	0.02497
11/05/91	0.330	0.18987
B. Peak load events (NO ₃ load > 0.0087 kg-N/ha/day):		
02/14/82	0.032	0.02647
03/02/87	0.064	0.01163
11/21/88	0.097	0.03915
01/03/89	0.079	0.01818
02/10/90	0.061	0.03756
04/27/90	0.059	0.02885

Table 16. Selected Peak NO_3 load and concentration events in the Fir Creek record.



Figure 26. Fir Creek NO_3 load and daily precipitation versus time for the peak load event of 02/10/90.



Figure 27. Fir Creek NO₃ concentration and daily precipitation versus time for the peak concentration event of 11/03/88.

Unfortunately, little was revealed by this process.

Inconsistent patterns were observed, with the environmental variable sometimes rising, sometimes falling, and sometimes remaining fairly steady in the vicinity of a NO_3 load or concentration peak.

This apparent inconsistency is actually a manifestation of the problem of low temporal data resolution. Without knowing the total form of the NO₃ load or concentration time series, the true time of initiation of a peak event is not known, nor is the true magnitude or timing of the maximum known. In fact, several maxima could occur within this 28-day window, and yet the single "peak" which registers in the data set may not correspond to any of these. Thus, it is not surprising that no consistent placement of the observed peaks on the time series pattern of other environmental variables was discernable.

C. Links to Suspended Sediment

Since the time series of NO₃ concentration has a very similar shape and pattern to a time series of suspended sediment load, and since the NO₃ samples are analyzed unfiltered, it was necessary to ask whether the NO₃ concentration peaks were in fact manifestations of high suspended sediment. If certain NO₃ peaks correspond to suspended sediment peaks, this would suggest that particulate NO₃ dominates the peaks, and that these peaks ought to be modelled separately in a manner parallel to the way sediment is modelled. Non-sediment peaks might then follow the pattern proposed by Johnson et al. (1969), whereby a soil water reservoir of relatively constant NO₃ concentration is diluted by precipitation.

However, no such link was discovered. As can be seen from Figure 28, the correlation between NO₃ concentration and suspended sediment concentrations is poor. Also, peaks in NO₃ concentration or load did not match the dates of peak suspended sediment concentration.



Figure 28. Fir Creek suspended sediment concentration versus NO₃ concentration.

D. Links to Snow-melt Events

It has often been observed in the literature that the annual average concentrations of NO₃ in precipitation exceeds that in stream water in the northwest. The same, in fact, is true of streams of the Bull Run (see Tables 4 and 12). Furthermore, some more-detailed studies have shown a pronounced decrease in NO₃ in throughfall (precipitation collected beneath a forest canopy) relative to precipitation in the absence of a canopy (Sollins and McCorison, 1981). Other observers have documented links between peak NO₃ concentration and spring snow melt (Clayton and Kennedy, 1985; Coates et al., 1976; Tiedemann et al., 1988).

This line of evidence leads to speculation that perhaps much of the nutrient transformation activity involving NO₃, particularly during the winter when the vascular plant community is dormant, may occur not in the soil, but in the forest canopy. A great variety of vascular and non vascular cryptograms (ferns, lichens, mosses, fungi) as well as a diverse microbial fauna and flora exists here, and comes into intimate contact with rainwater on its way to becoming throughfall. These organisms are known to rapidly become metabolically active when conditions become even momentarily favorable and even during the time when most vascular plants remain dormant.

Snow, however, short circuits its potential contact with these organisms by making its way to the forest floor in frozen, and presumably inert, form. A rapid melting of the snowpack could thus put a large quantity of relatively NO₃ -laden water into the stream. Therefore, it was speculated that many peak NO₃ events, particularly the peak NO₃ load events which tend to occur in late winter and early spring rather than in the autumn, might correspond to snow melt on the basin. Such was not the case, however. As can be seen from Figures 29 and 30, no correlation exists between the rate of snowpack ablation (in inches/day) and the stream NO_3 load, either for the North Fork subbasin, or for the Main Stem sub-basin which is close to the Blazed Alder SNOTEL site.



Figure 29. NO₃ load in the Main Stem Bull Run River versus snow-melt rate at the Blazed Alder (BA) SNOTEL site. Negative values correspond to snowpack ablation while positive values indicate snow accumulation.



Figure 30. NO₃ load in the North Fork Bull Run River versus snow-melt rate at the North Fork (NF) SNOTEL site. Negative values correspond to snowpack ablation while positive values indicate snow accumulation.

E. The Effects of Precipitation Chemistry

From the above discussion on precision and accuracy of the precipitation chemistry data, it is obvious that any interpretations of patterns or linkages gleaned from that data are speculative rather than definitive. It must also be remembered that the precipitation and stream chemistry data are fundamentally different in nature, the former being a one-week integrated sample and the latter a grab sample. Nevertheless, there is some value in examining the relationships between stream and rainwater chemistry, even if only in a conjectural sense.

Figure 31, which is a 90-day moving mean of both precipitation total nitrogen and Fir Creek NO₃ concentration, suggests a phase shift, with precipitation total nitrogen levels reaching their seasonal peaks 3 or 4 months earlier than the peak in stream water NO₃ level. The 90day moving mean was selected to provide sufficient curve smoothing to emphasize persistent patterns without being so long as to obscure seasonal effects. A similar pattern is seen in the corresponding areal loadings (Figure 32). This effect if even more apparent in Figure 33, which shows the seasonal shift from summer (WYDATE < 180) to winter (WYDATE > 180).

Attempts were made to correlate stream with precipitation NO₃ loads and concentrations using multiple regression. No significant correlation (at the P = 0.05 level) was found between NO₃ load for Fir Creek and either the precipitation NO₃ load (ANO3LD) or the antecedent precipitation NO₃ loads (ALD1 and ALD4). Likewise, no correlation existed between stream NO₃ load and precipitation total nitrogen loads (TANLD, TANLD1 and TANLD4), or between stream NO₃ concentration and precipitation NO₃ and total nitrogen concentrations (AIRNO3, AIRN1, AIRN4, TAN, TAN1 and TAN4). However, a significant inverse



Figure 31. Ninety-day moving means of total nitrogen $(NO_3 + NH_4)$ concentration in Headworks precipitation (stars and dotted lines) and NO₃ concentration in Fir Creek discharge (solid lines) versus time.



Figure 31. (Continued)



Figure 32. Ninety-day moving means of total nitrogen load in Headworks precipitation (stars and dotted lines) and Fir Creek discharge (solid lines) versus time. Total nitrogen refers to NO₃ + NH₄ in precipitation data and to NO₃ + total Kjeldahl nitrogen in stream data.







Figure 33. Precipitation versus Fir Creek NO₃ load. Solid dots represent the "summer" season (WYDATE > 180, or March 30 through September 30) and empty squares denote the "winter" season (WYDATE \leq 180, or October 1 through March 29).

(reciprocal) correlation was found to exist between stream NO_3 load (actually LNLD) and precipitation NO_3 and total nitrogen concentrations (AIRNO3 and TAN).

Figures 34 through 37 depict the net water-related nitrogen loading, that is, precipitation input minus stream output, on a weekly basis. The pattern shows no long term or season trends, and net loading is not significantly different from zero. It is important to note here that true watershed loading would consider other inputs (eg. nitrogen fixation) and outputs (eg denitrification), and would require an assessment of the spatial variability of precipitation chemistry across the watershed. Some sources suggest that concentrations of dissolved ions decrease with elevation (Likens et al., 1977) and with distance from air pollution sources (Schroder, et al., 1987).

Based on work in South Carolina, Richter et al. (1983) state that to obtain estimates of mean annual precipitation NO_3 concentrations from weekly samples would require roughly one collector site for every 50 ha to achieve a precision (95-percent confidence interval) of 10 percent of the annual mean; for NH_4 , comparable accuracy would require a collector for every 7 ha. Reynolds (1984), by contrast, suggests that a single collector is adequate for characterization of mean annual NO_3 concentration on a 600 ha



Figure 34. Net total nitrogen load on the Fir Creek sub-basin. Total nitrogen load is defined as precipitation input (of $NO_3 + NH_4$) minus stream discharge output (of $NO_3 + total Kjeldahl nitrogen).$



Figure 35. Net total nitrogen load on the North Fork sub-basin. Total nitrogen load is defined as precipitation input (of $NO_3 + NH_4$) minus stream discharge output (of $NO_3 + total$ Kjeldahl nitrogen).


Figure 36. Net total nitrogen load on the South Fork sub-basin. Total nitrogen load is defined as precipitation input (of $NO_3 + NH_4$) minus stream discharge output (of $NO_3 + total Kjeldahl nitrogen$).



Figure 37. Net total nitrogen load on the Main Stem sub-basin. Total nitrogen load is defined as precipitation input (of NO₃ + NH₄) minus stream discharge output (of NO₃ + total Kjeldahl nitrogen).

watershed in Great Britain. The spatial variability of precipitation chemistry on the Bull Run watershed may be much larger due to the larger range of elevations.

Medians of water-related NO₃ and total nitrogen concentrations and loads are summarized in Tables 17 and 18. The median is a better measure of central tendency for this type of data (which has appreciable skewness), particularly given the fact that the stream data is temporally stratified in such a way as to miss many of the peak events which strongly affect the mean. Median values obtained here are within the range expected for the Pacific Northwest (see Table 5).

Source	Median NO ₃ concentration, mg-N/l		Median Total nitrogen conc., mg-N/l
	Period of record ⁵		Period of record
	7/74-12/91	8/82-12/91	8/82-12/91
Fir Creek	0.041	0.049	0.102
North Fork	0.027	0.030	0.078
South Fork	0.025	0.026	0.076
Main Stem	0.036	0.038	0.083
Precipitation		0.086	0.144

Table 17. Medians of stream and precipitation NO₃ and total nitrogen concentrations.

⁵The period 8/82-12/91 is provided to allow comparison with the period of record for the precipitation chemistry data.

Source	Median NO3 loads, kg/ha/day		Median Total nitrogen loads, kg/ha/day
	Period of record		Period of record
	7/74-12/91	8/82-12/91	8/82-12/91
Fir Creek	0.00146	0.00169	0.00405
North Fork	0.00123	0.00129	0.00426
South Fork	0.00106	0.00103	0.00303
Main Stem	0.00184	0.00192	0.00443
Precipitation		0.00331	0.00534

Table 18. Medians of stream and precipitation NO_3 and total nitrogen loads.

VII. NUTRIENT RELATIONSHIPS ON THE WATERSHED

Earlier it was stated that NO_3 and total nitrogen (NO_3 + total Kjeldahl nitrogen) concentrations were well correlated, and that this fact justified the use of NO3 rather than total nitrogen in characterizing stream nitrogen patterns. The evidence for this claim is presented in Figure 38. The adjusted coefficients of variation (R^2) for this relationship are 0.74, 0.63, 0.62 and 0.18 for the Fir Creek, North Fork, South Fork and Main Stem sub-basins, respectively. The low R^2 for the Main Stem is due to 4 outlier points, the elimination of which results in an \mathbb{R}^2 of 0.78. On the average, NO₃ makes up about 50, 39, 36 and 46 percent of the total nitrogen in the Fir Creek, North Fork, South Fork and Main Stem sub-basins, respectively. When superimposed, graphs of total nitrogen and of nitrate correspond very closely with respect to the time of occurrence and relative magnitude of peaks. Computation of the NO3 to total nitrogen ratio also allowed the serendipitous discovery of six typographical errors in the data (points having NO3:TOTN ratios larger than 100 percent), which were subsequently removed from the analysis.

A final question for analysis was the correctness of the assumption that streams of the Bull Run watershed tend to be phosphorus limited (Aumen et al., 1990). Figure 39 depicts the ratio of total nitrogen to total phosphorus for the Fir Creek sub-basin. Theoretically, an N:P ratio of 7 (by weight) is optimum, as this value is characteristic of the tissues of most aquatic algae and macrophytes (Wetzel, 1983). When N:P > 7, the plant community is unable to fully utilize the available nitrogen because too little phosphorus is present. Thus, Fir Creek appears to be almost entirely phosphorus limited, sometimes strongly so.



Figure 38. Total nitrogen (NO3 + total Kjeldahl nitrogen) versus NO3 concentrations in Fir Creek.



Figure 39. Fir creek total nitrogen to total phosphorus ratio versus time. Horizontal line indicates biologically optimum value of nitrogen/phosphorus = 7.

However, it is perhaps more relevant to examine the ratio of NO_3 to PO_4 , which are the most predominant biologically available forms of nitrogen and phosphorus. As depicted in Figure 40, the Fir Creek is phosphorus limited for the majority of the time, but also seems to be marginally nitrogen limited for short periods during most years, averaging 13 percent of the total sample days. The occurrence of nitrogen limited conditions is most common for the North Fork subbasin, which tends to have higher phosphorus levels overall; this subbasin has $NO_3/PO_4 \leq 7$ on 79 percent of the days sampled (see Figure 41).

Tables 19 and 20 summarize the N/P ratio statistics for each sub-basin. Examination of the frequency of nitrogen-limited days by month or by season revealed no regular patterns (See Figure 42). However, the conclusion that all streams on the Bull Run system are nitrogen limited at all times is called into question by these observations. The biological implications of periodic shifts in limiting nutrient status is unknown, and would depend on such factors as the ability of organisms to store limiting nutrients for short periods of time.

Sub-basin	NO3-N/PO4-P ratio	Percent of days		
	Mean (±σ)	Median	sampled with $NO_3/PO_4 \leq 7$	
Fir Creek	19.1 (±16.2)	15.0	13	
North Fork	5.3 (±5.0)	3.7	79	
South Fork	13.3 (±9.2)	12.7	25	
Main Stem	20.7 (±15.5)	18.7	15	

Table 19. Mean and median ratios of NO_3-N/PO_4-P by weight, and percent of days sampled with $NO_3/PO_4 \leq 7$. σ is the standard deviation.

Table 20. Mean and median ratios of Total-N/Total-P by weight, and percent of days sampled with Total-N/Total-P \leq 7. σ is the standard deviation.

Sub-basin	Total-N/Total-P ratio by weight		Percent of days
	Mean (±σ)	Median	sampled with $N/P \leq 7$
Fir Creek	20.8 (±12.5)	17.3	1
North Fork	10.3 (±7.1)	8.6	37
South Fork	17.0 (±8.3)	15.3	3
Main Stem	22.7 (±12.9)	18.6	2



Figure 40. Fir creek NO₃ to PO₄ ratio versus time. Horizontal line indicates biologically optimum value of nitrogen/phosphorus = 7.











Figure 41. North Fork Bull Run River total nitrogen to total phosphorus ratio versus time. Horizontal line indicates biologically optimum value of nitrogen/phosphorus = 7.



Figure 42. Percent of total nitrate-limited days $(NO_3/PO_4 < 7)$ from the record falling in each month of the calendar year.

VIII. CONCLUSIONS AND RECOMMENDATIONS

Aumen et al. (1989) remarked that in terms of cost, attention and concern, the current water quality monitoring program on the Bull Run watershed is one of the most intense and sincere efforts in existence. No other record of comparable duration, accuracy, or level of detail exists for Western Oregon. Yet, any sampling scheme, by definition, extracts only a fraction of the total information possible, and as such will give incomplete coverage in frequency of measurements, in spatial completeness, and in duration of record sufficient to characterize extreme events (Aumen, et al., 1989). This study has addressed the overall resolution of the Bull Run data set in terms of its precision and accuracy, its sampling frequency in relation to natural variability, and its implications in terms of the type of predictive model it is possible to construct and the nature of the conclusions which can be definitively made concerning watershed processes.

The precision and accuracy of water nutrient data is driven by available technology as much as it is influenced by proper sample handling practice and attention to quality control in the laboratory. For the Bull Run data, there is probably little room for improvement in the latter two areas. Nevertheless, it was seen that only the NO₃ record had sufficient precision relative to its natural range and variability for patterns to be meaningfully interpreted and for modeling purposes. If a variable has too large a relative standard deviation (as does total Kjeldahl nitrogen and total phosphorus), or too many data points lying at or below the limits of detection (as does PO₄), no model will be possible.

The working regression model of NO_3 loads developed here for streams of the Bull Run Watershed could become a useful tool for predicting natural extremes and for discerning whether an observed

peak is expected on the basis of ambient conditions or might be a consequence of other causes, such as management activities or natural disturbance. From an academic point of view, this model of NO₃ load constitutes new information. The fit between this model and the data was good, as indicated by the relatively high coefficients of variation (66 to 74 percent of the variability of Log(NO₃ load) was explained by the model).

Current and antecedent precipitation were found to be strong drivers of NO₃ load, probably because both load and precipitation are linked to stream discharge. The 14-day cumulative discharge and the 14-day average maximum air temperature were correlated with NO₃ load, most likely acting as indices of seasonal variation. Thus, the model was seen to be a modestly useful inference tool as long as one is cautious about recognizing the limits of the statistical process and the surrogate nature of the predictor variables.

However, it was also seen how disappointingly limited in scope these deductions about watershed processes can be. This factor stems as much from the limited resolution of the data as it does from the complexity of the problem. A two week sampling interval, while probably adequate to characterize median concentration values (given a sufficiently long record), is not sufficient to characterize either the mean values or the frequency and magnitude of peaks. This is because the time between samples is long compared to the time scale on which changes occur in nutrient levels, and is long relative to the duration of peak events. Thus, the chances of capturing a peak event in the record are slim, and knowledge about the rapid changes which accompany an observed "peak" is nonexistent.

The same problem prevented any conclusions from being made using the graphical analysis of environmental variable behavior during time windows surrounding observed "peaks" in the record. Mathematically, the single peak in isolation has zero degrees of freedom, because it

consists of one data point. Thus, it becomes statistically impossible to establish correlations between this point and the other variables of interest within that time window. It had been hoped at the outset that knowledge of these other variables, which are either drivers or surrogates for drivers of nutrient transport processes, at a much finer scale of resolution, would fill in the gaps of information to the extent that more definitive conclusions could be made. Indeed, the availability of these other variables at higher resolution did allow the creation of time-integrated indices of antecedent conditions which were instrumental in the success of the NO₃ load model. However, the conclusions to be made about watershed processes remained weak and subjective. For those variables such as PO_4 which spend a significant amount of time below the limits of detection, even to statistically predict when a peak will occur would require more frequent sampling.

The precipitation chemistry data was even more problematic, as overall data precision was poor and did not include any provision to assess the magnitude of potentially large errors due to sample maturation. These limitations, together with the problem of insufficient knowledge about the spatial variability of precipitation chemistry over the watershed, forestalled any conclusions about areal nitrogen influx and efflux.

Since any sampling scheme will be limited, the design of a sampling protocol must be made with study objectives firmly in mind. Although a better understanding of processes controlling stream nutrients on the watershed would undoubtedly aid in management decisions and in water quality monitoring, that is not the main objective of the existing monitoring program. Rather, an assessment of whether nutrient levels are changing from those of the baseline period is the goal.

The current scheme of temporally-stratified grab samples is probably good for determining the median nutrient levels, and for

detecting long term trends in those median levels. The median is a good indicator of trend because it is relatively insensitive to infrequent peak events. However, grab sampling on two week intervals is not a good way to asses the frequency and magnitude of peak nutrient events or system variability, which, in the long run, may be more important water quality factors.

Grab sampling is also not a very good way to determine the average nutrient levels (or loads), since averages are sensitive to the occurrence of peaks. Rinella (1987) discovered that 70 percent of the annual suspended sediment transport on the Bull Run streams occurred during peak events that occupied only 3 to 4 days out of the year (1 percent of the time). If nutrient export is analogous, then most of the nutrient export may be going undetected, given the long sampling interval. Since reservoirs are long-term integrators of nutrient inputs, the reservoir nutrient dynamics are more responsive to the average nutrient load than to isolated peaks or to median levels.

These concerns have lead to a recommendation that the sampling scheme be changed from grab sampling at two week intervals to some form of automated flow-based sampling, in which sampling is more intensive during periods of high discharge (Aumen, et al., 1989). Currently, a flow-stratified random sampling scheme is being considered for total nitrogen and total phosphorus (Thomas and Lewis, 1992). The total range of possible discharges for a given stream would be proportioned into seven sub-ranges or strata (four corresponding to an increasing discharge and three to a falling discharge regime). A computer-controlled automated sampler would then collect samples at random times, the probability of sampling being

governed by the current discharge stratum. Thus, a pre-determined average annual number of samples would be spread evenly throughout the seven discharge strata⁶.

Such a scheme would allow better evaluation of mean and total loads (both seasonal and annual), and of peak loads, which are highly correlated with discharge, than does the current time-stratified sampling. Knowledge of peak concentrations would not be improved, however, since it remains unknown how to predict those peaks and sample accordingly.

This scheme would also make problematic the development or use of predictive models like the ones presented in this study. As with time-stratified sampling, serial autocorrelation would be present in data from flow-stratified random sampling as well, making a time series model (as opposed to a multiple regression model) necessary. However, highly erratic sampling intervals produced by the flowstratified scheme might prevent the meaningful application of a time series model, which depends on equally-spaced (or nearly equallyspaced) sampling intervals.

These concerns over serial autocorrelation do not apply if the objective is to compare mean nutrient concentrations or loads within like flow strata for the same seasons in different years, as is the case for the Bull Run water quality standards. Within a given flow stratum and season, the samples are random.

One recommendation which would help guide future sampling scheme adjustments would be to foster a research effort to determine the nature, magnitude and duration of nutrient peaks (both load and concentration). This might be achieved by conducting several intensive sampling efforts, each of about 10 days duration, in which

⁶Although telemetry would allow samples to be retrieved for analysis within 48 hours of collection, concerns over sample maturation changes preclude the use of this scheme for NO_3 . Total nitrogen may be less changeable. This assumption, however, needs to be periodically checked.

samples would be taken at 4-hour intervals during the season when nutrient peaks are expected. At this sampling frequency, the nutrient time series would be completely characterized. Capturing a series of peaks in this way would give needed clues as to the their statistical characteristics. Estimations of how much nutrient load is missed by the current sampling scheme could then be made.

The effort would also, hopefully, add to knowledge of what processes drive the peaks, and how to predict when peaks are likely to occur. If the timing of peaks can be predicted, even if somewhat inaccurately, it would be possible to combine the current timestratified sampling scheme with automated sampling which is activated only when a peak is likely, thereby capturing a detailed record from that elusive one percent of the time when most of the nutrient transport may occur. This would provide the most detailed and comprehensive picture of stream nutrient dynamics possible, without disrupting the continuity of a long and valuable record.

In summary:

1. The Bull Run stream nutrient data represents one of the longest, highest-quality records in existence for the Pacific Northwest. Yet, the ability to make inferences about watershed processes using these data remained weak due to data precision and resolution issues.

2. Of the four stream nutrients examined, only NO_3 was known to a precision sufficient to investigate time variability patterns. The others either exhibited poor precision (total Kjeldahl nitrogen and total phosphorus) or remained at or below detection limits for most of the time (PO_4) .

3. Poor data precision and a failure to quantify experimental error due to sample maturation changes precluded meaningful interpretation of the precipitation chemistry record. The available data indicated that average total nitrogen influx in precipitation may be nearly equal to stream total nitrogen load, but that precipitation total

nitrogen load may reach its seasonal maximum in the summer, three or four months earlier than the corresponding maximum in stream water. 4. A reasonably good model was developed to predict stream NO₃ load. The model was made possible by knowledge of the predictor variables at much higher time resolutions than existed for NO₃. However, this knowledge was not sufficient to fill in the gaps in the nutrient record or to greatly improve the model's capability to infer conclusions about watershed processes.

5. Nitrogen/phosphorus ratios indicated that although the four streams are predominantly phosphorus limited, each one (particularly the North Fork) is nitrogen limited at various times of the year. No seasonal pattern of nutrient limited status could be discerned.

6. Finally, this research underscored the importance of including data precision and resolution assessment in the design of any research or monitoring program, and in the interpretation of stream chemistry data.

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APPENDICES

APPENDIX A. DEFINITIONS OF VARIABLES CONSIDERED

What follows is a listing of the variables considered in the modeling process, their symbols, and notes on how they were computed. Variables given in **bold** type are those actually selected for the final model. Graphical displays of the two chosen dependent variables (LNLD and LNO3) versus each of the independent variables showing significant correlations with LNLD or LNO3 are given in Appendix B. "Log" refers to the base-10 logarithm.

A. Dependent Variables

NO3 : Instantaneous NO3 concentration in mg-N/1.

- TOTN : Instantaneous total nitrogen (NO₃ + total Kjeldahl nitrogen), in mg-N/l.
- NLD : Instantaneous NO₃ load in Kg-N/ha/day. Computed as NO3[·]CFS[·](2.4466)/(Sub-basin Area). If CFS is missing, then MCFS (daily mean discharge) is used instead.
- TNLD : Instantaneous total nitrogen load in Kg-N/ha/day. Computed as TOTN CFS (2.4466)/(Sub-basin Area). If CFS is missing, then MCFS (daily mean discharge) is used instead.

LNLD : Log(NLD), where NLD is instantaneous NO3 load.

LNO3 : Log(NO3), where NO3 is instantaneous NO3 concentration.

B. <u>Independent Variables</u>

1. Time Variables

- TIME : Time of sampling, in seconds past midnight, rounded to the nearest half hour. Used to match sampling time to instantaneous discharge (CFS).
- RTIME : Time of sampling, in seconds past midnight. Did not correlate with LNLD or LNO3.

DATE : Date of sampling. Used only for graphics.

- WYDATE : Day of the water year, beginning with October 1 (day 1) and ending with September 30 (day 365 or 366). Showed a non-linear correlation with LNO3 and LNLD which suggests the use of combinations of the sine and cosine as transforming functions. However, variance is unequal across the range (higher for small and large values of WYDATE), probably because the date of the beginning of the wet season is variable.
- SEASON1 : A sinusoidal index of season, computed as Cos(WYDATE 2π/365). Showed positive correlation with LNLD and LNO3, but interacted with LANG14 and TX14, which were superior indices of seasonality, and thus was eliminated by the stepwise procedure. SEASON2 : Another sinusoidal index of season, computed as
 - Sin(WYDATE $2\pi/365$). Showed a negative correlation with LNLD, and a week positive correlation with LNO3. However, SEASON2 also interacted with LANG14 and TX14, which were superior indices of seasonality, and thus was eliminated by the stepwise procedure.

2. Discharge Variables

CFS : Stream discharge at time of sampling, in CFS (ft³/sec). CFS readings were at half hour intervals, but these did not correspond exactly with the time of nutrient sampling. Thus, CFS readings were matched to nutrient measurements by rounding both the sampling time and the time of CFS measurement to the nearest half hour (using the variable TIME), resulting in a small potential mismatch (±15 minutes). No correlation with NO3 exists during any part of the year (see Figure 25). Not used in LNLD modeling because of colinearity.

- MCFS : Daily mean discharge. These were extracted from U.S. Geological Survey (USGS) records, and thus contain their estimated values for days when some or all of the 30-minute readings were missing. Displays a non-linear correlation with LNLD and a weak negative correlation with LNO3 which is better represented by the reciprocal, CFSR. Not used in LNLD modeling because of intrinsic colinearity.
- SUM7 : Sum of previous 7 day's cumulative discharge, in CFS'days. Computed by adding the previous 7 values of MCFS. Shows a nonlinear positive correlation with LNLD and a weak negative correlation with LNO3. However, SUM14 was better correlated with both variables and thus favored by the stepwise regression.
- SUM14 : Sum of previous 14 day's cumulative discharge, in CFS days. Computed by adding the previous 14 values of MCFS. Correlates negatively with LNO3 and positively with LNLD, but is better correlated to each after a log transformation (LSUM14).
- SUMCFS : Cumulative sum of MCFS values (including the current day's value) since the beginning of the water year, in CFS days. Correlated negatively with LNO3. Not correlated with LNLD.
- LCFS : Log(CFS). Not correlated with LNO3. Strong correlation with LNLD, but not used in LNLD modeling due to intrinsic colinearity.
- LCFSQ : [log(CFS)]². No correlation with LNO3. Strong correlation
 with LNLD, but not used in LNLD modeling due to intrinsic
 colinearity.

- CFSR : 1/CFS. Weak positive correlation with NO3, but strongly unequal variance across the range. Not considered for LNLD modeling due to intrinsic colinearity.
- LSUM14 : Log(SUM14). Negatively correlated with LNO3 and positively correlated with LNLD. Variance more equally distributed across the range than was the case with SUM14.

3. Hydrograph Placement Variables

- HSLOPE : Hydrograph slope, computed from readings 30 minutes apart, in CFS/hr. HSLOPE = (CFS_t-CFS_{t-30min})/0.5, where subscript "t" denotes the time of current reading. Did not correlate with either LNO3 or LNLD.
- HSLOPE4 : Hydrograph slope, computed from readings 4 hours apart, in CFS/hr. HSLOPE4 = $(CFS_t-CFS_{t-4br})/4$, where subscript "t" denotes the time of current reading. Did not correlate with either LNO3 or LNLD.
- HSLOPE6 : Hydrograph slope, computed from readings 6 hours apart, in CFS/hr. HSLOPE6 = $(CFS_t-CFS_{t-Gbr.})/6$, where subscript "t" denotes the time of current reading. Did not correlate with either LNO3 or LNLD.
- MHSLOPE : Hydrograph slope, computed from mean daily discharge (values 1 day apart), in CFS/hr. MHSLOPE = (MCFS_t-MCFS_{t-Iday})/24, where subscript "t" denotes the time of current reading. Of all the hydrograph slope variables, this was the only one to show statistically significant (P = 0.05) correlation with LNLD and LNO3. However, a graph of LNLD or LNO3 versus MHSLOPE shows a cusp at MHSLOPE = 0, indicating that this variable is a poor choice for modeling.

HCURVE : Hydrograph curvature, computed from readings 30 minutes apart, in CFS/hr². HCURVE = (HSLOPE_t-HSLOPE_{t30min})/0.5, where subscript "t" denotes the time of current reading. Did not correlate with either LNO3 or LNLD.

- HCURVE4 : Hydrograph curvature, computed from readings 4 hours apart, in CFS/hr². HCURVE4 = (HSLOPE4,-HSLOPE4,_HSLO
- HCURVE6 : Hydrograph curvature, computed from readings 6 hours apart, in CFS/hr². HCURVE6 = (HSLOPE6,-HSLOPE6,...)/6, where subscript "t" denotes the time of current reading. Did not correlate with either LNO3 or LNLD.
- MHCURVE : Hydrograph curvature, computed from readings 1 day apart, in CFS/hr². MHCURVE = (MHSLOPE,-MHSLOPE,.Iday)/24, where subscript "t" denotes the time of current reading. Not significantly correlated with either LNLD or LNO3, and has the same cusped functional form as MHSLOPE.
- R : Hydrograph recession index (the time, in days, since the rising limb of hydrograph ended). On a day of hydrograph rise, R = 0. On days when discharge is not rising, R is the number of days since the last day when discharge was rising. The hydrograph is said to be rising when the current mean daily discharge is greater than 1.1 times the mean discharge on the previous day. Used only as an intermediate step to compute HYST6, HYST8 and HYST95.
- HYST6 : Hydrograph hysteresis factor. HYST6 = 0.6^{R} . Correlates positively with LNLD and LNO3, but distribution of variance across the range is better with the variable HYST8.
- **HYST8** : Hydrograph hysteresis factor. HYST8 = 0.8^R. Correlates positively with LNLD and LNO3.

HYST95 : Hydrograph hysteresis factor. HYST95 = 0.95^R. Correlates positively with LNLD and LNO3, but distribution of variance across the range is better with the variable HYST8.

4. Precipitation Variables

PRECIPIN : Daily precipitation in inches. Positively correlated with LNO3 and LNLD.

- LSTPRCP : Previous day's precipitation in inches. Positively correlated with LNLD and LNO3, but somewhat better equality of variance across the range is obtained with the log transformation to LLSTPCP (see below).
- PREC3 : Total precipitation for the previous three day period (not counting the current day). Positively correlated with LNLD, but interacts with the better-correlated variable PREC7. Only weekly correlated with LNO3.
- PREC7 : Total precipitation for the previous seven day period (not counting the current day). Shows a strong positive correlation with LNLD and a much weaker positive correlation with LNO3.
- LPRECIPN : Log(PRECIPIN + 0.01). Correlates positively with LNLD and LNO3, but has poorer equality of variance across the range than PRECIPIN.
- **LLSTPCP** : Log(LSTPRCP + 0.01). Positively correlated to LNLD and LNO3, with somewhat better equality of variance across the range than is obtained with the variable LSTPRCP.
- AIRNO3 : Precipitation NO₃ concentration, in mg-N/l, for the week in which a stream sampling date falls. Values given in the NADP/NTN data are in mg-NO₃/l; these are divided by 4.426 mg NO₃/mg N to yield mg-N/l. Precipitation sampling period begins and ends on Tuesday morning. Showed a weak non-linear
correlation with LNO3 and LNLD. Not used for modeling due to loss of degrees of freedom (shorter length of record than stream variables).

- AIRN1 : Precipitation NO₃ concentration, in mg-N/l, for the week prior to the one in which a stream sampling date falls. Not correlated with LNO3 or LNLD.
- AIRN4 : Average precipitation NO_3 concentration, in mg-N/l, for the four-week period ending with the week in which a stream sampling date falls. Not correlated with LNO3 or LNLD.
- ANO3LD : Precipitation NO₃ load, in Kg-N/ha/day, for the week in which a stream sampling date falls. Computed from AIRNO3'PP/700, where PP is the weekly total precipitation at the NADP/NTN site in millimeters. Precipitation sampling period begins and ends on Tuesday morning. Not correlated with either LNLD or LNO3.
- ALD1 : Precipitation NO₃ load, in Kg-N/ha/day, for the week prior to the one in which a stream sampling date falls. Not correlated with either LNLD or LNO3.
- ALD4 : Average precipitation NO_3 load, in Kg-N/ha/day, for the fourweek period ending with the week in which a stream sampling date falls. Not correlated with either LNLD or LNO3.
- TAN : Precipitation total nitrogen (NO₃ + NH₄) concentration, in mg-N/l, for the week in which a stream sampling date falls. Values given in the NADP/NTN data are in mg NO₃/l and mg NH₄/l. To convert these values to mg-N/l, the NO₃ and NH₄ values are divided by 4.426 mg NO₃/mg N and 1.288 mg NH₄/mg N, respectively, before adding. Precipitation sampling period begins and ends on Tuesday morning. Displays a weak positive correlation with LNO3, and a weak negative or reciprocal correlation with LNLD.

- TAN1 : Precipitation total nitrogen $(NO_3 + NH_4)$ concentration, in mg-N/l, for the week prior to the one in which a stream sampling date falls. Not correlated with either LNLD or LNO3.
- TAN4 : Average precipitation total nitrogen $(NO_3 + NH_4)$ concentration, in mg-N/l, for the four-week period ending with the week in which a stream sampling date falls. Not correlated with either LNLD or LNO3.
- TANLD : Precipitation total nitrogen $(NO_3 + NH_4)$ load, in Kg-N/ha/day, for the week in which a stream sampling date falls. Not correlated with either LNLD or LNO3.
- TANLD1 : Precipitation total nitrogen (NO₃ + NH₄) load, in Kg-N/ha/day, for the week prior to the one in which a stream sampling date falls. Not correlated with either LNLD or LNO3.
- TANLD4 : Average precipitation total nitrogen $(NO_3 + NH_4)$ load, in Kg-N/ha/day, for the four-week period ending with the week in which a stream sampling date falls. Not correlated with either LNLD or LNO3.

5. Temperature Variables

- AIRTEMP : Sampling site air temperature at time of sampling, °C. Not correlated with LNO3. Shows a weak negative correlation with LNLD but this is better represented by TX14 (see below).
- H2OTEMP : Sampling site water temperature at time of sampling, °C. Not correlated with LNO3. Shows a weak negative correlation with LNLD which, again, is better represented by TX14 (see below).
- MTEMP : Daily mean water temperature at sampling site, °C. Shows a very weak positive correlation with LNO3, and a weak negative correlation with LNLD.
- MTEMP14 : Mean water temperature for the 14-day period ending the day prior to the day of sampling, °C. Displays a weak positive

correlation with LNO3, and good negative correlation with LNLD. Too many missing values were apparent for use in modeling.

- TMAX : Daily maximum air temperature at the Headworks, °C. Shows a negative correlation with LNLD (weaker than TX14), and no correlation with LNO3.
- TMIN : Daily minimum air temperature at the Headworks, °C. Shows a negative correlation with LNLD (weaker than TX14), and no correlation with LNO3.
- TX14 : Average maximum air temperature at the Headworks for the 14-day period ending the day prior to the day of sampling, °C. Negative correlation with LNLD, and weak positive or parabolic non-linear correlation with LNO3.
- TM14 : Average minimum air temperature at the Headworks for the 14-day period ending the day prior to the day of sampling, °C. Shows a negative correlation with LNLD (weaker than TX14), and no correlation with LNO3.

6. Solar Variables

LANGLEYS : Daily total solar influx, in langleys. Shows a weak negative correlation with LNLD and LNO3.

- LANG7 : Total solar influx for the seven day period ending the day prior to the day of sampling, in langleys. Shows a better correlation (also negative) with LNLD than LANGLEYS, but a similarly weak correlation with LNO3.
- LANG14 : Total solar influx for the fourteen day period ending the day prior to the day of sampling, in langleys. Shows a good negative correlation with LNLD, but interacts with the temperature variables (TX14). The latter are better for modeling purposes due to fewer missing values. Correlation with LNO3 is weak.

APPENDIX B. GRAPHICAL SCREENING OF INDEPENDENT VARIABLES

This section contains graphs of most of the independent variables mentioned in Appendix A against the two dependent variables, $Log(NO_3 \text{ concentration})$ and $Log(NO_3 \text{ load})$ (LNO3 and LNLD, respectively). Detailed definitions of variables are given in Appendix A.



Figure 43. LNO3 and LNLD in Fir Creek versus RTIME and WYDATE. See Appendix A for definitions of variables.



Figure 44. LNO3 and LNLD in Fir Creek versus SEASON1 and SEASON2. See Appendix A for definitions of variables.



Figure 45. LNO3 and LNLD in Fir Creek versus CFS and MCFS. See Appendix A for definitions of variables.



Figure 46. LNO3 and LNLD in Fir Creek versus LCFS and SUM7. See Appendix A for definitions of variables.



Figure 47. LNO3 and LNLD in Fir Creek versus SUM14 and SUMCFS. See Appendix A for definitions of variables.



Figure 48. LNO3 and LNLD in Fir Creek versus LSUM14 and MHSLOPE. See Appendix A for definitions of variables.



Figure 49. LNO3 and LNLD in Fir Creek versus MHCURVE and HYST6. See Appendix A for definitions of variables.



Figure 50. LNO3 and LNLD in Fir Creek versus HYST8 and HYST95. See Appendix A for definitions of variables.



Figure 51. LNO3 and LNLD in Fir Creek versus PRECIPIN and LSTPRCP. See Appendix A for definitions of variables.



Figure 52. LNO3 and LNLD in Fir Creek versus PREC3 and PREC7. See Appendix A for definitions of variables.



Figure 53. LNO3 and LNLD in Fir Creek versus LLSTPCP and AIRNO3. See Appendix A for definitions of variables.



Figure 54. LNO3 and LNLD in Fir Creek versus AIRN1 and AIRN4. See Appendix A for definitions of variables.



Figure 55. LNO3 and LNLD in Fir Creek versus ANO3LD and ALD1. See Appendix A for definitions of variables.



Figure 56. LNO3 and LNLD in Fir Creek versus ALD4 and TAN. See Appendix A for definitions of variables.



Figure 57. LNO3 and LNLD in Fir Creek versus TAN1 and TAN4. See Appendix A for definitions of variables.



Figure 58. LNO3 and LNLD in Fir Creek versus TANLD and TANLD1. See Appendix A for definitions of variables.



Figure 59. LNO3 and LNLD in Fir Creek versus TANLD4 and AIRTEMP. See Appendix A for definitions of variables.



Figure 60. LNO3 and LNLD in Fir Creek versus H2OTEMP and MTEMP. See Appendix A for definitions of variables.



Figure 61. LNO3 and LNLD in Fir Creek versus MTEMP14 and TMAX. See Appendix A for definitions of variables.



Figure 62. LNO3 and LNLD in Fir Creek versus TMIN and TX14. See Appendix A for definitions of variables.



Figure 63. LNO3 and LNLD in Fir Creek versus TM14 and LANGLEYS. See Appendix A for definitions of variables.



Figure 64. LNO3 and LNLD in Fir Creek versus LANG7 and LANG14. See Appendix A for definitions of variables.

APPENDIX C. GRAPHICAL RECORD OF STREAM NUTRIENT DATA

This section contains graphs of the complete record of NO_3 (both concentration and load), total nitrogen, PO_4 , and total phosphorus for the Fir Creek station, and of NO_3 concentration and load for the North Fork, South Fork and Main Stem stations.



Figure 65. NO₃ concentrations in precipitation. Horizontal bars indicate 95-percent confidence intervals for each measurement.







Figure 66. Total nitrogen $(NO_3 + NH_4)$ concentrations in precipitation. Horizontal bars indicate 95-percent confidence intervals for each measurement.







Figure 67. NO₃ concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement.











Figure 68. Total Kjeldahl nitrogen concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement.






Figure 69. PO₄ concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement.











Figure 70. Total phosphorus concentrations in Fir Creek. Horizontal bars indicate 95-percent confidence intervals for each measurement.



Figure 70. (Continued) Note that one point (TOTP = 0.137 on 11/25/91 at 16:00) is off the scale of the graph.



Figure 71. NO₃ loads in Fir Creek. Horizontal bars indicate 95percent confidence intervals for each measurement.







Figure 71. (Continued) Note that one point (NO₃ load = 0.190 on 11/5/91) is off the scale of the graph.



Figure 72. NO₃ loads in the North Fork Bull Run River. Horizontal bars indicate 95-percent confidence intervals for each measurement.



Figure 72. (Continued)







Figure 73. NO₃ loads in the South Fork Bull Run River. Horizontal bars indicate 95-percent confidence intervals for each measurement.



Figure 73. (Continued)



Figure 73. (Continued)



Figure 74. NO₃ loads in the Main Stem Bull Run River. Horizontal bars indicate 95-percent confidence intervals for each measurement.







Figure 74. (Continued)



Figure 75. NO₃ concentrations in the North Fork Bull Run River. Horizontal bars indicate 95-percent confidence intervals for each measurement.











Figure 76. NO3 concentrations in the South Fork Bull Run River. Horizontal bars indicate 95-percent confidence intervals for each measurement.











Figure 77. NO3 concentrations in the Main Stem Bull Run River. Horizontal bars indicate 95-percent confidence intervals for each measurement.







