LIMNOLOGICAL EFFECTS OF YELLOW PINE WATERSHED LITTER

by

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ABSTRACT

Selected chemical methods on natural and experimental infusion water were performed to determine the main effects of southwestern yellow pine litter on leachates. Pertinent literature is also reviewed. Reduction of alkalinity, color added to the water by needles, and high oxygen demands by leachates were the main negative effects observed. Positive effects of the leachates are addition of biogenic salts (high concentrations of phosphate and nitrate) and addition of organic matter. Main factors affecting import of litter into lakes are dryness of watershed, runoff rate, and buoyancy of litter. Direct estimates of organic import into Rose Canyon Lake during the 1966 summer rainy season are presented. From the data collected during this study, it appears that the inhibitory effects of pine needle leachates outweigh the relatively low trophic value contributed. Slow leaching of litter on the watershed is probably more beneficial to the fishery than import of whole litter into lakes.

INTRODUCTION

The importance of allochthonous organic matter (Ruttner, 1963) in ecosystems supporting fisheries has only recently received recognition. Teal (1957) documented the importance of organic import to a cold spring. Nelson and Scott (1962) studied the role of terrestrial detritus in stream production. McConnell (1963) and Glucksman (1965) estimated the relationship of organic import to gross photosynthesis and fish production in two small Arizona impoundments. Successful pond fertilization with hay and other organics is commonly practiced in the southeastern United States (Swingle, 1947). Warren and others (1964) increased production in an experimental trout stream by adding sucrose.

Bacterial food chains can link allochthonous material to higher trophic levels (Gorbunov, 1946). Direct ingestion of organic detritus by some invertebrates is also possible (Nelson and Scott, 1962). Waksman (1941) showed that bacteria can act as concentrators of small amounts of dissolved organic matter. Clarke and Gillis (1935) demonstrated that marine _Calanus_ can feed on bacteria, while Taylor and Sulcliffe (1964) maintained

Artemia on a diet of fine particulate organic matter. Putter (1907) believed that aquatic metazoans could subsist on dissolved organic matter, but his evidence has been refuted by others (Krough, 1931).

Much of central and southern Arizona's climate and topography provide an ideal situation for import of forest litter into small impoundments by flash floods. The typical desert climatic pattern of long periods of dry weather in the fall, spring, and early summer broken by precipitation during the winter and summer is characteristic of this area (Sellers, 1960). The summer rains, from mid-July to mid-September, are characterized by intense thunderstorm activity, while winter precipitation usually occurs in the form of gentle rain and snow (at higher elevations). Lowe (1964) reports that the spring drought is associated with higher temperatures and is the more severe. The steep slopes common on most forested watersheds in Arizona cause high runoffs following precipitation. The dryness of the watersheds preceding these high runoffs, especially during the summer rainy season, can transport large amounts of watershed litter. Artificial impoundments act as catch basins for floating litter which gradually sinks and becomes a part of the aquatic ecosystem.

The majority of trout lakes in the southern half of the state occur above an elevation of 7000 ft. Ponderosa pine is the dominant vegetation type on many of these watersheds. Most of the lakes are characterized by low alkalinity and low primary productivity (Kemmerer, 1965; Stewart, 1967) and, therefore, allochthonous debris may be important in determining chemical and trophic conditions in the lakes. The trophic value of organic and inorganic constituents of leachates and the inhibitory effects of oxygen depletion, color addition, and alkalinity reduction may play an important role in the ecology of these lakes. The factors affecting import such as time and amount of needle drop, precipitation and runoff rates, and litter floating time are important to understanding the effects.

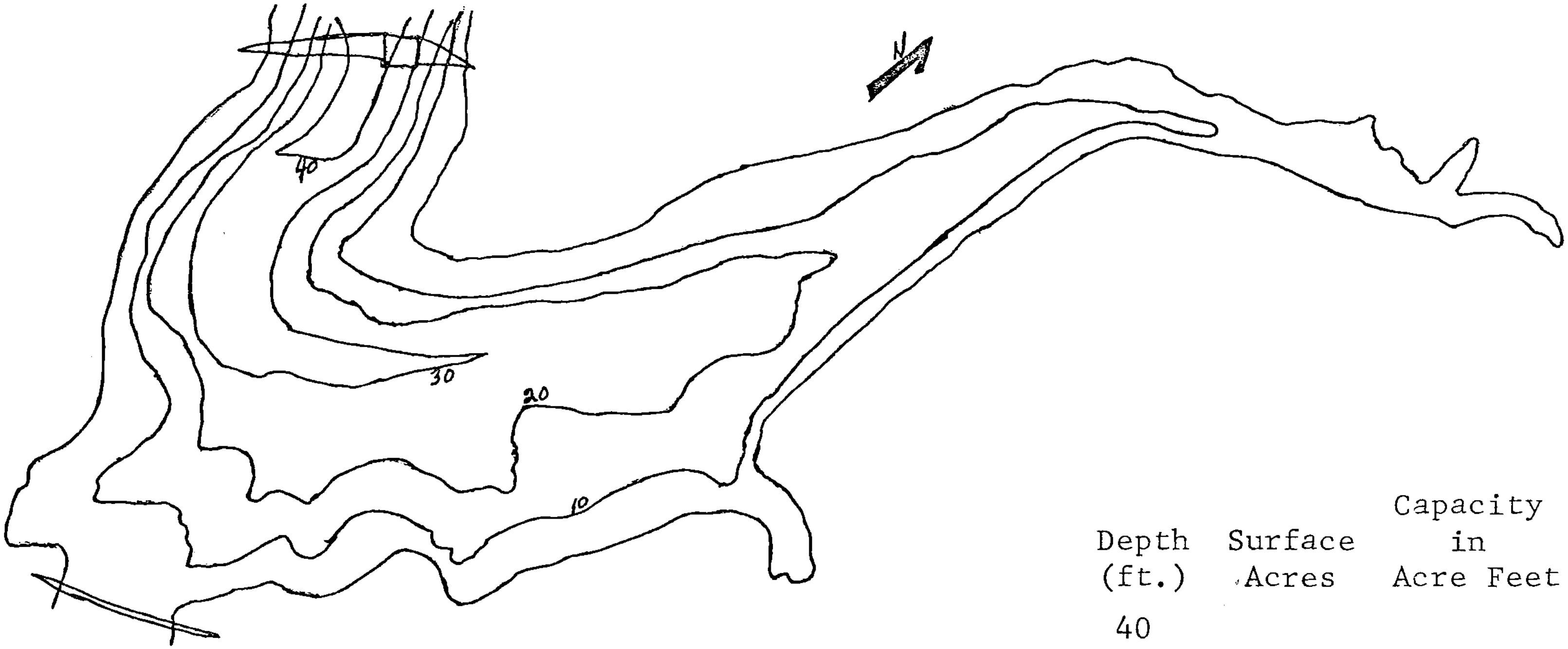
This study was undertaken to evaluate the physical, chemical, and trophic effects of pine litter in Arizona trout lakes.

STUDY AREA

Rose Canyon Lake, an impoundment situated on the southwestern slopes of the Santa Catalina Mountains about 35 road miles northeast of Tucson, was the principal study area. Rose Canyon was picked for the study because of its similarity in water chemistry and watershed characteristics to many of Arizona's soft water trout lakes (Kemmerer, 1965).

The dam was completed in 1958, and the reservoir covers an area of 7.33 acres at spillway level (Figure 1). Maximum depth of the lake is 40 ft.; mean depth, 15 ft.; shoreline length, 4225 ft.; average width, 250 ft.; and shoreline development factor, 2.1.

The fishery of the lake is based on catchable rainbow trout, *Salmo gairdneri* Richardson, which are stocked periodically during the spring, summer, and fall months, but are mostly "fished out" by winter. Bluegill sunfish, *Lepomis macrochirus* Rafinesque, and golden shiners, *Notemigonus chrysoleucas* (Mitchill), occur in the lake in large numbers. Largemouth bass, *Micropterus salmoides* (Lacepede), have also been introduced into the lake from unknown sources. Results of an electrofishing collection made on February 2, 1967, are given in Table 1. Kemmerer



Depth (ft.)	Surface Acres	Capacity in Acre Feet
40		
30		
20	2.45	17.9
10	4.61	53.4
0	7.33	112.2

Figure 1. Contour map of Rose Canyon Lake.

Table 1. Fish collected during one hour of electrofishing at Rose Canyon Lake February 2, 1967.

Species	Length Classes (total length in inches)	No. of fish
Bluegill Sunfish	>3	6
Lepomis macrochirus	2-3	34
Rafinesque	<2	32
Golden Shiner	>4	4
Notemigonus crysoleucas	3-4	12
(Mitchill)	<3	417
Largemouth Black Bass		
Micropterus salmoides	17.5	1
(Lacepede)		

(1965) reported green sunfish, *Lepomis cyanellus* Rafinesque, in August, 1964, but none was collected or reported during this study.

The area of the Rose Canyon watershed is steep to rolling (Figure 2). Granitic rocks dominate the geology of the area. Southwestern yellow pine, *Pinus ponderosa* v. *arizonica* Engelmanni, is the principal tree on the watershed. It occurs in certain southern Arizona mountain ranges above an elevation of about 7000 ft. (Lowe, 1964). Western yellow pine, *Pinus ponderosa* v. *scopulorum* Engelmanni, occurs at higher elevations in the Santa Catalinas and at the same elevation further north in the state (Lowe, 1964). Some mixed stands of oak also occur on the watershed, and

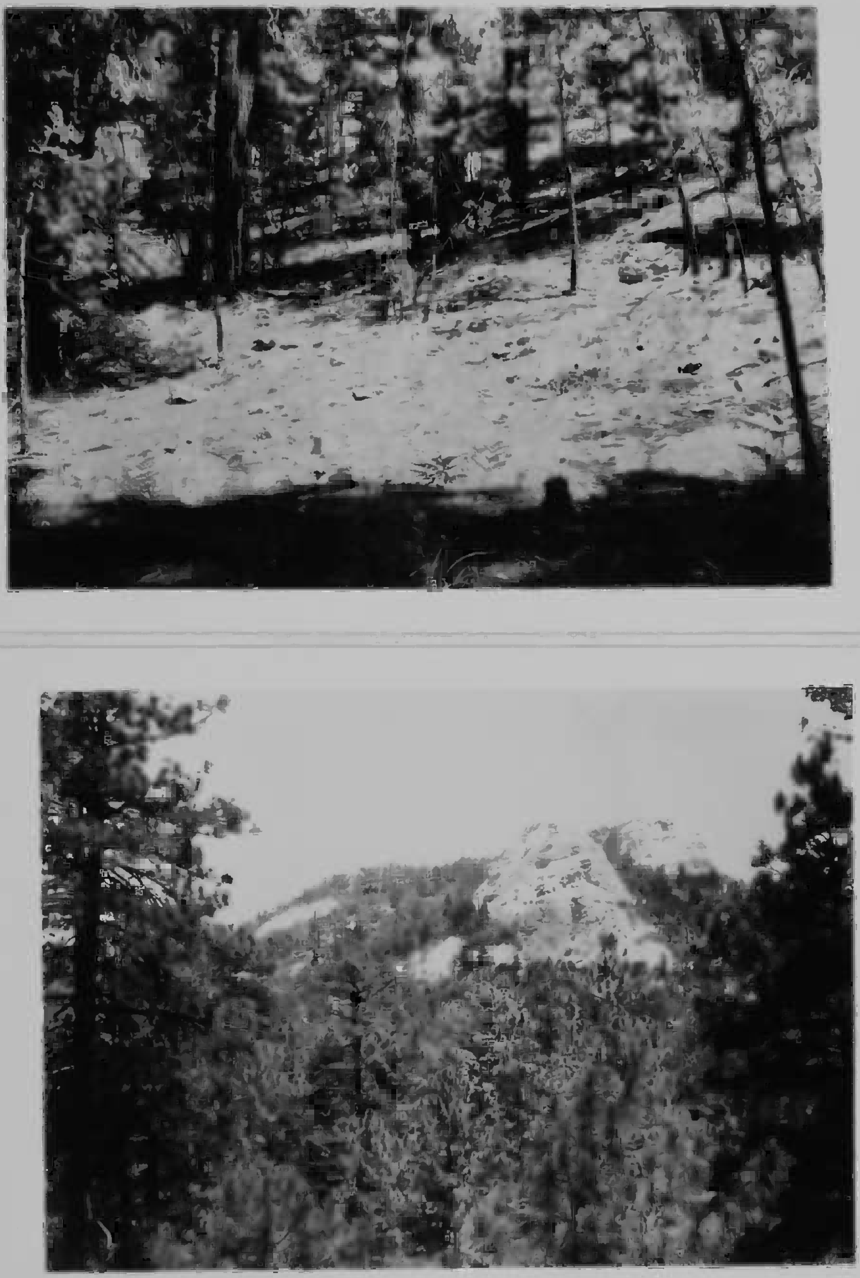


Figure 2. Representative views of the Rose Canyon watershed.

oak leaf import may be a significant constituent of allochthonous material entering Rose Canyon Lake, but it was not considered in this study.

Precipitation and temperature data from Palisades Ranger Station, approximately 1.75 miles north of the dam site, are given in Tables 2 and 3. Although the Ranger Station is almost 1000 feet higher (elevation 7990 ft.) than the lake (elevation 7000 ft.), some of the areas on the Rose Canyon watershed are nearly as high (7800 ft.). Slope exposure at the Ranger Station is the same as on most of the watershed (south). Shreve (1915) reports a 4.1° F. decrease in average annual temperature and a 4 to 5 inch increase in average annual precipitation per 1000 ft. increase in elevation in the Santa Catalina Mountains.

A limited amount of study was also done at Hawley, Fool Hollow, Becker, and Woods Canyon Lakes in east central Arizona. Morphometric data and watershed characteristics for these lakes are placed in the Appendix.

Table 2. Precipitation at Palisades Ranger Station. Precipitation values are in inches.

Year	Month	Total Precipitation	Number days with >0.5	>1.0	>1.5	>2.0	Snow, Sleet	Maximum Snow Depth
1965	January	3.18	2	1	0	0	13.0	9.0
	February	3.71	2	1	1	1	27.5	27.0
	March	2.16	1	1	0	0	14.5	17.0
	April	2.03	1	1	0	0	14.0	13.0
	May	T	0	0	0	0	-	-
	June	0.10	0	0	0	0	-	-
	July	5.56	3	2	2	0	-	-
	August	2.83	3	0	0	0	-	-
	September	0.20	0	0	0	0	-	-
	October	0	0	0	0	0	-	-
	November	5.52	5	2	2	0	-	-
	December	12.64	8	6	4	1	89.0	66.0
1966	January	3.04	2	1	0	0	34.0	53.0
	February	5.44	4	3	1	0	54.0	86.0
	March	0.36	0	0	0	0	4.0	36.0
	April	0.05	0	0	0	0	0	7.0
	May	0.03	0	0	0	0	-	-
	June	1.60	1	0	0	0	-	-
	July	4.03	4	1	0	0	-	-
	August	7.64	5	2	0	0	-	-
	September	7.36	4	4	1	1	-	-
	October	0.66	1	0	0	0	-	-
	November	1.94	2	1	0	0	8.0	1.5

Table 3. Average monthly temperatures at Palisades Ranger Station.

Year	Month	Mean Temperature (°F.) Minimum	Mean Temperature (°F.) Maximum
1965	January	28.8	46.3
	February	23.7	42.0
	March	27.4	45.7
	April	34.1	54.5
	May	39.3	63.4
	June	45.7	71.0
	July	55.0	74.7
	August	54.6	73.7
	September	48.5	67.2
	October	42.3	64.5
	November	37.0	52.1
	December	24.0	45.2
1966	January	21.5	42.0
	February	19.6	41.0
	March	27.0	51.7
	April	36.0	60.0
	May	43.7	69.7
	June	49.8	75.9
	July	54.7	77.4
	August	51.7	72.2
	September	47.5	68.5
	October	38.9	62.1
	November	34.4	55.4

MATERIALS AND METHODS

Field Water Collection

All water samples were collected in one-liter brown glass bottles. Rainwater and Thatcher (1960) believed that ion exchange occurred in this type of bottle, but Kemmerer (1965) found that ion exchange was negligible. Sub-surface water samples were taken with a one-liter brass Kemmerer water sampler manufactured by Foerst Specialties Company. All water samples were transported to the laboratory under refrigeration.

Water Analysis

All water was filtered through AA Millipore filters before analysis. Alkalinity, pH, and conductivity readings were taken before filtration. A LaMotte Chemical Company portable color comparator was used to determine hydrogen ion concentration. Conductivity was measured with a portable conductivity meter, Model RA-2A manufactured by Industrial Instruments, Inc. Phenolphthalein and methyl orange alkalinity, expressed as mg/l $CaCO_3$, were obtained by titration with $0.02N/H_2SO_4$. Phenolphthalein and brom cresol green-methyl red mixed indicators and 100 ml water samples were used in the determinations.

Anion analyses were done with a Bausch and Lomb Spectronic 20 Colorimeter. Hach Company procedures and reagents were used. One-inch test tubes were used in place of half-inch tubes because of better accuracy at low concentrations. The ions and the methods for their determinations are: ammonia nitrogen, direct Nesslerization method; nitrate nitrogen, Nitraver method; total phosphate, molydenum blue method; sulfate, Turbidimetric method; silica, molybdenum-blue-sulfite method; and total phenolics, tyrosine method.

Carbohydrates were determined by the phenol-sulfuric technique as described by Dubois et al. (1956). Results are expressed as mg/l glucose.

Metals were determined by spectrographic analysis performed by Efco Feed Company, Tucson, Arizona.

Chemical oxygen demands (COD) were used as a measure of total dissolved organic matter and were determined by the semimicro method as described by Maciolek (1962). Biochemical oxygen demands (BOD) of infusions were determined with a Hach manometric BOD apparatus, Model 1791 at about 25° C. Antibiotic solutions containing 13 mg penicillin G, 27 mg streptomycin, 35.5 mg polymixin B sulfate, and 250 mg activione per liter of distilled water were used in experiments to supress microbial activity to determine the nature of the oxygen demand.

Dissolved oxygen was determined by the Azide modification of the Winkler method (A.P.H.A., 1965). Reagent bottles with a determined volume of 127 ml were used in place of standard BOD bottles, and the entire contents of the bottles were titrated with 0.025 N phenylarsene oxide (PAO).

Temperature Stratification

Temperature readings, to the nearest 0.1° C., were taken at 1-ft. intervals with an electronic recording thermometer manufactured by Yellow Springs Instrument Company.

Litter Collection

Southwestern yellow pine needles for infusion experiments were collected on two dates. Winter leached litter subject to summer storm leaching and transport was collected on April 2, 1966; and unleached, newly fallen litter was collected on November 18, 1966. All needles were collected from hillsides on the Rose Canyon watershed.

Extraction Procedures

Experimental pine needle infusions were made in 1-gal. glass jars. Ten grams of needles per 3 liters water were used in the experiments. Weights are those of needles dried for two weeks at room temperature. Extraction temperatures are ± approximately 4° C. Distilled water leachings were made with copper distilled, deionized water. Tap water was from the campus water supply which averages about 140 mg/l methyl orange alkalinity.

Direct Estimation of Import

Direct estimates of import were made with electrically recoverable devices at Rose Canyon during the 1966 summer rainy season. The litter collectors consist of a plastic bucket 24 cm in diameter fixed to a tip-proof base of pine plank and light-walled steel conduit (Figure 3). Forty-seven buckets were set at 3m intervals along two transect lines covering the long axes of the lake (Figure 4). The recovery system, developed by McConnell (unpublished), depends on current from a "Tiny Tiger" generator passed through two chains dragged along the bottom setting off flashbulbs and releasing the floats and recovery lines. The plastic coating on the bulbs was removed so that the glass would break easily when the bulbs were set off. The

Figure 3. Photographs of recoverable litter collectors.

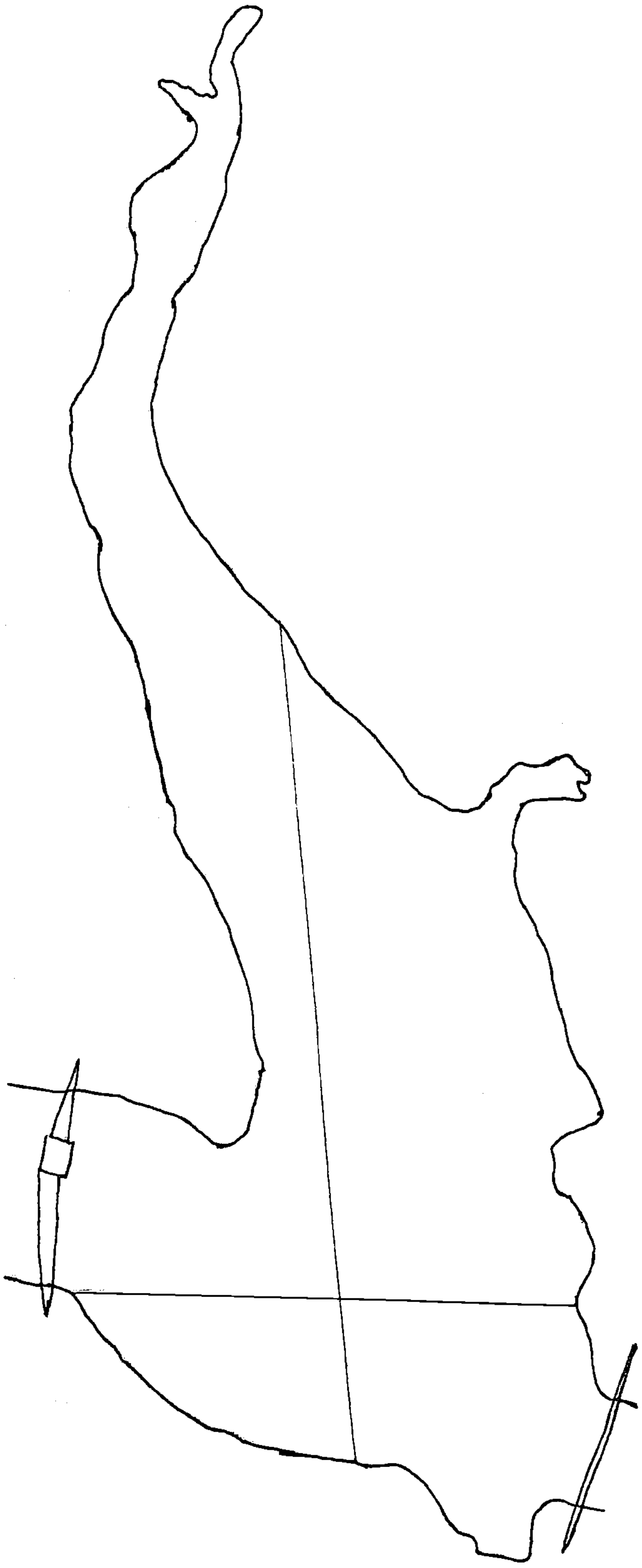


Figure 4. Location of transect lines in Rose Canyon Lake.

recovery system proved unreliable, and ten of the floats were released prematurely, probably by lightning. Although dredging proved impractical at Rose Canyon Lake, some estimates of allochthonous debris were made on other lakes with a 6- x 6-inch Eckman dredge manufactured by Foerst Specialties Company.

Lake and Watershed Characteristics

Weather data for the watershed were obtained from the Palisades Ranger Station. Watershed area was calculated from a USGS topographic map. Other watershed characteristics are personal observations. Lake morphometric data were taken from Arizona Game and Fish Department maps.

Buoyancy of Needles

Buoyancy of fasicle groups was tested in 150-gal. tanks. Groups of 20 fasicles were shaken for five minutes in 1-gal. glass jars three-quarters full of water to simulate wetting on the watershed. They were then poured into the tanks and the number afloat noted at intervals.

Certain minor modifications of the above-cited methods were made, and they are listed in specific sections and in table and figure captions and legends.

RESULTS AND DISCUSSION

Litter Drop

Although small amounts of needles fell throughout the year, the main drop was observed in the fall. Both in the Santa Catalina Mountains of southern Arizona and in the White Mountains of east central Arizona, the principal drop was observed to occur in October. Alway and Zon (1930) reported that 75 per cent of pine litter in a Minnesota forest fell between mid-June and mid-October. This pattern of litter fall leaves fresh debris on the ground over winter, and allows it to be packed and leached by winter snow fall. Flakes of bark and twigs appear to be a conspicuous part of watershed litter, and they may have limnologic significance, but they were not considered in this study.

Alway and Zon (1930) reported the average annual litter drop in a Minnesota pine forest as 1738 pounds per acre. They reported as much as 25 per cent variation between nearby plots, and almost as much from year to year on the same plots. Metz (1952) reported litter weights for a shortleaf and loblolly South Carolina pine forest at 2938-4476 pounds per acre per year needles and 288-1143 pounds per acre per year twigs, fruit, and bark. Chandler (1944) reports average litter drop for seven species of conifers in a New York forest as 2463 pounds per acre annually. Kramer and Kozlowski (1960), Metz (1952), and Chandler (1944) all report higher litter drop values for conifers than for hardwoods, but higher mineral content and decomposition rates (Kramer and Kozlowski, 1960) for hardwoods.

Canopy cover on the Rose Canyon Watershed (1500 acres) varies from 100 per cent in low-lying areas to close to zero on some slopes. If we assume an average needle drop of 1000 pounds per acre per year, there are 1.5 million pounds subject to leaching and transport annually.

Buoyancy

Buoyancy of air dry winter leached litter was tested under laboratory conditions. A scatter diagram of the results of six such tests is given in Figure 5. Needles began sinking rapidly after 24 hours, and mean floating time for all tests was 29.5 hours. Floating time is important to transport because litter must be sufficiently buoyant to remain afloat until it reaches the lake. Once it has reached the impoundment, the position in the lake where the litter sinks determines the type of long-term leaching and decomposition it is to undergo, aerobic or anaerobic.

Figure 5. Floating time for southwestern yellow pine fasticles in 150-gal. tanks. Results of six separate tests are presented in the graph.

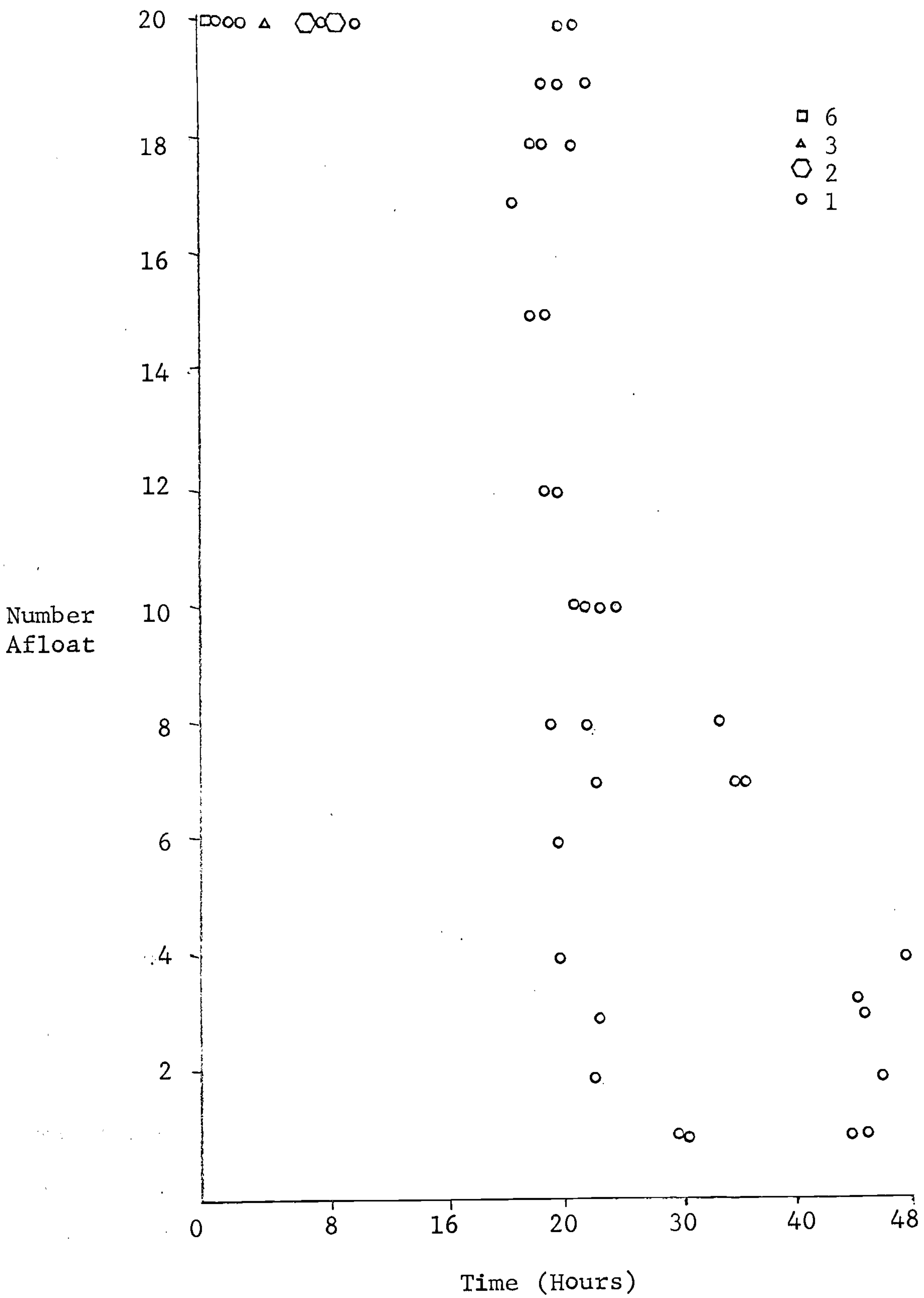

Number Afloat
20
18
16
14
12
10
8
6
4
2
0
8
16
20
30
40
48
Time (Hours)
□ 6
△ 3
⬡ 2
○ 1

Figure 5.

If the lake were almost full at the time of import, buoyant litter might be carried over the spillway by high runoff before it sank. This situation may have occurred at Rose Canyon during the 1966 summer rainy season, since the pine litter tested appears to be sufficiently buoyant, and the lake was at spillway level at the end of June.

Alkalinity and pH Changes

Reduction of alkalinity in infusion water was noted during the study. Data on alkalinity reduction are given in Figures 6, 7, and 8. Alkalinity reductions of up to 50 per cent took place in tap water infusions. High temperature 24-hour infusions and long-term infusions (Figures 7 and 8) showed greatest alkalinity reductions. High litter concentrations also showed greater reductions (Figure 7). Tap water blanks run along with room temperature and refrigerated infusions showed no decreases in alkalinity, but none was run at high temperatures, so reduction values for these infusions may be slightly high.

The mechanism in alkalinity reduction is unknown, but possibly it may be by the chelation and precipitation of calcium by complex organic ions. Alkalinity of infusion water increased after needles were removed and distilled water was added (Figure 8). This increase may have been due to the distilled water dissolving some of the

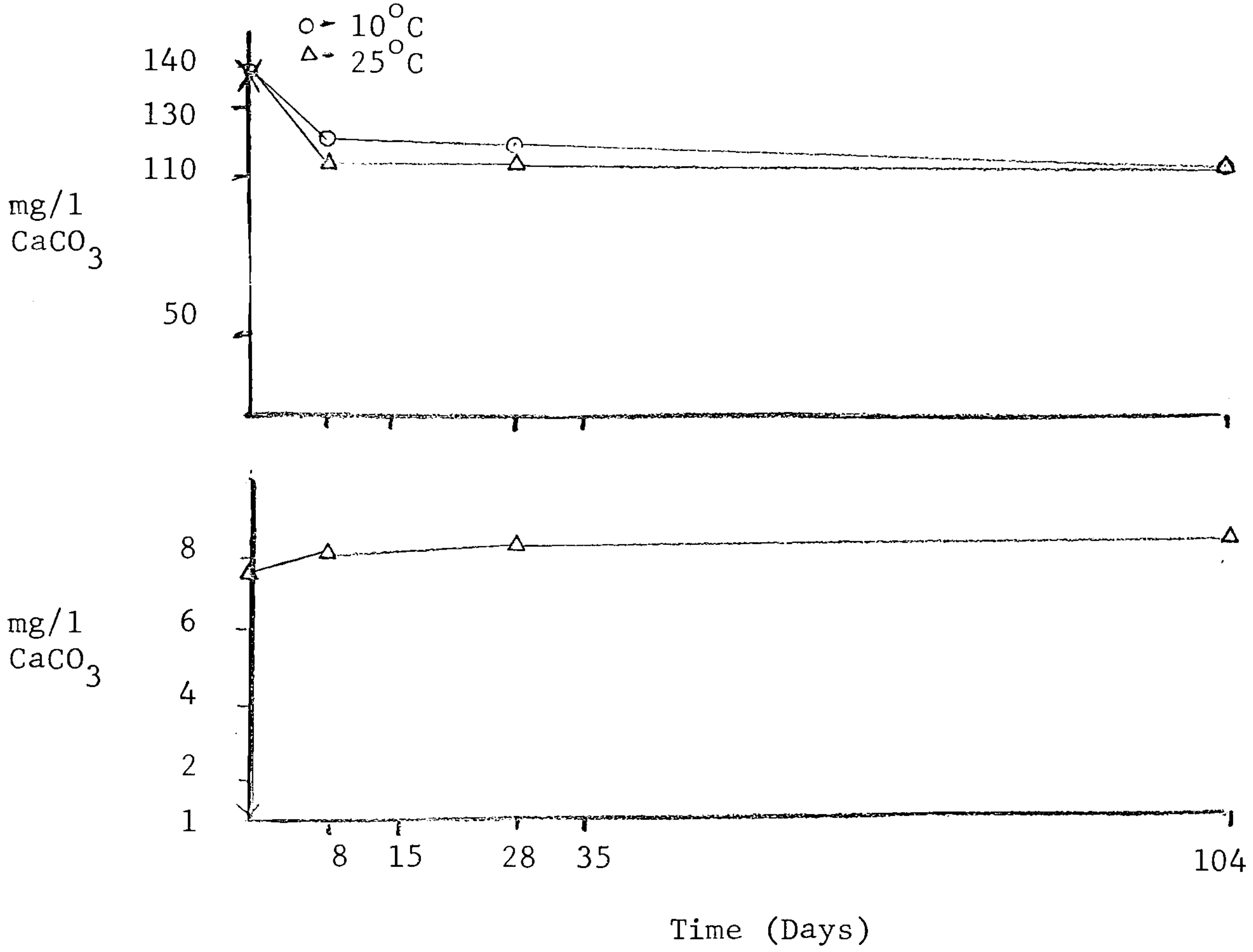


Figure 6. Alkalinity changes in 7-day tap (upper) and distilled (lower) infusion water after needles have been removed. Methyl orange alkalinities are given. An X on the alkalinity axis indicates the initial alkalinity of water before needles were added.

Figure 7. Alkalinity and pH changes in 24-hour tap infusion water after needles have been removed. Methyl orange alkalinities are given. An X indicates the initial alkalinity and pH before needles were added.

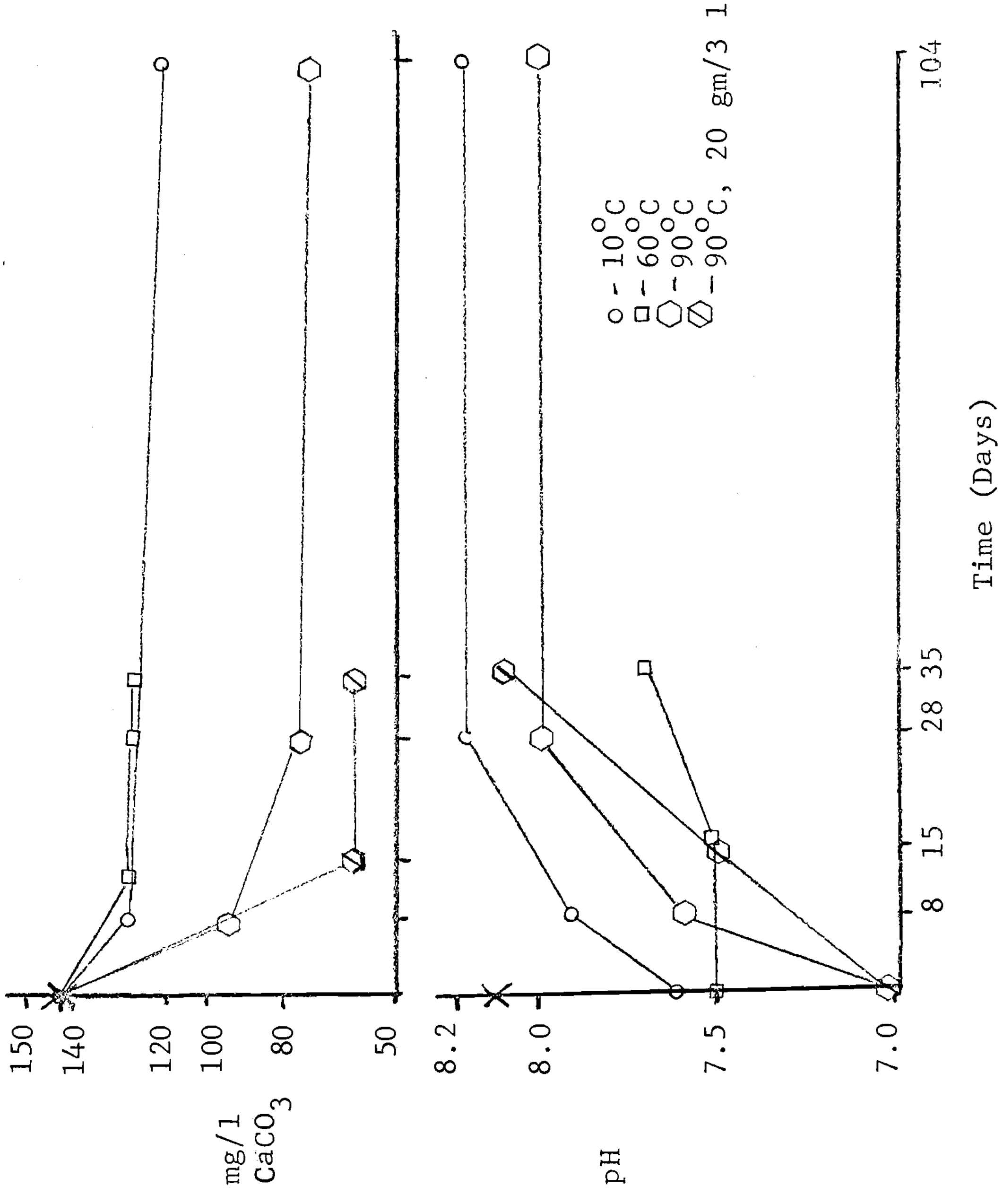

mg/1
CaCO$_3$
150
140
120
100
80
50
pH
8.2
8.0
7.5
7.0
8
15
28
35
104
Time (Days)
○ - 10°C
□ - 60°C
⬡ - 90°C
⬡ -90°C, 20 gm/3 1

Figure 7.

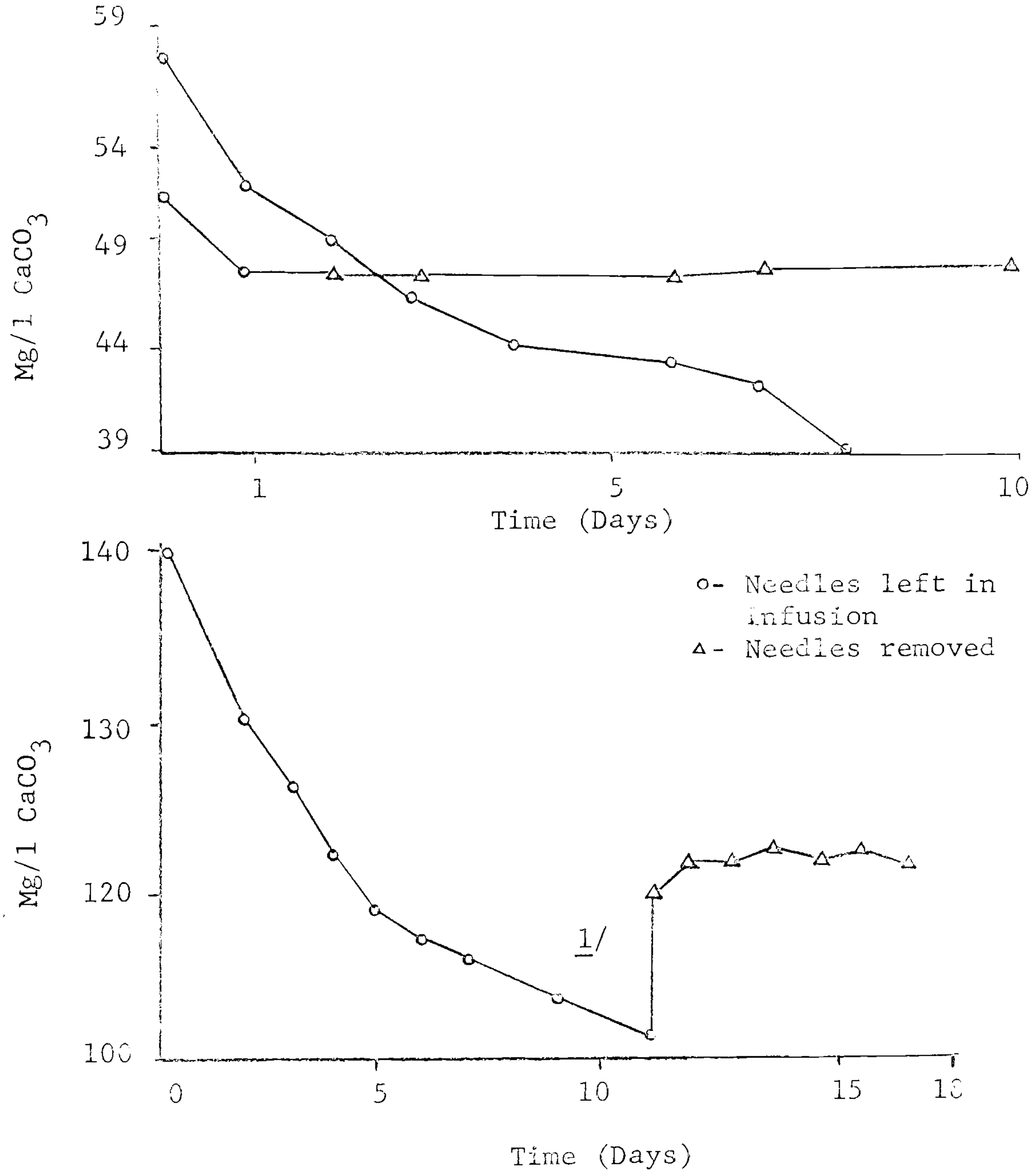


Figure 8. Effect of needle removal on alkalinity changes in mid-alkalinity range (upper) and in tap water infusions (lower). Temperature of infusions was 10°C, and methyl orange alkalinity values are given. Distilled water was added to bring alkalinity back into solution[1/].

precipitate. Perhaps the same mechanism responsible for low alkalinity in the classic bog lakes (Welch, 1952) causes alkalinity reduction in pine needle infusions.

Increase of alkalinity in distilled water infusions was also observed. "Alkalinity" is hard to interpret in this case because many substances can produce slight buffering effects in distilled water. High infusion temperatures and high litter concentrations showed greater alkalinity addition (Figure 9). The increase of alkalinity with increase in temperature sheds some doubt on the validity of alkalinity of distilled water infusions. Nykvist (1959) reports an increase in organic but not in inorganic compounds dissolved from pine litter with increases in temperature.

Changes in pH of infusions are given in Figures 7, 9, and 10. Data agree with those of Nykvist (1959), who reports pH changes in distilled water infusions of *Pinus silvestris*. After an initial drop, pH increased gradually with aeration in distilled water infusions. Tap water infusion pH dropped but rose to about the original level with aeration. Broadfoot and Pierre (1939) report lower litter pH and lower excess base for pine than for hardwood litter. Plice (1935) also noted low pH and low buffer capacity in several species of *Pinus*.

Figure 9. Alkalinity and pH changes in 24-hour distilled infusion water after needle removal. Needles were removed at zero time. Methyl orange alkalinities are given.

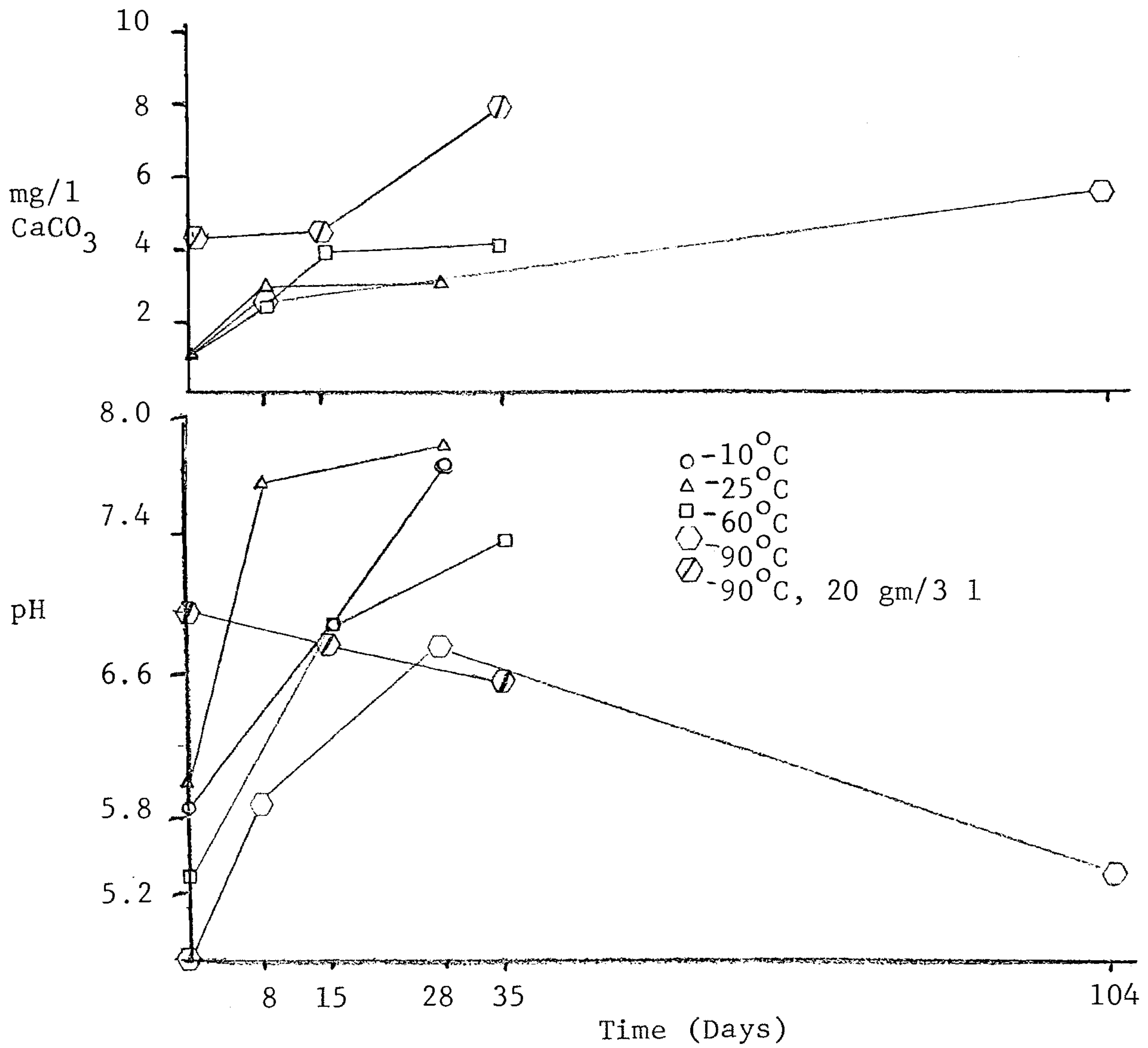

10
8
6
4
2
mg/1
$CaCO_3$
8.0
7.4
6.6
5.8
5.2
pH
○ -10°C
△ -25°C
□ -60°C
⬡ -90°C
⬡ -90°C, 20 gm/3 1
8
15
28
35
104
Time (Days)

Figure 9.

Figure 10. Changes in pH in 7-day tap (upper) and distilled (lower) infusion water after needles have been removed. Alkalinity values are methyl orange. An X on the pH axis indicates pH of water before needles were added.

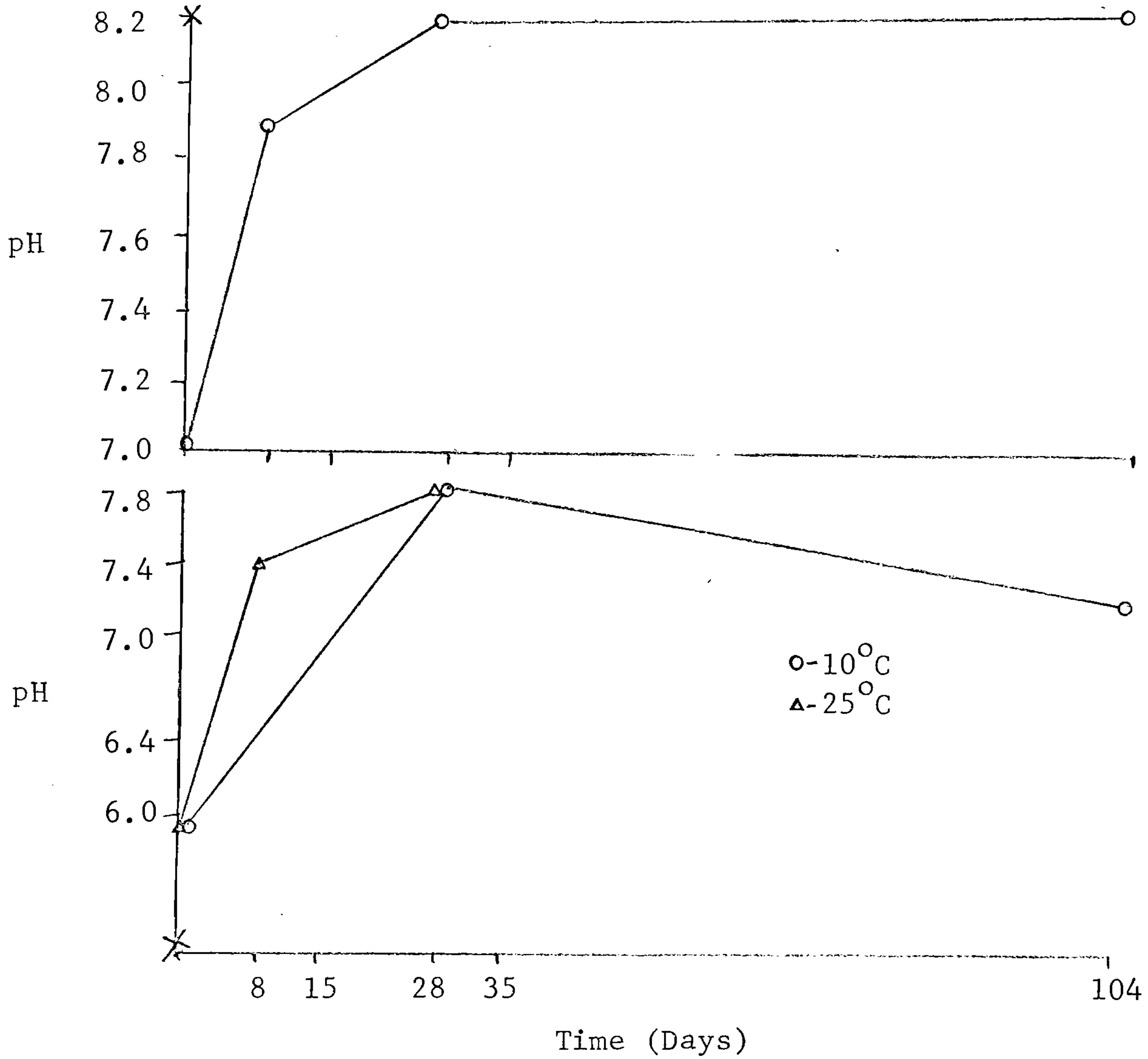

pH
8.2
8.0
7.8
7.6
7.4
7.2
7.0
pH
7.8
7.4
7.0
6.4
6.0
o-10°C
▵-25°C
8
15
28
35
104
Time (Days)

Figure 10.

Alkalinity, pH, and conductivity measurements for Rose Canyon Lake and inflow water are given in Tables 4 and 5. Inflows were characterized by low alkalinity due to the geology of the watershed. Low alkalinity problems in the lake were compounded by the flushing action of high runoff during the spring and summer of 1966. Kemmerer (1965) believed that alkalinity in the lake was derived mostly from calcareous dust carried to the area from the desert floor by convective currents and deposited on trees and ground litter. Alkalinity is apparently not derived from needles since alkalinity of inflow water did not increase during the period of maximum litter drop (Table 4).

Madguick and Ovington (1959) report large amounts of dissolved metals in precipitation in coniferous forests. Tamm (1951) also reports removal of calcium from tree crowns by precipitation.

Color

Pine needle infusions were characterized by a yellow-brown color. Shapiro (1957) reported greatest optical density of bog waters in the ultraviolet range. Greatest optical density of natural and infusion waters on the Spectronic 20 was on the "short" end of the scale. Measurements were made at 360 mμ for maximum optical density and at 500 mμ, a wave length near the center of

Table 4. Alkalinity, pH, and conductivity of inflow samples from Rose Canyon Creek.

Date of Inflow	Estimated Flow (cfs)	pH	mg/l $CaCO_3$	Conductivity (Micromhos at 10° C.)
12 August 1966	20.0	6.7	5.7	19
14 August 1966	<0.5	6.8	13.5	-
22 August 1966	<0.5	6.9	13.0	50
26 August 1966	<0.5	6.9	13.8	45
8 September 1966	<0.5	6.7	16.5	39
23 September 1966	<0.5	6.6	13.5	35
18 November 1966	<0.5	7.5	11.0	-
2 February 1967		No Inflow		
17 April 1967	1.0	6.9	13.0	-

Table 5. Alkalinity, pH, and conductivity of Rose Canyon Lake water.

	pH		mg/l $CaCO_3$		Conductivity (Micromhos at 10° C.)	
Date	Surface	Hypolimnion	Surface	Hypolimnion	Surface	Hypolimnion
20 September 1965	6.80	6.0	17.1	27.4	-	-
1 October 1965	6.50	6.5	18.0	34.2	-	-
15 November 1965	6.75	-	-	-	49	-
14 August 1966	6.80	-	13.5	-	-	-
22 August 1966	6.70	-	13.0	-	50	-
26 August 1966	7.50	-	13.0	-	40	-
8 September 1966	7.00	-	13.5	-	35	-
23 September 1966	6.80	5.9	11.5	31.0	30	35
18 November 1966	7.50	-	15.0	-	-	-
2 February 1967	7.40	-	23.0	-	-	-
17 April 1967	7.60	-	15.0	-	-	-

the visible spectrum. Optical densities of laboratory infusion water are given in Table 6. Optical density increased with temperature and with length of infusion. Winter leached needles produced higher optical density than newly fallen needles.

Color of laboratory infusion and natural water increased with aeration, then decreased with precipitation of a brownish floc. This observation tends to support the view of Ruttner (1964) that color from organic compounds in water is mainly colloidal. Shapiro (1957) reported that most of the color was removed from bog waters using an HA Millipore filter. He believed that the color was due to high molecular weight phenolic or enolic humolimnetic acids. Amount of color removed from infusion and lake water by AA Millipore filters varied greatly. Over 50 per cent was removed in some cases (Tables 6, 7, and 8).

Color in surface waters of a lake can significantly reduce the photic depth. Limitation of photic depth, calculated from the per cent transmission of unfiltered Rose Canyon Lake water at 500 mμ are presented in Table 7. Color in Rose Canyon was highest in the fall. Inflow color never reached high levels (Table 8). This observation suggests that color developed in the lake either from dissolved substances in the inflow or from litter falling or washing directly into the lake.

Table 6. Optical density of laboratory infusion water. One-inch tubes were used in measurements. Filtered water was AA Millipore filtered. All values are the means of three replicates and two separate determinations.

				Optical Density			
				360 $m\mu$		500 $m\mu$	
Extraction Temperature	Length of Infusion	Water	Needle Type	Filtered	Unfiltered	Filtered	Unfiltered
10° C	7 day	Tap	Old	0.080	-	-	-
25° C	7 day	Tap	Old	0.280	-	0.045	-
60° C	24 hour	Tap	Old	0.850	-	-	-
90° C	24 hour	Tap	Old	1.600	-	0.180	-
90° C*	24 hour	Tap	Old	1.600	-	-	-
10° C	24 hour	Distilled	New	0.065	0.072	0.010	0.02
25° C	24 hour	Distilled	Old	0.040	0.040	0.005	0.01
25° C	24 hour	Distilled	New	0.030	0.040	0.005	0.01

*Litter concentration 20 gms/31.

Table 7. Optical density of Rose Canyon Lake water. Calculated limitations of photic depth were made from 500 mμ unfiltered readings. AA Millipore filters and one-inch tubes were used.

Date	Optical Density				Calculated limitation of photic depth by optical density at 500 mμ
	360 mμ		500 mμ		
	Filtered	Unfiltered	Filtered	Unfiltered	
22 October 1965	0.040	10.080	0.010	0.020	100.0"
5 November 1965	0.065	0.130	0.020	0.050	40.0"
15 November 1965	0.025	0.103	0.010	0.025	80.0"
4 December 1965	0.037	0.149	0.025	0.035	57.0"
14 August 1966	0.092	0.165	0.010	0.040	50.0"
22 August 1966	0.060	0.120	0	0.025	80.0"
26 August 1966	0.060	0.140	0.020	0.060	33.3"
8 September 1966	0.050	0.075	0	0.005	400.0"
23 September 1966	0.120	0.130	0.015	0.035	57.1"
18 November 1966	0.115	0.200	0.020	0.060	33.3"
2 February 1967	0.050	0.110	0	0.020	100.0"
17 April 1967	-	0.140	-	0.020	100.0"

Table 8. Inflow optical density in Rose Canyon Creek.

Date	360 mμ		500 mμ	
	Filtered (AA)	Unfiltered	Filtered (AA)	Unfiltered
4 December 1965	0.050	-	-	-
12 August 1966	0.015	-	0.005	-
22 August 1966	0.025	0.040	0	0
26 August 1966	0.010	0.010	0	0
8 September 1966	0.005	0.010	0	0
23 September 1966	0.060	0.070	0.010	0.015
18 November 1966	0.030	0.030	0	0.005
2 February 1967	No Inflow			
17 April 1967	-	0.001	-	0

Oxygen Demand

Oxygen demands of 24-hour and continuous (litter left in bottles for the duration of experiment) infusions of winter leached and newly fallen needles are given in Table 9. Newly fallen needles showed slightly higher mean oxygen demands than winter leached needles, and more oxygen was consumed in continuous than in 24-hour infusions. Typical curves for oxygen demands are presented in Figure 11.

Antibiotics failed to effectively inhibit oxygen consumption in sterilized infusions, and five-day values were almost as high as controls (Table 10). Results are inconclusive, but it seems probable that at least a part of the oxygen demand is non-microbial. Strom (1931) and Lonnerbland (1931) attribute an oxygen demand other than microbial to the decomposition of allochthonous material (dy). Others (Eldridge, 1934) have reported high oxygen demands due to phenolic pollution. Mischonsniky (1934) believed that reduction in the oxygen concentration of water containing phenol may be due to "biochemical catalysts" brought into solution by phenol and reacting with it.

Oxygen was depleted in Rose Canyon Lake below a depth of 12 feet in the fall of 1965. Oxygen saturation was only about 60 per cent in surface water after turnover

Table 9. BOD of distilled water pine needle infusions at about 25° C.

Infusion	Needles	BOD (mg/l) at time (hours)										
		12	24	36	48	60	72	84	96	108	120	192
24 hour	New	10.3	20.0	22.5	23.0	27.8	-	28.0	28.0	30.0	30.0	
24 hour	New	11.0	23.0	26.0	27.0	30.5	-	33.5	33.5	34.0	34.0	
24 hour	New	12.0	25.3	27.8	30.3	34.6	-	37.6	37.6	37.6	38.1	
24 hour	New	13.0	27.0	30.5	32.0	36.5	-	39.0	39.0	41.5	42.5	
24 hour	Old	8.0	9.8	10.8	11.8	12.3	-	14.6	14.6	16.1	16.6	
24 hour	Old	6.0	7.0	7.0	7.0	7.0	-	9.2	9.2	11.5	13.0	
24 hour	Old	7.0	10.0	10.0	11.0	12.5	-	13.5	13.5	13.5	13.5	
Continuous	New	5.6	10.6	12.6	15.6	21.6	24.6	29.6	31.6	35.6	39.6	69.0
Continuous	New	6.0	10.0	13.0	18.4	26.0	30.0	37.0	40.0	46.0	50.0	84.0
Continuous	New	6.4	8.8	11.4	15.4	23.0	25.4	31.4	33.4	40.4	42.4	68.6
Continuous	New	6.8	9.8	11.8	15.8	23.4	26.8	31.8	35.8	41.8	43.8	77.2
Continuous	Old	5.6	9.6	11.6	16.6	23.6	25.6	29.6	31.6	37.6	39.6	63.2
Continuous	Old	6.0	6.0	6.0	12.0	18.0	20.0	22.0	23.0	24.0	25.0	32.0
Continuous	Old	4.6	8.6	11.6	17.6	24.0	26.6	31.6	33.6	39.6	41.6	72.2

Figure 11. Comparison of typical oxygen consumption curves for 24-hour infusion water and continuous infusions of pine needles in distilled water.

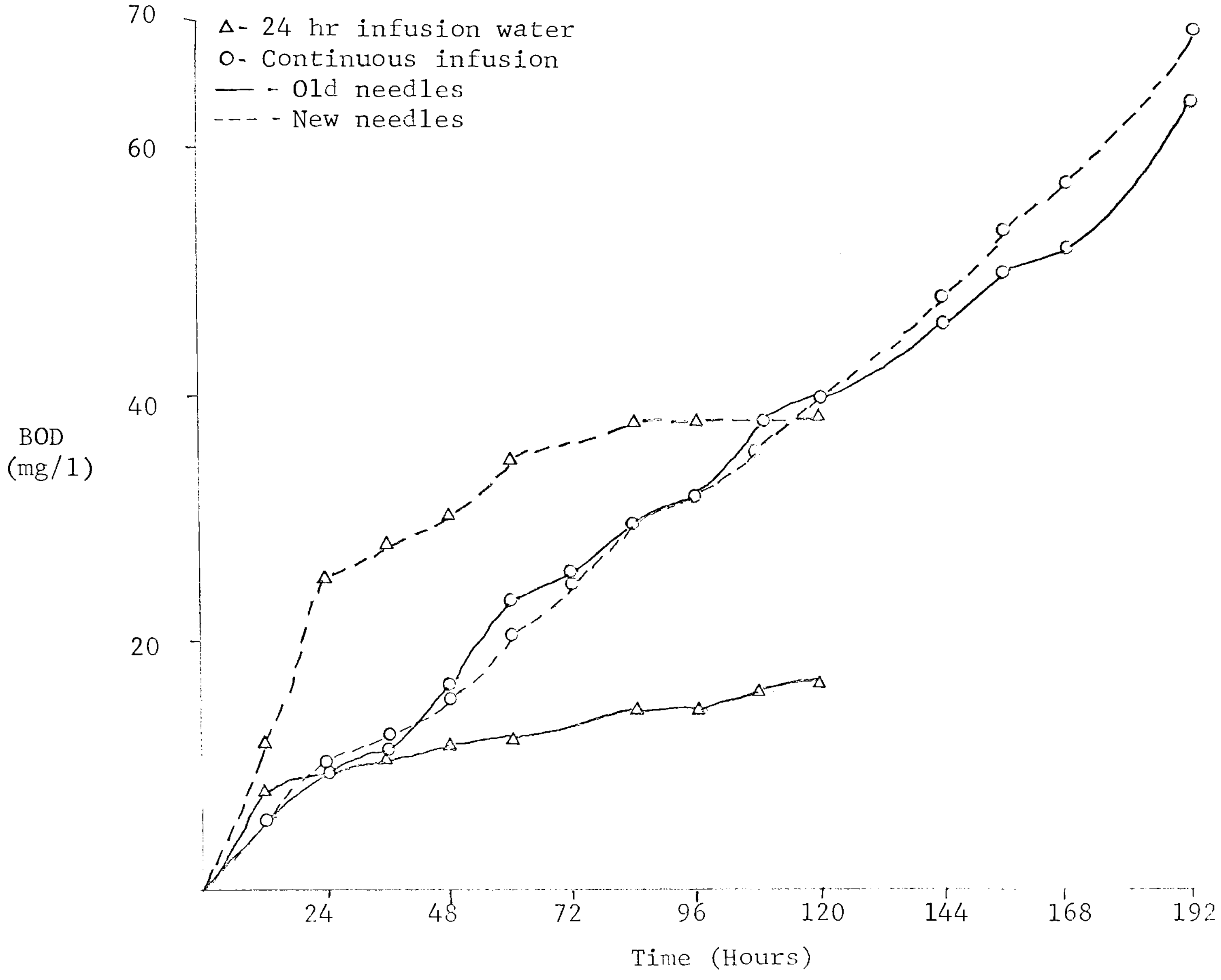

Δ- 24 hr infusion water
O- Continuous infusion
—— - Old needles
- - - - New needles
70
60
40
20
BOD (mg/1)
24
48
72
96
120
144
168
192
Time (Hours)

Figure 11.

Table 10. BOD in continuous, sterilized distilled water infusions at about 25° C.

	BOD (mg/l) at time (hours)						
Needles	24	48	72	96	120	144	168
Old	0.6	5.4	12.0	18.0	24.0	32.0	40.0
Old	0.2	6.0	12.0	18.0	23.0	28.0	36.0
Old	0.8	4.0	10.0	15.0	20.0	28.0	39.0
Old	0.2	7.4	14.0	20.0	27.0	34.0	46.0
New	0	6.0	12.0	18.0	26.0	33.0	40.0
New	0	4.0	10.0	16.0	21.0	26.0	36.0
New	0	8.0	20.0	26.0	30.0	38.0	52.0

on November 15 (Figure 12). Such high oxygen demands can only be attributed to allochthonous sources because of the lake's low autochthonous production. Kemmerer (1965) estimated productivity from gross photosynthesis at 155 gms $O_2/m^3/yr$. Primary production was probably even lower in 1966 because of lower alkalinity and the mechanical flushing action by high runoff. Representative temperature curves are also given in Figure 12.

Total Dissolved Organic Matter

Chemical oxygen demand (COD) was used as a measure of total dissolved organic matter. Results are reported as mg/l oxygen consumed and as mg/l glucose equivalents. This

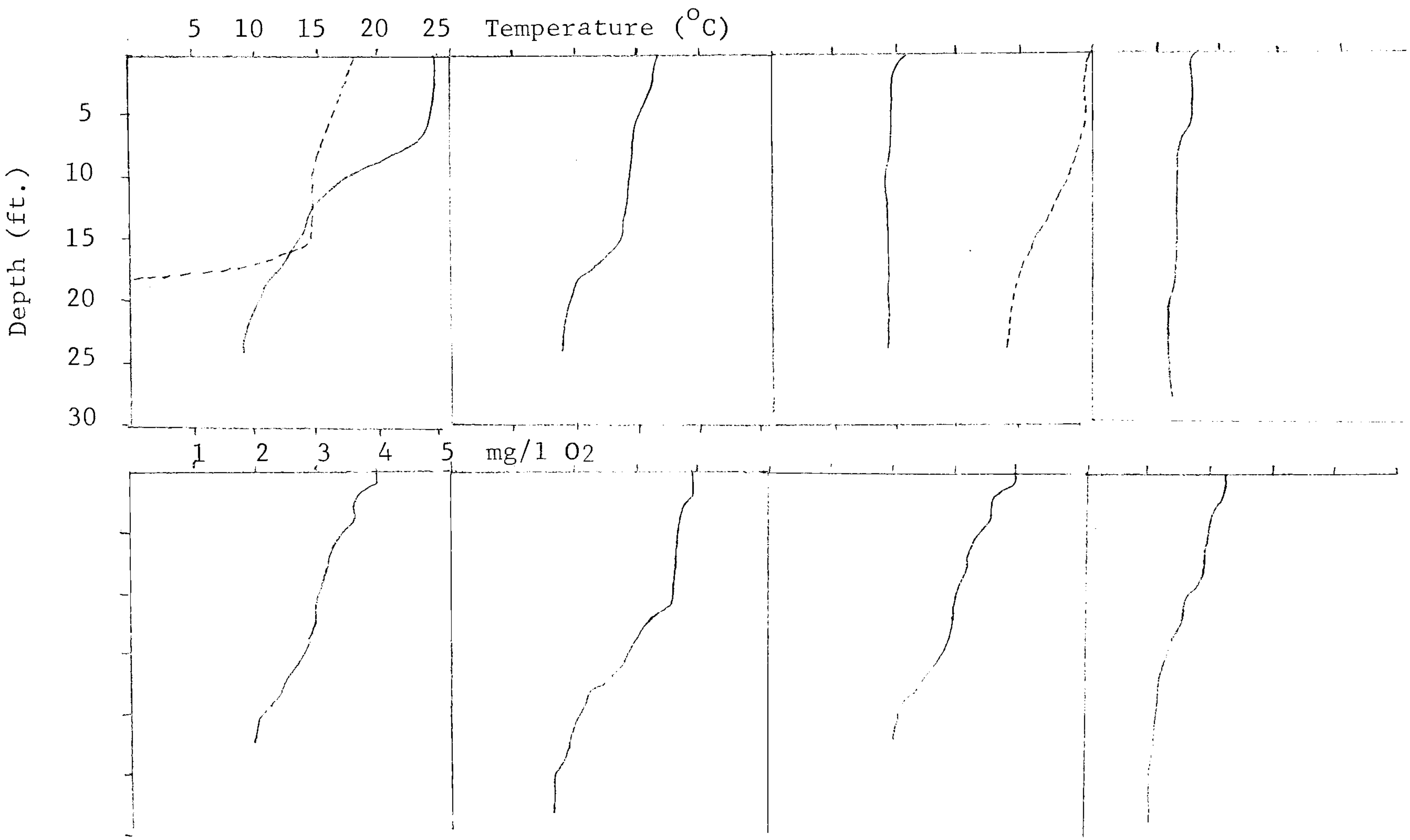


Figure 12. Representative temperature and oxygen profiles at Rose Canyon Lake. Broken lines are oxygen profiles.

test probably is a reasonably accurate measure of the total organic matter available to microorganisms, although some resistant substances not immediately used are also oxidized (A.P.H.A., 1965).

Chemical oxygen demands for infusion water are given in Table 11. Infusion temperature and duration had a marked effect on COD values (Figure 13). Seven-day values were almost double those of 24-hour infusions. These data agree with Nykvist's (1959), who reported increase in dissolved organic matter up to 43 days in distilled water infusions of *Pinus silvestris*. He also found that up to eight times as much organic matter was dissolved at 80° C. than at 25° C. Twenty-four hour infusion values and seven-day refrigerated values probably have more validity than long-term room temperature values because of microbial decomposition. Nykvist (1959) reports about 50 per cent reduction in organic matter of infusions after 43 days of aerobic storage.

It is difficult to explain the low COD values in relation to BOD values previously discussed. Chemical oxygen demands for comparable infusions were sometimes even lower than the corresponding BOD figures. Two possible causes for this discrepancy are volatilization of certain compounds during evaporation and evaporation temperatures too low to restrict microbial activity.

Table 11. Chemical oxygen demands (dichromate oxidation) of laboratory infusion water. All litter used was old needles.

Length of infusion	Temperature	Water	No. separate determinations	Range (mg/1 O_2)	Mean (mg/1 O_2)	Mean glucose equivalents (mg/1)
24 hour	10° C	Tap	3	13.5- 16.4	14.7	13.9
24 hour	10° C	Distilled	2	12.7- 15.7	14.2	13.4
7 day	10° C	Tap	2	29.8- 32.4	31.8	30.0
7 day	10° C	Distilled	2	30.8- 32.0	31.5	29.7
24 hour	25° C	Tap	3	38.2- 39.1	38.6	36.4
24 hour	25° C	Distilled	4	24.3- 30.6	27.2	25.7
7 day	25° C	Tap	3	71.7- 77.1	75.3	71.0
7 day	25° C	Distilled	2	83.3- 86.0	84.6	79.8
24 hour	60° C	Tap	3	123.4-126.6	125.1	118.0
24 hour	60° C	Distilled	2	137.8-144.2	141.0	133.0
24 hour	90° C	Tap	2	223.6-229.3	226.4	213.6
24 hour	90° C	Distilled	2	194.3-199.0	196.6	185.5
24 hour	90° C*	Tap	3	451.7-459.5	455.9	430.1
24 hour	90° C*	Distilled	2	474.9-521.5	498.2	470.0

*Litter concentrations 20 gm/3 liters.

Figure 13. Effect of extraction temperature on COD of short-term infusions. Each point represents the mean of two separate determinations.

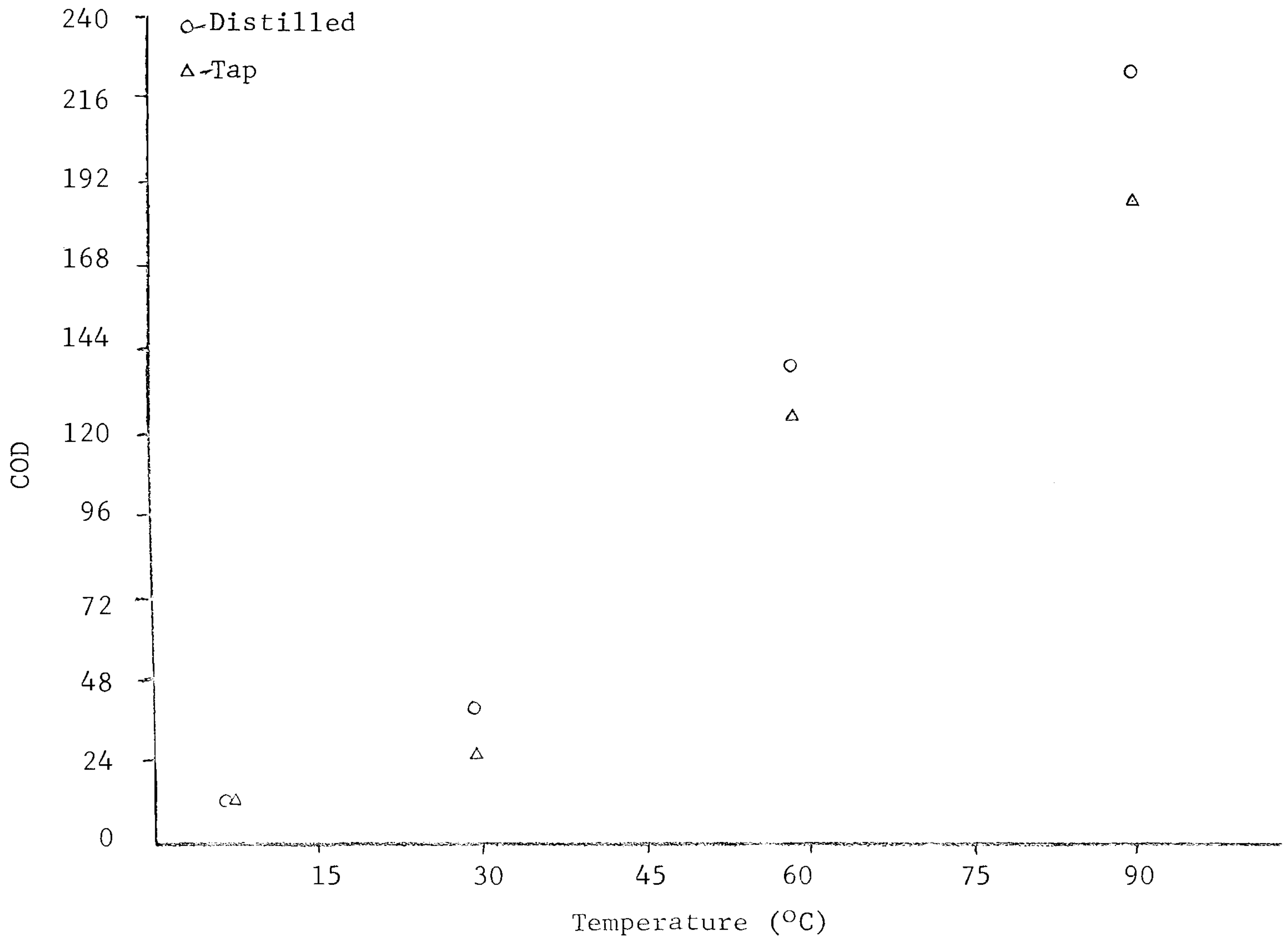

240
216
192
168
144
120
96
72
48
24
0
COD
ο-Distilled
Δ-Tap
15
30
45
60
75
90
Temperature (°C)

Figure 13.

Only one COD determination was made on inflow water. Oxygen demand of the August 12 flash flood water was 30.5 mg/l (28.7 mg/l glucose).

Phenolics

Total phenolic measurements, expressed as mg/l tannic acid (gallotannin), were made on infusion and natural waters. Measurements on infusion water are given in Table 12. Temperature had a marked effect on amount of phenolics extracted in short-term infusions (Figure 14).

In most lakes, phenolic concentrations are probably not accurate indicators of allochthonous import because decaying aquatic vegetation may also produce phenolics. Decaying Myriophylum from Becker Lake and Typha from Rose Canyon Lake produced high concentrations of phenolics under laboratory conditions. Klason (1935) reported phenolic substances ("lignin") from algae. Decaying Nostoc was tested, but no phenolic concentrations were detected during decomposition. Phenolics may prove to be fair indicators of allochthonous import in lakes with low autochthonous productivity.

Total phenolic measurements on Rose Canyon Lake and inflow water are given in Table 13. Concentrations measured in east central Arizona lake and inflow waters appear in

Table 12. Total phenolic measurements in laboratory infusions. All samples were AA Millipore filtered.

Temperature	Length of infusion	Water	Needles	No. separate determinations	mg/l tannic acid Range	Mean
10° C	24 hour	Distilled	Old	1	1.40	1.40
10° C	7 day	Distilled	Old	1	2.25	2.25
10° C	24 hour	Tap	Old	1	1.70	1.70
25° C	24 hour	Distilled	Old	1	1.75	1.75
25° C	7 day	Distilled	Old	2	4.8- 6.60	5.70
25° C	7 day	Tap	Old	2	3.7- 4.20	3.95
60° C	24 hour	Distilled	Old	1	7.20	7.20
60° C	24 hour	Tap	Old	1	7.30	7.30
90° C	24 hour	Distilled	Old	2	14.3-24.00	19.15
90° C	24 hour	Tap	Old	2	9.5-19.00	14.25
90° C*	24 hour	Distilled	Old	1	15.00	15.00
90° C*	24 hour	Tap	Old	1	15.50	15.50
10° C	24 hour	Distilled	New	1	1.55	1.55
25° C	24 hour	Distilled	New	2	2.9- 3.5	3.20
10° C	7 day	Distilled	New	1	4.25	4.25

*Litter concentrations 20 gm/3 liters.

Figure 14. Quantity of total phenolics extracted in 24 hours at different temperatures. Each point represents the mean of at least two separate determinations.

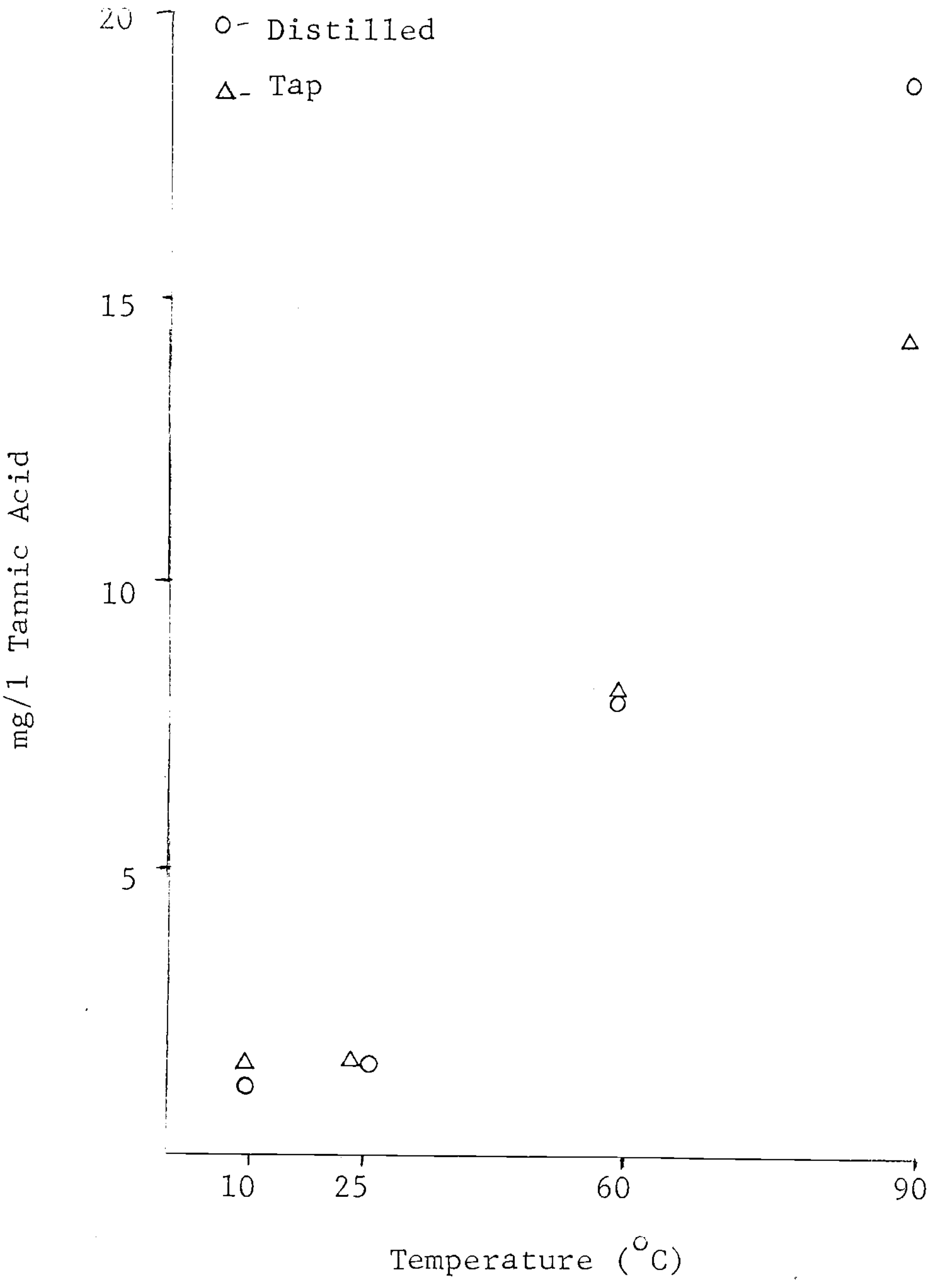

20
15
10
5
mg/1 Tannic Acid
O- Distilled
Δ- Tap
10
25
60
90
Temperature (°C)

Figure 14.

Table 13. Total phenolic measurements on Rose Canyon Lake and inflow water. Samples had been AA Millipore filtered.

	mg/l tannic acid		
	Lake		
Date	Surface	Hypolimnion	Inflow
22 October 1965	0.58	1.00	-
5 November 1965	0.50	2.25	-
15 November 1965	0.50	0.75	-
4 December 1965	0.70	0.75	-
13 August 1966	-	-	0.75
22 August 1966	0.35	-	0.05
26 August 1966	0.35	0.80	0
8 September 1966	0.38	0.75	0
23 September 1966	0.70	1.30	0.10
18 November 1966	0.30	0.50	0
2 February 1967	1.15	-	No inflow
17 April 1967	0.35	-	0.20

Tables 14 and 15. Phenolics in lake water appear to follow a cycle much the same as that of other nutrients. Fairly rapid decomposition in aerobic situations and preservation under anaerobic conditions has been demonstrated for certain tannin-like compounts (Zobell and Stadler, 1940). Steiner and Meloche (1935) demonstrated the slow decomposition of

Table 14. Phenolic distribution in lakes during summer stratification, September, 1965. Concentrations are expressed as mg/l tannic acid.

		mg/l tannic acid			
		Surface		Hypolimnion	
Lake	No. Samples	Range	Mean	Range	Mean
Hawley	2	0-0.2	0.10	0-0.250	0.13
Fool Hollow	2	0.15-0.2	0.17	0.075-0.625	0.35
Becker	2	0-0.3	0.15	0-0.200*	0.10
Woods Canyon	2	0.10-0.3	0.20	0.100-0.200	0.15

* Did not stratify.

Table 15. Phenolic concentrations in east central Arizona inflow waters.

Lake	Date	Inflow	mg/l tannic acid Un-filtered	mg/l tannic acid Filtered (AA)
Hawley	8 September 1965	Bever Dam	-	0
"	8 September 1965	Trout Creek	-	0
"	11 November 1965	Beaver Dam	0.50	0.100
"	25 November 1965	Trout Creek	0.50	0.350
"	25 November 1965	Beaver Dam	0.45	0.350
"	25 November 1965	Intermittent	0.30	0.130
"	25 November 1965	"	0.65	0.450
"	25 November 1965	"	0.25	0.140
"	2 February 1966	Trout Creek	0	0
"	2 February 1966	Beaver Dam	0	0
Fool Hollow	31 October 1965	Showlow Cr.	-	0.700
"	7 January 1966	"	0.25	0
"	7 January 1966	Fool Hollow	0.75	0.475
"	7 January 1966	Intermittent	0.55	0.500
Woods Canyon	26 March 1966	Chevlon Creek	0.25	0.200
Becker	26 November 1965	Diversion Ditch	0.50	0.200
"	25 February 1966	"	0.05	0

"lignin" in lake deposits. Waksman and Cordon (1938) showed that "lignin" retards cellulose decomposition, probably because of chemical bonding between the two compounds in wood.

Phenolics accumulate in the hypolimnion during the summer stratification because of the favorable conditions for their preservation (low pH, low oxygen, low temperature). Fall circulation brings about aeration and depletion of the phenolics by bacteria and fungi.

Strangely, highest inflow tannin at Rose Canyon was recorded during the flash flood of August 12 (Table 13). Fall and winter runoffs were generally low in tannins. The same was usually true for inflows of lakes in east central Arizona (Table 15). The temperature of runoff water may be the controlling factor in the amount of tannin extracted from litter. The same temperature factor may be important in the precipitation of phenolics in lakes. State of decomposition of litter may be another factor. During the winter litter is newly fallen, while the summer rains leach debris that has lain on the watershed for more than ten months.

Phenolic concentrations in lake water may be partly colloidal. Lake water samples filtered through AA Millipore filters lost all phenolic activity in some cases (Table 16).

Table 16. Phenolic analysis of filtered and unfiltered natural waters.

Lake	Source	mg/l tannic acid		% Loss
		Unfiltered	Filtered (AA)	
Hawley	Inflow	0.500	0.100	80.00
"	Inflow	0.450	0.350	22.20
"	Inflow	0.650	0.450	38.40
"	Inflow	0.300	0.130	56.70
"	Inflow	0.250	0.150	40.00
Becker	Surface	0.100	0.050	50.00
"	Surface	0.100	0.100	0
"	Surface	0.100	0.050	50.00
"	Surface	0.050	0	100.00
"	Inflow	0.500	0.200	60.00
"	Inflow	0.028	0	100.00
Fool Hollow	Inflow	0.550	0.500	9.10
"	Inflow	0.750	0.475	36.70
"	Inflow	0.250	0	100.00
Rose Canyon	Surface	0.500	0.500	0
"	Surface	0.750	0.670	10.70
"	Hypolimnion	0.750	0.500	33.30
"	Bottom	0.700	0.650	7.10
"	Inflow	0.300	0.100	66.70

Greatest reduction in phenolic activity seems to occur in water with high concentrations of phenolics and in inflow water. These colloids in inflow water may settle out once they reach the lake.

The nature of phenolics in pine litter has been explored by several investigators. Phenolic compounds reported from pine litter are presented in Table 17. Chief compounds found in *Pinus ponderosa* are leucocyanidin and dihydroquercetin (Hergert, 1960). Carbohydrate-linked phenolics in the form of glucosides are also important constituents of pine litter (Hergert, 1960), and they may be important nutrient sources for microorganisma.

Carbohydrates

Results of phenol-sulfuric analysis for total soluble carbohydrates are expressed as mg/l glucose because the identity of carbohydrates measured was unknown. Valid conclusions on soluble carbohydrates are probably limited to short-term infusions, since many bacteria and heterotrophic algae are efficient users of low concentrations (Wright and Hobbie, 1965). Relatively low concentrations of total carbohydrate were detected in infusions (Table 18). Newly fallen needles produced much higher concentrations than winter leached needles. This evidence indicates that

Table 17. Phenolic compounds reported from pine litter.

Compound	Source	Investigator
Misc. phenolics		
Dihydroquercetin*	Bark	Hergert (1960)
Dihydryquercetin* glucoside	Bark	"
Catechin	Bark, wood	"
Protocatechuic acid	Bark	"
Phloroglucinol	Bark	"
Caffeic acid (trans)	Bark	"
Ferulic acid (trans)	Bark	"
Coniferylaldehyde	Bark	"
Vanillin	Bark	"
Dihydromyricetin	Bark	"
Dihydromyricetin glucoside	Bark	"
Dihydrokaempherol	Bark	"
Myricetin	Bark	"
Quercetin	Bark	"
Gallocatechin	Bark	"
Epicatechin	Bark	"
Leucodelphinidin	Bark	"
Gallic acid	Bark	"
Flavonoids		
Pinocembrin	-	Geissman (1962)
Pinosilvin	-	"
Pinocembrin	-	"
Pinostrombin	-	"
Strobopinin	-	"
Cryptostrobin	-	"
Pinobanksin*	Heartwood	"
Strobobanksin	Wood, bark	"
Alpionone	Wood	"
Leucocyanidin* (3)	Wood	Hergert (1960)

*Notes compounds reported from *P. ponderosa*.

Table 18. Total soluble carbohydrate (phenol-sulfuric method) analysis of distilled water pine needle extracts.

				mg/l glucose	
Temperature	Length of infusion	Needles	No. separate determinations	Range	Mean
10° C	24 hour	New	3	0.62-0.62	0.62
25° C	24 hour	New	2	2.50-2.60	2.55
25° C	24 hour	Old	2	0.05-0.09	0.07
10° C	7 day	New	3	3.80-4.60	4.20

most of the soluble carbohydrates are either leached out or used up by organisms on the watershed during winter leaching.

Table 19 shows carbohydrates reported from pine litter by other workers. Much of the carbohydrate in pine litter may be present as polysaccharide (Dore, 1920; Kurth and Hubbard, 1951) and as polymers with phenolic compounds (Hergert, 1960). Hida _et_ _al_. (1962) report seasonal changes in the sugar content of Japanese pine needles. Parker (1957) measured higher sugar content in winter needles and related this higher concentration to freeze resistance.

This layer chromatography analysis of fresh yellow pine needle extracts by McConnell (unpublished) indicates that glucose and xylose are the main sugars present. Mannose, and possibly arabinose, rhamnose, and sucrose were also identified.

Cations

Results of spectrographic analyses for metals in a seven-day distilled water infusion of yellow pine needles are given in Table 20. The principal metals extracted were potassium, sodium, and calcium in order of importance. Concentrations of magnesium and manganese of more than one mg/l

Table 19. Carbohydrates reported from pine litter.

Worker	Source	Carbohydrates		
Dore (1920)	Wood*	Cellulose	57.72)	% dry weight
		Pentosans	3.49)	
		Mannan	6.37)	
		Galactan	0.78)	
Hergert (1960)	Wood*	Dihydroquercetin glucosides		
		Dihydromyricetin glucoside		
Hida _et al._ (1962)	Needles	Fructose		
		Glucose		
		Saccharose		
		Raffinose		
Kurth and Hubbard (1951)	Bark*	Pentosans	22.80)	% water extractives
		Galactan	25.30)	
		Glucosan	32.40)	
		Mannan	9.20)	
Parker (1957)	Needles*	Fructose	0.50)	% dry weight
		Glucose	1.30)	
		Sucrose	2.00)	
		Raffinose	2.00)	
Wolfrom and Tipson (1955)	Wood	Glucan	65.00)	% of sugars
		Mannan	12.50)	
		Xylan	13.00)	
		Galactan	6.00)	
		Arabanan	3.50)	

*Reported from _Pinus ponderosa_.

Table 20. Metals in a seven-day, 10° C. distilled water pine needle infusion. Litter concentration was 10 gm/l. Concentrations were determined by atomic absorption spectrophotometry.

Metal	mg/l
Molybdenum	<2.50
Chromium	<1.00
Lithium	<0.05
Calcium	3.70
Cobalt	<0.10
Copper	<0.10
Iron	<0.20
Magnesium	1.40
Manganese	1.12
Potassium	8.60
Sodium	3.90
Zinc	0.02
Nickel	<0.10
Lead	<0.50

were also reported. Most workers reporting analyses of pine litter report calcium, potassium, and sodium in order of importance as constituents of whole litter (Table 21). This evidence indicates that the calcium is probably present in the form of insoluble or slightly soluble compounds such as sulfates or it is mechanically bound in the litter. Broadfoot and Pierre (1939) found lower concentrations of metals in pine than in hardwood litter. Alway and Zon (1930) calculated that 17.2 pounds CaO and 2.6 pounds K_2O per acre per year were returned to the soil by needle drop in a Minnesota forest.

Extraction of metal salts from tree crowns by precipitation has been reported by several workers. Madguick and Ovington (1959) reported 33.8 kg calcium, 22.6 kg potassium, and 33.8 kg sodium per hectare per year removed from trees in a coniferous forest by precipitation. Tamm (1951) reported calcium, sodium, and potassium extracted from trees by precipitation. Dust on the trees may be the source of many metal salts (Kemmerer, 1965).

Anions

Results of analyses on laboratory infusions and lake and inflow water are given in Tables 22, 23, and 24. Infused needles produced high concentrations of ammonia- and nitrate-nitrogen. This is probably one of the most

Table 21. Metal analyses reported for <u>Pinus</u> litter. Values are percentages of oven dry weight.

Worker	Pine	% Ca	% Na	% K	% Mg	% Fe	% M	% S
Alway and Zon (1930)	Norway	0.66		0.130				
	White							
	Jack							
Ovington (1956)	Norway	0.95	0.02	0.430	0.11	0.013	0.04	0.16
Metz (1952	Shortleaf	0.59			0.19			
	Loblolly	0.43			0.15			
White (1954)	White			0.253				
	Red			0.231				
Garstka (1932)	Pitch	0.42						
	White							
	Jack							
	Norway							
Broadfoot and Pierre (1939)	Pitch	0.468-0.608						
	Scrub	0.382-0.544						
	White	0.576						
Plice (1934)	Scotch	0.6-0.8		0.65-0.74				
	Pitch	0.5-0.8						
	White	0.4-0.7						
	Red	0.3-0.4						
Askew (1937)	NewZealand	0.52-0.83			0.168-0.186	0.004-0.006	0.032-0.046	

Table 22. Infusion water anion analysis. All concentrations are expressed as mg/l. All values are the means of two separate determinations.

Length of infusion	Temperature	Needles	Water	Total PO_4	NO_3-N	NH_4-N	SO_4
24 hour	90° C	Old	Distilled	2.80	10.00	6.50	-
24 hour	90° C	Old	Tap	0.85	10.00	8.30	-
24 hour	60° C	Old	Distilled	0.44	4.80	4.90	0.5
24 hour	60° C	Old	Tap	3.80	4.95	3.60	-
24 hour	25° C	Old	Distilled	0.32	1.00	Turbid	-
24 hour	10° C	Old	Distilled	0.19	0.10	2.02	-
7 day	25° C	Old	Distilled	0.21	3.00	2.20	-
7 day	25° C	Old	Tap	0.47	2.65	2.50	-
7 day	10° C	Old	Distilled	0	0.80	4.70	0.5
24 hour	25° C	New	Distilled	0.25	1.15	Turbid	-
24 hour	10° C	New	Distilled	0.50	0.50	Turbid	-
7 day	10° C	New	Distilled	0.25	2.40	Turbid	-

Table 23. Anion analyses of Rose Canyon Lake water. Concentrations are expressed as mg/l.

Date	Situation	Total PO_4	NH_4-N	NO_3-N
26 August 1966	Surface	-	0.55	0.75
8 September 1966	Surface	0.29	0.81	0
23 September 1966	Surface	0.95	0.90	0.70
"	Hypolimnion	2.80	2.60	0.90
18 November 1966	Surface	0.17	0.71	0.40
2 February 1967	Surface	1.00	4.20	-
17 April 1967	Surface	1.17	Turbid	0.90

Table 24. Anion analyses of Rose Canyon inflow water. Concentrations are expressed as mg/l.

Date	Estimated flow (cfs)	Total PO_4	NH_4-N	NO_3-N	Si	SO_4
12 August 1966	20.0	0.10	0.90	1.10	0	4.0
14 August 1966	0.5					
22 August 1966	0.5	-	0.30	1.00	-	-
26 August 1966	0.5					
8 September 1966	0.5	2.29	0.30	0	-	-
23 September 1966	0.5	0.81	0.45	0.65	-	-
18 November 1966	0.5	0.21	0.20	0.10	-	-
2 February 1967	No inflow					
17 April 1967	1.0	0.65	Turbid	0.45	-	-

important limnological contributions of pine litter because soluble nitrogen compounds are readily available to both bacteria and photosynthetic algae. Inflow and lake water also contained appreciable concentrations of ammonia and nitrate nitrogen (Table 24).

Nitrogen percentages reported for pine litter are shown in Table 25. Values range from 0.3 to 1.82 per cent of oven dry weight. Birge and Juday (1927) demonstrated higher carbon-nitrogen ratios for allochthonous than for autochthonous organic matter in lakes.

Phosphorus is probably the most important nutrient to primary photosynthetic producers, and it is often a limiting factor in primary production (Bennett, 1965). Total phosphate measurements for infusion, lake, and inflow waters are given in Tables 22, 23, and 24. All water contained relatively high concentrations of phosphate.

Phosphorus percentages found in pine litter by other workers are presented in Table 25. Values varied from 0.06 to 0.13 per cent of oven dry weight.

The high concentrations of phosphate and nitrate in Rose Canyon Lake and inflow water are indicative of its low primary productivity. Phosphate is used up quickly in productive lakes, and concentrations are usually very low (Ruttner, 1963). This information suggests that inorganic fertilization of soft water lakes is a losing proposition.

Table 25. Nitrogen, phosphorus, chloride, and sulfur percentages prepared for Pinus litter. All values are based on oven dry weights.

Worker	Pine	% N	% S	% P	% Cl
Alway and Zon (1930)	Norway White Jack	0.74	0.08	0.13	-
White (1954)	Red White	0.40-1.09	-	0.20-0.30	
Metz (1952)	Shortleaf	0.45			
	Loblolly	0.31			
Coile (1937)	Shortleaf	0.80			
	Loblolly	0.40			
Broadfoot and Pierre (1939)	Pitch	0.46-0.57			
	Scrub	0.59-1.08			
	White	0.50			
Ovington (1956)	Norway	0.87		0.09	
Askew (1937)	New Zealand	0.82-1.26			0.07-0.15
Plice (1934)	White			0.06-0.08	

Trophic Value of Leachates

Dense bacterial and fungal "blooms" developed in infusions and in incubated lake and inflow water (Figure 15). These organisms would be available to filter-feeding invertebrates and to aufwuchs grazers. McConnell (unpublished) demonstrated significantly higher growth in filter-feeding

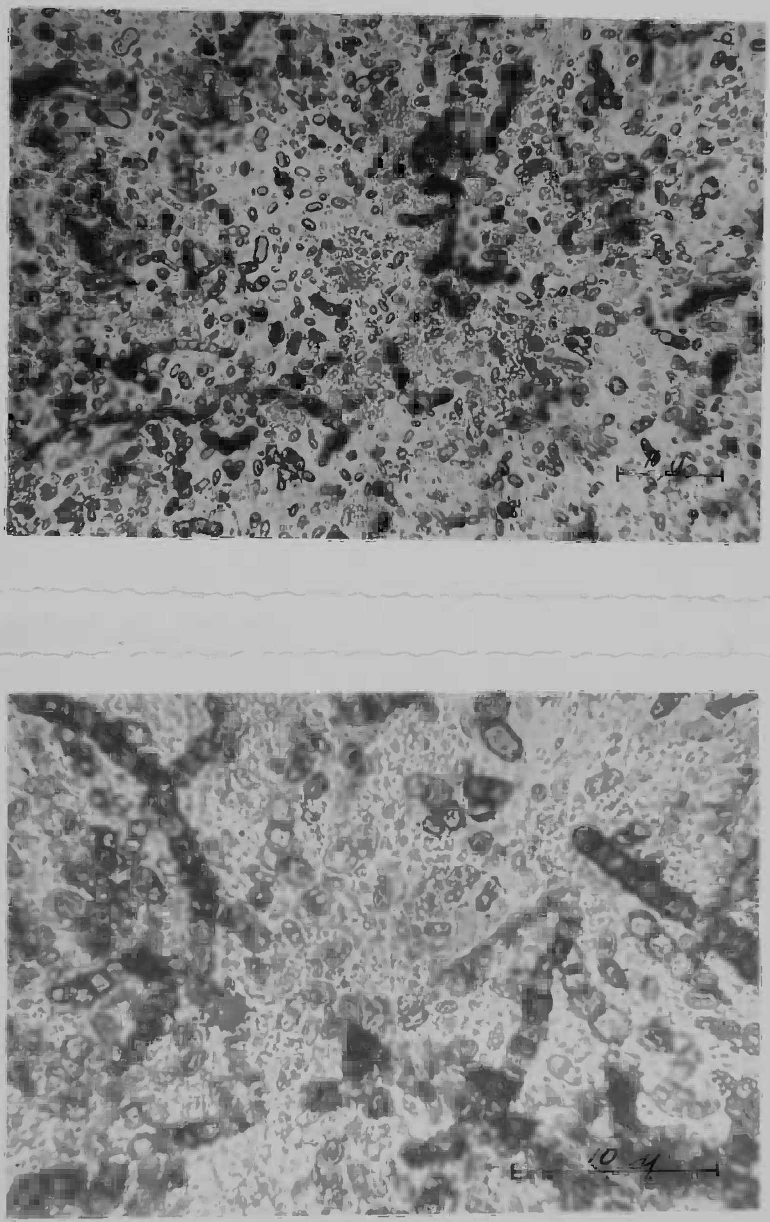


Figure 15. Photomicrographs of organisms developing in laboratory infusions of pine needles.

xenopus larvae in infused pine needle water. Swingle (1947) found higher fish production in ponds fertilized with pine needles.

Pine litter is undoubtedly of less trophic value than deciduous litter. Nykvist (1959) reports only a 3 per cent weight loss in pine litter after 40 days of leaching. Comparable weight loss in oak litter is more than 10 per cent (Nykvist, 1962). This author (1959) also reports that grinding greatly increases the solubility of pine litter.

Direct Estimates of Import

Estimates of import to Rose Canyon Lake from the 17 recovered litter collectors are given in Table 26. No pine needles were found in the collectors. Total allochthonous material present was one fir needle and one willow leaf. There was one observed flash flood (August 12) on the watershed during the sampling period. Possible reasons for the low estimate of import are uneven distribution of litter around inflows and close to the dam, and loss of floating litter over the spillway during periods of high runoff.

Direct estimates were made in four other lakes by Eckman dredge (Appendix).

Table 26. Estimate of allochthonous import to Rose Canyon Lake during the 1966 summer rainy season from recoverable litter collector data. Confidence limits are 80 per cent.

Total Samplers Placed	47
Date Placed	14 June 1966
Samplers Recovered Intact	17
Date Recovered	23 September 1966
Per Cent Recovery	35.8
Individual Sampling Area	329 cm^2
Pooled Sampling Area (17)	4659 cm^2 (0.4659 m^2)
Total Area of Lake Bottom	29,665 m^2
Weight of Material in Buckets	0.0475 gm ± 0.00318 gm
Estimated Total Import	3.0244 Kg ± 0.2025 Kg

SUMMARY AND CONCLUSIONS

The principal factors affecting pine litter import are precipitation and runoff rates, time of litter drop, and litter buoyancy. Favorable conditions are a dry fall, winter, and spring followed by the sudden onset of summer rains. Heavy winter precipitation tends to pack pine needles and make them more difficult to move. Dissolved organic matter is probably a proportionately more important allochthonous constituent on pine than on oak watersheds because of the better year round soil moisture conditions and more abundant humus at higher elevations.

Many of the trout lakes located in pine regions of Arizona are characterized by low alkalinity. The geology of the watersheds is the main factor influencing lake alkalinity. Combined with low innate alkalinity, alkalinity reduction by pine litter may be an important factor limiting primary production in Arizona trout lakes. Flushing of the lakes due to high runoff rates (at least in some years) also contributes to the low alkalinity problem.

Color contributed by pine needle leachates is another factor inhibiting primary production. Optical density of lake water was highest during the fall when one would expect high primary productivity. Inflow color never reached high levels, so it appears that color develops in the lake from dissolved organics or direct import.

Oxygen depletion in lakes due to high oxygen demands of organic materials is another important limnological effect of pine litter. Oxygen depletion in the hypolimnion may give rise to toxic conditions caused by sulfate reduction to H_2S. Oxygen demand may keep dissolved oxygen levels well below saturation for several weeks after fall turnover, and it may cause oxygen problems for trout in some Arizona impoundments. Although the nature of the oxygen demand by litter phenolics is unknown, at least part of it may be enzymatic.

Biogenic salts--phosphates and nitrates--are important constituents of leachates, and they are available to both primary producers and bacteria. The low alkalinity of most Arizona trout lakes, however, imposes restrictions on primary productivity, so that these nutrients may be of little benefit to photosynthetic organisms.

The trophic value of organic matter in allochthonous debris is another important consideration. The estimate of macroscopic organic import at Rose Canyon for the summer of 1966 is insignificant as the basis for a food chain.

The estimate of import is less than 1 per cent of Kemmerer's (1965) estimate of gross photosynthesis. Allochthonous material is undoubtedly more important to the lake than this estimate indicates. Two possible reasons for this underestimate are uneven distribution of litter in the lake and the trophic importance of dissolved organics.

Results of this study seem to indicate that in the case of pine litter and soft water trout lakes it is more desirable to have the litter leached on the watershed and not washed into the lakes. The low percentage of weight loss and the slow decomposition of pine litter could cause a litter buildup on lake bottoms. This mechanical effect coupled with alkalinity reduction, oxygen depletion, and color imparted to the water appears to outweigh the possible trophic value of pine litter.

APPENDICES

Appendix A. Selected morphometric characteristics of study lakes in east central Arizona.

Lake	Elevation (feet)	Surface Area (acres)	Maximum Depth (feet)	Mean Depth (feet)	Shoreline Development Factor
Hawley	8300	290	52	21	3.2
Becker	7000	110	20	10	1.3
Woods Canyon	7526	51	36	20	2.6
Fool Hollow	6256	149	61	20	3.3

Appendix B. Climatic data from study lakes in east central Arizona.

Lake	Mean Jan. Air Temp. (F)	Mean July Air Temp. (F)	Mean Yearly Precip. (inches)	Dominant Vegetation Type
Hawley	24	58	28	Mixed conifer
Becker	31	67	12	Grassland
Woods Canyon	28	63	20	Mixed conifer
Fool Hollow	32	68	18	Mixed

<u>Appendix C</u>. Color of lake water in east central Arizona. Optical density, using one-inch tubes, was measured at 360 mμ. Measurements were made during fall and winter, 1965-66.

	Optical Density					
	Surface			Bottom		
Lake	No. Samples	Range	$\bar{X}$	No. Samples	Range	$\bar{X}$
Hawley	5	0.010-0.030	0.024	3	0.020-0.06	0.0300
Becker	5	0.025-0.100	0.052	2	0.025-0.12	0.0690
Woods Canyon	2	0.027-0.070	0.046	2	0.025-0.15	0.0675
Fool Hollow	4	0.065-0.200	0.084	2	0.066-0.15	0.1080

<u>Appendix D</u>. Direct estimation of standing crop of allochthonous debris from Eckman dredge sampling in east central Arizona lakes.

Lake	No. Samples	Area Sampled (cm^2)	Estimate (gms/m^2)	80% Confidence limits (± gms)	Area of Lake (m^2)	Total Estimate for Lake (kg)	80% Confidence limits (± kg)
Hawley	18	3744	6.958	0.3461	1,173,630	7,836.120	392.99
Fool Hollow	18	3744	22.409	0.9222	603,003	13,512.690	556.09
Woods Canyon	20	4160	556.851	28.9856	206,397	114,932.380	5882.54
Becker	54	11232	2.586	0.0287	445,170	1,151.280	12.78

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