

AN ABSTRACT OF THE DISSERTATION OF
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STUDIES ON THE DISTRIBUTION AND FATES
OF DISSOLVED ORGANIC CARBON

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Dissolved organic carbon (DOC) is a complex mixture of compounds ranging from recalcitrant molecules highly resistant to microbial degradation to compounds essential to the activity and growth of microbes and algae. Regretably, commonly employed techniques presently used for measuring DOC fail to differentiate structural or biochemical characteristics. Identification of even a small fraction of the total DOC pool requires methods, many of which are expensive and time consuming. Therefore, providing an understanding of factors which govern the sources, concentration, and fate of DOC in aquatic ecosystems, furnishes a basis upon which to pursue more detailed research.

Initial research centered upon the distribution and transport of organic material in the Columbia River. Annual, diel, and main channel variability in DOC concentration for this major river was small, with maximum concentration less than twice minimum values. The relative annual constancy of DOC, in contrast to the inorganic nutrients nitrate and phosphate, indicated that a significant proportion of the DOC load reaching the Columbia was composed of recalcitrant compounds. Correlation of DOC concentration was best with physically controlled variables rather than nutrient concentrations affected by instream primary production or heterotrophic activity.

Further research was then initiated on two first-order streams where nutrient linkages between terrestrial and aquatic ecosystems are strongest. Two watersheds, one recently clearcut and the other an old-growth Douglas-fir forest were compared, since the impact of clearcutting upon DOC, nitrogen, and phosphorus dynamics is crucial to management of aquatic ecosystem in the Pacific Northwest. Solution nitrogen was more than tripled in the disturbed watershed. Increased nitrification and greater losses of dissolved organic nitrogen caused the elevated concentrations. Differences in the quality and quantity of DOC available to soil microflora in the two watersheds were hypothesized as important

factors in the observed nitrogen response. Concentrations of DOC actually reaching the two streams were generally low and relatively invariant, similar to the Columbia River, except during storms preceded by dry and usually warmer conditions. These pulsed inputs of water with elevated concentrations of DOC may constitute a major input of labile DOC to stream microbial populations.

Central to the reasoning that concentrations of DOC are normally dominated by recalcitrant compounds is the implicit argument that labile DOC is efficiently and rapidly removed from solution. The mechanisms and rates by which both biotic and abiotic uptake occurs were investigated using alder leaf leachate. Abiotic uptake was primarily associated with amorphous aluminum and iron oxides. Rapid equilibration occurred with up to 20% of the leachate susceptible to abiotic removal. Microbial uptake was kinetically slower but more efficient in processing the total DOC pool in the leachate. In one day, nearly 90% of the leachate was taken up. In two days, 97% was removed. Aquatic microbial populations were capable of processing almost the entire energy supply of DOC provided by the leachate.

STUDIES ON THE DISTRIBUTION AND FATES
OF DISSOLVED ORGANIC CARBON

by

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In the section for acknowledgements in my master's thesis, I suggested that I acknowledge no one as I did the whole damn thing myself. It was a lie then, and it would be even more so now.

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PREFACE

This thesis is the result of my investigations into the distribution and fates of dissolved organic carbon in aquatic ecosystems. It consists of three manuscripts which have or will soon be submitted for publication in various journals. The first paper, "Organic Carbon Transport in the Columbia River", has been submitted to Estuarine and Coastal Marine Science. It describes the annual cycle of organic material in transport in a large river system (Columbia River) and suggests some of the factors controlling both the quantity and form. The second paper, "Pathways and Mechanisms for Removal of Dissolved Organic Carbon from Leaf Leachate in Streams", has been submitted to the Canadian Journal of Fisheries and Aquatic Sciences (formerly the Journal of the Fisheries Research Board of Canada). The mechanisms and rates which control the removal of dissolved organic carbon are evaluated using leaf leachate as a source material. Both biotic and abiotic pathways are considered. The third paper, "Nutrient Response to Clearcutting in a First-order Stream in the Cascade Mountains", considers the response of an aquatic ecosystem to a common management practice, clearcutting. This paper is to be submitted to Ecological Monographs. Direct changes in dissolved organic carbon and other

nutrients are evaluated. Possible links between the quantity and quality of dissolved organic carbon and nitrogen dynamics are developed. Also, the importance of the timing and concentration of dissolved organic carbon and inorganic nutrient inputs for the functioning of aquatic ecosystems is considered.

The perspective throughout this work has been one of a chemist applying chemical data and techniques to ecosystem questions. Along the way, I have become increasingly cognizant of underlying ecological, biochemical, and microbiological processes affecting and being affected by dissolved organic carbon. The complexity of trying to decipher such a diverse pool of materials as constitutes dissolved organic carbon will require the efforts of numerous disciplines. In my own way, I took some of the tools with which I was familiar and approached general questions of distribution and pathways of removal and decomposition of this material. I nibbled at the edges of the big picture, but hopefully provided some understanding and direction for the next generation of research.

CHAPTER 1

ORGANIC CARBON TRANSPORT IN THE COLUMBIA RIVER

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ABSTRACT

Total organic carbon (TOC) levels in the Columbia River measured monthly from May 1973 to December 1974 ranged from a maximum of 270 $\mu\text{M}/\text{l}$ during late spring and early summer to a minimum of 150 $\mu\text{M}/\text{l}$ during late autumn. Sampling locations were directly behind the spillway at the Bonneville Dam, 230 km upstream, and at Kalama, Washington, 128 km upstream from the river mouth. The average annual TOC contribution from the Columbia River drainage to the northeastern Pacific is 4.9×10^{10} moles with an average concentration of approximately 195 $\mu\text{M}/\text{l}$. Of this TOC annual export, 89% is dissolved organic carbon (DOC) and 11% is particulate organic carbon (POC). The TOC and DOC levels were most highly correlated with oxygen saturation and discharge, while POC correlated more closely to high instream primary productivity as indicated by pH and oxygen supersaturation.

Variability of DOC in the main channel of the Columbia River from Portland, Oregon to the estuary during a June, 1974 cruise was minimal. The DOC concen-

trations ranged from 221-260 $\mu\text{M}/\text{l}$ with no significant upstream or downstream gradients. Diel variation also was slight, varying randomly during 24 hours between 235-257 $\mu\text{M}/\text{l}$. The relative annual constancy of the DOC in contrast to nitrate and phosphate is indicative of the refractory nature of a significant proportion of the dissolved organic load of the Columbia River.

The Columbia River is the second largest river on the North American continent with approximately 2×10^{11} m³ of water entering the Pacific Ocean annually from a basin of 670,000 km² (Fig. 1). The basin consists of about 85% forest and open range, 12% agricultural, and 3% urban land. The annual discharge for the Columbia River is about 58% that of the Mississippi and constitutes 1% of the total river input to the oceans worldwide.

Published data on the total organic carbon (TOC), dissolved organic carbon (DOC), and particulate organic carbon (POC) levels of large rivers on an annual basis are scanty. Malcolm and Durum (1976) reported the distribution of organic carbon for the Mississippi River, its tributaries the Ohio and Missouri, and three smaller rivers over a nine to eighteen month period. Albright (1977) measured DOC and POC for eight months in the Fraser River, British Columbia, another large North American river. P.M. Williams (1968, 1969) reported DOC concentrations of 100-250 $\mu\text{M}/\text{l}$ for the Amazon River, but a survey of the monthly TOC, DOC, and POC loads for the Amazon is not yet available. Measurements of organic loads in smaller drainages of the U.S. and Canada are summarized in Moeller et al. (1979).

The objectives of this study were fourfold: 1) To determine seasonal variations in concentration and partitioning between dissolved and particulate fractions of the organic load of the Columbia as a reference point for future studies on a basin being increasingly impacted by rapidly growing population, agriculture, and industry; 2) To examine natural seasonal variability in the concentration and form of organic matter relative to physical parameters of discharge rate and temperature, chemical parameters associated with the carbonate system, and nutrient distributions to provide predictive tools for estimating past and future export of organic matter by the Columbia River; 3) To assess upstream-downstream variability of organic load on the lower 200 km of the river for detectable point source inputs or for an organic carbon decrease due to processing before the estuary; 4) To carefully measure the annual organic carbon export for a major river for use in global carbon flux studies and for estimation of riverine input to the estuary and northeastern Pacific.

METHODS

Samples were taken monthly directly behind the spillway at the Bonneville Dam, 230 km upriver, and at Kalama, Washington, 128 km upriver from the river mouth

(Fig. 1). The Bonneville site is upstream from the confluence of the Willamette River and the large metropolitan area of Portland, Oregon and the Kalama site is 38 km downstream. Both sites provided access to the main channel. In addition, on June 1, 1974 a cruise on the R/V YAQUINA enabled sampling at sixteen points along the Willamette and Columbia River to the estuary at Astoria, Oregon (Fig. 1). Organic carbon was sampled dielly upriver from Astoria in river water with no measurable salt water influence.

Samples were drawn from a large volume wide-mouth sampler, filled at approximately 1-5 meters below the surface. Subsamples were then transferred to 1 liter glass bottles, which had been fired overnight at 465°C. Samples from two different depths were taken at each station. No major gradients were detected between the two samples at each station and the average concentrations have been reported. Bedload sampling was not attempted and our equipment precluded accurate sampling of near bottom gradients and bedload transport. The series of large dams on the mainstem of the Columbia was thought to reduce large particulate organic bedload transport to the estuary, but our calculation of POC export must be considered as a conservative estimate.

Oxygen samples were fixed at the sampling sites (Carpenter, 1965) and pH and water temperature measured.

Sample bottles were completely filled, stoppered tightly, and stored on ice until analyses immediately upon return to the lab. Alkalinity was measured by titration with 0.1000 N HCl (Park et al., 1969) and total carbon dioxide by a gas chromatography technique (Park et al., 1964). Phosphate, nitrate plus nitrite, and silicate were analyzed on a Technicon Autoanalyzer^R (Atlas et al., 1971). TOC, DOC, and POC were measured by wet oxidation with potassium persulfate ($K_2S_2O_8$) to CO_2 (Menzel and Vaccaro, 1964) on six replicate samples. The DOC was measured following filtration through 0.45 μm prefired silver filters. Average difference for six replicates determined directly and indirectly never exceeded 6 $\mu M/l$. Reproducibility of the TOC, DOC, and POC analyses was 4 $\mu M/l$ at a 95% confidence interval.

Controversy has centered upon the completeness of oxidation of organic material by the potassium persulfate wet oxidation method. Dry combustion methods (e.g. Skopintsev et al., 1966, Gordon and Sutcliffe, 1973, Sharp, 1973) yield concentrations consistently higher in organic carbon than the $K_2S_2O_8$ wet oxidation technique. However, P.J. Williams (1969) obtained only slightly higher recoveries with ultraviolet oxidation, averaging 10%. Also, measurement on 22 organic substrates by Menzel and Vaccaro (1964) and P.J. Williams (1969) using $K_2S_2O_8$ oxidation resulted in an average of 97.8% recovery,

with all but two compounds recovered in excess of 95%. Therefore, to further test for the completeness of oxidation of the organic material, a wide range of organic compounds were analyzed in solution at concentrations between 11 and 83 $\mu\text{M}/\text{l}$ for recovery by $\text{K}_2\text{S}_2\text{O}_8$ oxidation (Table 1). Attempts were made to include compounds both of high molecular weight and more refractory nature in addition to duplicating some compounds previously tested by others. Recoveries significantly below 100% for a wide range of compounds or for compounds abundant in natural waters would cause serious underestimates of the actual organic carbon present.

Average recovery for the 23 compounds was 93%. The markedly lower result for the chitin from cuttlebone may be a result of incomplete solubilization of the compound; chitin from a crustacean shell gave 91.3% recovery. Elimination of the cuttlebone chitin raises the average recovery to 95%. The high molecular weight proteinaceous compounds albumin, hemin, and casein yielded recoveries of 92.9, 90.0, and 87.0%, respectively. Humic acid, an abundant refractory component of many natural waters, was 98% recovered. Four compounds of lower molecular weight, glycogen, acetic acid, cysteine, and adenine yielded 80-90% recoveries. These compounds were likely volatilized during purging for the removal of inorganic carbon; this will constitute a substantial error where

significant quantities of volatile organics are present.

These tests confirm the findings of Menzel and Vaccaro (1964) and Williams (1969) that persulfate oxidized greater than 95% of organic matter in many compounds, and extends their findings to such substances as ATP, syringic acid, benzoic acid, and humic acid. High molecular weight proteins average 90% recovery while some volatile low molecular weight compounds averaged 87%. This does not definitively resolve whether $K_2S_2O_8$ seriously underestimates or dry combustion seriously overestimates organic carbon concentration. A yet unknown class of compounds in natural waters may be incompletely oxidized or, less likely, a very large proportion of the DOC may be volatilized in the $K_2S_2O_8$ procedure. However, our results suggest that recovery of DOC from the Columbia River will be underestimated by no more than 15% and we expect that recoveries will exceed 90%.

RESULTS

The Columbia River's flow and temperature during the period of sampling exhibited strong seasonal variability (Fig. 2). Temperatures ranged from 3°C in January to 21°C in August. River flow downriver of the Willamette River confluence was characterized by two distinct peaks of high discharge with minima occurring in late summer and early fall. The first peak was triggered by spring

runoff from snowmelt in the higher elevations of the basin, culminating in a maximal discharge in June. The second peak was produced by heavy rain during winter in western Oregon, swelling the Willamette River tributary to 40% of the total Columbia River flow. Numerous dams on the Columbia dampen the extremes of discharge historically associated with the river but the bimodal discharge pattern remains apparent. Extremes of discharge during 1974 ranged from .25 km³/day to 1.5 km³/day with an annual output of 230 km³/yr.

The pH at Kalama and Bonneville during the sampling period ranged from 7.45 to 8.51 (Fig. 3). Maximum pH was observed during early summer and minimum pH occurred during winter months. The pH at the downstream site was always lower than at the upstream site. This was a result of a major input of lower pH water by the Willamette River (Park et al., 1969).

Alkalinity at the two sites showed only small variation except for a distinct June 1974 minimum during extremely high spring snowmelt runoff (Fig. 3). The generally lower alkalinity at Kalama was attributable to the addition of lower alkalinity water from the Willamette River. Park et al. (1969) have shown that Columbia River alkalinity primarily consists of carbonate alkalinity (94%) with the surplus alkalinity likely resulting from the dissociation of organic acids.

Carbonate alkalinity is calculated from determination of pH, temperature, and total organic carbon dioxide.

Borate, phosphate, and silicate alkalinity has been shown to be negligible in the Columbia River (Park et al., 1969). Surplus alkalinity can therefore be estimated by the difference between total alkalinity and carbonate alkalinity. Calculations using the 1973 and 1974 data yielded 88% carbonate alkalinity and 12% surplus alkalinity.

Total carbon dioxide (ΣCO_2) for the Columbia River at Bonneville and Kalama was greatly decreased in June 1974 during peak runoff (Fig. 3). Late spring and early summer levels of CO_2 were generally lower than other times of the year indicative of the major snowmelt contribution. Winter decreases in ΣCO_2 at Kalama resulted from the high flow contribution of low ΣCO_2 water from the Willamette River.

The nutrient chemistry of the Columbia displayed distinct seasonal fluctuations. Park et al. (1970, 1972) clearly showed monthly nutrient variations throughout the Columbia River drainage; similar patterns were found in 1973 and 1974 (Fig. 4). Maximum nutrient concentrations occurred in late winter and minima in the summer. Both silicate and phosphate were strongly depleted in summer. Nitrogen was below the level of detection at either Bonneville or Kalama during five months of 1973 and in

July of 1974. The ratio of nitrate plus nitrite to phosphate varied from approximately 2:1 in summer to 19:1 in late winter.

Oxygen saturation displayed a definite seasonality (Fig. 2). Spring and summer months maintained oxygen supersaturations, often in excess of 110%. To what extent oversaturation was attributable to greater turbulence during increased river discharge or to primary production is unknown, although the general inverse relationship between the nutrient chemistry and O₂ saturation points to the potential importance of phytoplankton production as the O₂ source. It is probable that both factors are significant in producing supersaturation. Autumn and winter O₂ levels were near or slightly below saturation. Cooler temperatures, decreased light, and increased turbidity suppress primary production, and biological and chemical oxygen demand slightly decreased O₂ saturation below 100%.

The organic fraction of the Columbia River was dominated by DOC (Fig. 5). Spring and early summer maxima were apparent, but seasonal variability was much lower than for inorganic nutrients. The DOC concentrations ranged from 139-197 µM/l at Kalama and from 115-184 µM/l at Bonneville. Minima in both 1973 and 1974 occurred during late fall. Due to the domination of the DOC over POC, TOC fluctuations mirrored those of DOC.

The POC showed much greater variability with minima in late fall and winter (Fig. 5). Periods of high flow in late spring and early summer coupled with times of longer photoperiod coincided with the highest levels of POC. Asterionella species were observed on filters at the time of high POC in the June 1973 sample at Kalama. Cushing (1967) documented peaks of both Asterionella and Fragilaria sp. on the Columbia in the spring of 1964. The POC concentration ranged over more than an order of magnitude annually in contrast to the more invariant but higher DOC levels.

The concentration of all the organic fractions at Kalama was consistently higher than those found at Bonneville. A probable source, the Willamette River, was measured seasonally near its confluence. Since it was consistently lower in TOC, DOC, and POC than the mainstem Columbia, increases between the two sites must result from discharge of organic material into the Columbia from the large metropolitan areas of Portland, Oregon and Vancouver, Washington and their associated industry.

A cruise was undertaken in June 1974 on the lower 200 km of the Columbia River to measure the degree of variability for TOC, DOC, and POC. A plot of TOC versus distance from the river mouth demonstrates the absence of a downstream concentration gradient (Fig. 6). A range of

only 39 $\mu\text{M}/\text{l}$ or 16% of the average for all stations was encountered. Willamette River samples taken during the cruise again were lower in TOC and DOC, but with comparable POC concentrations to the Columbia.

A diel series of samples also were taken in June at a station 19 km from the river mouth to evaluate temporal fluctuations as a source of error in the budget calculations. Manny and Wetzel (1973) and Klotz and Matson (1978) observed significant diel cycles for a small stream and river, respectively, which could produce serious error in budgetary calculations. However, diel variability of TOC on the Columbia was low, ranging from 235-257 $\mu\text{M}/\text{l}$ with slightly higher but not significantly different concentrations at night (Fig. 7). The diel measurements all fell within the range of TOC values measured during the cruise the previous day. The time of day at which samples were taken does not appear to cause serious error in the calculated export of organic matter from the Columbia.

Using water year 1974, an annual chemical load was calculated from the average monthly flow and chemical measurements. The annual contribution from the Columbia River to the northeastern Pacific Ocean is given in Table 2. The organic carbon was partitioned into 4.4×10^{10} moles DOC and 0.5×10^{10} moles POC. The TOC was 89% DOC and 11% POC in 1974. The single largest

monthly input, accounting for 16% of the annual TOC, occurred in June, and over 50% of the TOC entered the estuary between April and July (Fig. 8).

Nutrient output in 1974, except for the organic carbon data, can be compared to 1966 and 1967 export calculated by Park et al. (1972), (Table 3). Allowing for the slightly greater runoff in 1974, little difference in the inorganic carbon output occurred in the basin. The nutrient elements in 1974 did show increased export, particularly for phosphate, which was approximately double the 1966 output and triple that of 1967. The effect of this increase in available nutrients on TOC, DOC, and POC is unknown.

Linear regression analysis (Draper and Smith, 1966) was used to test for correlation between the organic carbon fractions and the measured physical and chemical parameters (Table 4). For TOC, DOC, and POC at Bonneville and for TOC and DOC at Kalama, percent O₂ saturation explained the greatest amount of variation of the measured variables, and for POC at Kalama, percent O₂ saturation closely followed pH with a correlation coefficient, R² of .48. The correlation between the organic fractions and percent O₂ saturation was positive; increased O₂ saturation occurred during periods of higher organic carbon. Explanation for the significant correlations displayed by percent O₂ saturation with TOC, DOC, and POC

was probably due to the combined effects of physical and biological processes. Physical processes were associated with greater turbulence and flow velocity during high runoff which enhanced O₂ supersaturation and organic carbon load, particularly with passage over the numerous dams impounding the lower Columbia. Biological factors influencing O₂ saturation values and organic carbon concentrations were algal primary production and heterotrophic decomposition.

In an attempt to distinguish physically dominated processes from the biochemically linked processes influencing the correlation of percent O₂ saturation with TOC, DOC, and POC, a simple linear regression was performed on the dependent variables, TOC, DOC, and POC, for both Kalama and Bonneville with percent O₂ saturation excluded as a potential independent variable. A physical variable, flow rate, replaced percent O₂ saturation as the best predictor variable for TOC and DOC. Hydrogen ion activity, sensitive to biological activities such as photosynthesis and respiration, physical phenomena such as turbulence, and chemical weathering reactions, was then most highly correlated with POC.

DISCUSSION

The annual discharge of organic material from the Columbia River differed markedly from that of the Mississippi. Although the Columbia delivers three-fifths as much freshwater to the ocean as does the Mississippi, its organic load of 4.9×10^{10} moles was less than one-fifth of the 2.8×10^{11} moles carried by the Mississippi (Malcolm and Durum, 1976). The average annual concentration of TOC, DOC, and POC in the Mississippi River was 600, 283, and 317 $\mu\text{M}/\text{l}$, respectively, and 195, 174, and 21 $\mu\text{M}/\text{l}$ in the Columbia River. Thus the major difference between the Columbia and Mississippi, respectively, was found in the load of suspended particulate organic matter. The absolute annual export to the ocean by the Mississippi was 1.3×10^{11} moles or 1.59 million metric tons of DOC and 1.5×10^{11} moles or 1.77 million metric tons of POC. The Columbia, by comparison, delivered 4.4×10^{10} moles or .53 million metric tons of DOC and 0.5×10^{10} moles or .06 million metric tons of POC.

The variability in the carbon fractions in both the Columbia and Mississippi was greatest for particulate organics. Monthly DOC concentrations ranged from 139-197 $\mu\text{M}/\text{l}$ at Kalama on the Columbia and from 183-375 $\mu\text{M}/\text{l}$ at three sites on the lower Mississippi (Malcolm and Durum, 1976). POC displayed a more variable distribution

ranging from 2-72 $\mu\text{M}/\text{l}$ at Kalama to 92-508 $\mu\text{M}/\text{l}$ on the lower Mississippi. Seasonal trends showed slightly higher DOC concentrations from March - July for the Columbia, while POC varied widely with higher spring and summer levels. The Mississippi data do not allow a critical evaluation of the seasonal trends in DOC and POC as a maximum of seven data points yearly at one station were reported.

The TOC and DOC concentrations in the Columbia River appear to be linked to physical parameters. Reuter and Perdue (1976) argued that the majority of TOC in natural waters is from geopolymers eluted by meteoric waters from soil organic matter. If the primary source for the TOC and DOC were autochthonous compounds from primary production, a dilution effect would be predicted during times of increased runoff. Instead, both the TOC and DOC concentrations in the Columbia are positively correlated with discharge. In addition, the constancy of the TOC concentration along the lower 200 km of the river and throughout a diel study in June is indicative of the refractory nature of a significant proportion of the dissolved organic load.

For POC, primary production in the Columbia River is a potentially important source. Several observed chemical responses paralleled patterns which would be caused by primary production. Percent O_2 saturation was

closely correlated to pH; O₂ saturation was highest during summer months at the same time pH was at its maximum. If primary production was responsible for O₂ supersaturation during summer, pH would also be expected to be at a maximum as a result of fixation of CO₂. Algae were also identified on filters from these samples and were at least a portion of the POC. Highest levels of POC were observed during summer, the period during which primary production would be expected to be greatest. The Columbia River carries low concentrations of suspended organic carbon; monthly samples of plankton biomass near Hanford, Washington indicated that POC occasionally could be accounted for by primary producer biomass alone (Cushing, 1967). The series of impoundments on the Columbia River probably maximize the role of primary producers in this river. Impoundments tend to settle out POC, increase retention time, promote nutrient remineralization and, therefore, enhance total algal production.

Adequate annual organic carbon export budgets have been reported for only two of the twenty largest rivers, the Columbia and the Mississippi. No annual estimate for TOC, DOC, and POC has yet been published for the Amazon, which contributes 20% of all river water input to the oceans, although P.M. Williams (1968, 1969) has published DOC concentrations for sites near the river mouth which ranged between 100-250 $\mu\text{M}/\text{l}$. If 250 $\mu\text{M}/\text{l}$ is assumed as

an average DOC concentration, then the dissolved carbon exported yearly from the Amazon would be 1.4×10^{12} moles or about 17 million metric tons. Concentrations of TOC, DOC, and POC from the next four largest rivers after the Amazon (Congo, Orinoco, Yangtze, and Bramaputra) are not known.

In estimating the flux of organic carbon to the ocean from riverine input, the data from the Columbia and Mississippi point out the need for careful sampling of the suspended load. Published DOC values for the Amazon, Mississippi, and Columbia and the summary of DOC concentrations in smaller freshwater systems compiled by Moeller et al. (1979) suggest that, except for grossly polluted systems, DOC concentrations rarely range more than one order of magnitude annually. The assumption of an average world river DOC concentration between approximately 200-500 $\mu\text{M}/\text{l}$ based on the limited available data may therefore prove a good estimate. Conversely, Holland (1978) lists suspended sediment loads for the twenty largest rivers which range from 8 mg/kg for the St. Lawrence to 3400 mg/kg for the Ganges, a range of nearly three orders of magnitude. If the suspended sediment loads are indicative of the range of POC concentrations encountered in the largest rivers worldwide, careful sampling on an annual basis of the rivers with high suspended sediment loads and discharge must be undertaken

before an accurate global riverine carbon flux to the ocean can be estimated.

ACKNOWLEDGEMENTS

We wish to thank E. Seifert, L. Barstow, H. Cabrera-Muro and R. Kepler for excellent technical assistance and L. Gordon for laboratory facilities. We also thank Drs. C.E. Cushing, G.W. Minshall, J. Moeller, E. Suess, K. Cummins, and G.M. Ward for their comments and criticisms of the manuscript.

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TABLE LEGENDS

- Table 1. Percent recovery and standard deviation by potassium persulfate oxidation for selected organic compounds in solution at concentrations between 11 and 83 $\mu\text{M}/\text{l}$.
- Table 2. Monthly chemical input from the Columbia River into the northeastern Pacific Ocean during 1974.
- Table 3. Annual chemical budgets for the Columbia River in 1966, 1967, and 1974.
- Table 4. Best fit linear regression results with the organic carbon fractions at the Bonneville and Kalama sites as dependent variables and the measured physical and chemical parameters as potential independent variables.

Table 1. Percent recovery and standard deviation by potassium persulfate oxidation for selected organic compounds in solution at concentrations between 11 and 83 $\mu\text{M}/\text{l}$.

<u>Compound</u>	<u>Conc ($\mu\text{M}/\text{l}$)</u>	<u>Recovery (%)</u>	<u>Standard Deviation (%)</u>
Urea	42 & 83	102.0	1.4
2-AEP	33 & 67	101.9	0.9
Syringic Acid	11 & 18	101.4	5.9
L-tryptophan	33 & 67	101.0	4.9
Phloroglucinal dehydrate	33 & 67	100.9	1.3
ATP	33 & 67	100.8	5.2
L-lysine HCl	33 & 67	100.6	0.9
Sulfanilamide	33 & 67	100.0	0.1
Humic Acid	42 & 83	98.0	2.2
1,10-Phenanthroline	42 & 83	97.0	3.6
Glutathione	33 & 67	96.1	1.0
Benzoic Acid	42 & 83	95.0	3.1
Albumin	33 & 67	92.9	1.3
Mannitol	33 & 67	92.1	0.2
Vanillin	33 & 67	91.6	6.4
Chitin (crustacean shell)	17, 33 & 67	91.3	3.6
Hemin	42 & 83	90.0	4.1
D-glycogen	33 & 67	89.3	6.4
Acetic acid	42 & 83	88.0	3.3
L-cysteine HCl	42 & 83	88.0	2.8
Casein	42 & 83	87.0	2.1
Adenine	12 & 15	83.8	2.6
Chitin (cuttlebone)	17, 33 & 67	42.4	0.4

Table 2. Monthly chemical input from the Columbia River into the northeastern Pacific Ocean during 1974.

	<u>Jan.</u>	<u>Feb.</u>	<u>Mar.</u>	<u>Apr.</u>	<u>May</u>	<u>June</u>	<u>July</u>	<u>Aug.</u>	<u>Sept.</u>	<u>Oct.</u>	<u>Nov.</u>	<u>Dec.</u>	<u>Annual Export</u>
Phosphate (10^6 moles)	45.4	39.0	37.5	49.2	32.2	39.3	13.3	3.6	3.2	4.6	6.0	8.5	282
Nitrate (10^6 moles)	767	636	708	574	273	146	35	1	8	57	124	210	3,540
Silicate (10^8 moles)	58.2	49.0	60.0	71.7	66.8	62.0	30.0	13.1	10.5	13.6	16.4	23.8	475
Alkalinity (10^9 eq)	27.9	23.7	26.1	31.7	28.8	28.9	24.5	16.1	12.7	12.3	13.3	19.6	266
Total CO ₂ (10^9 moles)	26.8	21.2	25.7	30.3	26.7	22.5	17.3	12.1	10.8	11.3	11.8	15.6	232
Oxygen (10^9 moles)	11.7	9.5	9.0	11.0	11.3	12.9	7.4	3.8	3.0	3.3	3.7	5.3	92
TOC (10^8 moles)	48.2	42.6	48.0	60.0	61.0	78.3	49.1	26.4	18.5	17.5	17.7	24.6	492
DOC (10^8 moles)	44.7	40.1	43.9	52.1	54.0	67.1	40.0	21.4	15.8	16.9	17.5	24.4	438
POC (10^8 moles)	3.5	2.5	4.1	7.9	7.0	11.2	9.1	5.0	2.7	0.6	0.2	0.2	54

Table 3. Annual chemical budgets for the Columbia River
in 1966, 1967, and 1974.

Variable	1966	1967	1974
Water (liters)	2.0×10^{14}	2.3×10^{14}	2.5×10^{14}
Oxygen (moles)	6.9×10^{10}	7.4×10^{10}	9.2×10^{10}
Alkalinity (eq)	2.1×10^{10}	2.3×10^{11}	2.7×10^{11}
Total Carbon Dioxide (moles)	2.1×10^{11}	2.3×10^{11}	2.3×10^{11}
Phosphate (moles)	1.2×10^8	0.8×10^8	2.8×10^8
Nitrite + Nitrate (moles)	2.5×10^9	2.8×10^9	3.5×10^9
Silicate (moles)	3.3×10^{10}	3.5×10^{10}	4.8×10^{10}

Table 4. Best fit linear regression results with the organic carbon fractions at the Bonneville and Kalama sites as dependent variables and the measured physical and chemical parameters as potential independent variables.

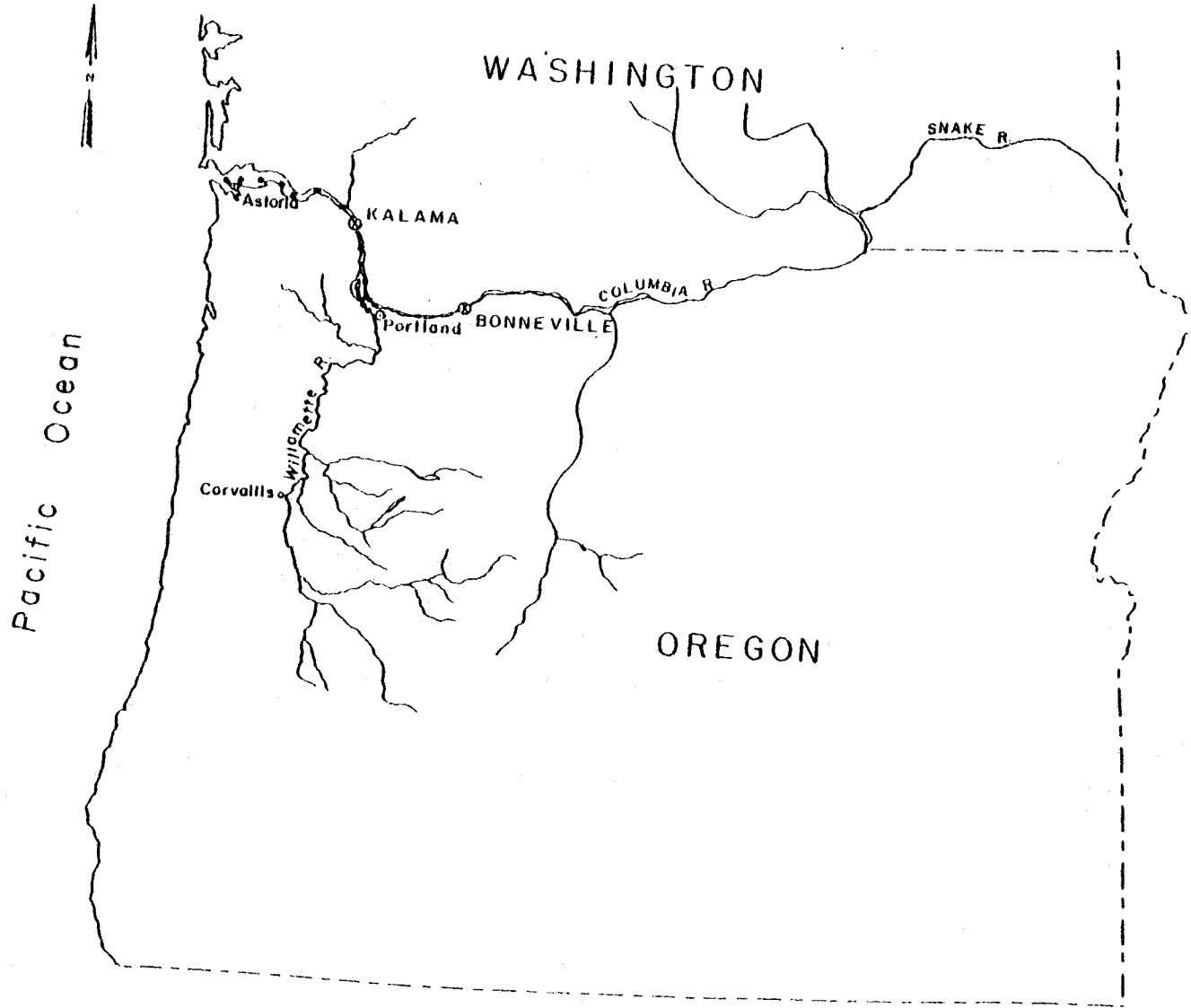
Site	Dependent Variable	Degrees of Freedom	Best x_1	R^2	f
Bonneville	TOC	19	O ₂ sat.	.83	73.58
Bonneville	DOC	19	O ₂ sat.	.67	30.43
Bonneville	POC	19	O ₂ sat.	.44	11.86
Kalama	TOC	19	O ₂ sat.	.45	13.31
Kalama	DOC	19	O ₂ sat.	.46	13.56
Kalama	POC	19	pH	.50	15.51

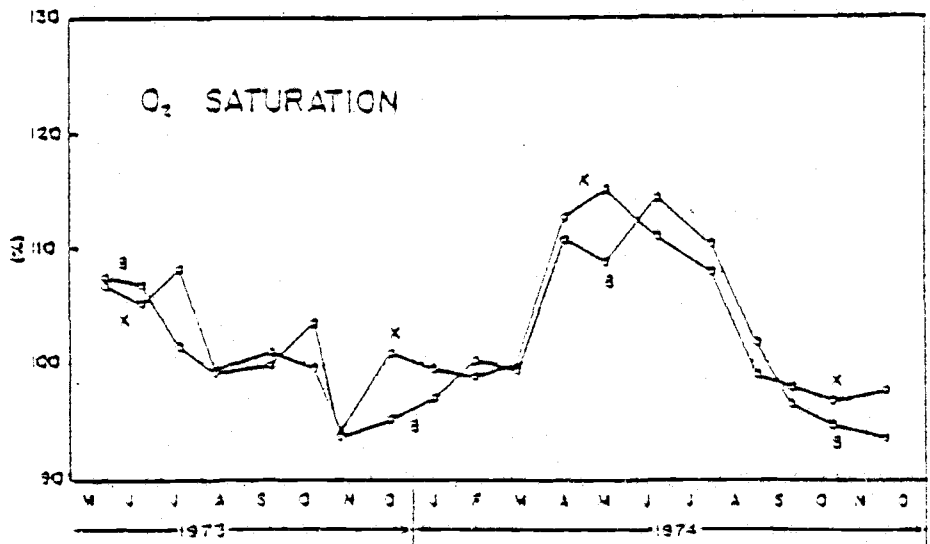
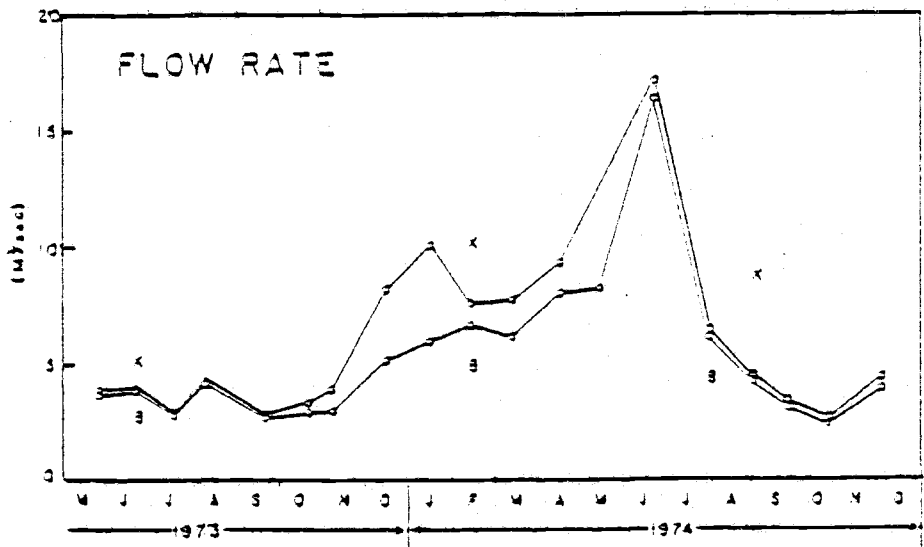
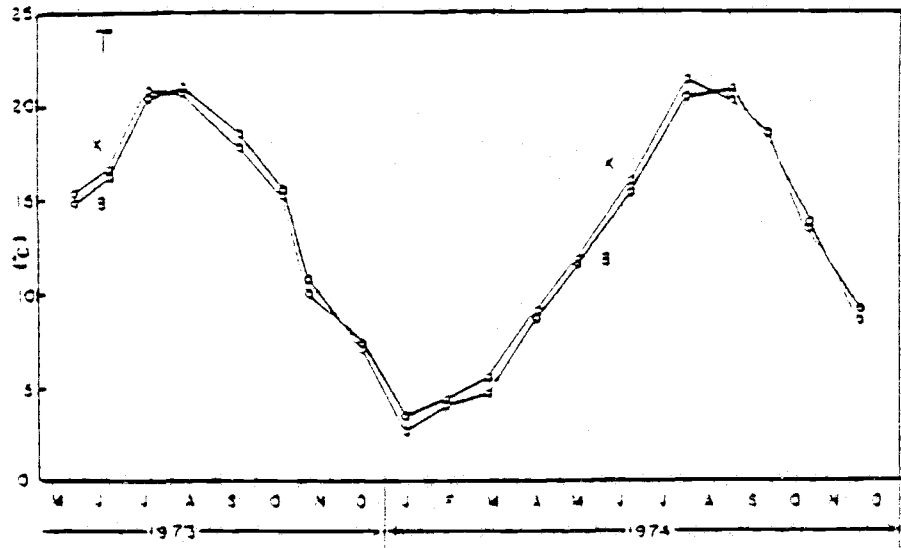
F test (1,19) at $p < .01$ is 8.18

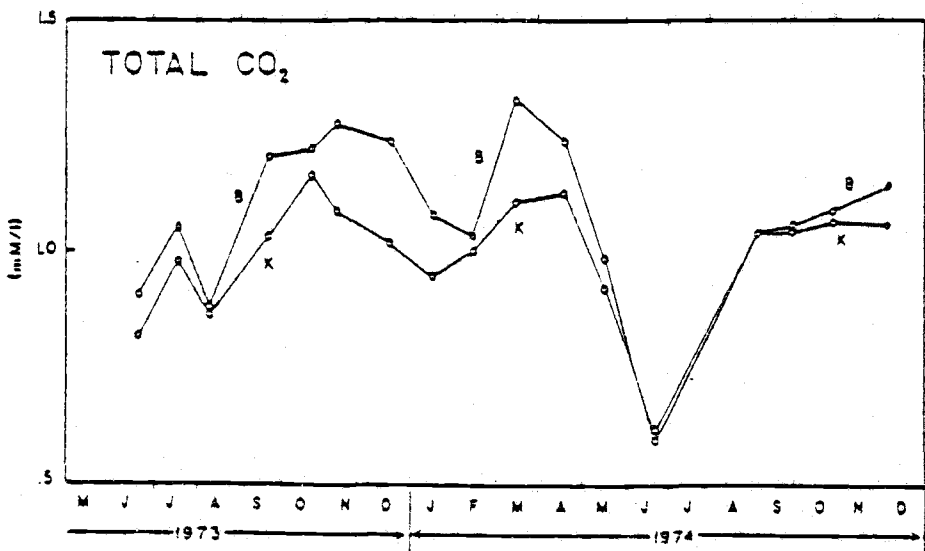
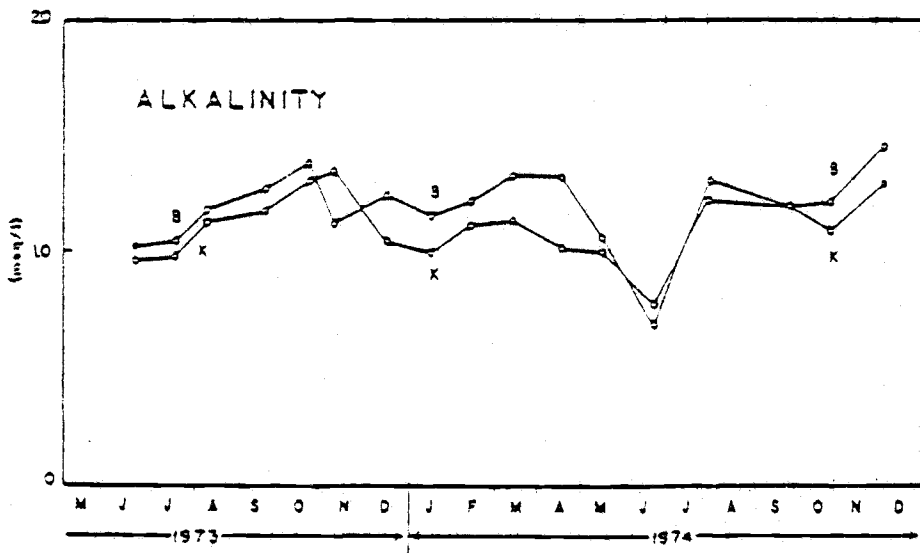
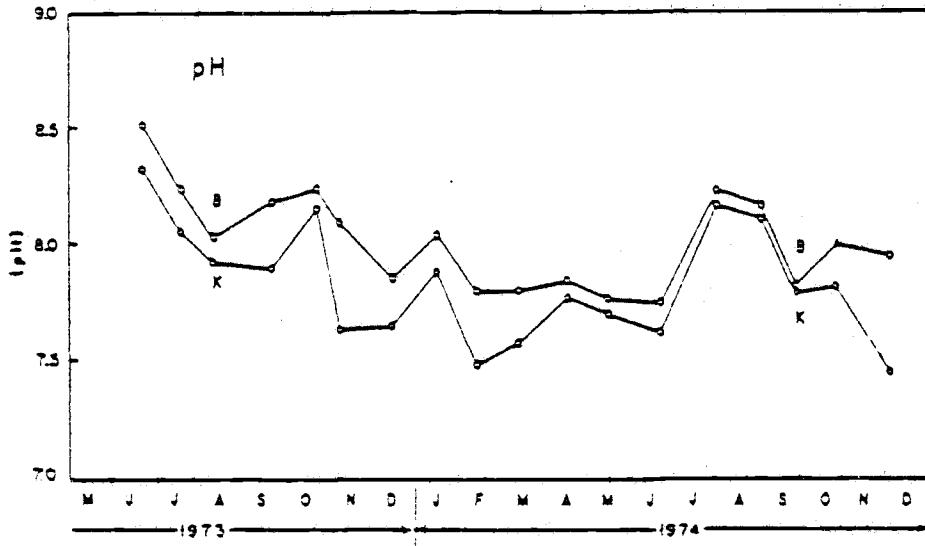
FIGURE LEGENDS

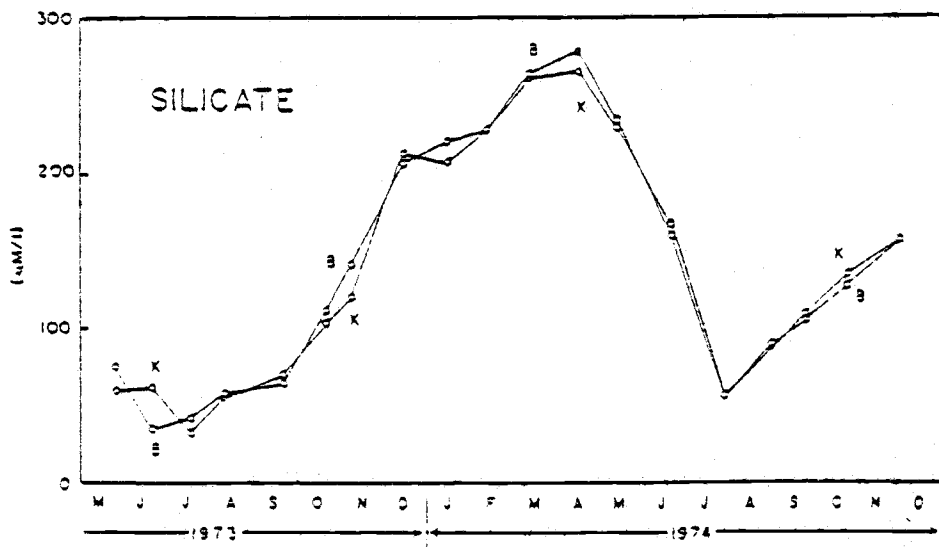
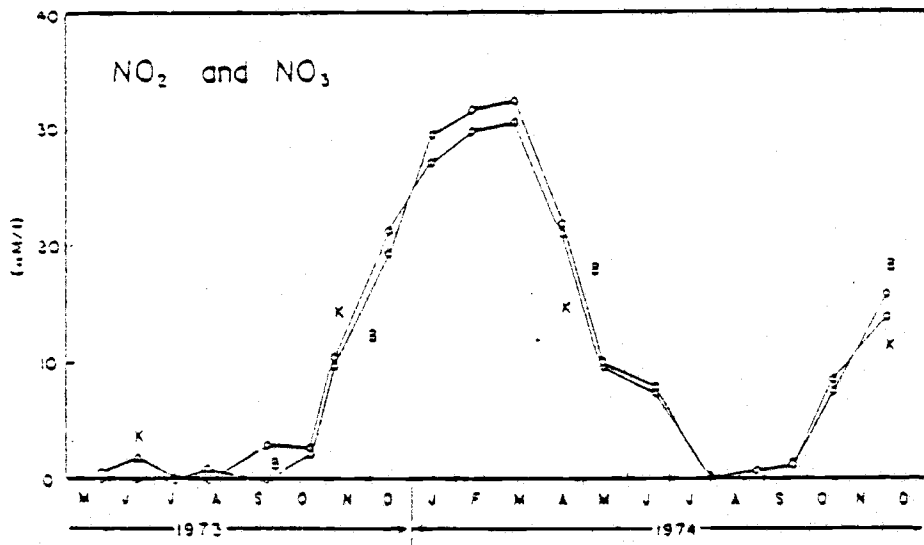
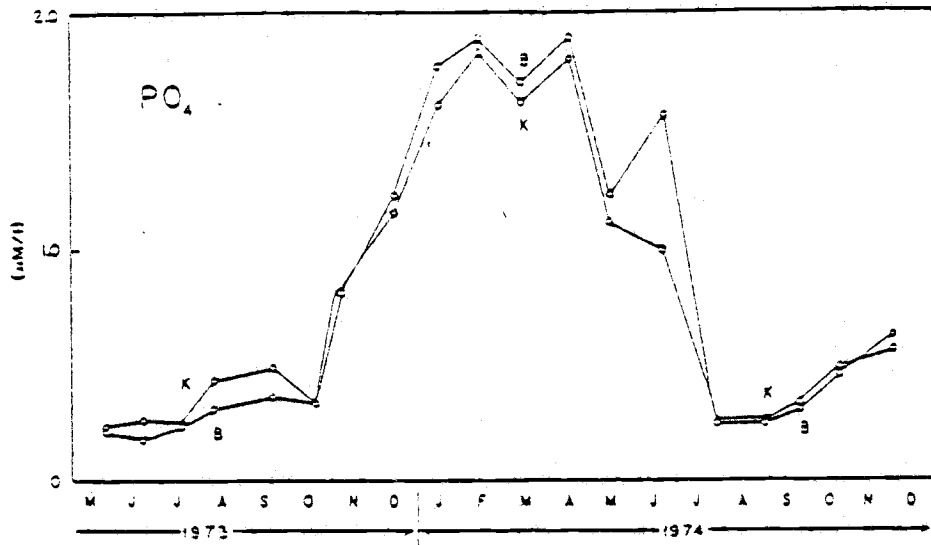
- Figure 1. The lower Columbia River with major tributaries. The Bonneville and Kalama sites are shown along with sampling locations, marked with darkened circles, for the June 1, 1974 cruise.
- Figure 2. Temperature, flow rate, and O₂ saturation at Bonneville and Kalama from May, 1973 to Dec., 1974.
- Figure 3. The pH, alkalinity, and ΣCO₂ at Bonneville and Kalama from May, 1973 to Dec., 1974.
- Figure 4. Phosphate, nitrite plus nitrate, and silicate at the Bonneville and Kalama sampling sites from May, 1973 to Dec., 1974.
- Figure 5. Organic carbon concentrations for the Columbia River at Bonneville and Kalama from May, 1973 to Dec., 1974 as TOC, DOC, and POC.
- Figure 6. The TOC, DOC, POC concentrations measured June 1, 1974 on the lower 200 km of the Columbia River. Samples collected in the Willamette River are enclosed in squares.
- Figure 7. A summer diel cycle for TOC, DOC, and POC sampled every four hours at a station 20 km upriver from Astoria, Oregon.
- Figure 8. The average monthly organic carbon input to

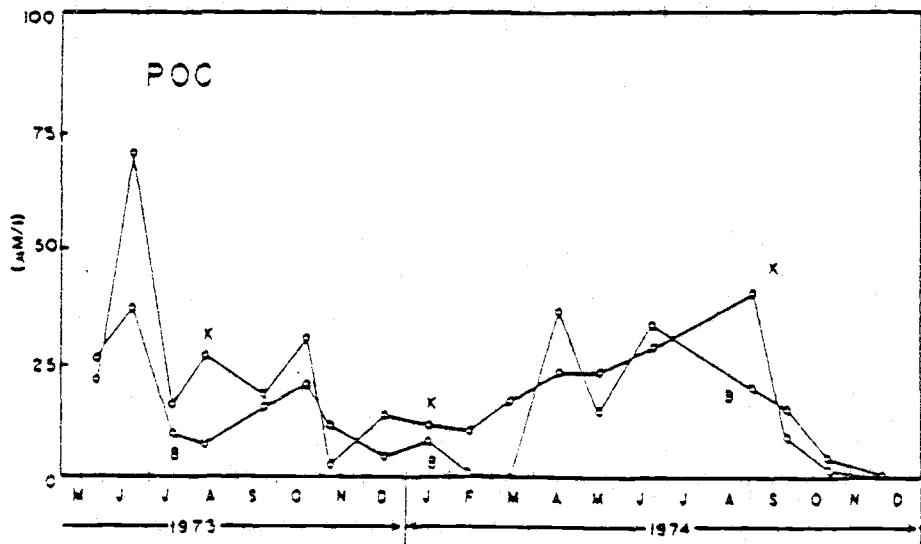
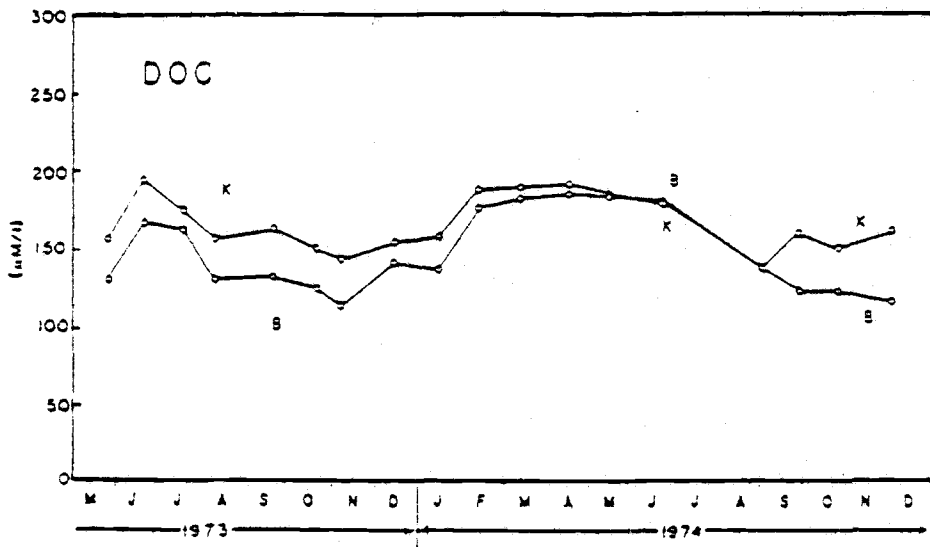
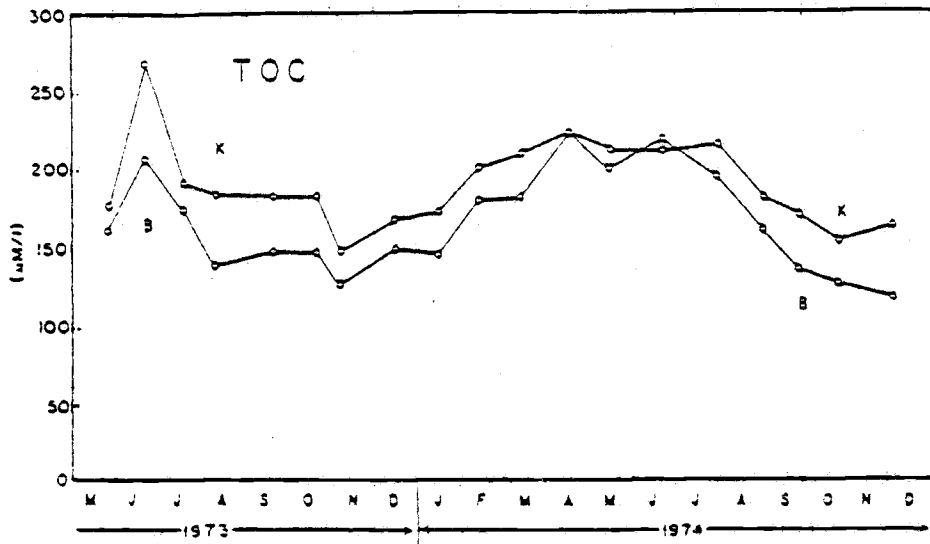
the estuary from the Columbia River in moles/
month as measured at Kalama, Washington from
June, 1973 to Dec., 1974.

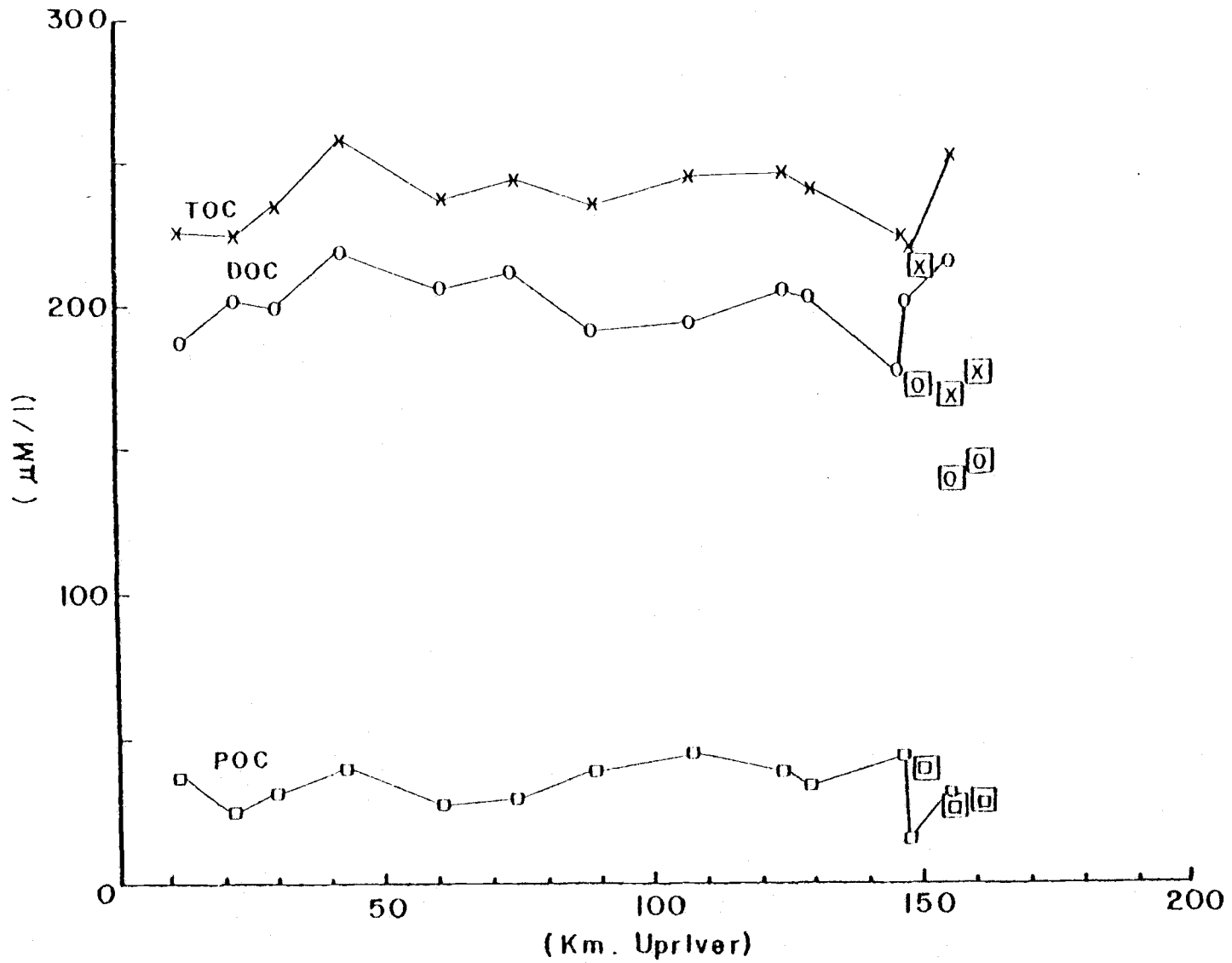


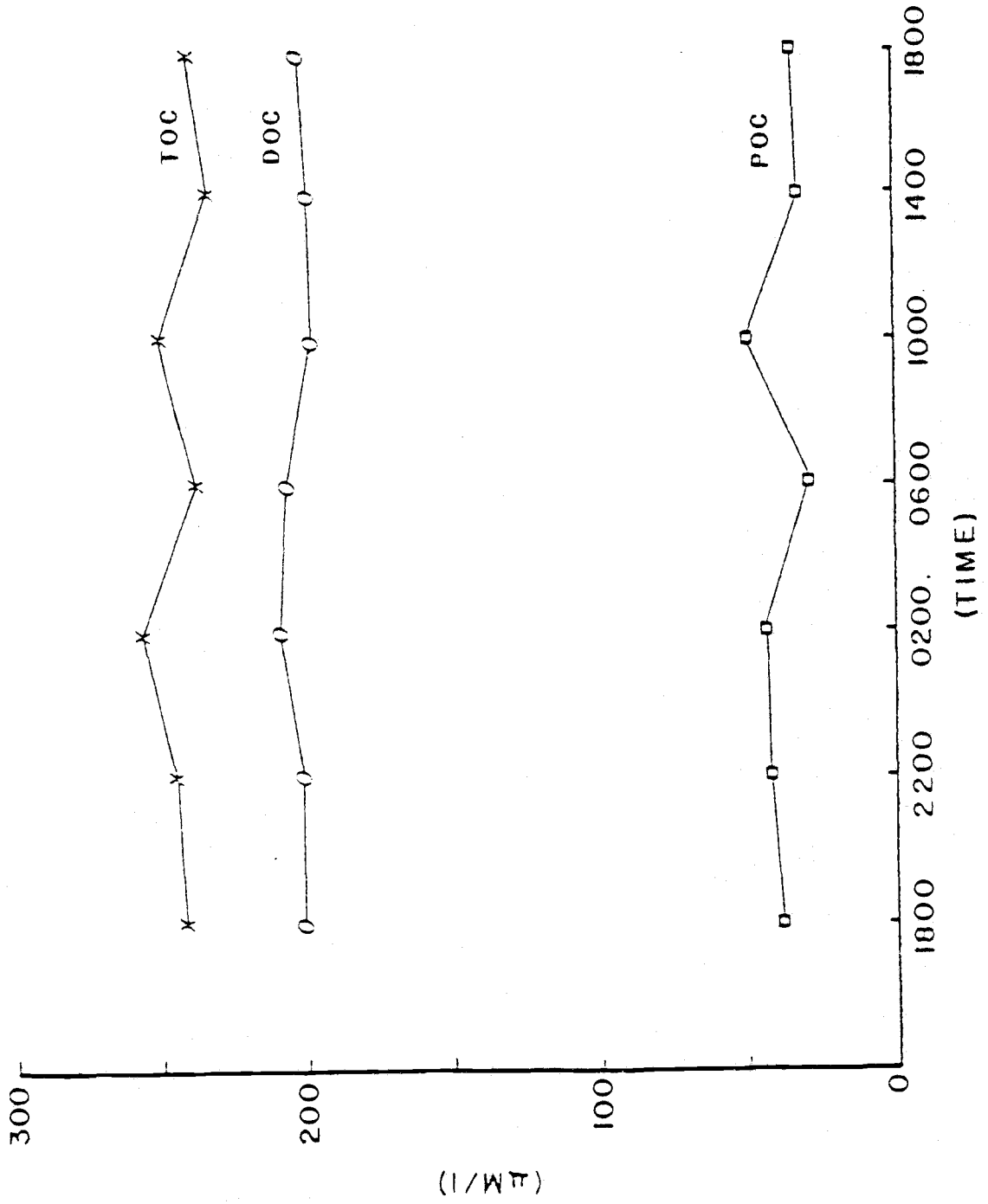


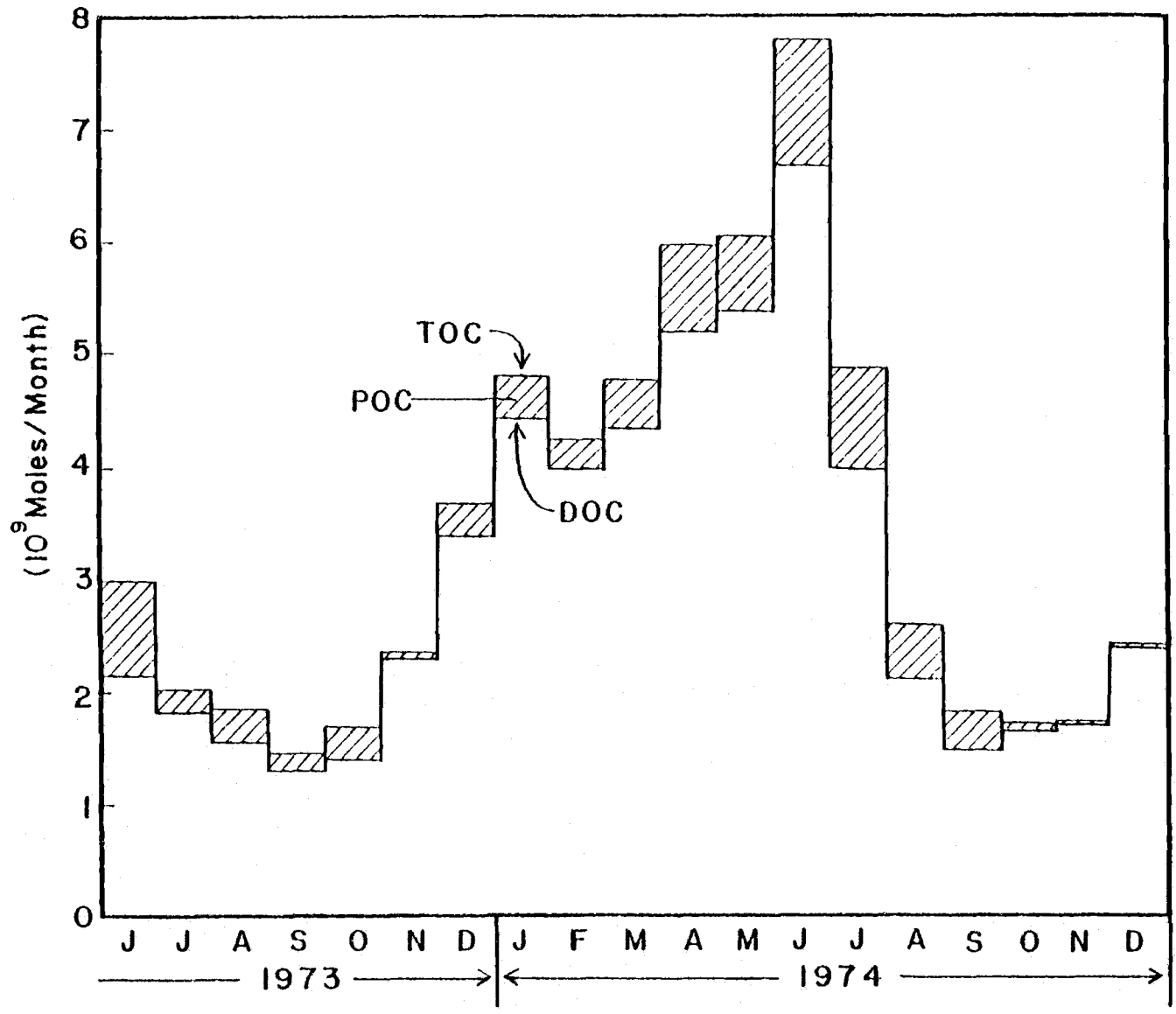












Chapter II

Running head: Dahm: Organic carbon pathways

Pathways and mechanisms for removal of dissolved
organic carbon from leaf leachate in streams

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Abstract

Removal of dissolved organic carbon (DOC) from the water resulting from adsorption and microbial uptake was examined. The mechanisms investigated are physical-chemical processes of adsorption to components of the stream sediment or water column and biotic processes associated with the microbial population. Adsorption was further separated into interactions involving (1) specific clay minerals, (2) amorphous solid phases of hydrous aluminum and iron oxides, and (3) fine particulate organic matter. Physical-chemical adsorptive mechanisms for alder (Alnus rubra) leachate removal exhibited rapid kinetic equilibration between the DOC and solid phases, but only a specific fraction of the DOC, likely containing certain chemical functional groups, was adsorbed. The amorphous aluminum and iron oxides possessed a much higher potential capacity than the clay minerals or fine particulate organics for DOC adsorption. Microbial uptake of DOC from the alder leachate was kinetically slower than adsorptive uptake but is much more efficient in processing the total DOC pool leached from alder leaves. Over a 48 h period, 97% of added ^{14}C labelled leachate was removed from solution by adsorption (approximately 20%) and microbial utilization (approximately 77%). The rate of microbial uptake was $45 \mu\text{gC/g sediment C/h}$ or $14 \text{ mg C/m}^2/\text{h}$.

The importance of dissolved organic carbon (DOC) in aquatic ecosystems is becoming increasingly apparent. Quantitatively, DOC is by far the most abundant form of reduced carbon in streams (Hobbie and Likens 1973, Wetzel and Manny 1977, Lush and Hynes 1978a, Moeller et al. 1979, Triska et al. 1979), rivers (Williams 1968, Malcolm and Durum 1976, Klotz and Matson 1978, Naiman and Sibert 1978), lakes (Wetzel and Rich 1973, Rich and Wetzel 1978), estuaries (Stephens 1967, Head 1976, Happ et al. 1977) and oceans (Williams 1975). The pathways and mechanisms for cycling these large pools of DOC represent critical transfers in the energetics of all aquatic ecosystems. In particular, processes which incorporate DOC into particulate form where either mineralization or further transfer up the food chain can occur are important steps in the transformation of DOC in these aquatic environments. Information which can differentiate physical-chemical processes of adsorption, flocculation, and aggregation of DOC from microbial uptake for a variety of heterogeneous natural inputs is needed. Knowledge of the mechanisms and factors controlling the uptake and degradation of the DOC load is essential.

For small headwater streams in relatively undisturbed localities, DOC plays an important role in stream budgets. Hobbie and Likens (1973) estimated 79% and 88% of the organic carbon export in two small northeastern U.S. watersheds to be in the dissolved state. Fisher and Likens (1973) calculated an annual energy budget for a second order northeastern stream in which export was 70% dissolved organic matter (DOM). In Augusta Creek of southwestern Michigan, 75% of the carbon in transport was DOC (Wetzel and Manny 1977). Triska et al. (1979) presented data for two

years from a high gradient first order stream in the Oregon Cascades which showed DOM to comprise 72 and 56% of total carbon export. DOC exceeds POC transport for streams throughout a wide geographical range and generally includes between 60 to 90% of the total carbon.

The chemical nature of the DOC in aquatic ecosystems is still largely unknown, largely because the heterogeneous mixture composing DOM defies separation and identification. Larson (1978) was able to classify only about 20% of the DOM as lipids, carbohydrates, phenols, proteins, or amino acids, after extensive effort on samples from a small Pennsylvania stream. Although potential sources for this DOM are numerous, soil eluates, leaf leachates, decomposing wood, aquatic plant material (algal and macrophytic), and decomposing forest litter likely provide major inputs for undisturbed streams. The degree of contribution from each of these sources will vary with the season and between systems. For example, McDowell and Fisher (1976) estimated that 42% of the total DOM in autumn for a small New England stream in a deciduous forest was derived from leaf litter. In streams where primary production exceeds respiration (Minshall 1979), the proportion of DOM derived from algal and macrophytic plants would likely be increased.

Studies involving leaf leachate utilization have included both microcosm and field estimates. Cummins et al. (1972) and Wetzel and Manny (1972) followed a number of chemical and biological variables in a large artificial stream following a 30 h exposure to hickory and maple leaves. Lock and Hynes (1975, 1976) studied the disappearance of DOC from four leaf species in small circulating bowls with and without

sediment, under sterile and unsterilized conditions, and with soft and hard water. Bott et al. (1977) studied microbial uptake of DO^{14}C from oak leaves in a small recirculating chamber. A field study using a mass balance approach (McDowell and Fisher 1976) calculated that 77% of autumnal leaf leachate was taken up during a 77-day period. Another field experiment in a small spring stream, utilizing cedar and sugar maple leachate calibrated against a conservative tracer (Na), measured 36-86% leachate uptake in about one hour (Lush and Hynes, 1978b). In all studies, a major fraction of the entering leaf leachate was removed from solution during the first few hours after addition.

Exact mechanisms, rates, and pathways of DOC removal for various compounds extracted from the leaf matrix remain obscure. Microbial uptake undoubtedly accounts for a significant fraction of the disappearance (Lock and Hynes 1975, 1976, Bott et al. 1977). However, Lush and Hynes (1973) demonstrated that abiotic reactions affected by pH, water chemistry, leaf species, and temperature, could cause a DOC drop of as much as 50% over 2.5 d. Lock and Hynes (1976) found that precipitation of maple leaf leachate in distilled water is negligible, but amounted to 20-25% in well water. When sediment was added, removal of maple leaf DOC increased dramatically with 85% removal in 24 h, and 98% in 48 h. The locus for sediment uptake was suggested to be at least 44%, and possibly up to 100% microbial. However, their experiment utilizing Tyndallized sediment suggested 30-40% abiotic uptake. Like biotic processes, abiotic uptake of DOC by stream sediment is expected to show a wide variation in efficiency dependent on numerous variables. Factors affecting abiotic uptake may include clay types,

sediment size distribution, pH, redox potential, water hardness, and 46 organic content.

In the Pacific Northwest, particularly in the coastal streams and rivers and in the riparian zones of clearcut forests, red alder (Alnus rubra) frequently dominates streamside vegetation. Therefore, leachate from alder was chosen as the DOC source in experiments designed to assay microbial and physical-chemical processes of DOC removal from the water column. Estimates for both the quantity of DOC removed and the relative rate of removal by abiotic and biotic pathways was sought. The physical-chemical mechanisms for uptake were further separated into interactions involving (1) specific clay minerals, (2) amorphous solid phases of hydrous aluminum and iron oxides, and (3) fine detrital particulate organic matter. These phases, in association with the microbial population, were considered to be the most important pathways for DOC uptake in streams of low dissolved solids and near neutral pH, characteristic of western Oregon.

MATERIALS AND METHODS

Red alder leaves were collected just before abscission. The leaves were dried 48 h at 50°C and then stored in a desiccator until use. The DOC solution was produced by 12-24 h of leaching at room temperature in filtered distilled water with constant agitation. High temperature extraction techniques were avoided, both to more closely duplicate stream leaching conditions and to avoid enhanced denaturation and solubilization brought on by the elevated temperature. Alder leaves labelled with ^{14}C were grown from seedlings in a $^{14}\text{CO}_2$ enriched atmosphere and leached in the same manner.

The secondary clay minerals used in adsorption studies were pure x-ray diffraction standards from Ward's Natural Sciences. Chlorite, kaolinite, and montmorillonite clays saturated with sodium were tested. Sufficient clay was used in the adsorptive experiments to preclude saturation of available uptake sites at the clay surface. Semi-quantitative information on the clay mineralogy of Cascade stream sediments was obtained, after density separation and saturation with K and Mg, by x-ray diffraction from a Cu K α radiation source (Harward et al. 1969).

The removal capacity of amorphous hydrous aluminum and iron was tested using pure electrolytically plated iron and high purity aluminum wire dissolved in redistilled 5N HCl. Small aliquots of concentrated aluminum or iron standards were added to known amounts of alder leachate and adjusted to pH 7 with 0.1N NaOH. The samples were agitated for 30 min, filtered, and Al, Fe, and DOC in the precipitate and solution were measured. A modified ferrozine method was used for Fe determinations

(Stookey 1970; Murray and Gill 1978), a catechol violet method for Al⁴⁸ (Dougan and Wilson 1974), and wet oxidation by potassium persulfate to CO₂ with subsequent determination by infrared analyzer for DOC (Menzel and Vaccaro 1964).

The definition used in this paper for DOC is arbitrarily defined as the organic carbon passing through a 0.4 μm Nuclepore^R filter. This is an arbitrary definition with many colloidal size particles, not truly dissolved organic molecules, smaller than this cutoff (Lock et al. 1977). Use of this traditional demarcation allows comparison with previous work. In a few cases, where leachate uptake was being tested in solutions containing high concentrations of clay particles, centrifugation at 3000 rpm for 5 min was used in lieu of filtration, since clogging was unavoidable.

Mercuric chloride (HgCl₂) was added at a concentration of 100 mg/l in all experiments where microbial processes were to be inhibited. An occasional plate count was performed to verify the lack of bacterial activity.

The determination of the amount of amorphous solid in 12 stream sediment samples and one seep utilized successive extraction with an oxalate buffer of pH 3 for two hours in the dark, followed by 3 min of boiling in 0.1N KOH solution (Dudas and Harward 1971). Only the finer particles of sediment, consisting of material passing through a 75 μm sieve, were analyzed. The oxalate buffer preferentially removes amorphous Fe, while the KOH solution extracts uncrystallized Al phases. The difference in sample weight before and after treatment, adjusted for the loss of organic material, estimates the amorphous inorganic sediment content.

Field studies investigating the uptake of DO^{14}C by stream sediment were performed in Oak Creek, a 3rd order stream. Stream sediment was carefully extracted from the upper 5 cm of a pool and sieved through a 4 mm sieve. One portion of the sediment was cleaned of organic material by repeated application of 35% hydrogen peroxide (H_2O_2). The cleaning process lowered the organic content from 2.6% to 0.6%. The sediment with low organic content from H_2O_2 oxidation and a second untreated aliquot of sediment were poisoned with HgCl_2 . Approximately 1400g of sediment including (1) freshly sieved unpoisoned sediment, (2) the HgCl_2 poisoned sediment, and (3) the H_2O_2 organic cleaned and HgCl_2 poisoned sediment were added to Plexiglass^R chambers with a recirculating pump (Bott et al. 1978). Ten liters of low organic carbon water were added to each chamber and the alkalinity adjusted to 30 mg CaCO_3 / liter, resulting in a pH between 7.1-7.4 for each chamber. These values for pH and alkalinity are within the range of measured values for streams in western Oregon. The chambers measure 38 cm long, 31 cm wide, and 10 cm high with a bottom surface area of .12 m².

Following 24 h of instream equilibration, 500 ml of ^{14}C labelled alder DOC, leached 12 h at room temperature, were added to each chamber. The alder leachate increased the DOC concentration 9.8 mg C/l. Samples were drawn every 5 min initially, with progressively longer sampling intervals during the first 24 h, and then every 4 h on the second day. Samples were filtered on prerinsed 0.4 μm Nuclepore^R filters and analyzed for total ^{14}C activity, DO^{14}C and DOC. The DO^{14}C was determined by acidifying the sample with 0.4 ml of 3% H_3PO_4 and purging

with O₂ for five min to remove ¹⁴CO₂. The ¹⁴CO₂ was determined by 50
difference. The cocktail consisted of a 10 ml water sample and
10 ml of New England Nuclear Aquasol II^R. Samples were radio-
assayed by liquid scintillation techniques (Beckman LS-150) and
corrections for background radioactivity and differences in
counting efficiency were made.

RESULTS AND DISCUSSION

The clay minerals to be tested for their capacity to adsorb dissolved organic carbon from alder leachate were determined by x-ray diffraction of sediment from four Cascade mountain streams. The predominant crystalline clay found in all sites was an intergraded chlorite (Singleton and Harward 1971). Secondary peaks for montmorillonite clay also were seen at each site. At two sites, traces of kaolinite also were present. Therefore, the crystalline clays chlorite, montmorillonite, and kaolinite were examined for their capacity to adsorb DOC leached from alder leaves.

Montmorillonite was most efficient in removing DOC from solution at pH 7 (Fig. 1), followed by chlorite and then kaolinite. The carbon adsorbed, expressed as milligrams removed per 100 milligrams of clay, plotted as a function of the DOC solution concentration shows montmorillonite followed by chlorite and then kaolinite in order of efficiency of DOC removal from solution at pH 7 (Fig. 1). The adsorptive capacity of montmorillonite accounted for about 0.8% of the available DOC leached from alder leaves over a concentration range of 2 - 224 mg C/l. The adsorptive uptake of DOC by chlorite was approximately 0.6%, and for kaolinite 0.5%. The vast majority of the DOC resulting from the leaching of a nitrogen-rich deciduous leaf was not susceptible to physical-chemical bonding to solid clay surfaces of montmorillonite, chlorite, and kaolinite. Coprecipitation with or adsorption to crystalline clay minerals by only a small fraction of the organic compounds released by leaching of leaf material is indicated. If significant displacement of DOC from

solution to the sediment is the result of abiotic processes, sediment 52 components in addition to crystalline clays must be participating.

Studies with soil solutions (Inoue and Wada 1968, and Wada 1977) have documented the high adsorptive capacity of uncrystalline amorphous clays and crystalline clays coated with amorphous inorganic material for dissolved organic matter, particularly humic and fulvic acids. The reduced resolution and peak heights of the x-ray diffraction patterns for the clay samples extracted from the four Cascade streams indicated a high percentage of poorly crystallized amorphous material. This observation was quantified by measuring the weight loss from fine detritus, collected from twelve first order streams and one seep, after successive acidic and alkaline dissolution treatments (Dudas and Harward 1971). The resulting weight loss, corrected for the loss of particulate organic matter, ranged from 7.9 to 27.4% (Table 1). Much of this amorphous material was thought to consist of uncrystallized aluminosilicate clays and hydrous oxides of iron and aluminum. Subsequent analysis of the extracted phase showed iron plus aluminum to constitute from 4.2 to 23.1% of the amorphous fraction (Table 1). The Elk Meadow seep sample was the most enriched in percentage amorphous iron and aluminum. The high percentage of amorphous material in the fine sediment is potentially a significant adsorbent of DOC, either by coprecipitation when dissolved metals enter oxygenated and neutral pH water or at the sediment-water interface.

Laboratory studies to assess the maximum potential for alder leachate uptake by coprecipitation with the hydrous oxides of aluminum and iron and a montmorillonite clay saturated with iron in the cation exchange positions at pH 7 (Scharpenseel 1968, Theng and Scharpenseel 1975) were

carried out in DOC solutions from 2 - 232 mgC/l. The carbon adsorbed (in milligrams per 100 mg of clay or metal) in the presence of excess metal or clay increased markedly over the crystalline clay uptake for both hydrous aluminum and iron oxides and montmorillonite pretreated with the amorphous iron coating (Fig. 2). Hydrous aluminum oxide was most effective as an adsorbent, removing approximately 33% of the carbon in solution. The hydrous iron oxide and montmorillonite clay perfused with amorphous iron were not significantly different, with a removal capacity of 26% of available DOC. This percentage is much greater than the 0.8% removal by sodium saturated montmorillonite alone. The amorphous phases of hydrous aluminum and iron oxide, either precipitating from the water column, where significant inputs occur, or associated with the sediment are potential sites for abiotic physical-chemical adsorption of one-quarter to one-third of the DOC released from alder leaves.

In assessing the capability for adsorption by the crystalline clays and amorphous hydrous metal oxides, an apparent linear relationship between the adsorption by weight as a function of DOC concentration resulted (Figs. 1 & 2). The form of these lines is strongly influenced by measurements made at DOC concentrations in excess of 10 mg C/l. In natural waters, DOC concentration is rarely above 10 mg C/l (Moeller et al. 1979) and increases in DOC concentration measured following leaf abscission in autumn is unlikely to exceed 1-2 mg C/l (McDowell and Fisher 1976). Therefore, the accuracy of DOC uptake curves at low DOC concentration is critical for estimating potential abiotic uptake by the sediment. For low concentrations of DOC, the maximum precision of the wet oxidation method (Menzel and

Vaccaro 1964) of analysis is approached. Use of uniformly labelled ^{14}C substrates may provide the necessary sensitivity to overcome the analytical problems and assess the linearity of abiotic DOC uptake at low concentrations.

An additional potential site for abiotic uptake of DOC is the particulate organic detritus of the sediment. Stevenson (1972) and Jackson et al. (1978) reviewed the capacity of humic acids to absorb hydrophobic organic compounds, especially toxic pesticides and herbicides. Khan and Schnitzer (1972) concluded that humic acid can firmly bind 2% or more by weight of hydrophobic organic compounds. For specific types of organic compounds, adsorption by humic colloids and particles may be a key factor in transport and breakdown.

Although abiotic uptake of alder leachate, primarily associated with amorphous components of the sediment, can potentially remove a significant fraction of the released DOC, a large percentage remains in solution. This fraction is either processed in solution or at the sediment-water interface by the microbial community or exported from the ecosystem. Utilizing a radioactively labelled ^{14}C alder leaf leachate, the rates and efficiency of DOC uptake with both an untreated sediment and the same sediment poisoned by HgCl_2 were measured. In addition, a third chamber was tested in which the sediment was pretreated with H_2O_2 to oxidize the particulate detrital organic material, and also poisoned with HgCl_2 . Any increased DOC uptake by the poisoned chamber with particulate organic material over the chamber cleaned of organic material with H_2O_2 is attributable to particulate organic - dissolved organic interaction.

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The initial response in each chamber, following the introduction of the labelled alder leachate, was a rapid decrease in DO^{14}C activity occurring predominantly in the first 10 min (Fig. 3). The decrease in the first 10 min removed between 18-23% of the DOC^{14}C in each chamber, and represents abiotic displacement of one fraction of the alder leachate to sedimented or suspended particles larger than $0.4 \mu\text{m}$. The sediment in the poisoned chambers displayed no further DO^{14}C uptake over the 48 h of the experiment. Water in the unpoisoned chamber, after approximately 1 hour, began a steady decrease in DO^{14}C activity. Fifty percent of the labelled organic fraction had been removed by 9.3 h after addition and 90% uptake was measured at 31.1 h. Within 48 h, 97% of the initial DO^{14}C activity was taken up by the sediment.

Radiocarbon removed from solution as DO^{14}C by the microbial population can either be incorporated into microbial biomass or metabolized and respired as $^{14}\text{CO}_2$. A measurable respiration response from the unpoisoned sediment appeared about 6 h after the leachate addition (Fig. 4). No measurable $^{14}\text{CO}_2$ was detected in either of the poisoned chambers. Metabolic $^{14}\text{CO}_2$ in the unpoisoned system increased steadily, after the 6 h lag period, until 22% of the labelled carbon was present in the inorganic carbon fraction. The fraction of DO^{14}C incorporated into microbial biomass is 57% over 48 h, assuming all of the rapid initial abiotic uptake of DO^{14}C is held unavailable to the microbial flora. Abiotic adsorption of DO^{14}C does not necessarily preclude eventual microbial uptake or mineralization, so the estimate of 57% for DO^{14}C incorporation into microbial tissue may be underestimated.

Abiotic decrease of the radiocarbon label from solution could result either through an actual decrease in the DOC concentration or through

exchange reactions between labelled compounds in solution and unlabelled adsorbed particulate organic carbon. If the adsorptive uptake of the DOC is dominated by (1) exchange reactions on the surfaces of the sediment with inorganic cations or anions, (2) formation of stable insoluble complexes with dissolved species in solution, or (3) bonding at the interface of solution and solid surfaces, total DOC concentration in solution will show a concomitant drop. However, if the $DO^{14}C$ uptake is largely the result of exchange reactions with adsorbed organic material, total DOC concentration will be reduced less than $DO^{14}C$ activity. In all three recirculating chambers, a definite drop in DOC concentration occurred over the first two hours (Fig. 5). Leachate concentration was calculated to increase the DOC concentration in each chamber by 9.8 mg C/l. The equilibrium DOC concentration before leachate addition for the sediment, sediment plus $HgCl_2$, and sediment plus $HgCl_2$ and H_2O_2 treatments was 1.4, 3.6, and 5.8 mg C/l, respectively. Two hours following addition of the DOC, there was a 34, 25, and 21% removal of total DOC from the unpoisoned, poisoned, and poisoned plus H_2O_2 oxidized treatments. In each treatment, decreases in total DOC concentration approximated $DO^{14}C$ uptake closely enough to indicate primarily DOC uptake, and not predominantly exchange of the radioactive compounds with unlabelled sediment organic matter. The small total DOC increase during times of peak sunlight intensity in the unpoisoned chamber may be a result of algal excretion (Jackson and Volk 1970), although algal biomass was small.

Previous work on the capacity of crystalline clays to adsorb DOC affirms the generally low affinity measured between alder leachate and kaolinite, chlorite, and montmorillonite. Evans and Russell (1959) studied the adsorptive capacity of bentonite and kaolinite saturated

with various cations for soil fulvic and humic acids. Kodama and Schnitzer (1974) reported adsorption of fulvic acid on kaolinite at pH 6.5 ranging from 2.2 - 3.4% by weight with increased adsorption on smaller clay particles. Rashid et al (1972) measured adsorption of a marine humic acid on chlorite and kaolinite and in no cases did adsorption exceed 0.4% by weight. Theng and Scharpenseel (1975) measured 2% adsorption of soil humic acid on sodium saturated montmorillonite. Hedges (1977) tested the uptake capacity of the organic compounds glucose, valine, and stearic acid on kaolinite and montmorillonite. Glucose and valine were not appreciably removed by either clay, but stearic acid was removed from 13 - 46% by weight over a concentration range of .01 to 1.0 mg/l. Alder leachate removal by the crystalline clays chlorite, kaolinite, and montmorillonite was uniformly low, below values reported for soil fulvic and humic acids (Fig. 1). The heterogeneous mixture of organic compounds released during leaching of alder leaves contained few compounds structurally susceptible to adsorption by the crystalline clays tested.

Rather than adsorption to crystalline clays, abiotic uptake of alder leachate was focused in the amorphous solids of the sediment and water column, which are largely composed of hydrous aluminum and iron oxides (Table 1). Greenland (1971) argued that humic and fulvic acid association with clay minerals in soils is governed by polyvalent metals at the clay surface, particularly iron and aluminum hydroxides. These bridging cations of hydrous

aluminum and iron can adsorb certain defined organic structures. Levashkevich (1966) demonstrated this adsorptive capacity between freshly precipitated iron and aluminum hydroxides and soil fulvic acids. Iron and aluminum hydroxide adsorbed 20-32 mg and 47-59 mg per 100 mg, respectively, at pH 5.0-5.5. Theng and Scharpenseel (1975) have documented the efficiency of ^{14}C labelled humic acid adsorption on montmorillonite with various bridging cations at the saturation sites. Fe^{+3} and Al^{+3} produce the greatest increase in uptake capacity. These results are in agreement with the measured alder leachate uptake by freshly precipitated iron and aluminum hydroxide and iron saturated montmorillonite (Fig. 2).

In the field tests utilizing recirculating chambers, the majority of alder leachate loss was from microbial uptake (Fig. 3). A significant and kinetically rapid abiotic removal occurred within minutes of the introduction of alder leachate, but overall disappearance over 48 h was primarily microbial. Cummins et al. (1972) and Lock and Hynes (1975, 1976) also attributed leaf leachate uptake in microcosm experiments to be primarily microbial. In addition, Sepers (1977) concluded that the utilization of dissolved organic compounds in aquatic environments is primarily attributable to the bacterial portion of the microbial community. For alder leachate, only 3% remained in solution after two days. The capacity of the microbial population for processing a diverse variety of organic structures from solution is clear. Rapid equilibration of the leachate with particular phases resulted in abiotic displacement to the sediment of one organic fraction released by the leaching process, where accumulation or microbial processing can proceed.

However, direct uptake from solution by the microbial community removed the greatest proportion of leached alder under the experimental conditions.

The biotic and abiotic rate and efficiencies of uptake of DOC are linked to numerous physical, chemical, and biological factors. Temperature, organic substrate concentration and structure, concentration of inorganic compounds such as nitrogen and phosphorus, grazing impacts from invertebrates and protozoans, pH, Eh, sediment type, and sediment size are examples of parameters potentially exerting an important influence on bacterial activity. Abiotic mechanisms of uptake are also influenced by pH, Eh, ionic strength of the solution, cation exchange capacity and saturating cations in the sediment, concentration of amorphous phases, temperature, sediment and clay types, DOC concentration and structure, and the concentration of divalent and trivalent cations such as Al, Fe, Ca, and Mg, both in solution and in the sediment. Attempts to compare results obtained under widely varying physical and chemical environments, both in the sediment and the water, should not lose sight of the inherent problems these variables can present.

Reported rates of leaf leachate DOC uptake both in microcosms and field experiments range over almost two orders of magnitude (Table 2). The rate of alder leachate removal in this study was $18 \text{ mg C/m}^2/\text{h}$, and is at the lower end of uptake rates reported. If abiotic adsorption is subtracted from the total, microbial uptake is $14 \text{ mg C/m}^2/\text{h}$. A second method for expressing DOC uptake is based on the organic fraction as the center of biotic removal. Uptake of DOC then is calculated as $45 \text{ } \mu\text{g C/g sediment C/h}$. Alternately, if the total uptake rate is calculated over the first 9 h of the experiment (corresponding to the time length used by Lock and Hynes (1975)), the rate becomes $43 \text{ mg C/m}^2/\text{h}$. Clearly,

the degree of initial DOC enrichment and the length of the experiment are important variables in a rate calculation, particularly where rapid abiotic uptake is coupled with microbial uptake, or where the organic substrate is markedly diminished during the early phases of the experiment. A removal rate calculated over the first 20 min following the alder leachate addition, when maximum abiotic removal occurred, is $442 \text{ mg C/m}^2/\text{h}$, similar to the rates determined by Lush and Hynes (1978b) in their field experiment. Although uptake rates of DOC vary widely depending upon ambient physical and chemical conditions, rapid and efficient removal of the majority of the DOC was observed in all cases. Inputs of DOC to streams from allochthonous riparian vegetation are removed and processed such that only a small fraction of this DOC is transported from the ecosystem. The focus for this uptake and processing is centered in the stream sediment and is largely microbial.

The rate and efficiency with which DOC is converted to bacterial biomass or adsorbed to particles control where in the stream system the DOC becomes available as potential food. Conversion to bacterial biomass and particles efficiently retains the majority of potential energy from alder leachate in a utilizable form for organisms otherwise unable to directly assimilate DOC. The efficiency and rate at which retention mechanisms operate upon other likely sources of DOC, such as aquatic plant lysates, soil eluates, conifer leachate, by-products of wood decomposition, and root exudates, need to be measured. If the majority of DOC entering streams is normally susceptible to efficient and rapid biotic or abiotic uptake, the biological significance of total DOC analysis is questionable. Instantaneous measurements of DOC concentrations are probably dominated by refractory compounds which

are less readily utilized than the quantitatively less abundant labile⁶¹ fraction. Compounds not adsorbed to soil or sediment and resistant to microbial degradation, may constitute much of the total analyzed DOC, while the tightly cycled and strongly retained sub-fraction comprises the portion of biological import. Future research should consider not merely the total DOC in solution, but concentrate on the quantity, quality, retention, and turnover of the biotically active fraction in stream ecosystems.

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Table 1. Distribution of amorphous material in the sediment fraction passing through a 75 μm sieve and collected on a 0.4 μm filter paper for 12 first order streams and one seep in the Oregon Cascades, and the percentage of Fe plus Al in the amorphous phase.

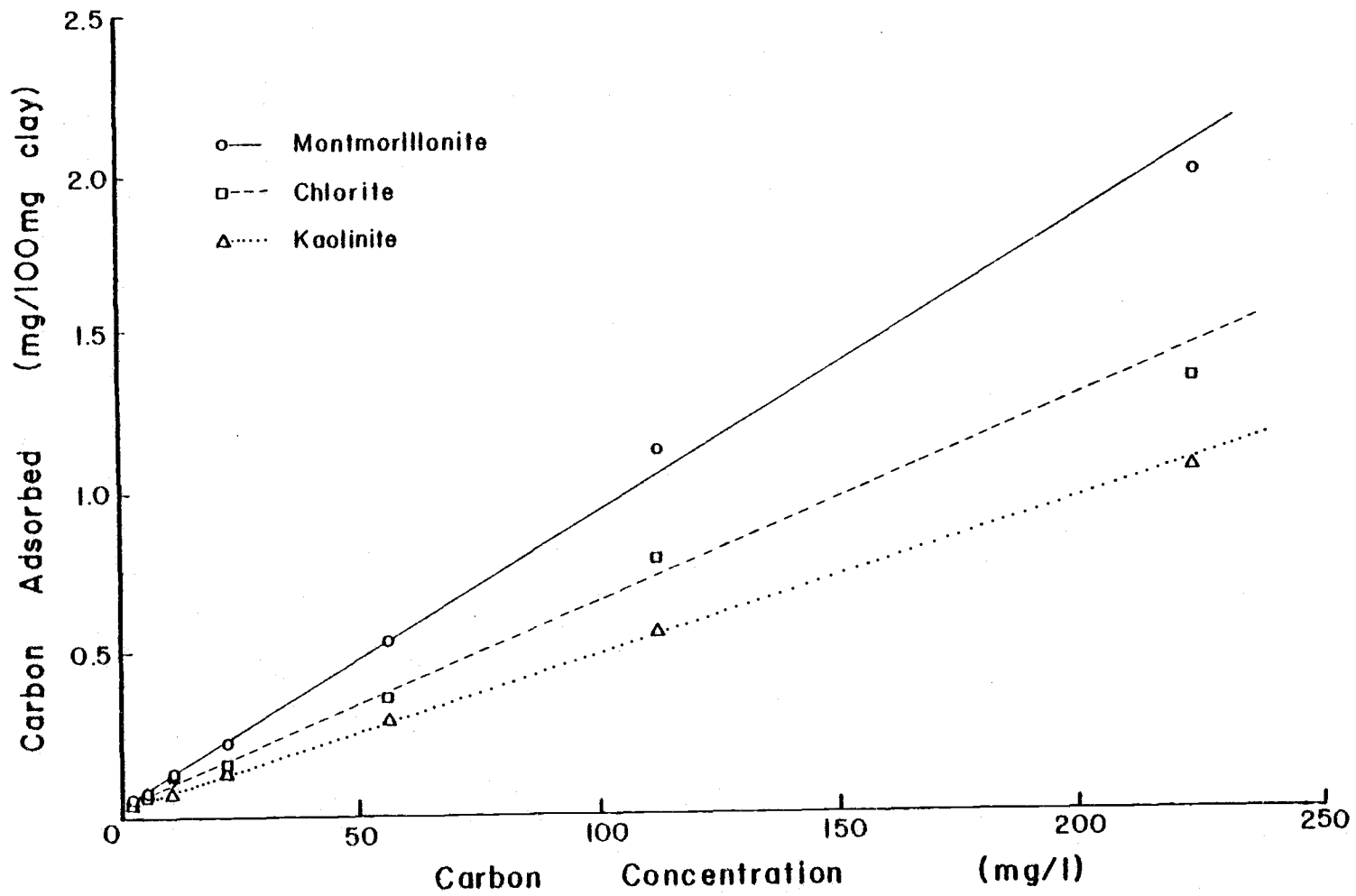
<u>Site</u>	<u>Amorphous Content (%)</u>	<u>Fe + Al in Amorphous Material (%)</u>
Elk Meadow Seep	9.8	23.1
Elk Meadow	11.8	13.0
WS10	7.9	14.6
Q101A	14.8	8.3
WS1	27.4	4.2
Ennis	22.8	4.5
B301	17.4	6.3
Doe	24.4	4.2
Quartz	9.6	12.1
Behms	12.1	12.3
Burwell	18.1	9.1
WS2	10.2	9.7
WS9	12.0	12.2

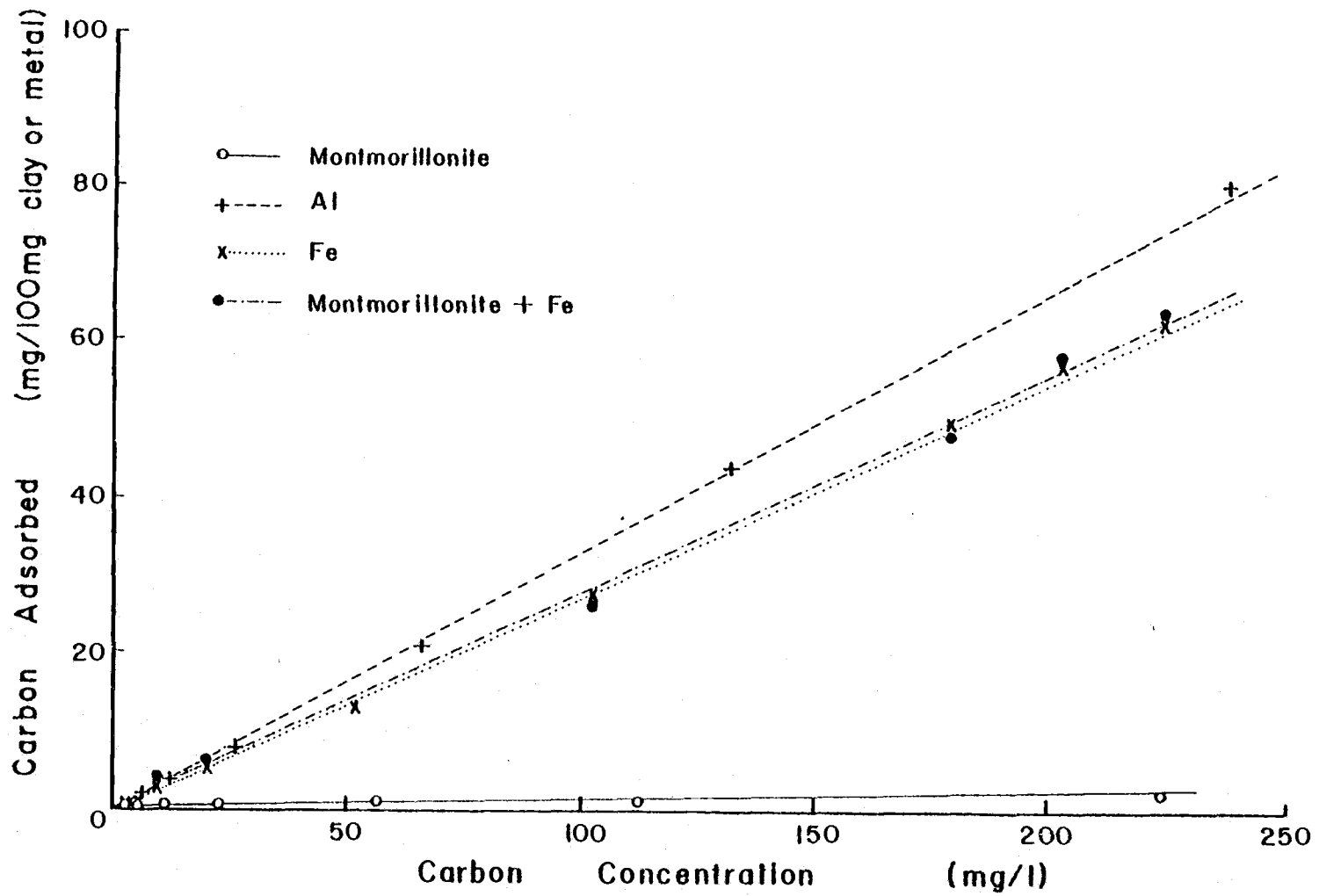
Table 2. Calculated rates of leaf leachate uptake per unit area per hour for reported microcosm and field experiments.

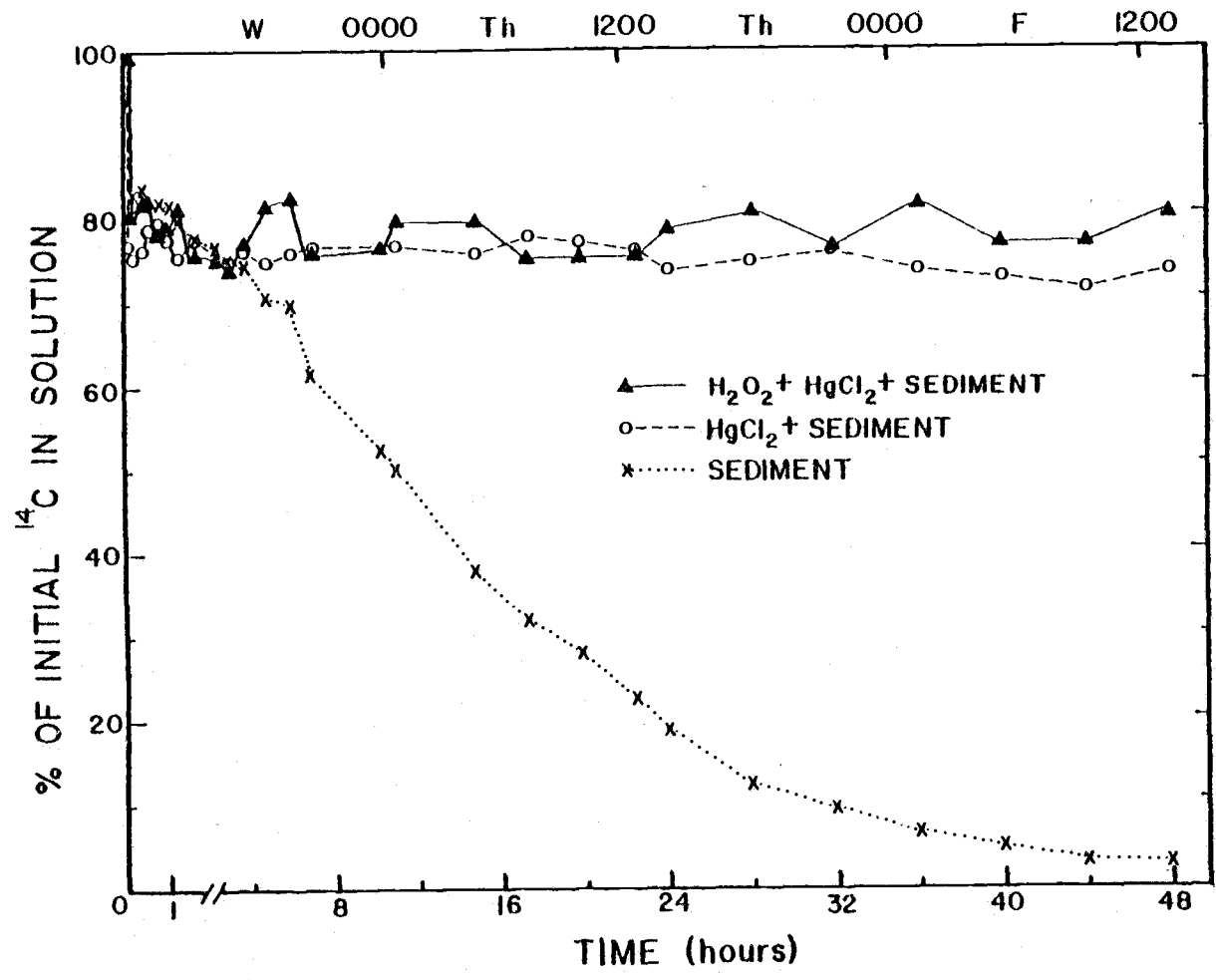
DOC Source	Time h	Uptake Rate (mg C/m ² /hr)	Reference	Comments
Hickory (<u>Carya glabra</u>) and Maple (<u>Acer saccharinum</u>)	48	220	Cummins et. al. (1972) and Wetzel and Manny (1972)	178-209 mg CaCO ₃ /l pH = 8.0-8.4 Large, recirculating stream
Aspen (<u>Populus tremuloides</u>)	9	120	Lock and Hynes (1975)	225 mg CaCO ₃ /l
Aspen (<u>Populus tremuloides</u>)	9	110	Lock and Hynes (1975)	5 mg CaCO ₃ /l
Maple (<u>Acer saccharinum</u>)	9	73	Lock and Hynes (1975)	225 mg CaCO ₃ /l
Maple (<u>Acer saccharinum</u>)	9	50	Lock and Hynes (1975)	5 mg CaCO ₃ /l
Pine (<u>Pinus resinosa</u>)	9	40	Lock and Hynes (1975)	225 mg CaCO ₃ /l
Pine (<u>Pinus resinosa</u>)	9	10	Lock and Hynes (1975)	5 mg CaCO ₃ /l
Cedar (<u>Thuja occidentalis</u>)	9	28	Lock and Hynes (1975)	225 mg CaCO ₃ /l
Cedar (<u>Thuja occidentalis</u>)	9	23	Lock and Hynes (1975)	5 mg CaCO ₃ /l Recirculating chamber
Cedar (<u>Thuja occidentalis</u>)	0.5	270	Lush and Hynes (1978)	200 mg CaCO ₃ /l
Maple (<u>Acer saccharinum</u>)	0.5	250-550	Lush and Hynes (1978)	pH = 7.8 Field experiment
Alder (<u>Alnus rubra</u>)	48	18	This paper	30 mg CaCO ₃ /l
Alder (<u>Alnus rubra</u>)	9	43	This paper	pH = 7.4 Temp = 15°C
Alder (<u>Alnus rubra</u>)	0.3	442	This paper	Recirculating chamber

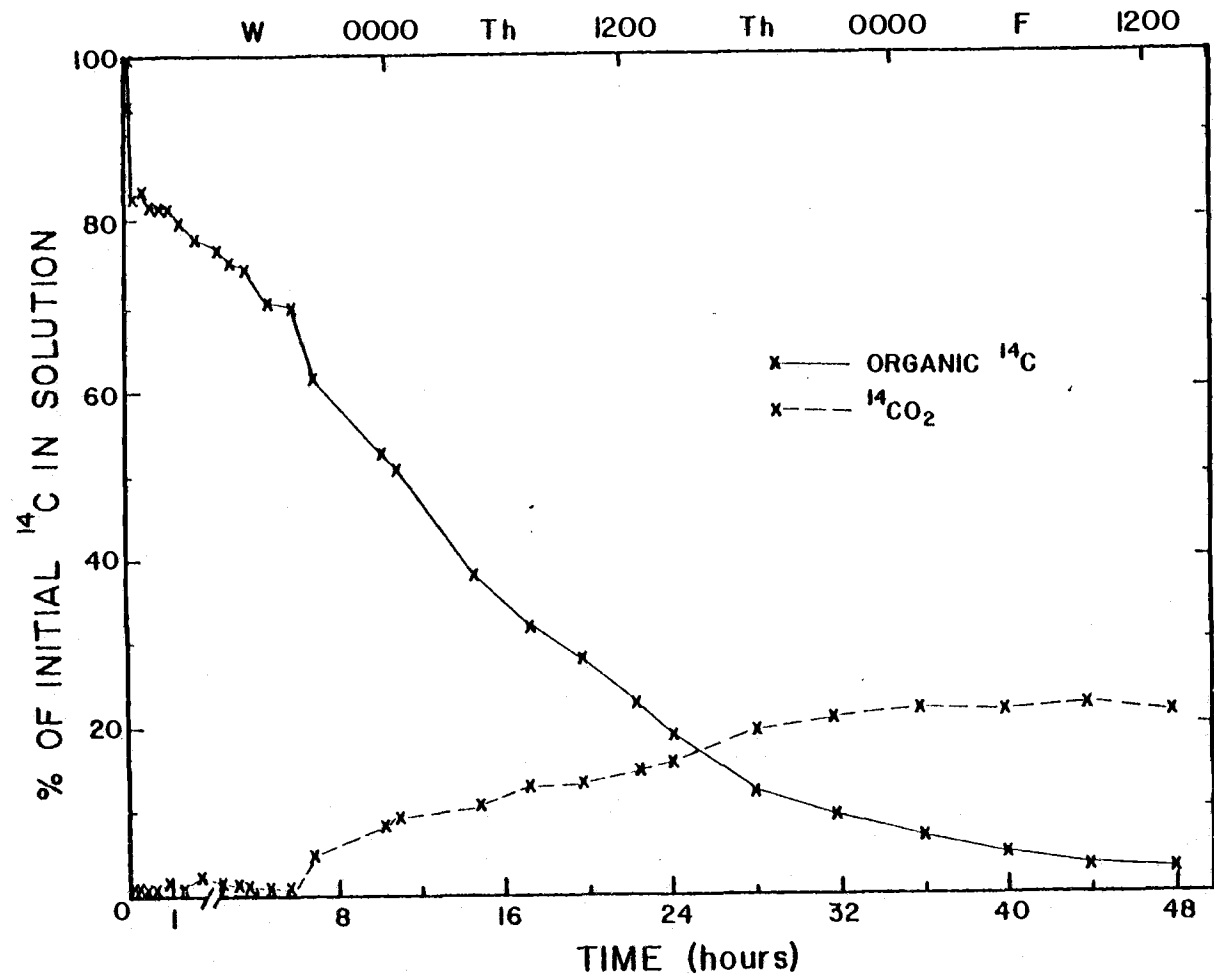
Figure Legends

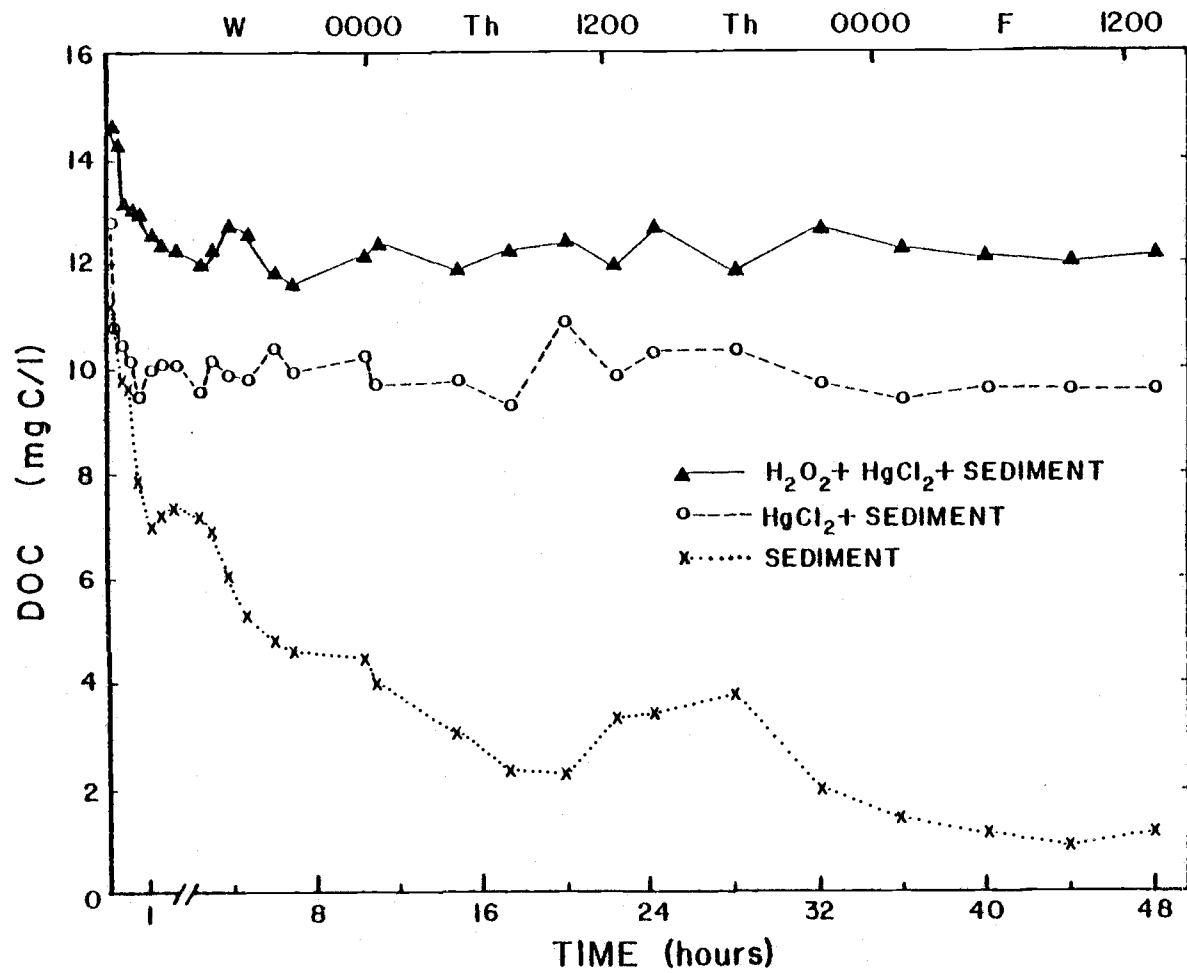
- Figure 1. Amount of DOC from alder leachate adsorbed from solutions of varying carbon concentration expressed in milligrams per 100 milligrams of clay using montmorillonite, chlorite, and kaolinite clays saturated with sodium.
- Figure 2. Amount of DOC from alder leachate adsorbed from solutions of varying carbon concentration by amorphous precipitates of Fe and Al and a montmorillonite clay saturated with Fe. The carbon adsorbed is expressed in milligrams per 100 milligrams of metal or clay. The montmorillonite clay saturated with sodium is shown for reference.
- Figure 3. Uptake of radiocarbon from the leachate of labelled alder leaves graphed as a percentage of the added DO^{14}C activity is plotted against time in hours for the three treatments tested in recirculating chambers.
- Figure 4. The disappearance of DO^{14}C from labelled alder leaves and the appearance of microbial respiration $^{14}\text{CO}_2$ is plotted against time for the chamber containing unpoisoned stream sediment. Carbon uptake and mineralization is graphed as the percentage ^{14}C relative to the amount initially added to the chamber.
- Figure 5. Concentration of total DOC (mg C/l) plotted against time for each chamber. Added DOC was calculated to raise the concentration 9.8 mg C/l. Background levels of DOC were 1.4, 3.6, and 5.8 mg C/l for the unpoisoned, poisoned, and poisoned plus H_2O_2 chambers, respectively.











CHAPTER III

Nutrient Response to Clearcutting in a First-order Stream
in the Cascade Mountains.

by

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ABSTRACT

Concentrations of dissolved nitrate (NO_3), total reduced nitrogen (N), phosphate (PO_4), and total phosphorus (P) have been measured for water years 1974 - 1978 in a first-order mountain stream, WS10, in the Cascade Mountains of Oregon, USA. Two years after sampling began, the 10.2 ha watershed was clearcut. Concurrently during water years 1977 and 1978, WS2, a second-order stream draining an old-growth coniferous forest 1.4 km southeast of WS10, was also monitored. In addition, on both watersheds, dissolved organic carbon (DOC) was measured intensively during most of water years 1977 and 1978 and ammonium (NH_4) during water year 1978.

In WS10, average annual stream NO_3 concentration increased from undetectable levels ($<3 \mu\text{g NO}_3\text{-N/l}$) before clearcutting to $62 \mu\text{g NO}_3\text{-N/l}$ in water year 1977, a drought period. Total NO_3 export increased steadily from .01 to .60 Kg/ha/yr in water year 1978. Total N concentration in solution during an annual cycle in WS10 increased from $33 \mu\text{g N/l}$ before clearcutting to $140 \mu\text{g N/l}$ in water year 1977. Distribution of N compounds in solution shifted from predominantly reduced forms to 44 and 38% NO_3 in water years 1977 and 1978, respectively. For comparison, annual N export from WS2 in 1978 was 90% in reduced compounds, mainly dissolved organic nitrogen

(DON). The NH_4 concentration for both streams annually averaged $<5 \mu\text{g NH}_4\text{-N/l}$ but with concentrations $>20 \mu\text{g NH}_4\text{-N/l}$ during summer months. Total P and PO_4 concentrations and export did not increase following clearcutting.

Average annual DOC concentration in WS10 during 1977, the second year after clearcutting, was 43% higher than WS2. Export was nearly three times as great (20 Kg/ha/yr versus 7.1 Kg/ha/yr). In water year 1978, annual DOC concentrations were nearly identical and export approximately 37% greater from WS10 (34.4 Kg/ha/yr versus 25.2 Kg/ha/yr). The ratio DOC/DON in water year 1978 was 39 in WS10 and 73 in WS2. The lowering of the DOC/DON ratio to values between 20-30 appears to enhance the competitiveness of chemoautotrophic nitrifying bacteria, thereby promoting nitrification in recently clearcut watersheds. Elimination of litterfall sources and death of root systems decreases competition for NH_4 from carbon oxidizing heterotrophic bacteria and root uptake.

Total N export in solution from WS10 was highest in water year 1978, equaling 1.6 Kg/ha/yr. This value is approximately triple precutting rates. Annual N losses in solution constituted 0.03% of total N capital in the watershed in water year 1978. Maximal annual solution losses did not exceed estimated precipitation and dry fallout inputs of 2.0 Kg/ha/yr. However, increased solar

radiation coupled with a tripling of average N concentrations in solution focus quantitatively small absolute watershed nutrient losses from clearcutting on the stream environment where significant structural and functional changes result.

INTRODUCTION

In the productive forests of the Pacific Northwest of North America, clearcutting is utilized more extensively than any alternative harvest method. Changes imposed on nutrient cycling by clearcutting forest ecosystems are concentrated in the streams which drain them. Streamflow (Hornbeck et al. 1970, Harr and McCorison 1979), suspended sediment (Beschta 1978), stream temperature (Brown and Krygier 1970), dissolved oxygen (Hall and Lantz 1969), and dissolved nutrient (Likens et al. 1970, Fredriksen 1972, Vitousek et al. 1979) changes have all been documented following clearcutting. This paper focuses on the dissolved nutrient responses following clearcutting of an old-growth conifer forest. Soluble nitrogen, phosphorus, and organic carbon are considered.

Nitrogen dynamics are of particular importance in Pacific Northwest watersheds, where the weathering of soil minerals provides no significant input. Overall cycling patterns for this biologically limiting element are strongly retentive (Sollins et al. in press). Vitousek et al. (1979) lucidly discussed mechanisms operating in disturbed ecosystems which are responsible for elevated stream NO_3 concentrations. They showed that trenching to eliminate root competition for NH_4 in 18 of

19 forest ecosystems throughout the U.S. increased NO_3 levels significantly. Gregory (1980) further demonstrated that elevated stream NO_3 in a first-order forest stream in the Cascade Mountains of Oregon, when coupled with increased light input, stimulated primary production. Since clearcutting increases light input, the timing, concentration, and form of nitrogen inputs become critical factors for primary production in streams draining clearcut areas and for the nutrient export they provide to larger downstream aquatic ecosystems (Triska et al. in press).

Clearcutting also affects the sources and timing of dissolved organic energy input. Elimination of the canopy removes a major source of allochthonous energy to the stream ecosystem (Fisher and Likens 1973), while stimulation of instream primary production can provide additional organic material. Therefore, shifts in the origin and concentration of DOC and DON can impact the stream directly by alteration of heterotrophic microbial activity from changes in DOC and DON quality (Lock and Hynes 1975) or indirectly by altering the quantity of DOC and the DOC/DON ratio in soil solutions. Coats et al. (1976) and Sollins et al. (in press) have suggested that the reduced C/N ratios may create favorable conditions for nitrification. If correct, similar streams, draining a clearcut watershed with increased

concentrations of NO_3 , should contain dissolved organic matter with lowered ratios of DOC/DON. In comparison, a nearby old-growth coniferous forest stream with low NO_3 concentration and a continuous supply of high C/N litterfall would have higher ratios of DOC/DON.

The goal of this study was to examine stream nutrient response to perturbation of the watershed by routine clearcutting and timber removal practices used in the Pacific Northwest. We sampled the stream both before and after treatment and established a control in a nearby old-growth site. Intensive sampling, emphasizing high flow events, provided us with improved accuracy in estimating nutrient output and temporal variability in concentration. Three main objectives were: 1) to accurately measure the loss of dissolved N, P, and organic carbon from a clearcut and an old-growth conifer watershed; 2) to determine temporal variability over multiple annual cycles for the concentration of dissolved N, P, and organic C in streams flowing from logged and unlogged ecosystems; and 3) to measure changes following clearcutting in the type of N compounds in streamwater.

STUDY SITES

This study was conducted on the west slope of the Cascade Mountains of Oregon in the H.J Andrews Experimental Forest, 72 km east of Eugene, Oregon. Two gauged watersheds located 1.4 km apart were compared (Figure 1). A maritime climate exists with distinct seasonal rainfall patterns. Annual precipitation at a meteorological station within 3 km of both watersheds averaged 240 cm. Over 80% of precipitation occurred between October and April from long-duration, low-intensity frontal storms.

Watershed 10 (WS10) is a first-order stream (Strahler 1964) draining 10.2 ha with a southwesterly aspect. Elevation at the stream gauging station is 430 m, and the watershed rises to a maximum elevation of 670 m at the southeastern ridge line. Overall slope of the stream channel is 45% with side slopes ranging up to 90%. Residual and colluvial clay loam soils derived from pyroclastic rocks overlay highly weathered andesitic tuff and breccia bedrock to an average depth of approximately 130 cm (Harr and McCorison 1979). The soils have extremely high conductive capacity to stream channels, therefore overland flow does not occur (Harr 1977). Streambed structure consists of a series of small pools, mainly created behind large organic debris, connected by riffles generally running on bedrock.

Dominant forest vegetation in WS10 was 350-550 year old Douglas fir (Pseudotsuga menziesii) mixed with western hemlock (Tsuga heterophylla) and western red cedar (Thuja plicata). During May - July of 1975, WS10 was clearcut. A running skyline system was used to yard all logs and unmerchantable scrap >20 cm in diameter or >2.4 m in length to a single uphill landing. A scrap pile was burned, but the entire watershed was not broadcast burned.

Watershed 2 (WS2) is a second-order stream at the gauging station draining 60.3 ha with a northwesterly aspect. Elevation ranges from 525 m at the weir to a ridgetop maximum of 1070 m. Stream channel gradient is 40% with side slopes up to 100%. Soil and bedrock type, streambed structure, and dominant forest vegetation are similar to WS10.

METHODS

Stream Sampling

Stream chemistry was sampled routinely on WS10 since October 1973 and on WS2 since October 1976. Sampling was designed to intensively monitor fall storms. Biweekly samples, coupled with fall storm sample collections, were taken in water years 1974 and 1975. In water year 1976, weekly sampling was initiated. During water year 1977 and most of 1978, samples were taken every three days.

Streamwater samples were collected at the weirs in 500 and 1000 ml polypropylene bottles. Bottles were washed with detergent, acid rinsed, and then rinsed with distilled H₂O. Sample bottles were thoroughly rinsed with streamwater from the collection site before a sample was collected. Samples for DOC were drawn into 250 ml glass bottles which were pre-fired at 500°C before use. Samples to be analyzed for NH₄ were acidified after sample collection with 1 ml of 1N H₂SO₄.

Once collected, the samples were refrigerated and transported to the laboratory as rapidly as possible. Samples for analysis of nitrogen and phosphorus were frozen until analyses could be performed. Triplicate DOC samples were sealed into ampules as quickly as possible after arrival.

Stream Discharge

Daily average streamflow for each watershed was obtained from concrete trapezoidal flumes with a cutoff wall to bedrock. Gauge height, measured by 120° V notch weirs connected to continuous strip-chart recorders, was converted to discharge per second with calibration curves. It was possible to obtain hourly discharge records during storm events. Peak discharge for both watersheds occurred December 13, 1977. Discharge was 117 and 446 l/sec for WS10 and WS2, respectively. Late summer and early fall low flows were 0.2 and 0.6 l/sec for WS10 and WS2.

Chemical Methods

DOC is defined here as the organic carbon passing through a 0.4 μm glass fiber filter, pre-fired at 350°C to remove organic contaminants. It is recognized that many colloidal size particles, not truly dissolved organic molecules, are smaller than this traditional cutoff (Lock et al. 1977). Triplicate aliquots of 5 ml from the filtered samples were acidified, potassium persulfate was added, the samples were purged to remove inorganic carbon and then the samples were sealed in ampules. Following oxidation of the organic material, the CO_2 was determined

with an infrared analyzer (Menzel and Vaccaro 1964). Reproducibility at a 95% confidence interval was 0.05 mg C/l.

A modified Kjeldahl technique was used for the analysis of the low total reduced N (organic N + NH_4) present in forested Oregon streams (Holcombe et al. in press). Minimum detectable concentration was .003 $\mu\text{g N/l}$ and recovery of a variety of organic N compounds always exceeded 92%. Direct measurement of NH_4 was begun in water year 1978 on a Technicon Autoanalyzer^R II. Determination was by a modified phenol-hypochlorite method (Solorzano 1969). DON was calculated by subtracting NH_4 concentrations from the total reduced N levels. The cadmium reduction method (Strickland and Parsons 1972) was used to determine NO_3 plus NO_2 . Subsequent analyses for NO_2 were undetectable and nitrogen determined with this method will be considered to be only NO_3 . Autoanalyzer techniques for NO_3 supplanted manual methods in water year 1978. All data is reported as micrograms of nitrogen per liter. Minimum detectable concentration for NH_4 , NO_3 , or NO_2 was .002 $\mu\text{g N/l}$.

Total P was determined after acid hydrolysis with potassium persulfate and sulfuric acid. The molybdate blue method of Murphy and Riley (1962) was used for both PO_4 and total P determinations. The molybdate blue

method is not specific to the PO_4 anion and all data reported as PO_4 may contain small amounts of other molybdate reactive phosphorus compounds. Manual methods were replaced in water year 1978 with autoanalyzer determination. Minimum detectable concentration for total P was $.005 \mu\text{g P/l}$ and $.002 \mu\text{g P/l}$ for PO_4 .

Stream Nutrient Export and Concentration

A computer program was written to estimate daily, monthly, seasonal, and annual concentration and total export for the nutrients DOC, NO_3 , NH_4 , total reduced N, total P, and PO_4 . Daily average streamflow and the nutrient data obtained from grab samples were the basis for the calculation. An attempt to utilize regressions of nutrient concentration on streamflow to predict solute concentration and transport (Johnson 1979) was unsatisfactory due to the poor correlation between concentration and discharge over an annual cycle. Instead, the average measured nutrient concentration was multiplied by discharge for all days when grab samples were taken. If multiple samples were analyzed during one day, the average value for all measurements was used. On days when no sample was taken, a linear interpolation was made between the concentrations determined on the samples nearest in time on each side of the date with no nutrient

data.

The method employed has the advantage of taking into account temporal variability affecting nutrient availability for stream transport. Fall freshets following dry summers export much higher concentrations of nutrient material than late winter storms, after months of intermittent precipitation. Since sampling was designed to carefully monitor storm events, an accurate estimate of nutrient transport and concentration was obtained in these watersheds with rapidly fluctuating discharge (Figures 2 and 3). A regression estimate, averaging a complete annual cycle, yields a single estimate for each rate of discharge with no consideration of prior hydrological or climatic characteristics. For some ecosystems this is satisfactory (Johnson et al. 1969, and Johnson 1979), but was not applicable to nutrient solutes in Oregon Cascade streams or woodland and farmland watersheds of the mideast (Taylor et al. 1971).

RESULTS AND DISCUSSION

Phosphorus

Phosphorus abundance in the bedrock of the central Oregon Cascades was high (James 1978). Losses of dissolved P exceeded losses of dissolved N in WS2 and WS10 before tree harvest. Export from WS2 was 0.93 kg/ha/yr in water year 1978, but only 0.14 Kg/ha/yr in the drought period. A similar decrease in dissolved P output during the drought year also occurred in WS10. Average annual input of dissolved P by precipitation amounted to approximately 0.2 Kg/ha/yr (Fredriksen 1975). Weathering reactions with bedrock or soil minerals ultimately provided the majority of dissolved P in both watersheds. Output of dissolved P in WS10 and WS2, except during the drought conditions, surpassed any undisturbed forest ecosystem reported by Hobbie and Likens (1973), Likens and Bormann (1974), or Feller and Kimmins (1979).

Clearcutting did not produce increased concentrations or total export of dissolved P (Table 1). Likens and Bormann (1974) reported an approximate doubling of solution P output following deforestation. However, the measured increase equaled .01 Kg/ha/yr in a deciduous forest, where P was tightly recycled. In WS10, the five

year average for dissolved P transport was 1.06 Kg/ha/yr. A response of the magnitude observed by Likens and Bormann (1974) after deforestation would have remained undetected against the normally high dissolved P concentrations.

Based on five years of measurements in WS10, dissolved P export was 42% organically bound and 58% inorganic PO_4 . Phosphorus export from WS2 was 63% organic P and 37% inorganic PO_4 for water years 1977 and 1978. The difference in the proportions between the two watersheds reflected the consistently lower PO_4 concentration in WS2 (Figures 4 and 5). Solution losses of dissolved P were minimized during the drought year. Lowest average annual concentrations occurred during water year 1977 and together with reduced discharge resulted in total outputs for dissolved P of 30% and 15% of the other years on record for WS10 and WS2, respectively (Table 1). Such variability points out the danger inherent in estimating long term nutrient fluxes based upon single annual estimates. Hydrologic and climatic conditions strongly affected annual nutrient output.

Seasonal fluctuations in total dissolved P were closely linked to climatic influences on precipitation and decomposition (McColl 1972). Long warm summers allowed accumulation of soluble P in the soil, but

without adequate precipitation for transport of large quantities of P to the stream. Autumn storms flushed the soil system, elevating dissolved P concentrations with only small increases in discharge. Increases occurred mainly in organic P concentration. The interval between periods of rainfall, the amount of precipitation, and recent temperature influenced the concentrations of nutrients in water entering the stream (Feller 1977).

The PO_4 concentration was remarkable constant throughout all seasons (Figures 4 and 5). Constancy throughout annual sampling periods even with wide ranges of streamflow and temperature, suggested equilibration between the soil matrix and solution, probably involving iron and aluminum compounds. The role of biological uptake on PO_4 concentration was small. Solubility equilibria given by Stumm and Morgan (1970) for phosphates, iron, aluminum, and calcium allow an equilibrium P concentration in solution to be calculated at various pH values. WS2 and WS10 were near neutral pH with low calcium content (<10 mg Ca/l). At pH 6 to 7, aluminum phosphate or hydroxylapatite control solubility, and equilibrium dissolved P concentration is predicted to be about 25 $\mu\text{g P/l}$. Annual average concentrations of PO_4 for WS2 and WS10 ranged from 22-50 $\mu\text{g P/l}$. Meyer (1979) has also suggested that organic matter content in addition to aluminum mineral equilibria may exert control

on soluble P concentration. This possibility cannot be ruled out as an additional factor in WS10 and WS2.

Physical-chemical equilibration between weathering and precipitation inputs with aluminum and calcium compounds, and possible organic matter, regulate PO_4 concentration more strongly than biological controls in these watersheds.

Nitrogen

Nitrogen was considered the biologically limiting element for plant growth in WS2 and WS10 (Sollins et al. in press). Recycling conserved the available N and low concentrations occurred in stream water flowing from the watersheds. Losses from streamflow were greatly exceeded by inputs from precipitation and nitrogen fixation (Sollins et al. in press). Consequences of clearcutting on the concentration and biogeochemical cycle of N can greatly affect instream and downstream aquatic ecosystem structure and function (Cummins 1974).

Total dissolved N is defined as reduced N (organic N and NH_4) plus NO_3 . Before clearcutting in WS10, the average dissolved N concentration was 33 μg N/l over nearly a two year period (Table 2). For two years in WS2, the concentration of total dissolved N averaged 36 μg N/l. The first year following clearcutting saw a

slight increase to 49 $\mu\text{g N/l}$. During drought conditions in water year 1977, the average dissolved N level increased to 140 $\mu\text{g N/l}$. In water year 1978 elevated concentrations continued with average annual solution N levels of 85 $\mu\text{g N/l}$. A comparison between water years 1974 and 1975 with 1977 and 1978 showed a tripling in dissolved N from 33 $\mu\text{g N/l}$ to 101 $\mu\text{g N/l}$.

Export of total dissolved N has increased steadily each year since clearcutting (Table 2). Disturbance effects on soluble N loss did not peak the first or second year after commercial clearcutting as reported for deciduous forests of the northeast (Bormann and Likens 1979). Biotic regulation of N losses has not been reestablished three years after cutting. As revegetation of the watershed proceeds, continued N concentration and streamflow monitoring will determine the resilience of this coniferous forest ecosystem to N cycling, where resilience is defined as the relative rate of recovery after perturbation (Vitousek et al. 1979). This lag in ecosystem response to deforestation must be considered in predicting instream and downstream consequences of N addition on water quality.

Total dissolved N export in solution from WS10 in water year 1978 amounted to 1.6 Kg/ha/yr. This value is triple precutting rates. Total watershed N capital is estimated at 4930 Kg/ha/yr, mainly composed of soil

organic matter (Sollins et al. in press). Maximum annual solution losses therefore constitute 0.03% of total N. Maximum annual solution losses of N were exceeded by estimated annual precipitation and dry fallout inputs of 2.0 Kg/ha/yr (Sollins et al. in press). Even following disturbance, WS10 remained highly retentive for elemental N, unless denitrification was a significant source of loss. Estimates of denitrification were unavailable on either WS2 or WS10.

Average reduced N export from WS10 increased approximately 30% after clearcutting (Table 2). Immediate increases were detected the first year after harvest. Slash and organic debris left by the logging operation provided an abundant supply of leachable residue. Total reduced N export during the drought year was comparable to preclearcut estimates, but average concentration was at a maximum. Average annual concentration of reduced N during the drought year was 53% higher in WS10 than WS2 (Figures 6 and 7). Reduced N concentration and export remained elevated the third year after cutting and were similar to first year values (Figures 8 and 9).

Ammonia was analyzed only during water year 1978 (Figures 8 and 9). No increases in streamwater concentration or export were observed in WS10 compared to WS2. Likens et al. (1970) also found no NH_4 response following clearcutting. Concentration and export of NH_4 were low in both watersheds. Only in summer months was the con-

concentration of NH_4 consistently above detectable 97
levels. Summer concentrations averaged $21 \mu\text{g NH}_4\text{-N/l}$
on both watersheds.

Concentrations of DOC can be estimated on WS2 and WS10 during water year 1978 when both total reduced N and NH_4 were analyzed. In both watersheds, DON was the dominant form in which N loss occurred in streamflow (Table 2 and Figures 10 and 11). For watersheds in the White Mountains of New Hampshire, Vitousek (1977) calculated low concentrations of DON relative to NO_3 , but Gosz (1978) reported forested watersheds of New Mexico where DON transport outweighed inorganic forms. In ecosystems where N is tightly recycled the importance of DON to stream communities may be enhanced. The predominance of DON to inorganic N compounds may however result from stable refractory compounds essentially unavailable to the aquatic community. Manny (1972) measured a progressive increase in the percentage of UV-refractory DON downstream in Michigan with maximum values of about 70% of the DON in spring months. Fall measurements by Manny and Wetzel (1973) ranged from 20-60% UV-refractory DON on the same stream. Quantitative estimation of biologically labile and refractory components in the DON pool and their temporal variability in N starved streams is necessary to judge the potential availability of DON to the stream biota.

Nitrate response in disturbed ecosystems has

received great attention due primarily to the dramatic increases observed and its implications to water quality. Likens et al. (1970), Fredriksen (1971), Pierce et al. (1972), Aubertin and Patrie (1974), and Vitousek et al. (1979) reported increased NO_3 losses after clearcutting. WS10 also showed dramatically increased NO_3 export, but only after a year delay. Water year 1976, the first complete water year after deforestation, did not produce a significant increase in NO_3 export when compared to WS2 or to data from WS10 before clearcutting (Table 2). Hydrologically, water year 1976 maintained near normal discharge. Either the rate of nitrification was not sufficient to produce measurable increases in NO_3 or processes delaying nitrate loss prevented increased NO_3 in the stream. Water year 1977 showed a pronounced shift to an average of $62 \mu\text{g NO}_3\text{-N/l}$ compared to undetectable levels ($<3 \mu\text{g NO}_3\text{-N/l}$) in undisturbed systems (Figure 6). Nitrate accounted for 44% of the total N in WS10. The wetter conditions of water year 1978 decreased the average annual concentration of NO_3 in WS10 to $32 \mu\text{g NO}_3\text{-N/l}$ but total export continued to increase to $.60 \text{ Kg N/ha/yr}$ (Figure 8). Once again NO_3 accounted for over one third (38%) of the N transport.

Vitousek et al. (1979) suggested that N uptake by regrowing vegetation, N immobilization, lags in nitrification, and a lack of water for transport are most

important in delaying or preventing solution losses of NO_3 . The delay in NO_3 response, which occurred the first year after cutting on WS10, could be attributable to all possibilities except a lack of water for transport. First, clearcutting does not result in immediate root death. Viable root systems from the removed vegetation could compete for available NH_4 for up to a year (Kermit Cromack, personal communication). Secondly, the accumulation of NH_4 in solution or on cation exchange sites could be prevented or delayed through immobilization by heterotrophic bacterial decomposers. Conifer litter, which was abundant the first year after cutting as broadcast burning was not employed, produces leachate with a high carbon/nitrogen ratio (Sollins et al. in press). Stimulation of the heterotrophic carbon oxidizing aerobic bacteria, by an abundance of oxidizable leachate, would produce a concurrent high demand for NH_4 . The availability of such an energy base would decrease with time as additional litterfall would be lacking. Thirdly, nitrification could lag either through allelochemical inhibition (Rice and Pancholy 1972, 1973) or a low initial population of nitrifiers (Vitousek et al. 1979). Belser (1979) concluded that the hypothesis of allelochemical inhibition has no solid data to support or deny it. Also, Belser (1979) reported generation times for nitrifying bacteria in soil mixtures of six

days or less. Such generation times argue against a year delay in establishing a nitrifying population if favorable conditions existed. Further study of root uptake after tree removal, allelochemical inhibition on nitrifiers from clearcut slash, and the response of heterotrophic carbon oxidizing bacteria is necessary to determine if one or a combination of these mechanisms delayed NO_3 losses to the stream.

Nitrate concentrations in WS10 reached a maximum value of 268 $\mu\text{g NO}_3\text{-N/l}$ during the early stages of the first storm in late February of the drought year (Figures 2 and 6). Much larger increases in NO_3 concentration were measured by Vitousek et al. (1979) in 16 of 19 lysimeter studies in forested ecosystems throughout the U.S. where root uptake was inhibited ($>1400 \mu\text{g NO}_3\text{-N/l}$). Although measured concentrations of NO_3 in WS10 would not constitute a positive response based on the criteria established by Vitousek et al. (1979), increases in NO_3 can be more significant in aquatic systems which are potentially N limited. Interpretation of the consequences of increased N to streams following clearcutting should address both absolute changes in dissolved N concentration and the N demand in aquatic ecosystems into which the disturbed watershed drains.

Following warm summer temperatures with little precipitation, fall storms normally discharge the highest

annual amounts and concentrations of dissolved N (Figures 6 - 11). However, during the drought year, increased stream discharge did not occur until February, delaying export of the majority of solution losses of N that year until winter. Feller (1977) reported maximum nutrient losses in southwestern British Columbia during winter. Coats et al. (1976) showed that streams with spring snowmelt had maximum losses of N in spring. Climatic influences such as temperature, precipitation type and pattern, and growing season affects both annual and seasonal variability in N export. Both the quantity and timing of N inputs is important in predicting aquatic ecosystem response.

Total dissolved N losses in WS10 can be compared to dissolved N export summarized by Likens and Bormann (1974). Maximum export of 1.6 Kg N/ha/yr (Table 2) in water year 1978 was half or less of any of the nine disturbed forest ecosystems reported. Only undisturbed forests of the Pacific Northwest had outputs similar or less than WS10. Influenced by different geology and climate, forests of all types conserve most strongly nutrients vital to the maintenance of the ecosystem. In many watersheds of the Pacific Northwest, the vital nutrient is N.

Patterns of nutrient output in streamwater measured at the base of a watershed were, at times, significantly

changed by aquatic biota. This pattern was particularly true for N, and to a lesser extent P, in WS10 during summer low flow. Increased solar radiation to WS10 following clearcutting greatly stimulated aquatic primary productivity (Gregory 1980). Algal metabolism utilizes inorganic nutrients but cells may release both organic and inorganic compounds. Since, NO_3 concentrations during summer months were lower than any other season of the year (Figures 6 and 8), uptake of nutrients by a very active algal community altered the form and timing of N losses from the watershed.

Nutrient output from the watersheds reflected both terrestrial and aquatic processing and should not be interpreted simply as loss from the terrestrial system. Both heterotrophic microbial communities, mainly bacteria and fungi, and aquatic primary producers were involved. Clearcutting shifted the relative importance of each component, but both were active. For example, diel patterns of NO_3 in WS10 before clearcutting revealed only minor shifts, but increased after logging. Such alteration was most apparent at low flows. Light and an increased NO_3 supply in streamwater produced an abundant algal community in WS10 which in turn impacted N dynamics (Gregory 1980).

Dissolved organic carbon

Studies which report DOC concentrations of streams and rivers are few, even though Wetzel and Rich (1973) have termed DOC as functionally the most important component in the detrital carbon trophic structure for lake systems. Moeller et al. (1979) summarized available studies providing adequate data to permit estimation of annual mean DOC concentration and output for any stream or river. Seventeen streams smaller than fourth-order were found. Most of these estimates were based on monthly or longer sampling intervals and none linked DOC concentration directly to instream measurements of microbial metabolism and productivity. Leachate studies (Lock and Hynes 1976, Bott et al. 1977, and Lush and Hynes 1978) in recirculating chambers and a small spring stream have shown that the readily leachable fraction from leaves is rapidly assimilated by stream microbial populations. The importance of such labile DOC material to higher trophic levels of stream communities through microbial uptake is not known. Intensive sampling in WS2 and WS10 provided a measurement of the timing and quantity of DOC output and possibly an indirect indication of the potential quality of the soluble reduced carbon.

Average seasonal and annual concentrations and

output of DOC in WS2 and WS10 were calculated for water years 1977 and 1978 (Table 3). Fall estimates in water year 1977 were based on samples collected beginning November 22, 1976 and the sampling interval was lengthened to every third week beginning April 26, 1978. Average annual concentration of DOC in WS10 during 1977 was 43% higher during water year 1977 than in WS2. Export of DOC was nearly three times as great from WS10 than WS2 in water year 1977 (20.6 versus 7.1 Kg/ha/yr). Higher concentrations of DOC in late winter and spring, combined with greater annual water yield per hectare from the clearcut watershed, produced the increased export (Figures 12 and 13).

Water year 1978, the third year after clearcutting and a return to near normal rainfall patterns, produced nearly identical average annual concentrations of DOC in WS2 and WS10 (Figures 14 and 15). Export was approximately 37% greater from WS10 (34.4 versus 25.2 Kg/ha/yr). Higher export was due to the nearly 50% greater annual water yield per hectare from WS10.

Concentration of DOC in WS10 dropped 47% from an annual average of 2.74 mg C/l in water year 1977 to 1.87 mg C/l in water year 1978. Concurrent decrease in WS2 was only 8%. Dilution during the wetter year may explain the general decrease on both watersheds, but the much greater decline in WS10 was likely attributable to

limited renewal of fresh leachable litterfall.

Differences in DOC concentration during recovery of the disturbed stream probably reflected differences in quantity, quality, and timing of allochthonous inputs.

Output of DOC based on two years of monthly sampling was reported for two watersheds of the Hubbard Brook Experimental Forest, New Hampshire (Hobbie and Likens 1973). One watershed drained a deciduous forest and the other had been cut 20 months before sampling began. Output of DOC was identical from each stream and averaged 10.3 Kg/ha/yr. Two year averages for WS2 and WS10 were 16.2 and 27.5 Kg/ha/yr, respectively. The summary of DOC output from smaller streams and rivers in North America reported by Moeller et al. (1979) ranged from 2.1 to 54.2 Kg/ha/yr.

Hobbie and Likens (1973) stated that since concentrations of DOC did not change appreciably with discharge or season, monthly sampling would not be much improved by increased sampling intensity. However, Manny and Wetzel (1973) concluded that DOC concentrations after an autumn rain were double the annual average. Mixing of low DOC subterranean ground water with variable but higher DOC water from subsurface run-off was suggested as the primary variable affecting DOC concentration. Our sampling schedule, which included measurement every third day between storms and every four hours during

spates, enabled evaluation of the errors of a less rigorous sampling frequency on estimates of DOC concentration and output.

DOC data from WS10, calendar year 1977, were recalculated for average DOC concentration and export using monthly discharge and the DOC value collected nearest the middle of the month. Export was estimated as 26.9 Kg/ha/yr and average annual concentration as 1.55 mg C/l. Values obtained using the complete data set were 43.2 Kg/ha/yr for export and 2.50 mg C/l for an average annual concentration. The 60% difference was primarily attributable to increased DOC concentrations during storms, particularly those following dry low flow periods.

Temporal variability in DOC concentration was closely linked to prior climatic conditions and streamflow (Figures 2, 3, and 10-12). Periods of low flow or following large storm events were characterized by low relatively invariant concentrations of DOC. For example, in late November and December 1977 (early in water year 1978) a series of large spates thoroughly flushed both WS2 and WS10 (Figure 3). Concentration of DOC remained low in both watersheds until small storms, following drier weather, occurred in late April (Figures 14 and 15). During summers, when little or no precipitation falls, DOC again was low and relatively constant. Baseline

levels of DOC in WS10 have averaged about 1.0 mg C/l higher than WS2. Logging residues, extensive exposure of unvegetated mineral soil, and increased erosional rates on WS10 were likely sources for the observed difference. Both streams responded to small storm events after dry low discharge periods with rapid increases in episodic pulses of high DOC concentration up to ten times baseline levels. Drought conditions in water year 1977 were punctuated by a number of low intensity storms (Figure 2). Each small increase in the hydrograph corresponded to increased concentrations of DOC, usually two to five times the levels between storms, until larger storms in late February and early March flushed out the readily leachable DOC fraction and no concentration changes accompanied higher streamflow. This pattern, whereby concentration changes in DOC occurred only when both increases in streamflow and a regenerated source of DOC in the watershed exists, resulted in poor correlation between DOC concentration and stream discharge. Instead, small and moderate size storms, preceded by dry spells and generally warmer temperatures, produced instream conditions with the greatest concentrations of soluble reduced carbon.

The role of these pulsed inputs of greater dissolved potential energy on the functioning of the aquatic ecosystem has not been investigated. Microbes may be a

primary food source for benthic organisms (Ward and Cummins 1979). Since the rate of microbial activity is related to the availability of energy in the ecosystem, periodic enrichment of streamwater during small storms may be an important factor in providing an energy base for higher trophic communities. The significance of such episodic increases of DOC depends upon the chemical nature of the added material. Lower baseline concentrations of DOC may well represent recalcitrant organic molecules insusceptible to microbial degradation by the soil microflora (Alexander 1975). Increased concentrations of DOC during storms could represent a flushing of recalcitrant organic material built up in the soil or a shunting of more labile material directly and more quickly to the stream from the litter layer and upper soil horizons. Whether higher DOC concentrations provide an increased supply of labile energy-rich compounds which stimulate stream microbial activity or simply represent a flushing of stored refractory material with little utilizable energy is not known. The possible link between temporal variability in DOC and measurements of microbial activity needs to be established.

DOC/DON Ratio

Water year 1978 provided an opportunity to compare

the integrated monthly concentration of DOC and DON in WS2 and WS10 (Figure 16). The ratio of DOC/DON in WS10 was 39, nearly half the ratio of 73 in WS2. Since average annual DOC concentrations in WS10 have been similar or higher than WS2, the reduced ratio resulted from greater DON in WS10. Ratios of DOC/DON never dropped below 50 in WS2 but were approximately 20 for seven of twelve months in WS10.

Differences in DOC/DON ratios in streamwater flowing from WS2 and WS10 may in part explain the greater nitrate production in the clearcut watershed. Coats et al. (1976) found that greater nitrification was correlated to lower C/N ratios. Jansson (1958) noted that the addition of carbonaceous material decreased nitrogen mineralization while the addition of highly nitrogenous compounds increased nitrification. WS2, with a continuous input of carbon-rich and nitrogen-poor litterfall, yielded streamwater with almost no NO_3 and higher DOC/DON ratios. WS10, with no litterfall input, contained much higher NO_3 values and a much lower DOC/DON ratio.

We hypothesize that clearcutting stimulates nitrification and produces the observed quantities and forms of instream dissolved N in two ways. First, clearcutting interrupts the input of fresh litter to the forest floor. The C/N ratio of litterfall in the coniferous forests of the Oregon Cascades is about 100

(Sollins et al. in press). Leaching and decomposition of this material releases labile dissolved organic compounds containing little N. Carbon oxidizing heterotrophic bacteria utilize this resource base, but concurrently place a high demand on all available N, organic and inorganic. Clearcutting effectively removes for a period of time the reduced energy normally supplied by fresh litterfall. Decomposition of logging residues, older litterfall, roots, and soil organic material continues, but the input eventually is reduced and the available dissolved compounds become more recalcitrant. This resource limitation reduces the activity and number of viable DOC and DON degrading heterotrophic bacteria. The NH_4 and DON escapes rapid uptake and utilization. Secondly, clearcutting removes plant root competition for NH_4 . Nitrifiers, which must compete in an old-growth forest with both roots and heterotrophic bacteria for NH_4 , suddenly are the beneficiaries of massive root death. Since in situ activities of nitrifiers are commonly limited by the production rate of ammonium (Alexander 1965), decreasing root competition favors increased NO_3 production. In the old-growth conifer system, root uptake and carbon oxidizing heterotrophic bacteria out-strip slower growing nitrifiers for the available NH_4 . In sites where slash is not burned, clearcutting first results in a lag period during which the sudden flux of

additional high C/N litter is metabolized by soil heterotrophs. Gradually, as the more easily decomposed slash is metabolized, heterotroph NH_4 demand is decreased. Nitrifiers then have a better competitive opportunity. This hypothesis does not support the contention of Rice and Pancholy (1972, 1973) that allelochemical inhibition from tannin buildup in climax ecosystems inhibits nitrification.

This hypothesized alteration of the microbial population and microbial activity could then be used to attempt to explain the observed differences in concentration and form of N and DOC in WS2 and WS10. Neither stream had elevated concentrations of NH_4 . Increased nitrification together with soil heterotrophs in WS10 could have prevented an increase of NH_4 to the stream after clearcutting. However, WS10, after a lag phase, began leaking NO_3 . Quantitatively, NO_3 input has increased steadily since clearcutting. Reestablishment of vegetation and new sources of litterfall are predicted to shut down gradually the leaching out of NO_3 from WS10. The pattern for DON is less distinctive, although WS10 displayed a concentration about double that of WS2 in water year 1978. A large fraction of the measured DON in both watersheds is likely to be refractory. A reduced population of heterotrophic bacteria in WS10, due to removal of the canopy, would have allowed an increase

in labile DON output to the stream. The magnitude of increase is not as great as for NO_3 but quantitatively was substantial. Losses of DON would also be predicted to diminish as revegetation occurred.

Meanwhile, concentrations of DOC showed only minor quantitative shifts. WS10 contained higher concentrations of DOC than WS2 in water year 1977, particularly during low discharge. Leaching and decomposition of the abundant slash, now one to two years old, could have generated the additional DOC. However by water year 1978, no difference in DOC concentration was observed between watersheds. The similarity in concentration of DOC between the logged and old-growth stream would be expected if much of the DOC entering both streams was composed of recalcitrant molecules insusceptible to microbial degradation (possibly derived from soil humus or wood). If the heterotrophic microbial flora of WS2 is effectively degrading all but refractory DOC, the average annual concentration of DOC primarily measured the recalcitrant material. Since primary production was catastrophically reduced by clearcutting, labile DOC entering WS10 was lowered and the average annual concentration dominated by recalcitrant compounds. Differential inputs of potential DOC sources in both watersheds were efficiently degraded to similar concentrations of DOC, probably composed of stable, refractory

compounds. Only during storm events, preceded by periods of lower discharge, were concentrations of DOC significantly elevated. The affect of these pulsed inputs of water with higher DOC, possibly composed partially of more labile energy-rich compounds on stream processes has not been investigated. Nor has the importance of canopy removal on the interaction of carbon oxidizing heterotrophs and nitrifiers been established. Both questions are linked to the quality and quantity of DOC in the watershed and stream. Impact on stream structure and function may be considerable and requires further consideration.

CONCLUSIONS

(1) A first-order stream, WS10, draining a recently clearcut coniferous forest quadrupled its average annual concentration of dissolved N during the second year after harvest. Third year levels remained about triple those of a nearby control stream, WS2, in an old-growth forest.

(2) Soluble N in WS2 and WS10 before clearcutting was dominated by organic N. Over 90% of dissolved N was in a reduced state. About 10% of the reduced N was NH_4 . Clearcutting increased the percentage NO_3 in solution from less than 10% to 44 and 38% in water years 1977 and 1978.

(3) Total export of dissolved N from the clearcut watershed has increased steadily each of the first three years following disturbance. Export reached 1.57 Kg N/ha/yr in water year 1978, nearly triple the value before harvest. Maximum export constituted about 0.03% total N capital per hectare. Inputs still exceeded stream export. Even following disturbance, WS10 tightly conserves elemental N.

(4) Increased NO_3 concentrations did not appear in WS10 during the first year after clearcutting. Most likely, either continued root activity, immobilization of NH_4 by heterotrophic bacteria decomposing the abundant fresh logging residues, or a combination of the two mechanisms delayed immediate NO_3 response.

(5) Instream primary production altered WS10 export

of nutrients. Seep concentrations of nitrogen, and to a lesser extent phosphorus, are decreased during transport downstream. Instream uptake is highest during summer low flow.

(6) Concentrations and export of total P and PO_4 over an annual cycle were unchanged after clearcutting. Climatic variations, such as the drought conditions of water year 1977, increased concentrations and decreased total export, but differential effects between the old-growth and clearcut watershed were undetectable.

(7) Phosphate in both streams remained relatively invariant, regardless of discharge or season. Soluble PO_4 appeared to be controlled by an equilibrium with aluminum minerals and possibly hydroxylapatite and organic matter in the soils and stream. Biotic regulation of PO_4 concentration was minimal.

(8) Export of DOC from WS10 was triple WS2 during the drought water year of 1977. Concentration of DOC also was significantly higher in WS10, particularly during reduced flow. Decomposition of abundant slash left after logging is suggested as the additional source. In water year 1978, the third year after cutting, concentrations of DOC were approximately equal in both watersheds. Export was slightly higher in WS10, reflecting higher water yield from the clearcut watershed.

(9) The average annual ratio of DOC/DON in

streamwater from WS10 was consistently 50% lower than that in WS2. The lower ratio is primarily due to increased DON, rather than decreased DOC. It is hypothesized that the lower ratio occurs because of decreased heterotrophic bacterial activity in the forest floor. Elimination of fresh litterfall after clearcutting temporarily removes a major food base to the heterotrophs and populations decline. Less of the available DON is immobilized by soil heterotrophs and more enters the stream. The decreased competition from carbon oxidizing heterotrophic bacteria and elimination of root uptake could also provide increased NH_4 availability and promote greater nitrification.

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Table 1. Average annual concentration and output of total dissolved phosphorus (TDP), inorganic phosphate ($\text{PO}_4 - \text{P}$), and organic phosphorus (by difference) in WS2 and WS10 is given for water years 1974 - 1978.

Water Year	Stream	Discharge (Km ³)	TDP	PO ₄ -P (µg P/l)	Org P	TDP (Kg P/ha/yr)	PO ₄ -P (Kg P/ha/yr)	Org P
1974	WS10	.23	58	36	22	1.31	0.80	0.51
1975	WS10	.15	88	50	38	1.31	0.76	0.55
1976	WS10	.20	52	35	17	1.00	0.67	0.33
1977	WS10	.08	49	27	22	0.37	0.20	0.17
1978	WS10	.19	72	35	37	1.33	0.65	0.68
1977	WS2	.22	37	23	14	0.14	0.08	0.06
1978	WS2	.86	65	22	43	0.93	0.32	0.61

Table 2. Average annual concentration and output of total dissolved nitrogen (TDN), reduced nitrogen (RN), nitrate (NO₃), ammonia (NH₄), and dissolved organic nitrogen (DON) in WS2 and WS10 is given for water years 1974 - 1978. Reduced N is NH₄ plus DON. DON is calculated by difference.

Water Year	Stream Discharge (Km ³)	TDN	RN	NO ₃ (µg N/l)	NH ₄	DON	TDN	RN	NO ₃	NH ₄	DON
							(Kg N/ha/yr)				
1974	WS10	.23	.026	.025	.001	-	.58	.57	.01	-	-
1975	WS10	.15	.044	.043	.001	-	.65	.64	.01	-	-
1976	WS10	.20	.049	.047	.002	-	.93	.90	.03	-	-
1977	WS10	.08	.140	.078	.062	-	1.06	.59	.47	-	-
1978	WS10	.19	.085	.053	.032	.004	1.57	.97	.60	.08	.89
1977	WS2	.22	.055	.051	.004	-	.20	.19	.01	-	-
1978	WS2	.86	.031	.028	.003	.003	.44	.39	.05	.05	.34

Table 3. Average seasonal and annual concentration and output of DOC in WS2 and WS10 during water years 1977 - 1978 is given.

Water Year	Stream	Dis-charge (Km ³)	Average Concentration (mg C/l)					Export (Kg C/ha)				
			F	W	Sp	Su	Total	F	W	Sp	Su	Total
1977	WS10	.08	1.64*	2.89	2.59	5.19	2.74	2.1*	10.9	5.2	2.4	20.6
1978	WS10	.19	2.23	1.02	1.76†	2.57†	1.87	24.7	4.8	3.6†	1.3†	34.4
1977	WS2	.22	1.72*	1.93	1.56	3.58	1.92	0.4*	3.4	2.2	1.1	7.1
1978	WS2	.86	1.73	1.62	2.22†	2.54†	1.77	14.9	6.2	3.1†	1.0†	25.2

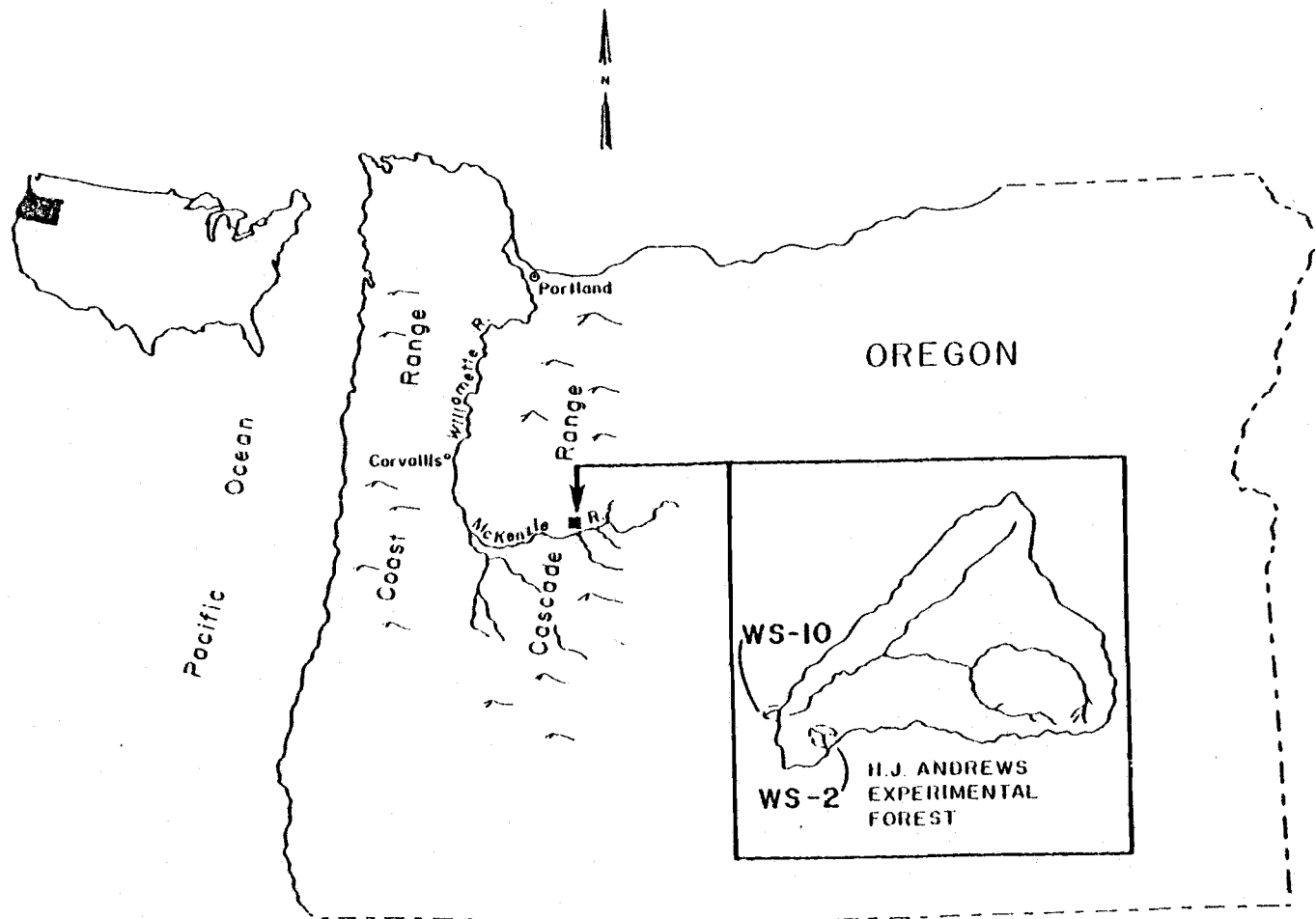
† Based on samples collected every third week after April 26, 1978.

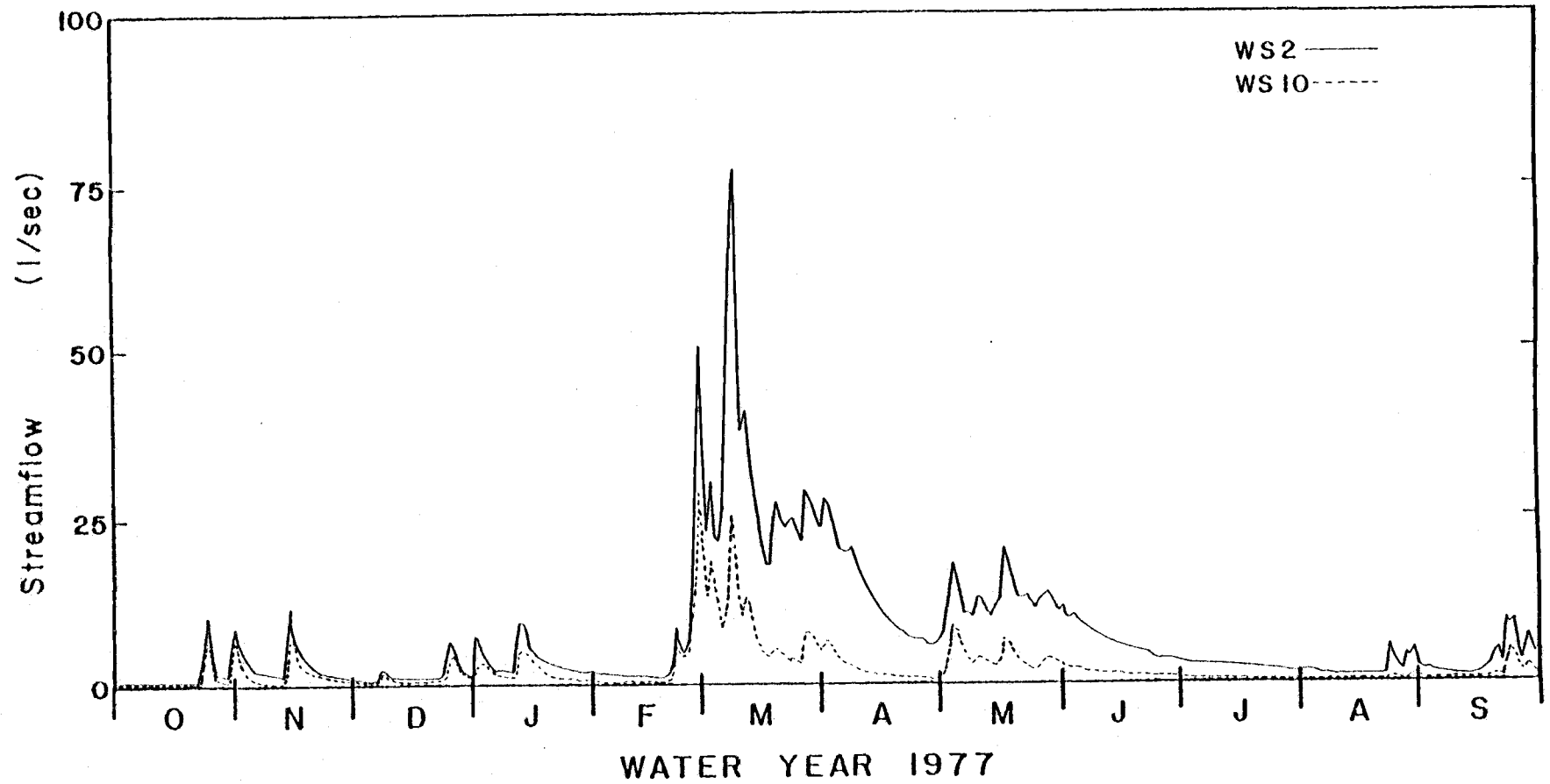
* Based on samples collected starting November 22, 1976.

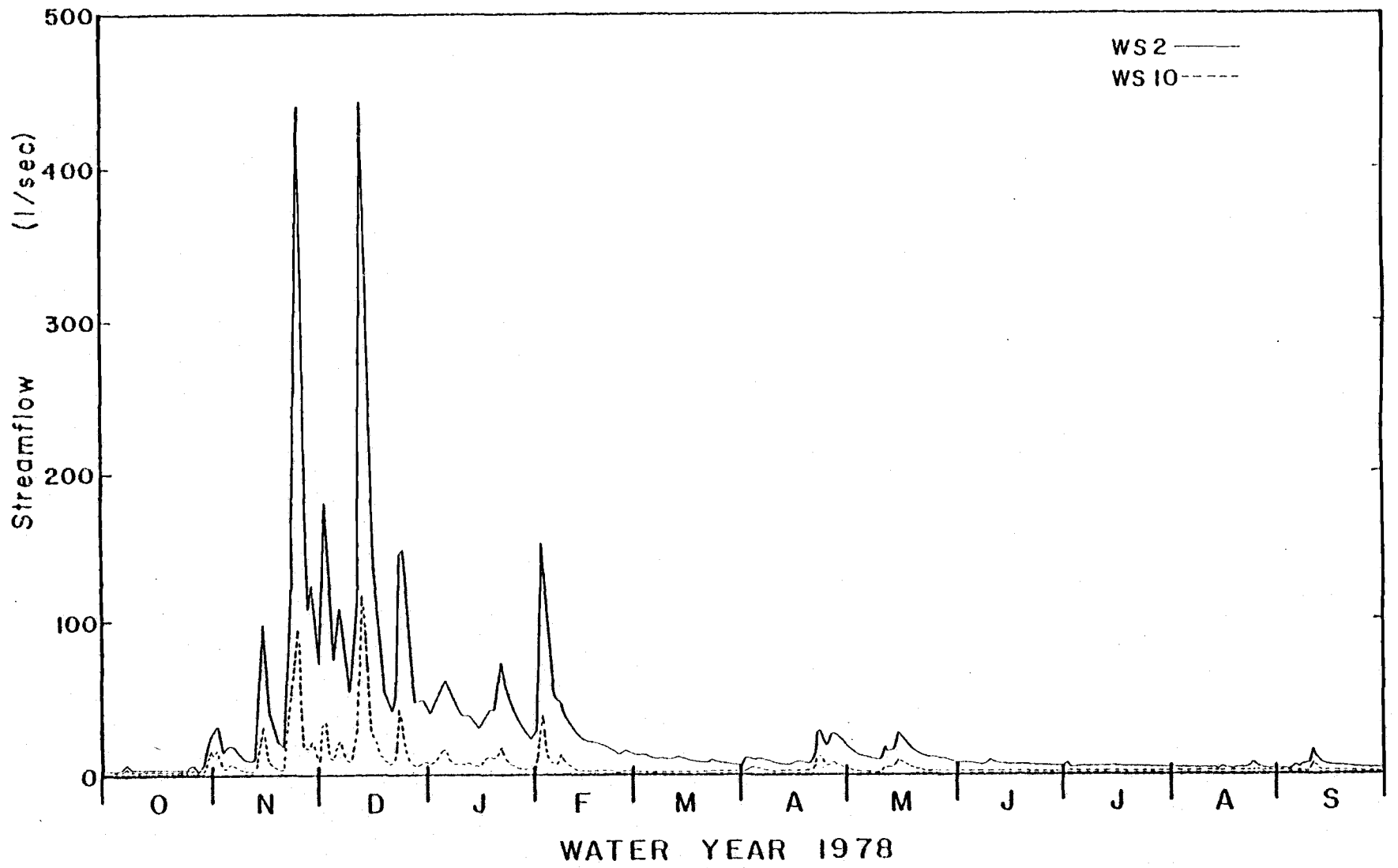
FIGURE LEGENDS

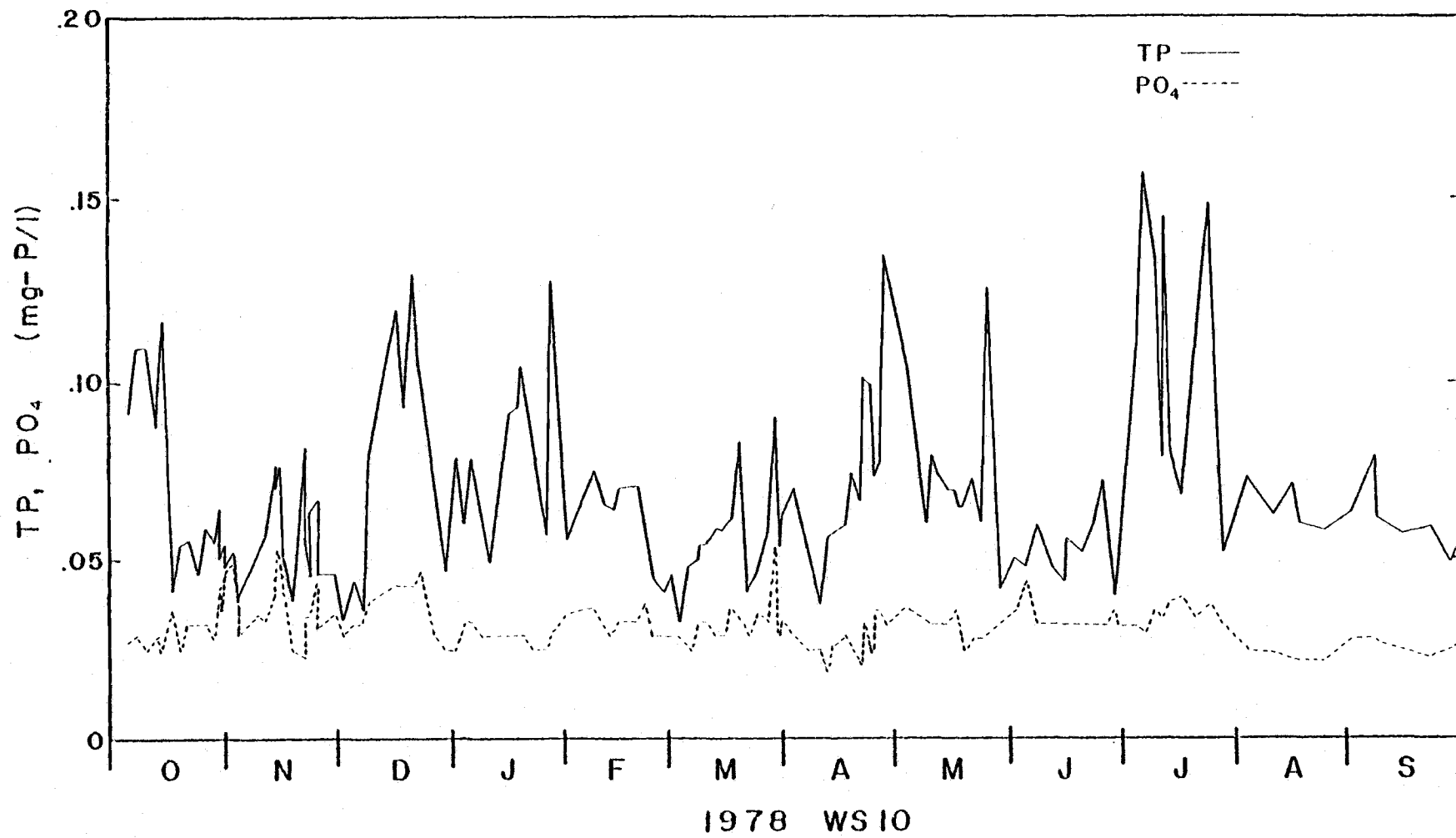
- Figure 1. Location of WS2 and WS10 in the H.J Andrews Experimental Forest in the Cascade Range of Oregon, USA.
- Figure 2. Streamflow in WS2 and WS10 during water year 1977.
- Figure 3. Streamflow in WS2 and WS10 during water year 1978. Note the change in scale for streamflow as more normal discharge patterns followed a drought year.
- Figure 4. Concentration of dissolved total phosphorus (TP) and phosphate (PO_4) in mg P/l in WS10 during water year 1978.
- Figure 5. Concentration of dissolved total phosphorus (TP) and phosphate (PO_4) in mg P/l in WS2 during water year 1978.
- Figure 6. Concentration of dissolved reduced nitrogen (RN) and nitrate (NO_3) in mg N/l in WS10 during water year 1977.
- Figure 7. Concentration of dissolved reduced nitrogen (RN) and nitrate (NO_3) in mg N/l in WS2 during water year 1977.
- Figure 8. Concentration of dissolved reduced nitrogen (RN), nitrate (NO_3) and ammonium (NH_4) in mg N/l in WS10 during water year 1978.

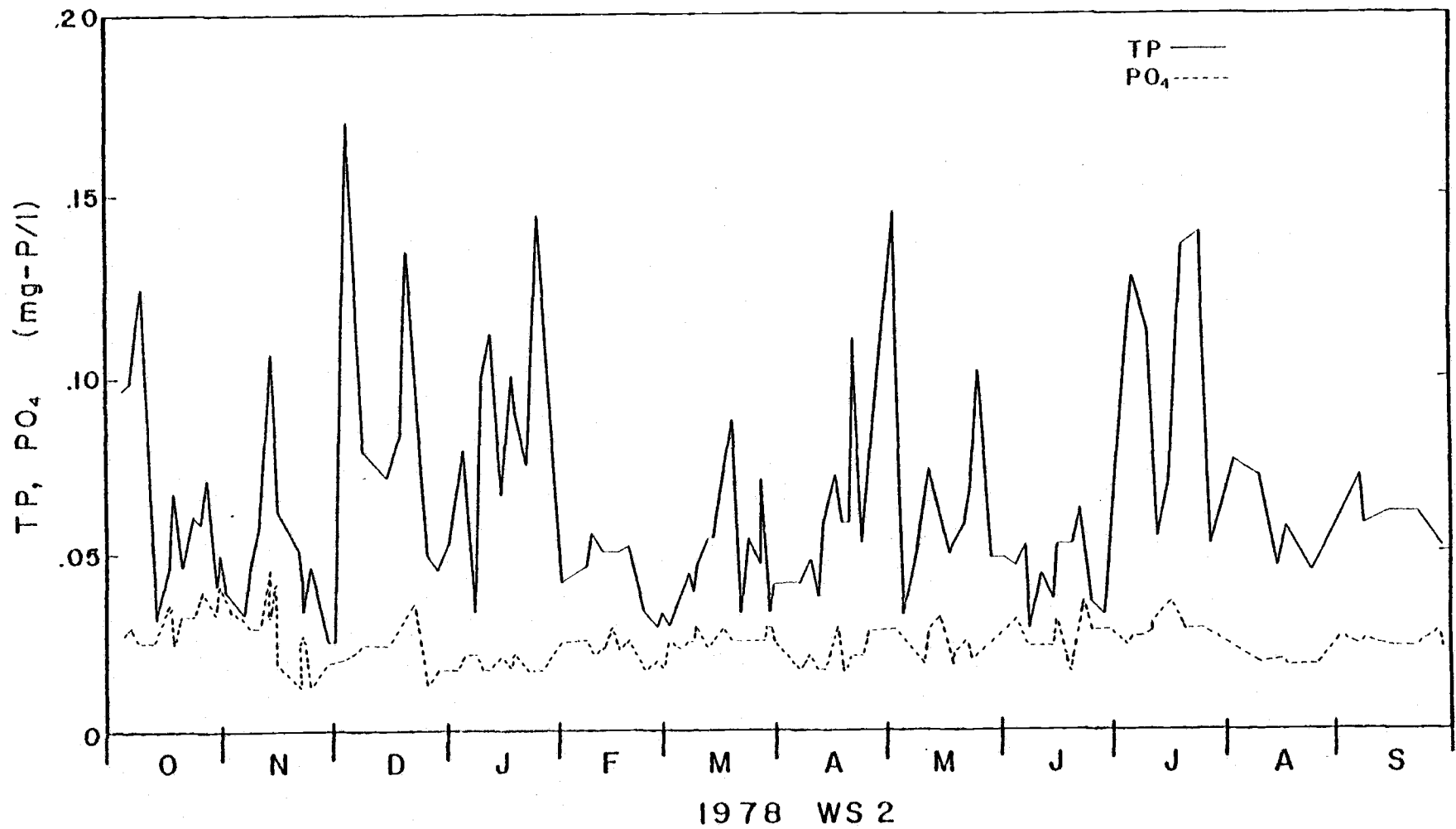
- Figure 9. Concentration of dissolved reduced nitrogen (RN), nitrate (NO_3), and ammonium (NH_4) in mg N/l in WS2 during water year 1978.
- Figure 10. Concentration of dissolved organic nitrogen (DON) in mg N/l in WS10 during water year 1978. DON is obtained by difference between reduced nitrogen (RN) and ammonium (NH_4).
- Figure 11. Concentration of dissolved organic nitrogen (DON) in mg N/l in WS2 during water year 1978. DON is obtained by difference between reduced nitrogen (RN) and ammonium (NH_4).
- Figure 12. Dissolved organic carbon (DOC) concentration in mg C/l in WS10 during water year 1977.
- Figure 13. Dissolved organic carbon (DOC) concentration in mg C/l in WS2 during water year 1977.
- Figure 14. Dissolved organic carbon (DOC) concentration in mg C/l in WS10 during water year 1978.
- Figure 15. Dissolved organic carbon (DOC) concentration in mg C/l in WS2 during water year 1978.
- Figure 16. Ratio of DOC/DON in WS2 and WS10 obtained by dividing average monthly export of DOC and DON. Average monthly export was estimated from grab samples and daily discharge.

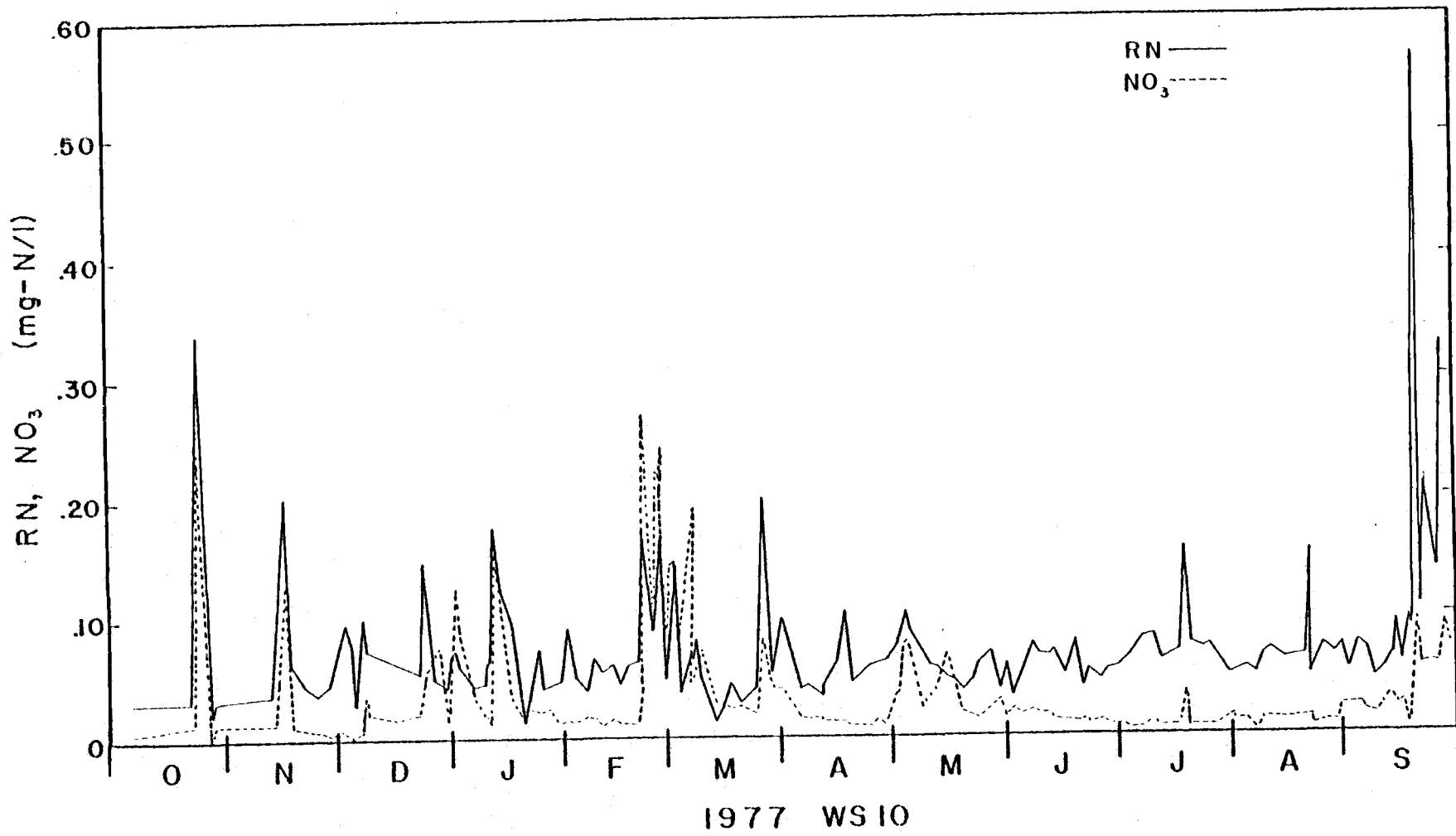


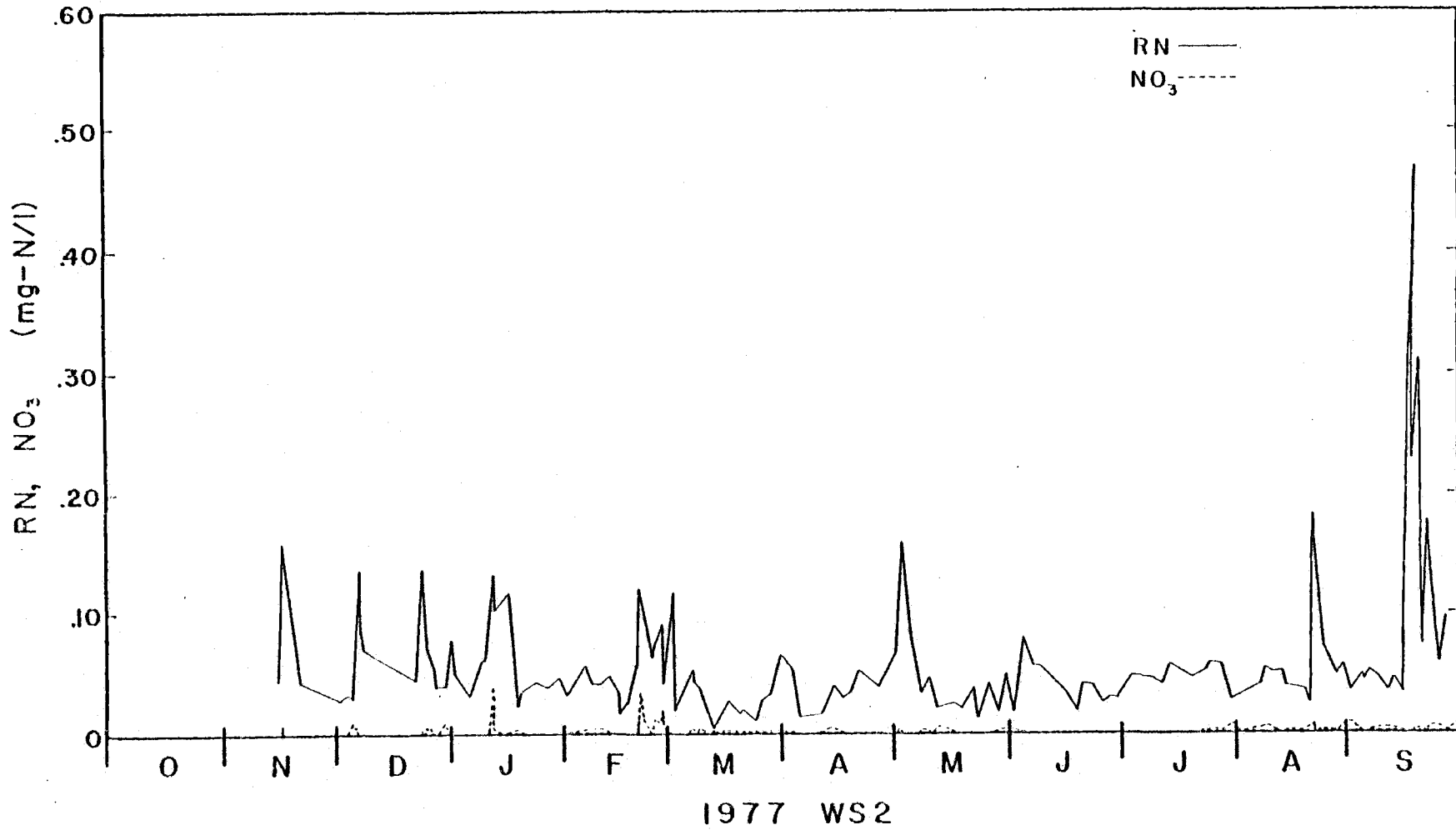


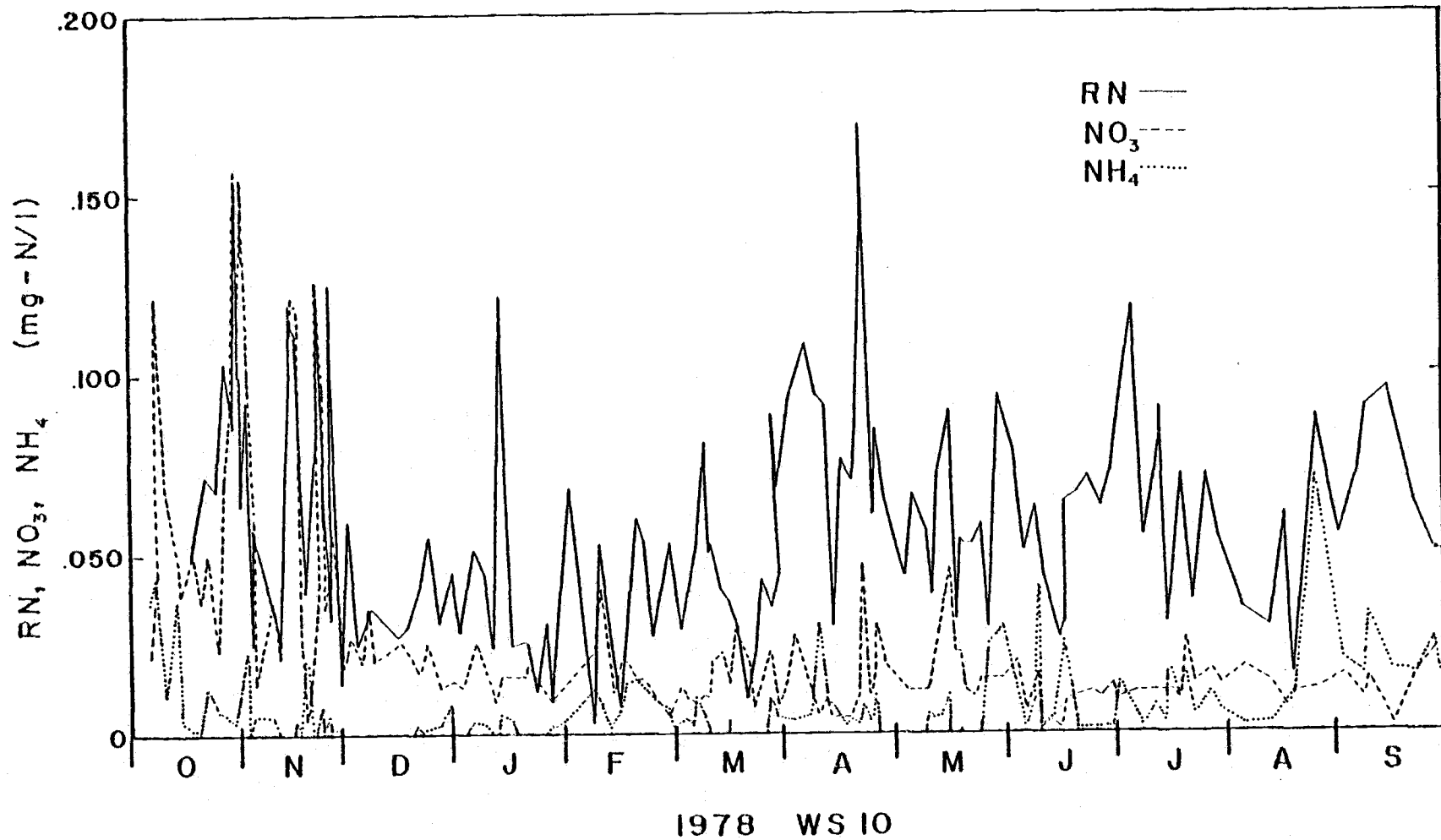


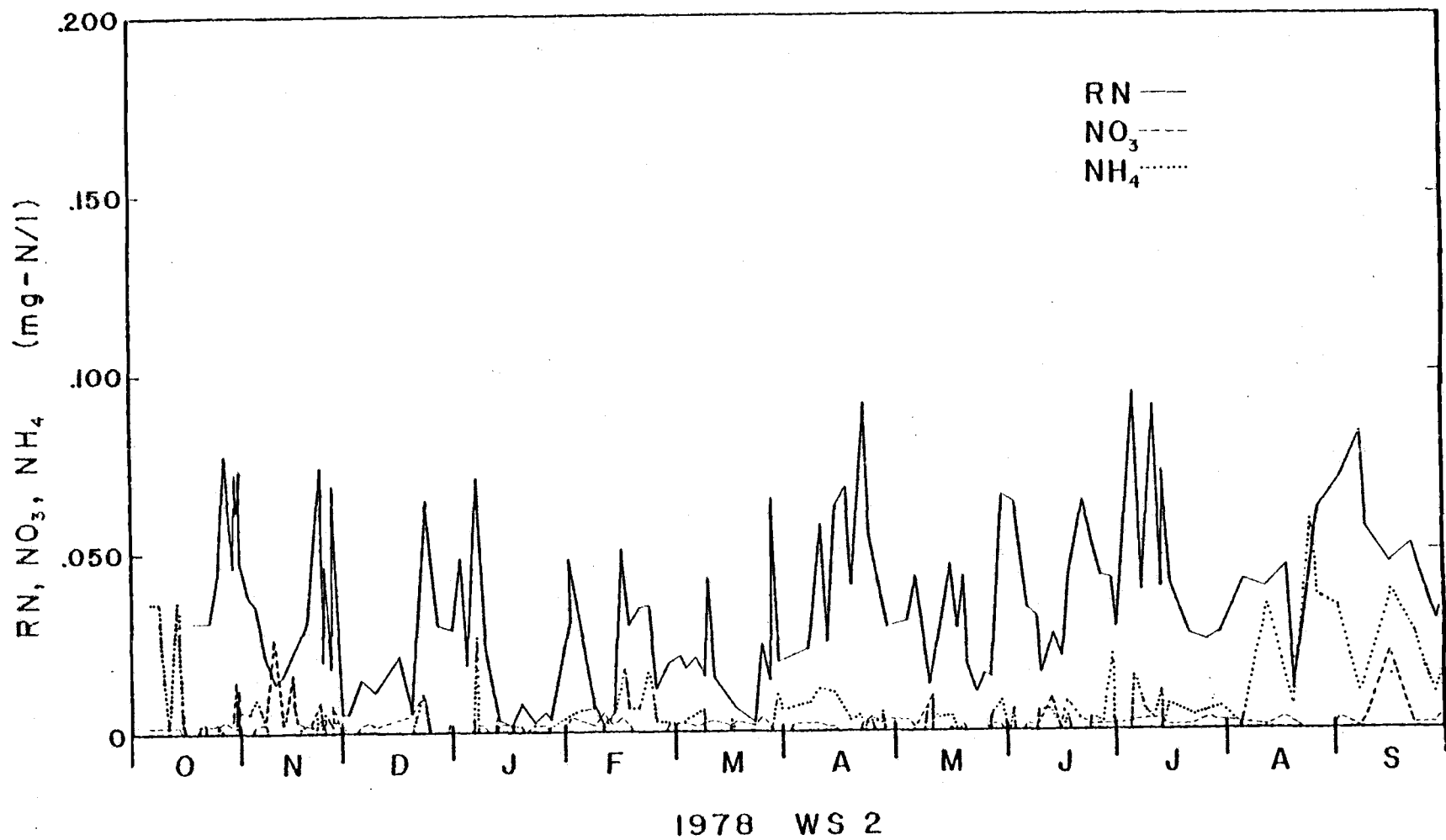


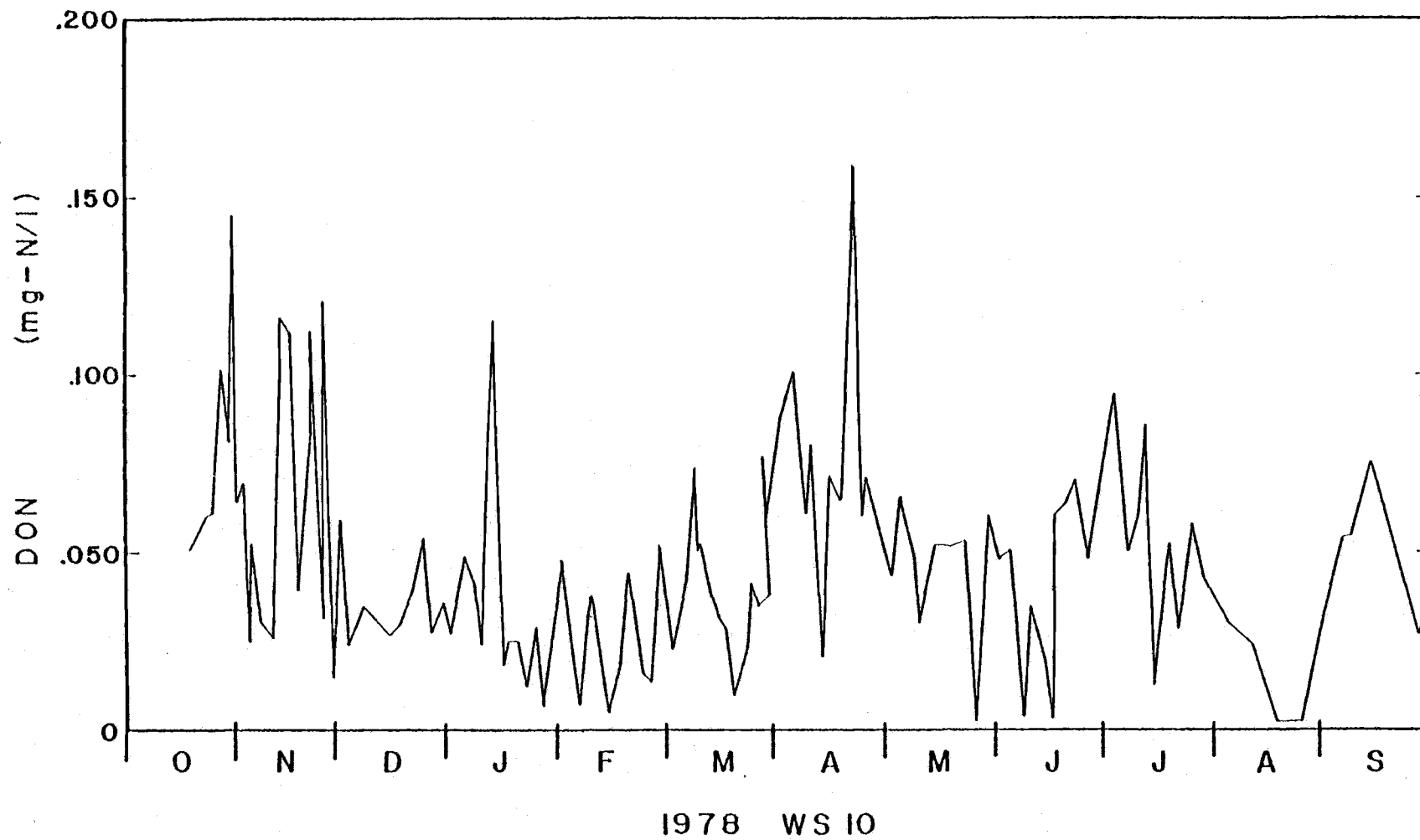


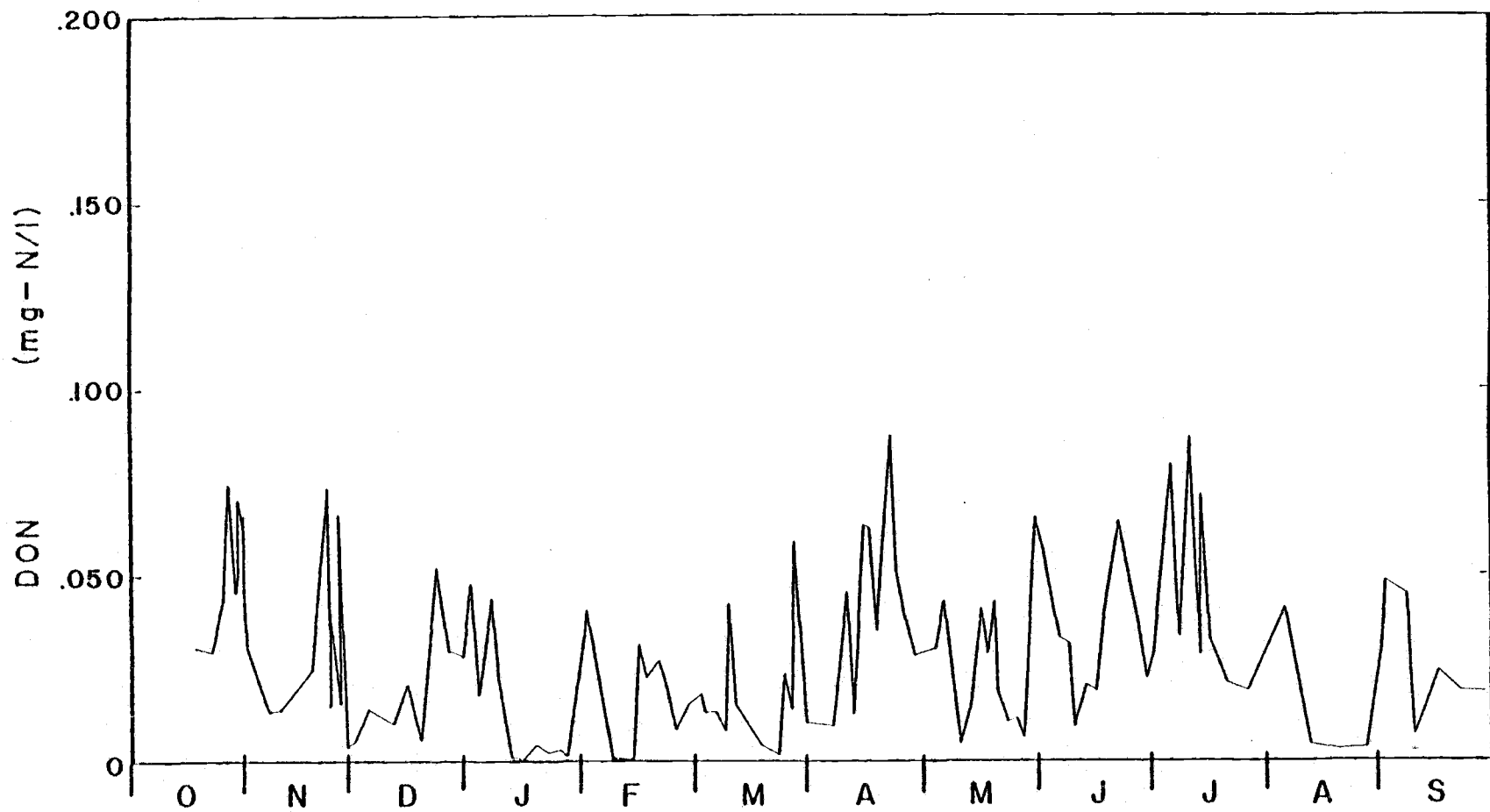












1978 WS 2

