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STREAM ORGANICS TO
EVALUATE LAND MANAGEMENT

Technical Completion Report

Project No. 3109-146
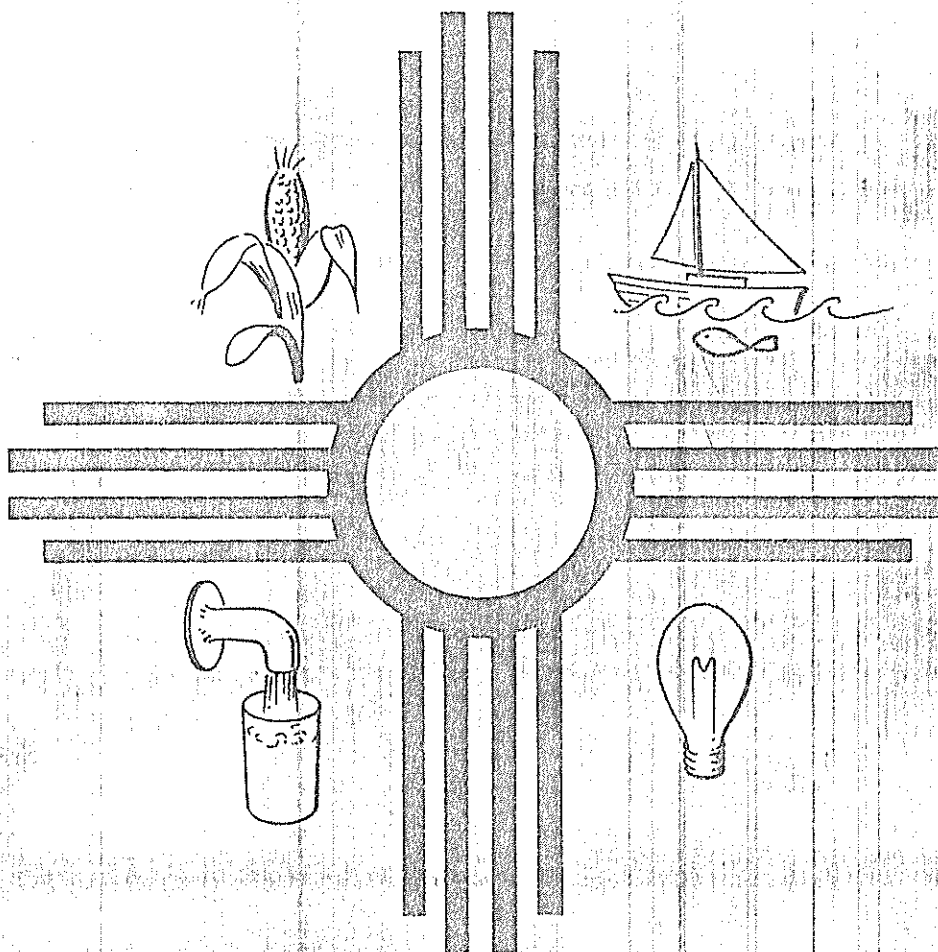
New Mexico Water Resources Research Institute

STREAM ORGANICS TO EVALUATE

LAND MANAGEMENT

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ABSTRACT

The type and amount of organic matter, particulate and dissolved, present in surface water has a very real effect upon the ecological status of the stream itself as well as downstream ecosystems. The objectives of this study were to evaluate the quantity of certain N and C compounds in stream water from 4 communities; pine and juniper, mixed conifer, spruce and fir, and aspen. These studies were performed on gauged watersheds to calculate absolute quantities. Significant differences were found between the streams of different vegetational communities. Concentrations of inorganic N and dissolved C compounds were highest in the stream water of the mixed conifer community. For each community the highest concentrations of all compounds occurred during the high stream discharge following snow melt. Concentrations of tannin and lignin also were highest in the mixed conifer community while phenol concentrations were high in both the mixed conifer and aspen communities. A number of factors are involved including organic matter accumulation, decomposition rates, plant tissue composition, evapotranspiration, and stream discharge.

ACKNOWLEDGEMENTS

INTRODUCTION

The type and amount of organic matter, particulate and dissolved, present in surface water has a very real effect upon the ecological status of the stream itself as well as downstream ecosystems. Effects are varied ranging from increasing soil fertility by release of phosphates (Johnston 1956, 1959), potassium and trace elements (Henderson and Duff 1963) to very detrimental effects such as: inhibition of root growth by lignin degradation products (Borner 1955, 1956, Prill et al. 1949), inhibition of nitrification by mercapto compounds (Frederick et al. 1957), fouling commercial anion-exchangers used to treat surface water (Frisch and Kunin 1960), a source of carcenogenic hydrocarbons (Borneff and Fisher 1961), and unpleasant discoloration by "yellow organics" (Shapiro 1957, Lamar and Goerlitz 1966, Christman 1970). The macromolecular nature of the yellow organics remains speculative but the phenolic nature has been well established.

Organic acids, both aromatic and aliphatic, are prominent in soils and surface waters as a result of plant exudates and plant tissue decomposition. The most prominent among the phenolic acids are p-hydroxybenzoic, vanillic, ferulic, and p-coumaric; among the aliphatics, acetic, formic, succinic, butyric, oxalic, and malic. These acids are strongly linked to bacterial action (Wang et al. 1967). Phenolic acids and organic acids, in general, are normal components of soil and surface waters, however, bacterial transformations prevent their accumulation beyond a steady-state level. The equilibrium level of low molecular-weight

organic acids in the soil solution is likely to be highest when plant residues are undergoing active decomposition (Stevenson 1968). This level is a characteristic of the vegetation community. Management operations are known to alter decomposition processes and may affect the quantity and type of organics in the soil and entering surface water. If accumulation in soil or surface water does occur these compounds exert their growth-inhibitory properties in many ways (Lingspysa and Lackwood 1962, Borner 1955, 1956, Prill et al. 1949). Concentrations as low as 10 ppm for synthetic p-hydroxybenzoic, ferulic, and p-coumaric acids caused inhibitory effects on rye and wheat root growth. Federal safety standards for drinking water report a recommended maximum limit of 0.001 mg/l for phenols as of 1961 (Public Health Service Drinking Water Standards 1961). McGauhey (1968) reports work by W. Alexander on toxicity levels of phenols on fish. A lethal dose for perch is 9 mg/l with an exposure time of one hour; the lethal dose for rainbow trout is 6 mg/l with an exposure time of 3 hours.

Studies of organics in surface water normally are concerned only with concentrations. Studies of organics in the surface water of a gauged watershed are non-existent. We feel studies of organics on gauged watersheds are extremely important in that it is possible to calculate total organic output (i.e. concentration times stream discharge). This data will allow us to evaluate not only the quantities of various organics from individual vegetation communities but the total quantity delivered to downstream ecosystems.

OBJECTIVES

The original objectives of this study were to: 1) evaluate the quantity and quality of organics in surface water from different vegetation types on the Tesuque Watersheds in the Sangre de Cristo Mountains; and 2) evaluate any change in surface water organics as a result of watershed management procedures. The management activity originally identified in this study was a light thinning (25%) in aspen vegetation by the Forest Service to increase water yield. The thinning was not performed during the fall of 1973 as originally planned, therefore, conclusions cannot be made regarding this practice. This report will deal primarily with the organics in streams from natural vegetation types.

PROCEDURES

The research was performed on the Tesuque watersheds in the Sangre de Cristo Mountains of New Mexico (Figure 1). These watersheds are gauged and except for a small aspen watershed, have about 10 years of calibration data. The aspen watershed (3.4 ha) was gauged in 1973. The study area covers an elevational gradient of 1310 m (2423 m - 3734 m) and a number of vegetation communities. Four watersheds were studied for stream organics which represent 4 distinct vegetation communities (Table 1).

Organic Carbon

Organic carbon was analyzed by the wet dichromate oxidation procedure of Maciolek (1962). Biweekly or monthly stream samples were collected from each watershed and refrigerated ($2^{o}C$) until analysis, usually within 48 hours. Analyses were made on the
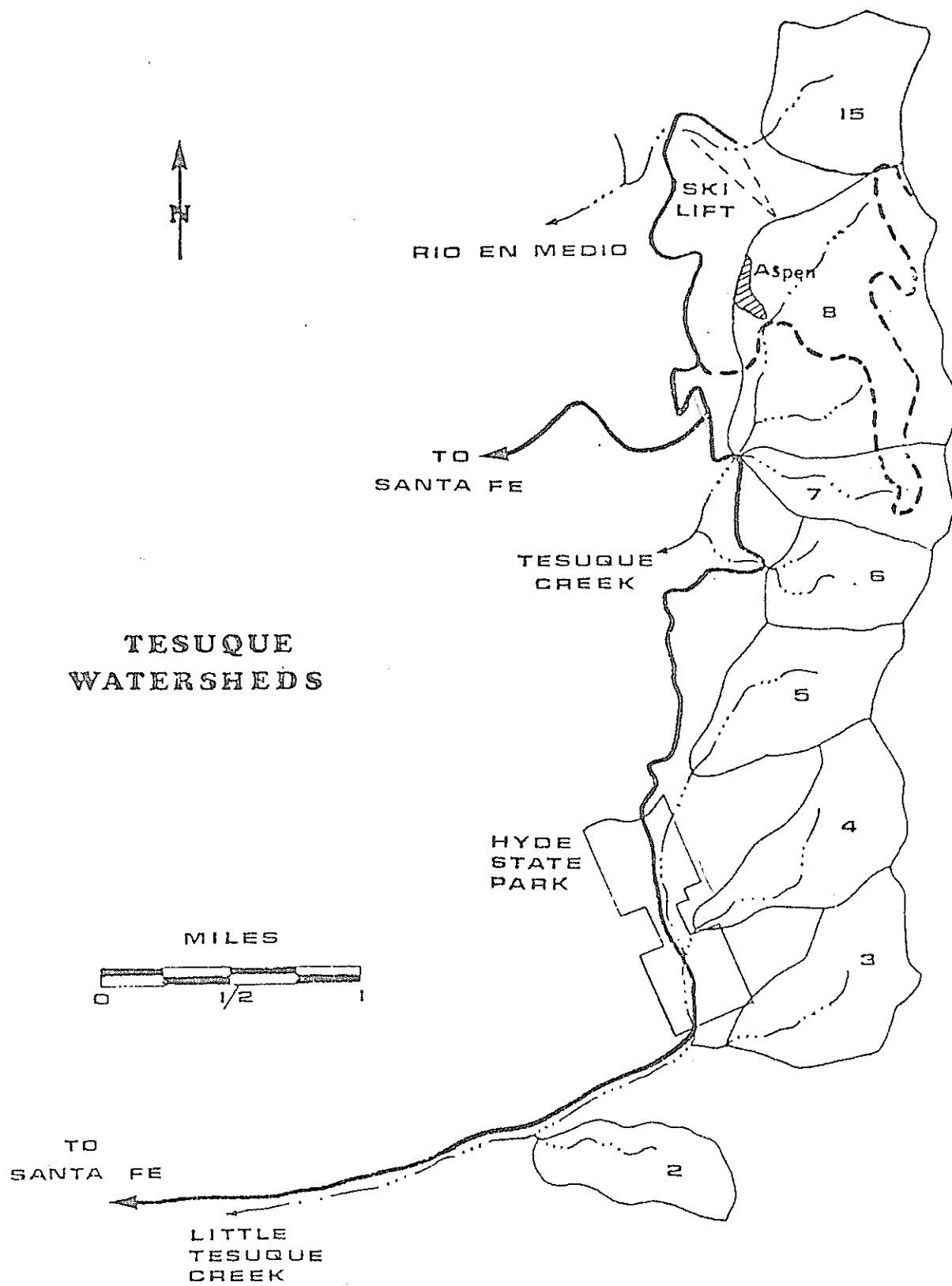
Figure 1. Tesuque Watershed Study Area. All watersheds
are gauged.

Table 1. Characteristics of study watersheds; elevation, vegetation, stream discharge, evapotranspiration

| | Watershed | | | |
Item	2	4	Aspen-1	15
Elevation (m)				
maximum	2850	3383	3232	3734
minimum	2423	2621	3110	3231
Vegetation (ha)				
pinon-juniper	10	0	0	0
pine	106	0	0	0
mixed conifer	0	100	0	0
aspen	0	0	3.4	0
spruce-fir	0	80	0	123
subalpine grassland	0	0	0	40
total (ha)	116	180	3.4	163
Runoff (cm)				
1973-74 water year	0.96	2.74	18.86	27.94
Evapotranspiration (cm)				
1973-74 water year	59.5	44.6	30.5	30.5

sample for total carbon and dissolved carbon. Dissolved carbon analyses were made on a sample after filtering with a 0.45 u Millipore filter. Particulate carbon was assumed to be equal to the difference between dissolved and total carbon.

Total Nitrogen

Inorganic ammonia nitrogen (NH_4^+) was analyzed by distillation and Nesslerization (Standard Methods 1971). Nitrate nitrogen (NO_3^-) was analyzed by the ultraviolet procedure (Standard Methods 1971). Total nitrogen was analyzed by the micro-kjedhal procedure of McKenzie and Wallace (1954). Organic nitrogen (NH_3) was calculated by subtracting inorganic NH_4^+-N from the total N analysis.

Stream Organics

Phenols:

Phenol activity in natural and domestic water supplies could be reduced by such interfering agents as chlorine, a strong oxidizing agent, alkaline pH, phenol decomposing bacteria and enzymes released by these organisms. This requires that a procedure for preservation be used. Initially we used the procedure outlined by EPA in Standard Methods of Water Analysis, however, chlorine is probably not present in these natural waters in high concentrations and the use of the strong reducing agents sodium arsenite and ferrous sulfate were unnecessary. Further, it was found that ferrous sulfate reacts with chlorine to give ferrous chloride and this reacts irreversibly with phenols to give a colored complex and thus destroying the phenol. In our procedure phosphoric acid was added to take care of alkaline pH. The preservation procedure adapted was a combination of recommendations

from EPA and personal communication with Dr. R. Cooper, University of New Mexico. All sample bottles were washed with sulfuric acid-dichromate solution and rinsed with demineralized water. One ml of 1:9 H_3PO_4 (A.R.) was added to each 100 ml of sample collected. The bottles were filled completely to eliminate oxygen. They were capped tightly and shaken to distribute the H_3PO_4. All samples were stored in the dark and kept chilled until analysis was begun. Dark storage prevents photo-oxidation of the organic constituents. It was found that samples should be processed within 5 days of collection.

Phenolic compounds of surface waters normally are analyzed using the 4-aminoantipyrine colorimetric method (EPA 1971). This assay is based on the reaction of 4-aminoantipyrine and a phenolic compound in the presence of potassium ferricyanide at pH 10.2.
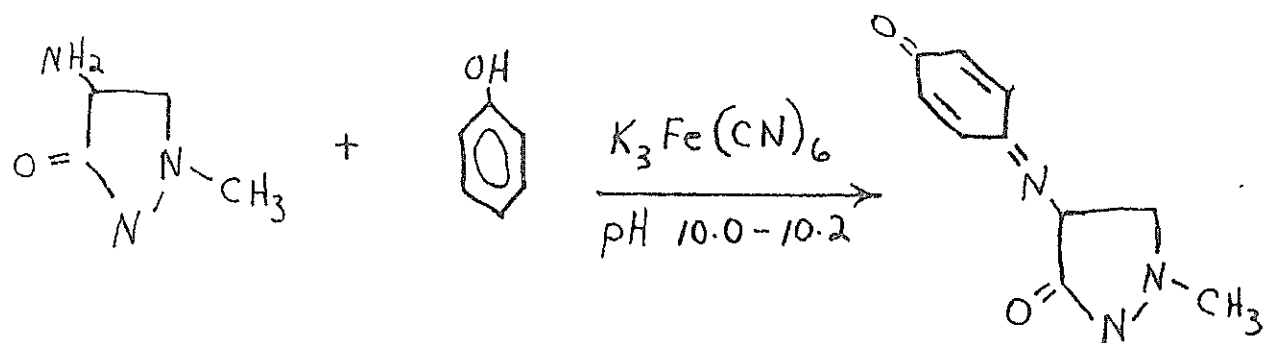
Additional research on this method of determining phenolic acid concentrations revealed that although the method is highly specific and sensitive (0 - 100 ppb) it has severe limitations when applied to natural waters for two reasons: The 4-amino-antipyrine complex occurs only with phenolic compounds in which the para position is not blocked by an aryl, alkyl, nitro,

benzoyl, nitraso on carbonyl group (i.e. in general the para substituted phenols don't react), and substituted phenols that do react have different molar absorbitivities (ϵ) than the unsubstituted phenol which is normally used as the standard. Tests of the absorbtivity (ϵ) for ortho and para substituted phenols demonstrated that standard procedures yield concentration readings lower than the actual concentration of test samples. For these reasons concentrations reported in this study under-estimate actual concentrations.

Tannins and Lignins:

Tannins and lignins are by-products of biological oxidation of plant tissue. A routine analysis for tannins and lignins developed by the Hach Chemical Co. was used for analysis in this laboratory. The procedure used is restricted to 0 - 15 mg/l of tannin and lignin read as tannic acid. All turbid samples were filtered through Hach paper #1894-57 prior to analysis.

Specific Phenols:

In addition to preservation with H_3PO_4, water samples were concentrated to be able to identify specific phenols. The freeze concentration procedure of Shapiro (1961) was the method chosen. For our system we used a 5.0 gallon lined stainless steel can with 3/4 inch styrofoam tops, variable speed motor with rheastatic control, nalgene stirring rods, a chest freezer (2 x 6 ft) and a 2 inch thick styrafoam cover for the freezer. Maximum sample size was 18 1; this allowed for expansion as freezing took place in the can. The motor speed was adjusted to a rate that just prevented splashing. The freeze-out took about 60-70 hours. Quantitative

freeze concentrations of phenol and some substituted phenols were made in order to determine the efficiency of the process. Concentrations used for this test were similar to those found in stream water during the year. The cone of concentrated water was collected and brought to volume and developed with 4-aminoantipyrene. The recovery efficiency for phenol was 80%.

The analysis for specific phenols followed procedures out-lined by Hathway (1960) and Whitehead (1964). As stated in the introduction we were interested in studying vanillic, syringic, p-coumaric, p-hydroxybenzoic and ferulic acids. We attempted to isolate, characterize, and semiquantitatively assess these 5 phenolic acids. The procedures just mentioned were developed for analysis of phenolic compounds in plants and soil hence the applicability of the procedures to phenolic compounds in surface waters was unknown.

For the isolation procedures we used 15-20l of water and the results indicate that a larger quantity should have been used. Samples were preserved with 1:9 H_3PO_4 (1 ml/100 ml of sample) and freeze concentrated to small volumes. This concentrated water sample was extracted with organic solvents, reduced in volume again and applied to Whatman No. 1 chromatographic paper for descending chromatography. The paper was dried and the colorimetric assay used required spraying the plates with p-nitroaniline diazoacelate and developing with 1.0 M NaOH. By the use of standard compounds the level of detection by this colorimetric assay was shown to be approximately 5 ug. When the 5 phenols were mixed, applied as a single spot on the paper and developed in isopropanol/ammonia/water (10:1:1) for 22 hours at $22^{\circ}C$, there was sufficient separation

that each phenol could be identified. Starting at the origin and progressing to the solvent front the phenols appeared in the order syringic, vanillic, ferulic, p-hydroxybenzoic, and coumaric.

Watersheds 15 and 4 showed trace amounts of phenolic compounds when analyzed by the above methods. A problem with the method was apparent when stream water samples were used because of a large residue which formed at the origin of the chromatagraphic paper. The color development of this residue showed that phenols were contained within the residue. Using the solvent system of butanol, pyridene and water we were still not successful in obtaining a separation of the acids of interest. Color development still showed some trace of the acids at the origin, however. The yellow residue was probably a mixture of organic compounds and these could be responsible for binding the phenols in a complex that is not soluble in the solvent systems used. From cation analyses on stream water we know that Ca^{++} and Mg^{++} concentrations are high and might very well be responsible for the complexes formed during the freeze concentration process. Our approach to this problem for future research would be to dialyze the stream sample before starting the concentrating procedure or if the volume prohibits this then at least dialyze at some point before concentration is complete.

Using IR, NMR and UV data we hoped to confirm our hypothesis on the nature of the compounds. The scan from IR indicated phenols were present which supports our analyses using the 4-aminoantipyrine colorimetric method. There was insufficient material for NMR analysis.

Using Bio-gel columns which separate by molecular weight

Table 2. Weighted average concentrations (mg/1) of N and C for 4 study watersheds during the period October 1973-September 1974. The ratios of inorganic N/organic N and dissolved C/particulate C reflect differences in decomposition rates.

	Watershed			
	2	4	Aspen-1	15
NH_4-N	0.31	0.40	0.18	0.13
NO_3-N	0.56	1.02	0.46	0.30
Org. N	0.040	0.035	0.200	0.130
Diss. C	4.23	5.96	2.16	0.87
Part. C	0.44	0.57	0.25	0.24
$\dfrac{\text{Inorg N}}{\text{Org N}}$	21.75	40.57	3.20	3.31
$\dfrac{\text{Diss C}}{\text{Part C}}$	9.61	10.46	8.64	3.62

we found that compounds are in fact complexed. The yellow acids
recovered from watershed 4 stream water and run on the Bio-gel
columns averaged 200,000 in molecular weight. This indicates a
significant amount of complexing.

Because of the difficulty in developing analyses for specific
phenols there was insufficient time to analyze for xanthones,
flavonoids, and heavy metal content of the organics as originally
outlined.

RESULTS AND DISCUSSION

The research involved the analysis of levels of several
organic compounds, carbon, and nitrogen in stream water from a
number of gauged watersheds having different vegetational communities.
Microbial populations and decomposition rates were expected to be
different in these communities as well as the quality and quantity
of organics in the stream water.

In terms of carbon and nitrogen, water quality differs in
each of the watersheds as shown in Table 2. Since the discharge
rate affects concentrations the data are presented as weighted
average concentrations. A significant feature of table 2 is the
higher concentrations of inorganic nitrogen and carbon in the
stream water draining mixed conifer vegetation (W-4). This is
significant since we would expect higher rates of decomposition
in this vegetation type because of higher productivity and more
favorable moisture and temperature conditions (Gosz 1975).
Faster rates of decomposition combined with greater productivity
should cause higher mineralization rates and an increased potential

for the loss of soluble material to drainage streams. The ratios
of inorganic N/organic N and dissolved C/particulate C in table
2 support this view. The drainage water of mixed conifer
vegetation has higher concentrations of inorganic N (NH_4^+, NO_3^-)
and dissolved C than of organic N or particulate C relative to
other vegetation types. Presumeably this occurs as a result of
more rapid and complete decomposition processes. The influence
of different discharge rates on loss as well as nutrient recycling
efficiency will be discussed later in this report.

The conclusion that the fastest decomposition rates occur
in mixed conifer vegetation seems logical when considering the
climax coniferous communities of the area (i.e. pinon-juniper,
pine, mixed conifer, spruce-fir). Aspen vegetation, a successional
species, might be an exception since the higher base element
content of deciduous vegetation normally allows rapid decomposition
(Gosz et al. 1973, Thomas 1970). The thin layer of organic matter
on soil under aspen vegetation might be viewed as evidence
supporting rapid decomposition in this community. Other factors
such as litter fall and organic matter accumulation must be
considered when comparing aspen with mixed conifer vegetation.
It is conceivable that the relatively low concentrations of C
and N in stream water from aspen vegetation is a result of much
smaller quantities of soil organic matter available for decomposi-
tion. In contrast, decomposition in coniferous communities occurs
on large quantities of organic matter, the result of many years
of accumulation. Our current studies are quantifying the organic
matter accumulation of all of the vegetational communities.

The low levels of inorganic N in stream water from aspen vegetation may be the result of more efficient nutrient cycling associated with the higher productivity of successional species (Odum 1971). Whether aspen productivity is higher than that of mixed conifer vegetation is unknown at this time.

Concentrations of phenols and tannins plus lignins also vary among the vegetational communities (Table 3). The weighted average concentration of tannin plus lignin is highest in the stream draining mixed conifer vegetation. This also supports the view that of the coniferous communities decomposition rates are highest in the mixed conifer vegetation. Tannin and lignin represent relatively decay resistant compounds and we would expect their concentrations to increase in organic matter in proportion to decomposition.

Among coniferous communities concentrations of phenols in stream water are highest in the mixed conifer community. Among all vegetation types the highest concentrations occur in aspen which may be an indicator of rapid decomposition since phenols are slowly decomposed or it may be a matter of the higher concentrations of phenols characteristic of aspen vegetation. Dormaar (1971) reports the polyphenol content of aspen leaves as 160 mg per g of leaf tissue.

In view of the relatively undisturbed condition of the study watersheds, the levels of phenols found in stream water were rather supprising. Using the federal safety standard of 0.001 mg/l phenol there were few times when the stream water of the study watersheds could have been considered safe for human consumption. This becomes even more significant when we consider that

our results underestimate actual phenol concentrations (see procedures). This certainly warrants further study.

The temporal patterns for concentrations of C and N compounds were similar for all watersheds. Concentrations of NO_3-N, NH_4-N, organic N, dissolved C, particulate C, lignin, tannin, and phenols were highest during the spring months concurrent with the high stream discharge period resulting from snow melt. The combination of high concentration and high discharge caused a large proportion of the year's total loss to occur in a short period of time. Tables 4 and 5 show total losses of C and N compounds for a one-year period. Losses of C and N during the two-month period of April and May accounted for from 32% (W-15) to 57% (W-4) of the year's total. This emphasizes the importance of the interaction between the decomposition process and stream discharge. High rates of decomposition provide abundant material which can enter the drainage stream. Significantly, when we express the loss of C and N compounds per cm of discharge the mixed conifer watershed showed the greatest rate of loss. The only exception seems to be for the loss of phenols which had the greatest rate loss in the aspen watershed. We feel that the reason for this is the high phenol content of aspen leaf tissue. Total loss of C and N per year was highest at the higher elevations (W-15, Aspen) because of the much higher stream discharge at those elevations (Tables 1,4,5), however, concentrations of C and N compounds in that water were relatively low.

It is indeed significant to look at evapotranspiration in the study watersheds (Table 1). The highest evapotranspiration

Table 3.　Weighted average concentrations of lignin plus tannin and phenol in the stream water of 4 watersheds

Watershed

	2	4	Aspen-1	15
Lignin + Tannin (mg/l)	3.3	4.2	3.4	3.1
Phenol (ug/l)	2.9	4.0	5.3	1.9

Table 4. Total losses of C and N from 4 study watersheds during the period October 1973-September 1974. Values are in g/ha unless otherwise indicated.

	Watershed			
	2	4	Aspen-1	15
NH_4-N	30	108	335	367
NO_3-N	54	274	862	825
Org. N	3.5	10	369	359
Tot. N	87.5	392	1566	1551
Diss. C	409	1611	4079	2433
Part. C	42 (9.4%)	153 (8.7%)	463 (10.2%)	670 (21.6%)
Tot. C	451	1764	4542	3103

$$\frac{\text{Tot C (g/ha)}}{\text{Discharge (cm)}}$$

	2	4	Aspen-1	15
	469.8	643.8	240.8	111.1

$$\frac{\text{Tot N (g/ha)}}{\text{Discharge (cm)}}$$

	2	4	Aspen-1	15
	91.1	143.1	83.0	55.5

Table 5. Total losses of lignin plus tannin and phenols from 4 study watersheds during the period October 1973-September 1974. Values are in g/ha unless otherwise indicated.

| | Watershed | | | |
	2	4	Aspen-1	15
Lignin + Tannin	317	1150	6732	8661
Phenol	0.30	1.10	10.50	5.31

$$\frac{\text{Lignin + Tannin (g/ha)}}{\text{Discharge (cm)}}$$

| 330 | 420 | 340 | 310 |

$$\frac{\text{Phenol (g/ha)}}{\text{Discharge (cm)}}$$

| 0.31 | 0.40 | 0.53 | 0.19 |

(cm of water) occurred in the mixed conifer watershed (W-4) which can be associated with the higher productivity of that vegetational community (Rosenzweig 1968). Thus, mixed conifer vegetation demonstrated the greatest ability to reduce stream discharge and dampen storm runoff. This is indeed fortunate because of the abundant material that could enter the stream resulting from decomposition processes. It also suggests that as a mixed conifer community gets to an overmature stage (low productivity), evapotranspiration may decrease and decomposition and discharge rates may increase causing significant increases in stream organics. This probably would occur for every vegetational community but the effect would be greatest in the mixed conifer community.

Future Research

Our major difficulty in this research project concerned the separation and analysis of specific organic compounds. The major reason for this difficulty was the lack of valid procedures for the analysis of organics in fresh waters. Many of the analytical procesures were developed for polluted waters (industrial phenols) or for organics in soils. The different phenols found in streams and their low concentrations require that specific methods be developed at all stages from preservation to final analysis. We have identified some specific methodology and are continuing research on other phases of this problem.

Our research to date indicates that organics in stream water do vary as a result of the biotic and abiotic factors associated with different vegetational communities. The concentrations found indicate that even under natural conditions these waters

are of marginal quality. More research is needed on what can be considered safe for human consumption. Is this level the same for industrial phenols as well as phenols resulting from decomposition processes. This requires the use of bioasseys. Finally, land management practices must be studied for their effects on the quantity and quality of stream organics. However, this research must await the development of quantitative analysis procedures.

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