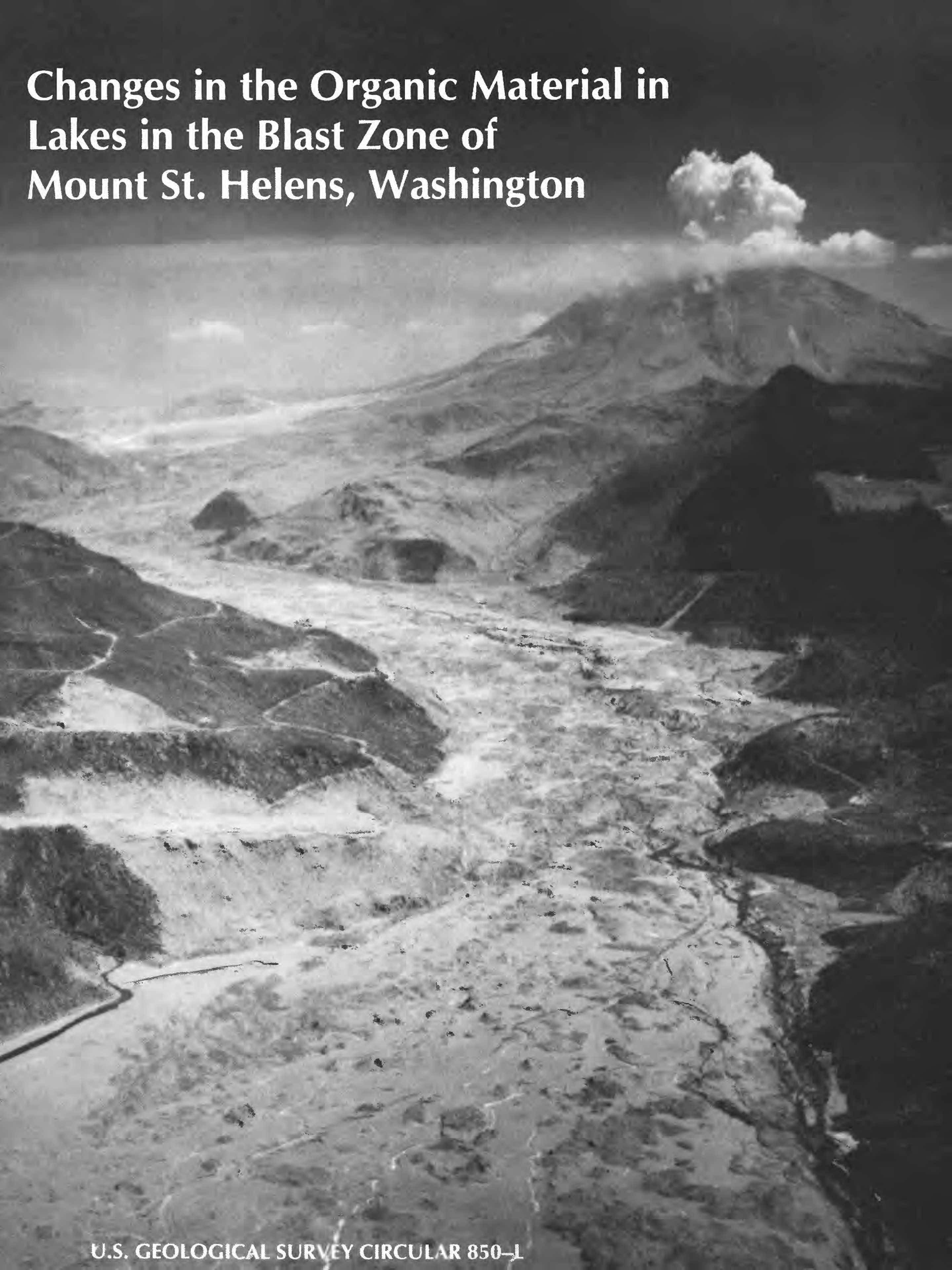
Changes in the Organic Material in Lakes in the Blast Zone of Mount St. Helens, Washington



U.S. GEOLOGICAL SURVEY CIRCULAR 850–L

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By D. M. McKnight, J. M. Klein, and R. C. Wissmar

Hydrologic Effects of the Eruptions
of Mount St. Helens, Washington, 1980

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Multiply	*By*	*To obtain*
foot (ft)	0.3048	meter (m)
acre	4046.87	square meters (m^2)
mile	1.609	kilometer
acre-foot	0.001233	cubic hectometer (hm^3)

HYDROLOGIC EFFECTS OF THE ERUPTIONS OF
MOUNT ST. HELENS, WASHINGTON, 1980

CHANGES IN THE ORGANIC MATERIAL IN LAKES IN THE BLAST ZONE OF MOUNT ST. HELENS, WASHINGTON

By Diane M. McKnight, John M. Klein and Robert C. Wissmar

ABSTRACT

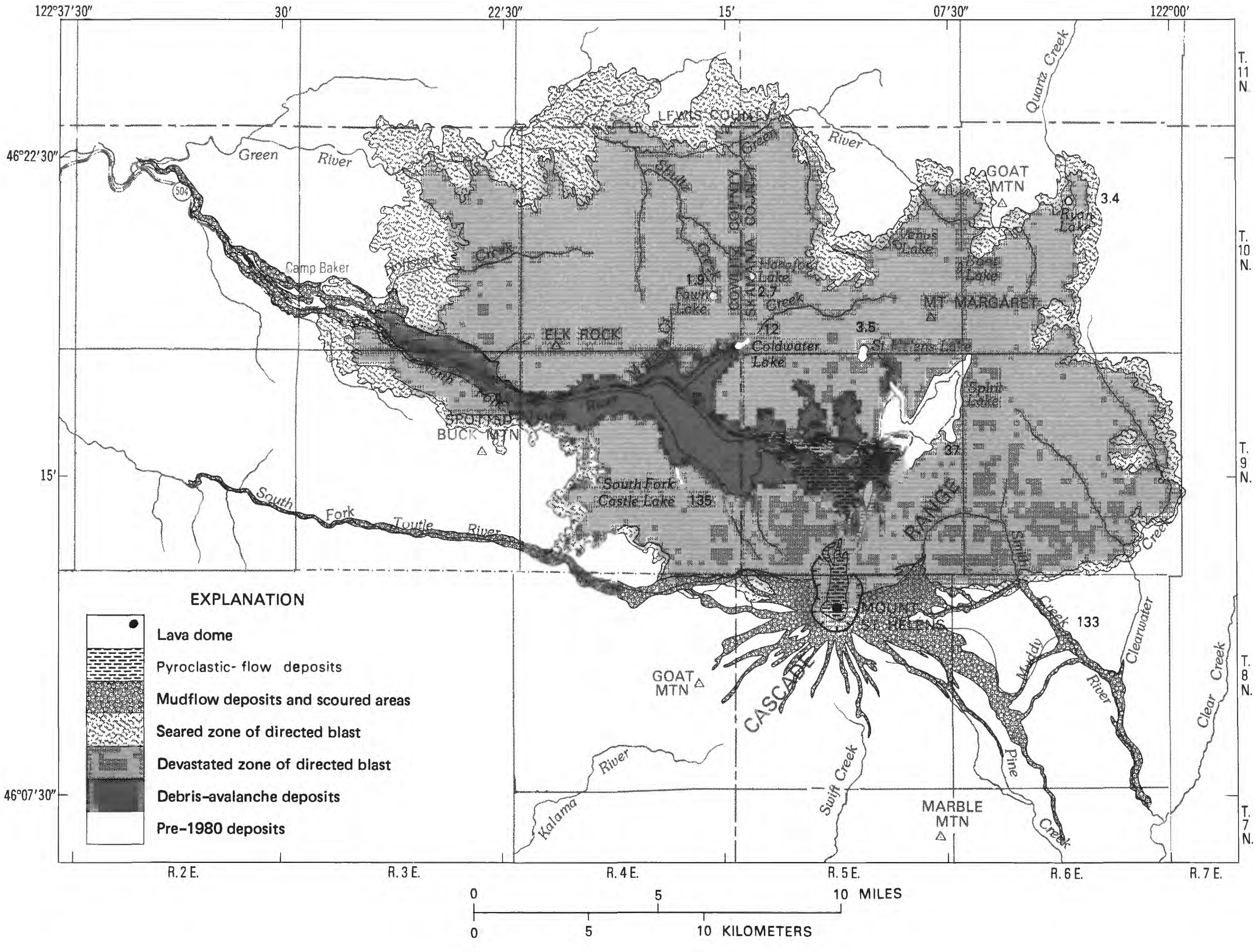
The productive conifer forest that had surrounded Mount St. Helens, Washington, was destroyed by the cataclysmic eruption of the volcano on May 18, 1980. Large quantities of organic material were introduced into the nearby surface waters, either as soil and plants incorporated into pyroclastic, mudflow, or debris-avalanche deposits, or as blowndown timber swept into lakes by the lateral blast of hot volcanic gases. The resulting major increases in the concentration of dissolved organic material were one of the most significant changes in the water chemistry of surface waters of the blast zone. The concentrations of dissolved organic material were greater in lakes directly associated with pyroclastic, mudflow, and debris avalanche deposits, than in lakes receiving only ash deposits and blowndown timber. In these lakes, increases in dissolved organic material were correlated with dense bacterial populations, and large increases in the concentrations of dissolved manganese, iron, and sulfur. The majority of the dissolved-organic material was higher molecular-weight, yellow organic acids similar in their general properties to aquatic fulvic acids found in most surface waters. Many of the specific organic compounds identifiable by gas chromatography—mass spectrometry were derived from the pyrolysis of plant and soil organic material.

The major changes in the organic chemistry of the blast-zone lakes between late summer 1980 and spring 1981 can be attributed to the tremendous inflow of rain and snowmelt. For example, the decrease in the dissolved organic carbon concentration of South Fork Castle Lake from 135 milligrams carbon per liter on September 11, 1980, to 10 milligrams carbon per liter on May 1, 1981, is attributable to the almost 14-fold increase in lake volume. Aquatic fulvic acids continued to be the major fraction of the organic material, and the refractory nature of humic substances is the major explanation for the persistence of the dissolved organic material in these lakes. During the spring and summer of 1981, there were some changes in the chemical nature of the aquatic fulvic acids, such as a decrease in sulfur content. There appeared to be two minor sources of dissolved organic material in these lakes. In Spirit and South Fork Castle Lakes, the hypolimnion became anaerobic during the summer and the concentrations of dissolved organic carbon increased, indicating that anaerobic decomposition of organic material in the volcanic deposits covering the lake bottoms was a small, but continuing source of dissolved organic material. The other minor source was dissolved organic material leached from volcanic ash and dead plant material. Many of the organic compounds identified in surface waters within the blast zone in the summer of 1980 were not identified in surface waters within the blast zone in the late spring of 1981, probably because of the considerable dilution by rain and snowmelt. The few compounds that were identified in the late spring of 1981 probably were transported into the lakes with rain and snowmelt that had leached volcanic debris.

INTRODUCTION

The May 18, 1980, eruption of Mount St. Helens in southwestern Washington caused massive and widespread destruction. A once-productive forest on the north slopes of the mountain was completely pyrolyzed and burned; with increasing distance from the mountain, trees were uprooted and stripped of bark, branches, needles, and leaves. In sheltered areas such as North Coldwater Creek, many of the trees were blown over, burned and charred in the intense heat and then buried in the hot debris and mud. Still others were swept downstream in the mudflow before being buried. Accordingly, there was a significant physical, chemical, and biological alteration of the aquatic environments within the devastated blast zone.

Concentrations of many inorganic chemical constituents increased in the lakes and streams from the dissolution of inorganic material contained in the pyroclastic material, mud, ice, and ash. Additionally, because of the tremendous quantity of vegetation pyrolysed by the blast and eventually deposited in the aquatic environment, great increas-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R. 4 E.
R. 5 E.
R. 6 E.
R. 7 E.
Green River
504
Camp Baker
LEWIS COUNTY
COWLITZ COUNTY
SKAMANIA COUNTY
River
Quartz Creek
GOAT MTN
Ryan Lake
3.4
Venus Lake
Fawn Lake
1.9
Hanaford Lake
2.7
Creek
MT MARGARET
ELK ROCK
12
Coldwater Lake
3.5
St. Helens Lake
Spirit Lake
37
SPOTTED BUCK MTN
River
South Fork Castle Lake
135
South Fork Toutle River
RANGE
CASCADE
MOUNT ST. HELENS
GOAT MTN
Smith Creek
133
Muddy River
Clearwater Creek
Clear Creek
Pine Creek
Swift Creek
Kalama River
MARBLE MTN
EXPLANATION
Lava dome
Pyroclastic- flow deposits
Mudflow deposits and scoured areas
Seared zone of directed blast
Devastated zone of directed blast
Debris-avalanche deposits
Pre-1980 deposits
0 5 10 MILES
0 5 10 KILOMETERS

es occurred in the concentration of dissolved organic material. Greater concentrations of dissolved organic material occurred in those lakes and streams directly associated with pyroclastic, mudflow, and debris avalanche deposits, than in those water bodies into which only ash and timber were deposited (fig. 1). Extremely abundant microbial populations accompanied these increases in dissolved organic material and probably were caused by these increases (Wissmar, Devol, Staley, and Sedell, 1982; Baross and others, 1982; Staley and others, 1982).

Analysis of water samples collected from Sprit and Coldwater Lakes during the summer of 1980 following the eruption showed that much of the dissolved organic material was similar to aquatic-fulvic acids from more typical environments (McKnight and others, 1982). Pereira and others (1982) identified many specific organic compounds, which were similar to many of the compounds observed in Kraft pulp-mill wastes, thus concluding that the pyrolysis of plant and soil material in the blast zone was indeed the major source of dissolved-organic material.

In this report, data are presented that describe changes in the organic material in several of the blast-zone lakes in the summer of 1981, 1 year after the major eruption of Mount St. Helens. Data are presented for: (1) The distribution of dissolved and suspended organic material in these lakes; (2) the fractionation of the dissolved-organic material into hydrophobic and hydrophilic solutes; (3) the characterization of aquatic humic substances; and (4) the identification of low molecular-weight organic acids and neutral-organic compounds. Determining the changes in the dissolved organic material is an important part of the overall study of the limnological recovery of these lakes.

DESCRIPTION OF BLAST-ZONE LAKES

Studies of the dissolved organic material in the summer 1980 showed that differences between lakes were related to differences in the way lakes had been physically altered by the May 18, 1980, eruption. The general physical, chemical, and biological characteristics of blast-zone lakes are described here to provide a background for discussing the changes in organic constituents.

FIGURE 1 (facing page).—Blast zone of Mount St. Helens showing the dissolved organic-carbon concentrations, in milligrams per liter, of several lakes sampled on September 11, 1980.

PHYSICAL CHARACTERISTICS

Lakes in the blast zone (fig. 1) can be divided into two major groups: (1) Those that were formed or directly impacted by mudflow, debris avalanche, or pyroclastic deposits (Spirit Lake, South Fork Castle Lake, and Coldwater Lake); and (2) those in the area where timber was blown down or scorched by the blast of hot volcanic gases, and a thick layer of volcanic ash was deposited (including St. Helens, Fawn, Hanaford, and Ryan Lakes).

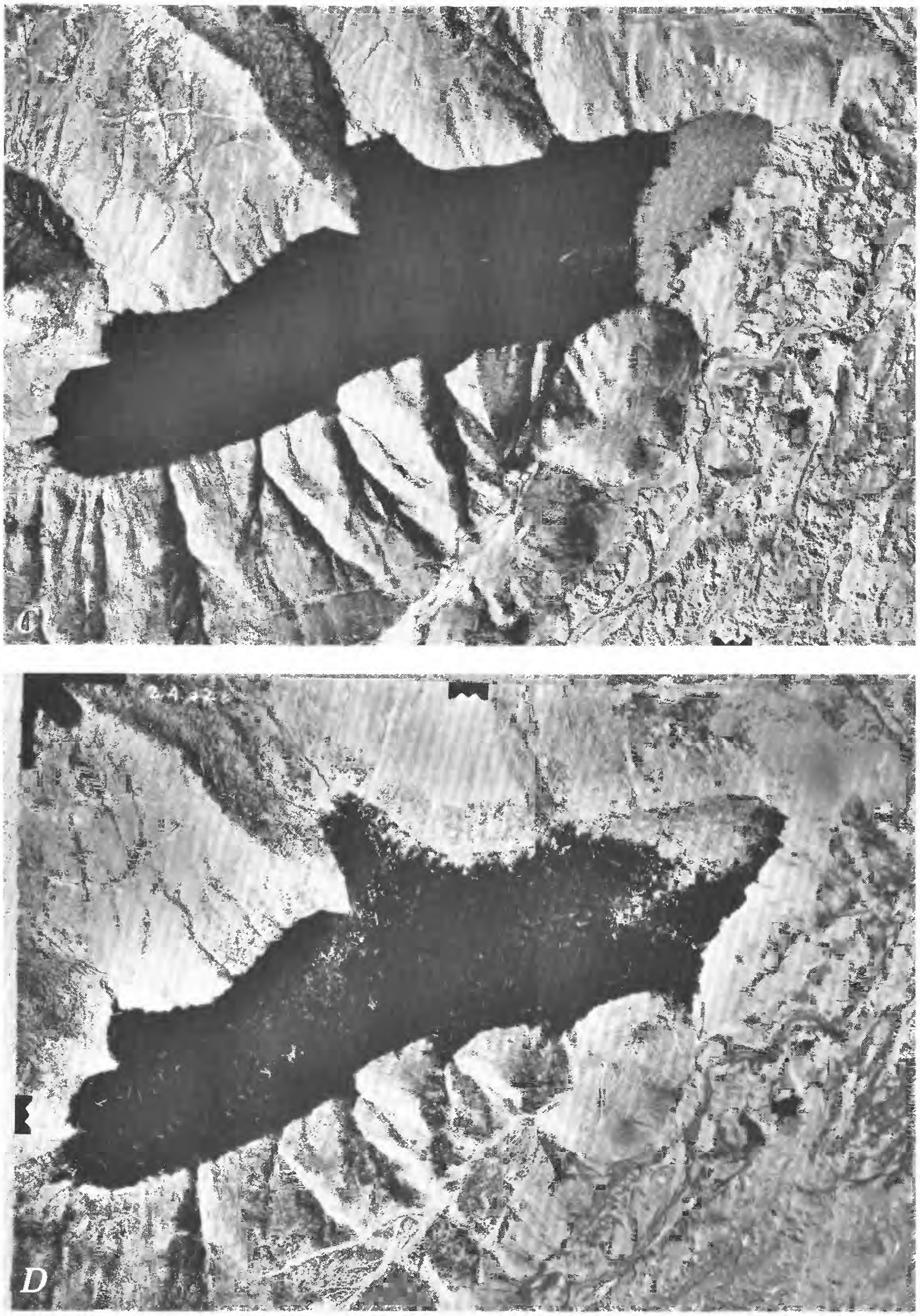
South Fork Castle and Coldwater Lakes are new lakes that were formed by two small creeks being dammed by the debris avalanche and mudflow that filled the upper Toutle River Valley. The volume of water in these lakes greatly increased during the winter and spring of 1981. Aerial photographs of South Fork Castle Lake (fig. *2A, B, C,* and *D*) clearly show that the lake greatly increased in size from November 11, 1980, to March 1, 1981. The volume of South Fork Castle Lake increased by about 14 times from 1,100 acre-feet on September 30, 1980, to 14,960 acre-feet on May 27, 1981; and the volume of Coldwater Lake increased by about 6 times from 10,800 acre-feet on October 31, 1980, to 67,600 acre-feet on May 31, 1981 (U.S. Geological Survey, October 1981, unpublished data). The volume of both lakes increased more slowly through the summer and fall of 1981.

As shown in figure 1, pyroclastic-flow deposits entered and partly filled Spirit Lake during the May 18, 1980, eruption. The areal size and elevation of Spirit Lake continued to increase from snowmelt and rainfall because the original outlet, the North Fork Toutle River, was blocked by the debris avalanche. Unlike the two newly formed lakes, there was a limited volume increased from 126,000 acre-feet on November 22, 1980, to 169,000 acre-feet on May 31, 1981.

During and after the May 18, 1980, eruption, trees, shrubs, and other organic debris were swept into Spirit, South Fork Castle, and Coldwater Lakes, and the lake surfaces were partly covered with floating logs from the summer of 1980 through the fall of 1981. However, the major source of dissolved-organic material in these lakes has been pyrolyzed plant and soil material in volcanic deposits that cover the lake bottoms.

Many of the lakes in the second group in the timber blowdown-zone and scorch-zone also had large numbers of floating logs covering their surface. Generally, those lakes in the Mt. Margaret area that were covered with ice at the time of the erup-

FIGURE 2.—Aerial photographs of South Fork Castle Lake on: A-July 20, 1980; B-November 11, 1980; District Office,



C-March 1, 1981; and D-July 27, 1981. Photographs from the U.S. Geological Survey, Washington Tacoma, Washington.

tion (including St. Helens, Fawn, and Hanaford Lakes) were not as severely affected as some of the lakes farther away from Mt. St. Helens that were not covered with ice. In fact, small fir trees that probably had been buried by snow at the time of the eruption were observed along the banks of St. Helens Lake, which drains into Spirit Lake. By studying these lakes in the blown-down zone, we can distinguish between the effects of the mudflow, debris avalanche, and pyroclastic deposits, and the effects of the blown-down logs and the denudation of the watersheds.

CHEMICAL CHARACTERISTICS

INORGANIC CONSTITUENTS

The inorganic chemistry of blast-zone lakes was altered by dissolution of magmatic and lithic deposits (Wissmar, Devol, Nevissi, and Sedell, 1982). Increases in major cations, anions, and trace metals generally were greatest in the first group of lakes associated with mudflow, debris avalanche, and pyroclastic deposits, as illustrated by selected pre- and post-eruption data for Spirit Lake (table 1) obtained by Dion and Embry (1981). Similar data was obtained by Wissmar, Devol, Nevessi and Sedell (1982). The pH of these lakes remained between 6.0 and 8.0, buffered by carbonic acid and dissolved organic acids.

During the winter and spring of 1981, dissolved inorganic constituents were diluted by rainfall and snowmelt. For example, the data for major cations and trace metals in South Fork Castle Lake on September 11, 1980, and on May 1, 1981, show that the concentration of most of these constituents decreased by about four fold (table 2). The volume of the lake increased by about 14 times during this interval, which indicates that dissolution of volcanic deposits in the watershed continued to be a source of dissolved inorganic constituents. The changes in the inorganic chemistry of lakes in the second group varied with the position of the lake relative to different blast deposits (Dion and Embrey, 1981; Wissmar, Devol, Nevissi, and Sedell, 1982).

TABLE 1.—*Concentrations of selected major cations, anions, and trace metals in Spirit Lake, March 28, 1980, and June 30, 1980*

[Date from Dion and Embry, 1981: mg/L, milligrams per liter; μg/L, micrograms per liter]

Constituent	March 28, 1980	June 6, 1980
Major cations, in mg/L		
Calcium, Ca	2.8	74
Magnesium, Mg	0.6	13
Sodium, Na	2.0	68
Major anions, in mg/L		
Chloride, Cl	1.5	86
Sulfate, SO_4	1.0	190
Trace metals, in μg/L		
Iron, Fe	6	5,000
Manganese, Mn	10	8,800

TABLE 2.—*Concentrations of some major cations and trace metals in South Fork Castle Lake on September 11, 1980, and April 30, 1981*

[mg/L, milligrams per liter; μg/L, micrograms per liter]

Constituent	Sept. 11, 1980	April 30, 1981
Major cations, in mg/L		
Calcium, Ca	74.3	21.4
Magnesium, Mg	16.7	4.4
Sodium, Na	82.3	18.6
Trace metals, in μg/L		
Copper, Cu	28	14
Iron, Fe	1,970	640
Manganese, Mn	4,570	1,120
Lead, Pb	38	33
Zinc, Zn	38	33
Strontium, Sr	373	97

ORGANIC CONSTITUENTS

The increase in the concentration of dissolved organic carbon (DOC) in blast-zone lakes has been discussed by Dion and Embrey (1981), Wissmar, Devol, Nevissi, and Sedell, (1982), Pereira and others (1982), and McKnight and others (1982). During the summer of 1980, DOC concentrations were greatest in South Fork Castle, Coldwater and Spirit Lakes. For example on September 11, 1980, the DOC of South Fork Castle Lake was 135 mg C/L (milligrams carbon per liter). The DOC concentrations also were affected by the dilution of the lakes by snowmelt; the DOC of South Fork Castle Lake on May 1, 1981, was 10 mg C/L. Comparison of this data with the 14-fold increase in lake volume indicates that there were no major new sources of dissolved organic material in the snowmelt.

BIOLOGICAL CHARACTERISTICS

As described by Baross and others (1982), Wissmar, Devol, Staley, and Sedell, (1982), and Staley and others (1982), extensive bacterial populations and anaerobic conditions developed within weeks after the May 18, 1980, eruption in the most severely impacted lakes. Dense bacterial populations (as many as $2x10^7$ cells per milliliter) were correlated with high DOC, manganese, sulfur and iron concentrations, as anaerobic degradation of organic material and oxidation of reduced metals were the major energy sources. Baross and others (1982) concluded that nitrogen-cycle reactions regulated microbial processes in these lakes.

Rain and snowmelt entering these lakes during the winter and spring of 1981 destratified and oxygenated these lakes (Dahm and others, 1982). However, as the summer progressed, the lakes became stratified and microbial degradation of organic material from volcanic deposits on the lake bottoms resulted in anaerobic conditions, increased bacterial activity, and increased concentrations of reduced metal species in the bottom waters.

METHODS

Samples were collected from both the epilimnion and hypolimnion in cleaned, precombusted glass bottles and stored on ice during transport to the U.S. Geological Survey laboratory in Lakewood, Colorado. Here the samples were stored at 4°C (degrees Celsius) until analysis. One hundred milliliters of sample were filtered through precombusted Gelman GFC glass fiber-filters.[1] The filtrate was analyzed for DOC, after acidification and purging of inorganic carbon dioxide, with a Beckman 915-C carbon analyser. The filters were frozen and subsequently analyzed for suspended organic carbon (SOC) by the Oceanographic Method (Strickland and Parsons, 1972).

The fractionation of dissolved organic material into hydrophobic and hydrophilic solutes was performed as described by Leenheer and Huffman (1976) by Huffman Laboratories, Denver, Colorado. Aquatic fulvic acids were isolated from filtered (0.45 micrometer Selas silver membranes) lakewater samples using XAD-8 resin following the method described by Thurman and Malcolm (1981), with the exception that humic acids were not separated. Elemental analysis of the freeze-dried fulvic acids were performed by Huffman Laboratories using various combustive methods. Carboxylic acid and phenolic content was determined by potentiometric titration (Thurman and Malcolm, 1981). Molecular weight was calculated from measurement of the radius of gyration by small angle X-ray scattering (Thurman and others, 1982). Carbohydrate content was determined by the phenol-sulfuric acid and method using a 4 percent phenol solution and glucose as a standard.

The gas chromatography-mass spectrometry methods described by Pereira and others (1982) were followed without deviation. To summarize, unfiltered samples that had been stored at 4°C, were extracted with ether, to obtain neutral and acidic fractions. The organic-acid fraction was then methylated with diazomethane; and both fractions were analysed with a Finnigan 4000 computerized gas chromatograph-quadropole mass spectrometry system.

Identification of specific organic compounds was based on the mass spectral library fit (FIT values generally were about 950, with 1000 being a perfect fit) and more importantly on comparison of the relative retention time (RRT) with RRT values reported by Pereira and others (1982). Pereira and others (1982) had confirmed many of their organic compound identifications by analysing standard compounds and by high-resolution mass spectrometry.

RESULTS AND DISCUSSION

DISSOLVED AND SUSPENDED ORGANIC CARBON

Results of the DOC and SOC analyses for the summer of 1981 are presented in table 3 and figures 3-6 for Spirit, South Fork Castle, Coldwater and St. Helens Lakes. As described previously (fig. 1), Spirit Lake received pyroclastic deposits; South Fork Castle and Coldwater Lakes were formed when the debris avalanche filled the North Toutle River Valley, and St. Helens Lake was in the zone of blown-down timer that received significant inputs of debris from the lateral blast and significant ashfall. The DOC concentrations in all four lakes decreased

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[1] Any use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

TABLE 3.—*Organic carbon in four representative lakes in the blast zone of Mount St. Helens during the summer, 1981*

[DOC, dissolved organic carbon; SOC, suspended organic carbon; mg C/L, milligrams carbon per liter.]

Lake	Date sample collected	Epilimnion		Hypolimnion	
		DOC (mg C/L)	SOC (mg C/L)	DOC (mg C/L)	SOC (mg C/L)
Spirit Lake	4/30	17.4	--	--	--
	7/16	14.6	0.6	16.5	2
	8/3	15.2	.2	17.6	.5
	8/28	15.3	.4	17.4	.6
	9/28	15.0	.5	17.1	.7
South Fork Castle Lake	5/1	10.2	--	--	--
	7/21	7.7	.8	9.6	3.1
	8/4	6.2	.4	7.6	.5
	8/27	6.7	.2	13.0	1.6
	9/28	7.4	.3	9.9	--
Coldwater Lake	4/30	6.9	--	--	--
	6/17	4.0	--	6.5	.2
	7/16	5.3	.6	4.6	.60
	8/5	4.7	.60	6.9	.8
	8/27	6.0	.4	5.0	.1
	9/27	5.6	.3	4.2	.6
St. Helens Lake	6/25	1.5	.4	1.4	1.1
	7/16	1.7	.5	1.2	.8
	8/3	1.6	1.2	1.2	.2
	8/27	1.4	.6	1.4	.4
	9/28	1.9	.3	1.3	.4

significantly during the winter and spring from dilution by rain and snowmelt. For example, the DOC concentration in Spirit Lake decreased from 37 mg C/L on September 11, 1980, to 17 mg C/L on April 30, 1981; and the DOC concentration of South Fork Castle Lake decreased from 135 mg C/L on September 11, 1980, to 10.2 mg C/L on May 1, 1981. However, DOC concentrations in Spirit, South Fork Castle, and Coldwater Lakes were still much greater than in Spirit Lake before the May 18, 1980, eruption (0.8 mg C/L) and much greater than in other lakes in the Cascade Range.

SPIRIT LAKE AND SOUTH FORK CASTLE LAKE

Several trends are apparent in the data from Spirit Lake and South Fork Castle Lakes (figs. 3 and 4). First, DOC concentrations were much greater than SOC concentrations; these are typical

TABLE 4.—*Fractionation of dissolved organic carbon in surface waters in the blast zone of Mount St. Helens*

[DOC, dissolved organic carbon; mg C/L, milligrams per liter.]

Lake	Date sample collected	Depth zone	DOC (mg C/L)	Hydrophobics (percent)			Hydrophilics (percent)		
				Acids	Neutrals	Bases	Acids	Neutrals	Bases
Spirit Lake	9/11/80	Epilimnion	37.3	41	12	2	43	1	2
	4/30/81	Epilimnion	17.4	41	10	0	44	0	5
	7/22/81	Epilimnion	15.1	40	9	0	46	2	3
	8/31/81	Epilimnion	16	40	9	0	40	1	8
		Hypolimnion	16.1	33	13	0	50	0	4
South Fork Castle Lake	9/11/80	Epilimnion	3.5	24	7	0	63	3	3
	5/1/81	Epilimnion	10.2	36	11	0	47	3	3
	7/22/81	Epilimnion	7.9	40	9	0	44	5	2
	8/31/81	Epilimnion	7.4	37	8	0	48	2	4
		Hypolimnion	8.9	35	12	0	45	4	3
Coldwater Lake	9/11/80	Epilimnion	11.7	30	9	0	56	4	1
	4/30/81	Epilimnion	6.9	30	19	0	43	4	4
	7/22/81	Epilimnion	5.7	30	17	1	43	6	4
St. Helens Lake	9/11/80	Epilimnion	3.5	39	29	0	32	0	0
	7/22/81	Epilimnion	1.4	29	0	0	36	13	21
Ryan Lake	7/22/81	Epilimnion	3.4	30	18	0	47	0	5
Fawn Lake	9/11/80	Epilimnion	1.9	31	6	0	63	0	0
	7/22/81	Epilimnion	2.9	29	19	0	39	9	4
Hanaford Lake	9/11/80	Epilimnion	2.7	10	51	0	32	0	5
	7/22/81	Epilimnion	2.3	22	24	0	38	9	7

for freshwaters other than large rivers. Second, throughout the summer of 1981, the DOC and SOC concentrations generally were greater in the hypolimnia of these lakes than in the epilimnia. The same trend is found in the data collected by Wissmar and Devol (University of Washington, unpublished data, January 1982), and by Dahm and others (1982). Dahm and others (1982) also observed a marked increase in the DOC in the hypolimnion of South Fork Castle Lake in August 1981. Both of these lakes were aerobic in early May, but gradually became stratified with decreasing dissolved-oxygen concentrations in the hypolimnia in July (Dahm and others, 1982). The concentrations of dissolved ferrous iron and methane also increased in the hypolimnia from late June through August (Dahm and others, 1982). These data indicate that a major source of dissolved organic material was anaerobic decomposition of organic material in the volcanic deposits covering these lake bottoms. Rapid aerobic biodegradation or chemical reactions, such as photolysis, in the epilimnion also may be responsible for the lesser DOC values in the epilimnion.

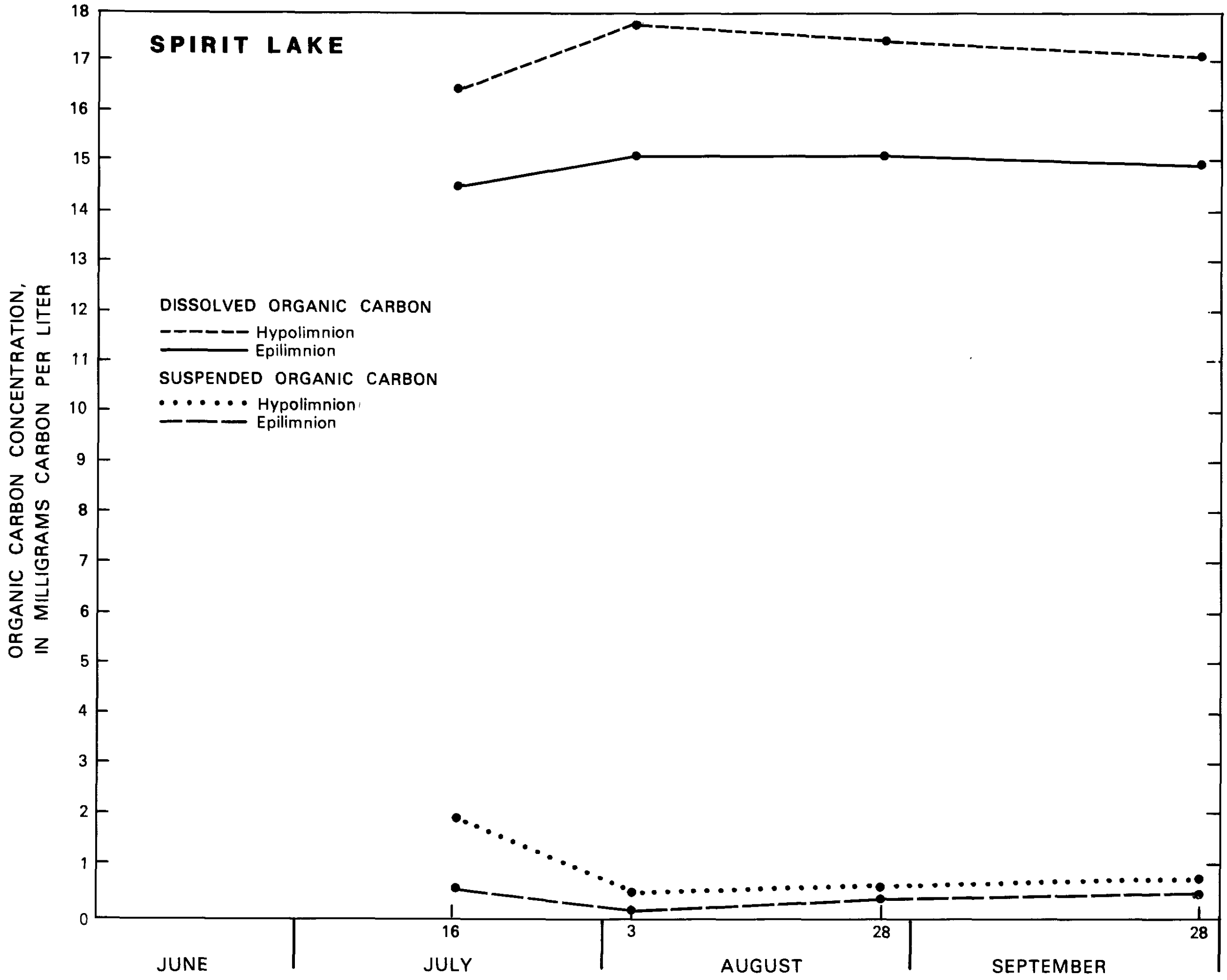

FIGURE 3.—Concentration of dissolved and suspended organic carbon in the epilimnion and hypolimnion of Spirit Lake during summer 1981.

The third major trend in DOC data for Spirit and South Fork Castle Lakes is that the epilimnetic DOC concentrations did not change much in these lakes during the summer of 1981. As explained previously, the lake volumes did not increase much during the summer, so dilution of chemical constituents was not a major effect. For example, the volume of South Fork Castle Lake only increased 13 percent from 14,960 acre-feet on May 27, 1981, to 17,290 acre-feet on September 30, 1981. The constancy of the epilimnetic DOC concentrations further indicates that most of the dissolved organic material was in the form of relatively refractory substances that were not being utilized as a substrate by micro-organisms at a significant rate. This conclusion is further supported by data presented in the following section which shows that the majority of the dissolved organic material could be characterized as humic material. The DOC concentrations in the hypolimnion of Spirit Lake also were stable, whereas the DOC concentrations in the hypolimnion of South Fork Castle Lake fluctuated significantly, increasing from 7.6 to 13 mg C/L during August. These fluctuations may have been related to temporal or spatial variations in the decomposition of benthic volcanic deposits in South Fork Castle Lake.

COLDWATER LAKE

In Coldwater Lake, DOC and SOC concentrations were not consistently greater in the hypolimnion (fig. 5) than in the epilimnion. The failure of dissolved organic material to accumulate in the

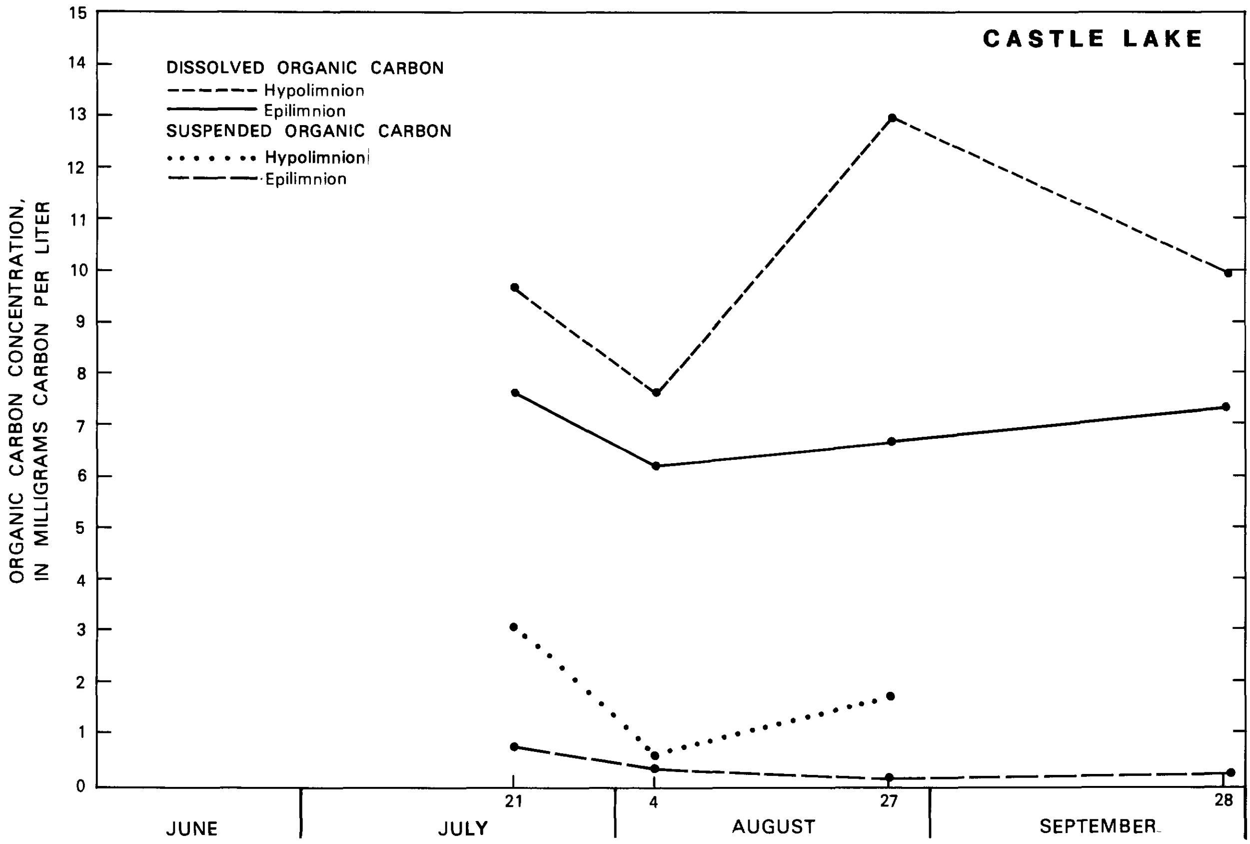

FIGURE 4.—Concentration of dissolved and suspended organic carbon in the epilimnion and hypolimnion of South Fork Castle Lake during summer 1981.

hypolimnion probably was related to the continued presence of dissolved oxygen at depth until late August. Dahm and others (1982) concluded that biodegradation of organic material in the volcanic deposits underlying the lake probably was comparable to biodegradation in Spirit and South Fork Castle Lakes, based on similar rates of methane production. Leaching and decomposition of the logjam covering Coldwater Lake also may have contributed organic material to the surface water of the lake.

ST. HELENS LAKE

In St. Helens Lake (fig. 6), in the timber blowdown zone, DOC concentrations had decreased from 3.0 mg C/L in September 1980, to about 1.5 mg C/L throughout the summer of 1981. These concentrations are typical of other lakes in the Cascade Range. For example, the DOC concentration of Spirit Lake during the spring before the May 18, 1980, eruption was 0.8 mg C/L, and the DOC concentration of Merrill Lake, a small lake outside of the blast zone 10 miles southwest of Mount St. Helens, was 1.0 mg C/L on May 1, 1981.

FRACTIONATION OF DISSOLVED ORGANIC MATERIAL

Results of the fractionation of dissolved organic material in blast-zone lakes in September 1980, and in the summer of 1981 are compared in table 4. The general trends indicate: (1) Hydrophobic and hydrophilic acids consistently comprise between 73 percent and 87 percent of the DOC in Spirit, South Fork Castle, and Coldwater Lakes; and (2) although these hydrophobic and hydrophilic acids are the two most important classes in the lakes in the zone of blown-down timber, the results are more variable, especially for St. Helens Lake, than in the other lakes. There are no obvious explanations for most of this variability in the data from the lakes in the zone of blown-down timber. The predominance of the organic-acid fractions has been observed for a wide range of surface waters (Stuber and Leenheer, 1978).

TABLE 5.—*Characteristics of aquatic fulvic acids isolated in samples from lakes in the blast zones of Mount St. Helens*
[meq/g, millequivalents per gram; μg/mg, micrograms per milligram; A, angstroms; C, carbon; H, hydrogen; O, oxygen; N, nitrogen; P, phosphorus; S, sulfur; Cl, chlorine]

Lake and date sample collected	Elemental analysis (percent by weight)								Functional groups (meq/g)		Carbohydrate contents (µg/mg)	Radius of gyration A
	C	H	O	N	P	Ash	S	Cl	Carboxylic acid	Phenol		
Spirit Lake												
9/11/80	51.6	4.92	37.5	1.00	0.2	1.06	4.31	0.39	5.16	1.7	18	10.6
4/30/81	50.6	4.9	40.0	.36	----	1.8	2.35	.25	5.29	1.0	64	8.7
7/22/81	50.5	4.7	37.0	.63	----	0.32	1.93	----	5.8	1.2	53	7.9
8/31/81	50.1	4.76	36.2	.64	----	3.82	2.41	----	5.2	1.0	57	10.8
South Fork Castle Lake												
9/11/80	51.7	4.96	37.7	.67	.2	.10	2.14	1.25	5.52	2.8	----	6.5
5/1/81	51.4	5.04	38.7	.54	----	2.6	1.09	.18	5.0	.87	43	10.2
7/22/81	----	----	----	----	----	----	----	----	6.4	1.05	71	8.7, 10.6
8/31/81	----	----	----	----	----	----	----	----	6.13	.93	76	9.2
Coldwater Lake												
4/30/81	53.6	5.21	38.4	0.31	----	1.8	.84	.18	6.0	1.16	53	----
Merrill Lake												
4/30/81	51.3	4.97	39.5	0.73	----	1.38	.49	.39	4.34	.83	72	----

In the epilimnion of Spirit Lake, the hydrophilic- and hydrophobic-acid fractions were almost equal, and the proportion of organic material in the different fractions was remarkably constant from September 1980 to August 1981. This result is consistent with the characterization of the major fractions, organic acids, as refractory aquatic-humic substances (McKnight and others, 1982). In late August, a sample was analysed from the hypolimnion, where active microbial degradation of organic material was indicated by methane production, and by anoxic conditions below a depth of 16 feet (Dahm and others, 1982), or a depth of 26 feet (S.S. Embrey, October 1982, U.S. Geological Survey, unpublished data), and by greater DOC concentrations. In this sample, hydrophilic acids were a larger fraction than hydrophobic acids, which may be characteristic of the production of dissolved organic material from anaerobic degradation of organic material in the underlying volcanic deposits (McKnight and others, 1982).

In South Fork Castle Lake, DOC concentration was extremely high in September 1980 and the hydrophilic-acid fraction was much greater than the hydrophobic acid fraction. By early May 1981, after the lake volume had been greatly increased by oxygen-saturated rain and snowmelt, the total organic-acid fraction had not changed much (87 percent to 83 percent of the DOC), but the hydrophobic-acid fraction had increased in importance. As a result, the fractionation of organic carbon in Spirit Lake and South Fork Castle Lake was more similar in the summer of 1981 than in 1980. From the volume and DOC data for South Fork Castle Lake, we can conclude that there was approximately the same total quantity of dissolved organic material in the lake from September 1980 to May 1981, which leads to a further conclusion that there are no major sources or losses of dissolved organic material during this time. If this second conclusion is correct, then the increased importance of the hydrophobic acid fraction may have been caused by chemical processes occurring as the lakewater became saturated with dissolved oxygen during the spring snowmelt.

In South Fork Castle Lake there was not as much difference between the samples from the epilimnion and the hypolimnion in August as there was in Spirit Lake. At one South Fork Castle Lake sampling site, Dahm and others (1982) found that there was some dissolved oxygen present in the hypolimnion, although the concentration was less than in the epilimnion. A few days later at a different site in South Fork Castle Lake, S.S. Embrey

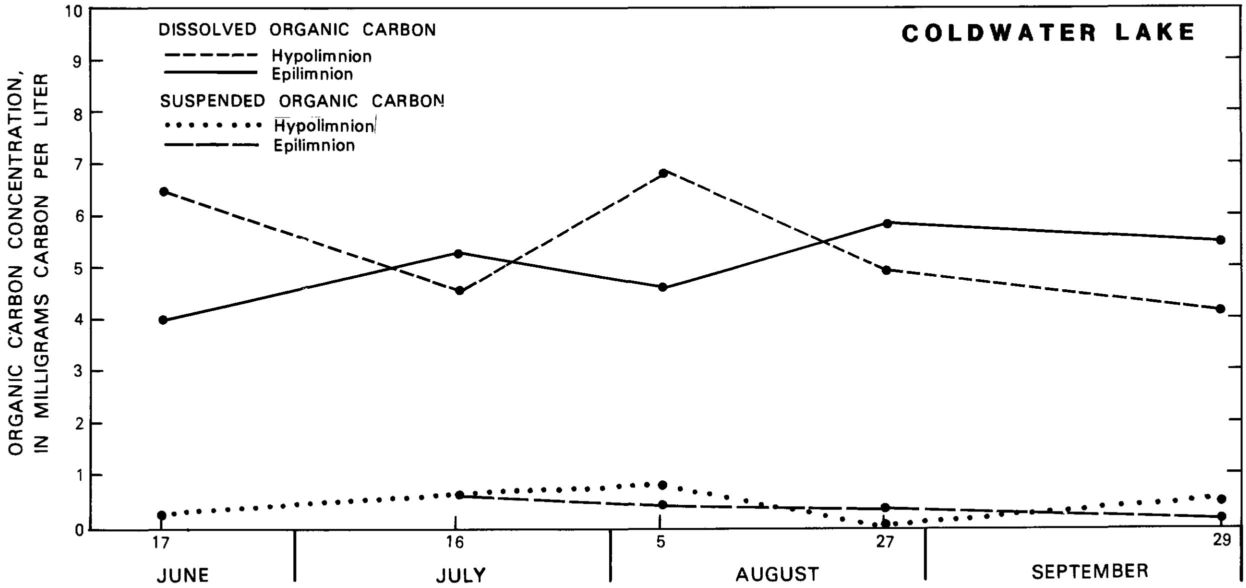

FIGURE 5.—Concentration of dissolved and suspended organic carbon in the epilimnion and hypolimnion of Coldwater Lake during summer 1981.

(1982) found that the lake was oxygenated to a depth of 49 feet; whereas, Spirit Lake was found by both groups of researchers to be anoxic below a depth of 26 feet. The more anoxic conditions in Spirit Lake than in South Fork Castle Lake probably explain the greater importance of hydrophilic acids in the hypolimnetic waters of Spirit Lake than in the hypolimnetic waters of South Fork Castle Lake.

In Coldwater Lake, the organic material also became more hydrophobic between September 1980 and April 1981; however, the increase was in the hydrophobic-neutral fraction rather than the hydrophobic-acid fraction. The hydrophobic-neutral fraction may have been humic substances with less ionizable functional groups.

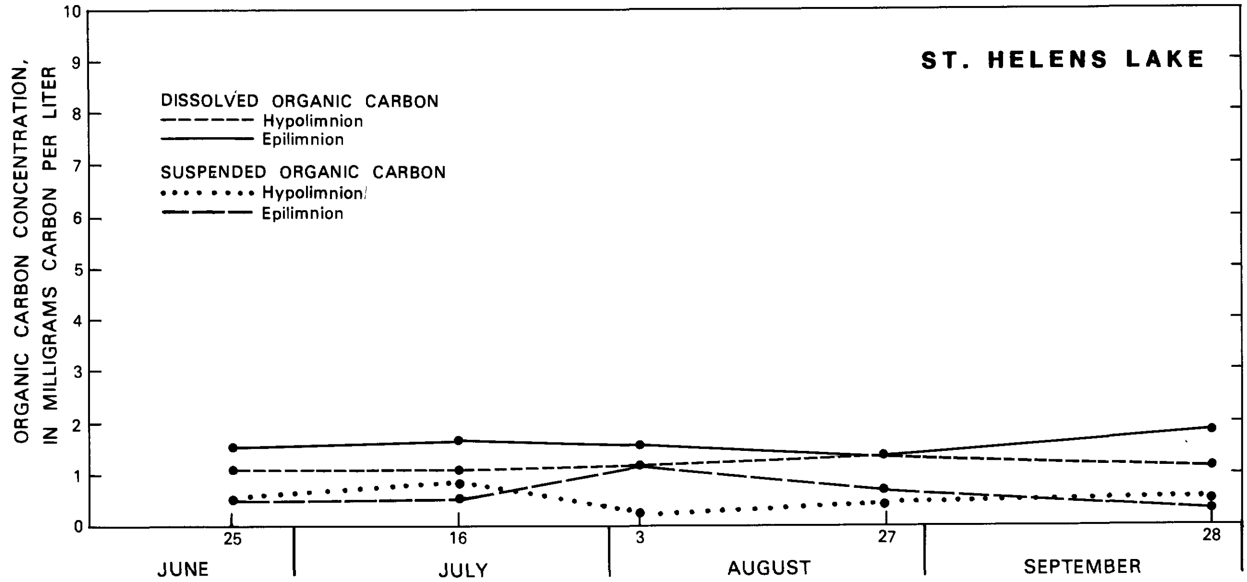

FIGURE 6.—Concentration of dissolved and suspended organic carbon in the epilimnion and hypolimnion of St. Helens Lake during summer 1981.

TABLE 6.—*Neutral organic compounds identified in a sample from South Fork Castle Lake, on March 27, 1981*

[RRT, relative retention time; FIT, mass-spectral-library fit]

Compound	RRT	FIT
1. Cycloheptane	0.21	950
2. Cyclopentanone,3-methyl-	.22	942
3. Benzene,ethyl-	.24	973
4. Cyclohexanone	.28	949
5. Benzene,(1-methylethyl)-	.33	929
6. Disulfide,1,1-dimethylethyl,methyl-	.34	948
7. Trisulfide,dimethyl-	.40	978
8. Phenol	.42	952
9. 7-Oxabicyclo,[2.2.1]heptane,1-methyl-4-(1-methylethyl)-	.47	990
10. Benzene,1-methyl-4-(-1-methylethyl)-	.49	960
11. 2-Oxabicyclo,[2.2.2]octane,1,3,3-trimethyl-	.50	995
12. Phenol,2-methoxy-	.51	942
13. Ethanone,1-phenyl-	.55	976
14. Phenol,-methyl-isomer	.57	982
15. Bicyclo,[2.2.1]heptane-2-one-1,3,3-trimethyl-	.59	963
16. Bicyclo[2.2.1]heptane-2-one-1,7,7-trimethyl-	.67	977
17. Phenol,-ethyl-isomer	.72	973
18. 3-Cyclohexen-1-methanol,α,α,4-trimethyl-	.72	963
19. Ethanone,1-(methylphenyl)-	.73	966

In lakes located in the timber-blowdown zone, the concentrations of DOC were lesser than in lakes associated with the mudflow, debris-avalanche, and pyroclastic-flow deposits. As in Coldwater Lake, the hydrophobic-neutral fraction was an important fraction in the July samples from Ryan, Fawn, and Hanaford Lakes. However, no consistent trends were indicated in the comparison between September 1980 and July 1981.

CHARACTERIZATION OF AQUATIC HUMIC SUBSTANCES

Generally, aquatic humic substances are yellow, high molecular-weight organic acids; and they account for between 30 and 80 percent of the dissolved organic material in surface and ground waters. Most aquatic humic substances can be further described as aquatic fulvic acids, which are soluble at low pH. The characterization of aquatic humic substances from Spirit Lake and South Fork Castle Lake was discussed by McKnight and others (1982). The most unusual characteristic was large sulfur content; for example, 4.31 percent in fulvic acid from Spirit Lake compared with 0.49 percent in fulvic acid from Merrill Lake. There are several possible chemical pathways whereby sulfur could have been incorporated into the organic material, such as reaction with sulfur dioxide in the blast of volcanic gases or with dissolved hydrogen

TABLE 7.—*Neutral organic compounds identified in a sample from South Fork Castle Lake, May 1, 1981*
[RRT, relative retention time; FIT, mass-spectral-library fit]

Compound	RRT	FIT
1. Cyclopentanone,3-methyl-	0.23	920
2. Trisulfide,dimethyl-	.41	985
3. Benzene,(1-methylethyl)-	.44	935
4. Phenol,2-methoxy-	.52	872
5. 2-Cyclopenten-1-one,2,3,4-trimethyl-	.55	972
6. Ethanone,1-phenyl-	.56	917
7. Ethanone,1-(methylphenyl)-	.73	983
8. 1-H-inden-1-one,2,3-dihydro-	.87	903

sulfide in the anaerobic waters. By comparing the elemental-analysis data presented in table 5, the sulfur content in fulvic acids from both Spirit Lake and South Fork Castle Lake decreased by about a factor of 2 between September 1980 and May 1981. The sulfur content of the fulvic acid in Spirit Lake did not change much throughout the summer of 1981. Until the nature of the sulfur in the fulvic acid has been determined, it is not possible to explain the decrease in sulfur content.

Other than the difference in sulfur contents, the elemental compositions of the aquatic fulvic acids in the lakes did not change during the year. Also, they were very similar to the elemental composition of fulvic acid from Merrill Lake, outside the blast zone.

There are two interesting trends in the data for the functional-group content of the aquatic fulvic acids. The first trend is that the carboxylic-acid contents, which are assumed to be those functional groups that have been titrated at pH 8, are greater in fulvic acids from the blast zone lakes than in fulvic acid from Merrill Lake, which should represent the reference aquatic fulvic acid for lakes in the Cascade Range. The carboxylic-acid content of the fulvic acid from Merrill Lake also is at the lower end of the range of values reported for other aquatic fulvic acids, between 4 and 6 meq/g (milliequivalents per gram) (Thurman and Malcolm, 1981). It also is interesting to note that the carboxylic-acid content and the carbohydrate content of the fulvic acid from South Fork Castle Lake was greater in July and in August of 1981, than in May of 1981.

The second trend is that the phenol content of fulvic acids from both Spirit and South Fork Castle Lakes decreased between September 1980, when the lakes were completely anaerobic, and May 1981, when the lakes were oxygen-saturated. The decrease in phenol content may have resulted from phenol-condensation reactions occurring under oxygenated conditions. This hypothesis is supported by the significant increase in the molecular size (radius of gyration) of the fulvic acid from South Fork Castle Lake during the same period (table 5). Aerobic biodegradation of phenols also may explain the decrease in phenol content of the fulvic acids.

To summarize, the general characterization data show that fulvic acids from the blast-zone lakes were chemically changed as the lakes were aerated and diluted by rain and snowmelt during the winter and spring of 1981. However, the chemical reactions causing these changes cannot be identified without a more detailed structural characterization of the fulvic acids.

IDENTIFICATION OF ORGANIC COMPOUNDS

Organic acids and neutral organic compounds were identified using gas chromatography-mass spectrometry by Pereira and others (1982) and McKnight and others (1982), in surface-water samples and volcanic-ash samples collected from the blast zone during the summer of 1980. Their results showed that the major source of organic carbon in the blast-zone lakes was pyrolyis of plant and soil organic material. They found that compounds of particular interest were terpenes; di-, tri-, and tetrasulfides; resin acids; and insect juvenile hormones. When compared with the data from the summer of 1980, the data presented here on the organic compounds present in the blast-zone lakes 1 year after the May 18, 1980, eruption, provide insight into the degradation and transport of organic material in surface waters of the blast zone of Mount St. Helens.

SOUTH FORK CASTLE LAKE

It was anticipated that during the snowmelt period the dissolved organic material in the blast-zone lakes associated with mudflow, debris-avalanche and pyroclastic-flow deposits would be altered by dilution, oxidation, and addition of organic compounds leached from volcanic debris in the watershed. For this reason, samples from South Fork Castle Lake were analysed from the beginning (March 27, 1981) and end (May 1, 1981) of the major snowmelt period.

NEUTRAL ORGANIC COMPOUNDS

Several terpenes were present in South Fork Castle Lake in March 1981 (compounds 9, 11, 15, 16, and 18 in table 6). Two of the terpenes (compounds 9 and 11) were not found in South Fork Castle Lake the previous summer (1980), but were found in Coldwater Creek (W.F. Pereira, U.S. Geological Survey, unpublished data, January 1981) and Coldwater Lake (in Supplementary Data at the end of the report). The other three terpenes (compounds 15, 16 and 18) were found in South Fork Castle Lake the previous summer (1980). However, no terpenes were found in May 1981 (table 7) at the end of the snowmelt; degradation under oxygenat-

TABLE 8.—*Comparison of neutral organic compounds identified in samples from South Fork Castle Lake, September 11, 1980, and before (March 27, 1981) and after (May 1, 1981) aeration and dilution by snowmelt*

[x, present; -, absent]

Compound	Sept. 11, 1980	March 27, 1981	May 1 1981
1. Cycloheptane	-	x	-
2. Cyclopentanone,3-methyl-	x	x	x
3. Benzene,ethyl-	-	x	-
4. Cyclohexanone	-	x	-
5. Disulfide,1,1-dimethylethyl-,methyl-	x	x	-
6. Trisulfide,dimethyl-	-	x	x
7. Benzene,(1-methylethyl)-	-	x	x
8. Phenol	x	x	-
9. 7-Oxobicyclo,[2.2.1]heptane,1-methyl-4-(1-methylethyl)-	-	x	-
10. Benzene,1-methyl-4-(1-methylethyl)-	x	x	-
11. 2-Oxabicyclo,[2.2.2]octane,1,3,3-trimethyl-	-	x	-
12. Phenol,2-methoxy-	-	x	x
13. 2-Cyclopenten-1-one,2,3,4-trimethyl-	x	-	x
14. Ethanone,1-phenyl-	x	x	x
15. Phenol,-methyl isomer	x	x	-
16. Bicyclo,[2.2.1]heptane-2-one,1,3,3-trimethyl-	x	x	-
17. Bicyclo,[2.2.1]heptane-2-one,1,7,7-trimethyl-	x	x	-
18. Phenol,-ethyl isomer	-	x	-
19. 3-Cyclohexen-1-methanol,α,α,4-trimethyl-	x	x	-
20. Ethanone,1-(methylphenyl)-	x	x	x
21. 3-Cyclohexen-1-methanol,α,α,4-trimethyl,-(5)	x	-	-
22. 1 H-inden-1-one,2,3-dihydro-	x	-	x
23. Phenol,5-methyl-2-(1-methylethyl)-	x	-	-

TABLE 9.—*Organic acids identified in a sample from South Fork Castle Lake, March 27, 1981*

[RRT, relative retention time; FIT, mass-spectral-library fit]

Compound	RRT	FIT
1. Pentanoic acid,3-methyl,methylester	0.43	842
2. Butanedioic acid,dimethylester	.56	900
3. Cyclohexanecarboxylic acid,methylester	.58	987
4. Benzoic acid methylester	.63	990
5. Octanoic acid,methylester	.64	888
6. 2-Thiabicyclo/3.1.0/Hex-3-ene-3-carboxylic acid,methylester	.65	902
7. Hexanoic acid,methylester	.67	888
8. Pentanedioic acid,methylester	.69	926
9. Pentanedioic acid,3,3-dimethyl,dimethylester	.76	906
10. Benzoic acid,2-hydroxy-,methylester	.76	989
11. Benzoic acid,3-methyl,methylester	.78	942
12. Heptanoic acid,methylester	.80	925
13. Benzenepropanoic acid,methylester	.89	987
14. Benzoic acid,3-methoxy-,methylester	.96	973
15. Heptanedioic acid,dimethylester	.97	984
16. Benzoic acid,-(1-methylethyl)-,methylester isomer	.97	964
17. Benzoic acid,-(1-methylethyl)-,methylester isomer	1.05	973
18. Benzoic acid,3-hydroxy-,methylester	1.09	966
19. Octanedioic acid,dimethylester	1.10	996
20. Benzenedicarboxylic acid,dimethylester isomer	1.10	941
21. Benzenedicarboxylic acid,dimethylester isomer	1.16	725
22. Benzeneacetic acid,3-hydroxy,methylester	1.16	966
23. Benzenedicarboxylic acid,dimethylester isomer	1.18	976
24. Benzenepropanoic acid,4-hydroxy,methylester	1.20	874
25. Nonanedioic acid,dimethylester	1.22	994
26. 1,4-Benzenedicarboxylic acid,2-(acetyloxy)-, dimethylester	1.29	942
27. 1,2-Benzenedicarboxylic acid,4-methyl,dimethylester	1.30	885
28. Cyclohexanecarboxylic acid,4-(1,5-dimethyl-3-oxohexyl)-methylester isomer	1.57	984
29. Cyclohexanecarboxylic acid,4-(1,5-dimethyl-3-oxohexyl)-methylester isomer	1.62	961

ed conditions or dilution by snowmelt are possible explanations.

Most of the phenolic compounds present in the summer, 1980 and early spring 1981 (compounds 8, 12, 14, and 17 in table 6) had disappeared by May 1981, with the exception of phenol, 2-methoxy (compound 4, table 7). With the development of oxygenated conditions, phenolic compounds would be involved in oxidative-coupling reactions. Additionally, aerobic biodegradation of phenols may have occurred. Dilution during the spring snowmelt also may explain the failure to detect phenolic compounds in May 1981. Phenol, 2-methoxy, a probable decomposition product of vanillin and other lignins, was the least abundant phenolic compound in March 1981, but was the only phenolic compound detected in May 1981 and its concentration had not decreased. This indicates a continuing input of phenol, 2-methoxy to South Fork Castle Lake during the spring snowmelt. It is important to emphasize that phenol, 2-methoxy, and the other identified compounds, represent only a small percentage (less than 1 percent) of the dissolved organic material. Therefore, the conclusion that specific organic compounds entered the lake with rain and snowmelt is consistent with the conclusion that the dissolved organic material, mainly aquatic fulvic acid and hydrophilic acids, behaved conservatively and that there were no major new inputs of dissolved organic material.

Several ketones were found in South Fork Castle Lake on all sampling dates (compounds 2, 14, and 20 in table 8). Another ketone, 1 H-inden-1-one, 2,3-dihydro-, which was found in volcanic ash (Pereira and others, 1982), was not present in March 1981, but was present in May 1981, indicating that this compound entered the lake with snowmelt that had been in contact with volcanic ash in the watershed.

The changes in organic sulfide compounds are also interesting. Disulfide, 1,1-dimethyl ethyl-, methyl was present in South Fork Castle Lake in September 1980 and in March 1981, but was not detected in May 1981, when the lake was saturated with dissolved oxygen. However, trisulfide, dimethyl- was present in March 1981 and was still present in May 1981, despite the oxygenated conditions.

TABLE 10.—*Organic acids identified in a sample from South Fork Castle Lake, May 1, 1981*

[RRT, relative retention time; FIT, mass-spectral-library fit]

Compound	RRT	FIT
1. Benzoic acid,-(1-methylethyl)-methylester isomer	1.06	829
2. Decanoic acid,8-methyl-,methylester	1.61	970
3. Heneiocsanoic acid,methylester	1.80	971

ORGANIC ACIDS

The organic acids followed the same pattern as the terpenes and phenolic compounds: persistence over the winter until the end of March, and then disappearance by the beginning of May with the snowmelt runoff (1981). This is true for the fatty acids, dicarboxylic acids, and their derivatives (compounds 1, 2, 5, 7, 8, 9, 12, 15, 19, and 25 in table 9) and for all but one of the aromatic acids (compounds 4, 10, 11, 13, 14, 16, 18, 20, 21, 22, 23, 24, 26, and 27 in table 9). The resin acids and insect juvenile hormones found in September 1980, were of interest because of their potential toxicity to aquatic organisms. Two of the four resin acids (compounds 28 and 29) that had been found in the September sample from South Fork Castle Lake also were found in March, but even these compounds were not found in May (tables 10 and 11). From these data, it can be concluded that most of the change in the organic chemistry of South Fork Castle Lake was a result of dilution by snowmelt in the spring.

SPIRIT LAKE

Samples collected from Spirit Lake on August 7, 1980, and September 11, 1980, were analysed previously (Pereira and others, 1982 and McKnight and others, 1982). Only a few of the compounds identified in the August 7, 1980, sample analysed by Pereira and others (1982) were found in the September 11, 1980, sample, analysed by McKnight and others (1982), indicating that degradative processes already had begun in the summer of 1980. In this study, a sample collected on April 30, 1981, was analysed; the data are presented in tables 12 and 13. In comparing the Spirit Lake data with the South Fork Castle Lake data, it is important to keep in mind that the dilution effect was much greater (14-fold) in South Fork Castle Lake than in Spirit Lake.

NEUTRAL ORGANIC COMPOUNDS

Very few of the neutral organic compounds found in Spirit Lake during the fall of 1980 were found in

April 1981 (table 12). Further, most of the neutral compounds found in Spirit Lake in April 1981 also were found in South Fork Castle Lake at the same time. This provides additional support for the conclusion that compounds persisting in Spirit and South Fork Castle Lakes in May were brought into the lakes with the snowmelt that had leached volcanic ash and dead plant material.

ORGANIC ACIDS

The organic acids found in Spirit Lake in April 1981 (table 13) were predominantly: (1) Fatty acids, dicarboxylic acids and their derivatives (compounds 1, 2, 5, 11, 12, and 14 in table 13) and (2) aromatic acids (compounds 3, 4, 6, 7, 8, 9, 10, and 13 in table 13). Many of these organic compounds also were found in Spirit Lake in September 1980, and in volcanic ash (table 13), and could have been brought into Spirit Lake with snowmelt that had leached volcanic ash and dead plant material. The potentially toxic resin acids and insect juvenile hormones found in Spirit Lake in August 1980 were not found in September 1980 or in April 1981, which indicates that they probably will not re-enter the blast-zone lakes with the snowmelt at concentrations great enough to be of ecological significance.

COLDWATER LAKE

In the summer of 1980, black water containing large quantities of dissolved organic material was flowing in Coldwater Creek. Pereira (U.S. Geological Survey, unpublished data, January 1981) identified many organic compounds, including terpenes and resin acids in Coldwater Creek. However, in September 1980 the surface water of Coldwater Lake was not as enriched in dissolved organic carbon (15 mg C/L) as Coldwater Creek (150 mg C/L), and only seven neutral organic compounds were identified (see Supplementary Data at the end of the report). Four of these compounds were terpenes, including cineole, fenchone, and terpinen-4-ol. No organic acids were identified in Coldwater Lake in September 1980.

NEUTRAL ORGANIC COMPOUNDS

Only three neutral organic compounds could be identified in the sample from Coldwater Lake collected on April 30, 1981 (table 15). These compounds were similar to compounds identified previously in blast-zone waters. As observed in South Fork Castle and Spirit Lakes, terpenes did not persist as detectable concentrations after the spring snowmelt.

ORGANIC ACIDS

In contrast to September 1980 when no organic acids were identified in Coldwater Lake (Supplementary Data at the end of the report), many organic acids were identified in the April 30, 1981, sample. These organic acids were mainly fatty acids, dicarboxylic acids, and their derivatives (compounds 1, 4, 11, 13, and 14 in table 16) and aromatic acids (compounds 2, 3, 5, 6, 7, 8, 9, 10, and 12). As was true in South Fork Castle and Spirit Lake, most (10 of 14) of the organic acids present on April 30, 1981, in Coldwater Lake also had been found in volcanic ash (table 16). This again supports the conclusion that leaching of volcanic ash was an important source of low molecular-weight organic compounds in blast-zone lakes during the spring snowmelt.

TOUTLE AND COWLITZ RIVERS

Samples from the Toutle and Cowlitz Rivers were collected on June 16, 1981. No neutral organic compounds which could be attributed to the effects of the Mount St. Helens eruption were identified in these samples. Dissolved organic material in surface waters draining the blast-zone area may have been removed in these rivers by chemical reactions, such as adsorption by sediments, or may have been decreased in concentration by dilution. The fatty acids and aromatic acids identified in these rivers (table 17) may have originated in the blast zone, but also may be normal organic constituents in these rivers. Because there is no pre-eruption data available for the Toutle and Cowlitz Rivers, it is not possible to distinguish between organic compounds associated with the May 18th eruption and normally present organic compounds. However, we can conclude that the resin acids and insect juvenile hormones that were found in blast-zone lakes in the summer of 1980, and which may be toxic to aquatic organisms, are not present in detectable concentrations in the Toutle and Cowlitz Rivers.

SUMMARY AND CONCLUSIONS

The major changes in the organic chemistry of the blast zone lakes between late summer 1980 and

TABLE 11.—*Comparison of organic acids identified in samples from South Fork Castle Lake and in volcanic ash*

[x, present; -, absent]

Compound	South Fork Castle Lake			Volcanic ash
	Sept. 11, 1980	March 27, 1981	May 1, 1981	1980
1. Butanoic acid,3-methyl-,methylester	x	-	-	-
2. Pentanoic acid,2-methyl-,methylester	x	-	-	-
3. Pentanoic acid,3-methyl-,methylester	x	x	-	-
4. Pentanoic acid,4-methyl-,methylester	x	-	-	-
5. Benzene,methoxy-	x	-	-	-
6. Phenol	x	-	-	-
7. Ethanedioac acid,diethylester	x	-	-	-
8. Hexanoic acid,4-methyl-,methylester	x	-	-	-
9. Benzene,1-methoxy-4-methyl-	x	-	-	-
10. Butanedioic acid,dimethylester	-	x	-	x
11. Cyclohexanecarboxylic acid,methylester	x	x	-	-
12. Penol,2-methyl-	x	-	-	-
13. Benzoic acid,methylester	x	x	-	x
14. Phenol,2-ethyl-5-methyl-	x	-	-	-
15. Octanoic acid,methylester	-	x	-	x
16. 2-Thiabicyclo 3.1.0 hex-3-ene-3-carboxylic acid,methylester	x	x	-	-
17. Hexanoic acid,methylester	-	x	-	-
18. Pentanedioic acid,methylester	-	x	-	-
19. Pentanedioic acid,2-methyl-,dimethylester	x	-	-	-
20. Benzeneacetic acid,methylester	x	-	-	x
21. Pentanedioic acid,3,3-dimethyl-,dimethylester	-	x	-	-
22. Benzoic acid,2-hydroxy-,methylester	x	x	-	x
23. Benzoic acid-,methyl-,methylester isomer	x	x	-	x
24. Heptanoic acid,methylester	-	x	-	-
25. Octanoic acid,2-methyl-,methylester	x	-	-	-
26. Hexanedioic acid,dimethylester	x	-	-	x
27. Benzenepropanoic acid,methylester	x	x	-	-
28. Benzoic acid,3,5-dimethyl-,methylester	x	-	-	-
29. Benzoic acid,3-methoxy-,methylester	x	x	-	x
30. Heptanedioic acid,dimethylester	x	x	-	-

TABLE 11.—*Comparison of organic acids identified in samples from South Fork Castle Lake and in volcanic ash*—Continued

Compound	South Fork Castle Lake			Volcanic ash
	Sept. 11, 1980	March 27, 1981	May 1, 1981	1980
31. Benzoic acid,-(1-methylethyl)-,methylester isomer	x	x	-	x
32. Benzoic acid,-(1-methylethyl)-,methylester isomer	x	x	x	x
33. Benzoic acid,3-hydroxy-,methylester	-	x	-	-
34. Benzoic acid,4-methoxy-,methylester	x	-	-	x
35. Benzeneacetic acid,3-methoxy-,methylester	x	-	-	-
36. Octanedioic acid,dimethylester	x	x	-	x
37. 1,2-Benzenedicarboxylic acid,dimethylester	x	x	-	x
38. Benzoic acid,2,3-dimethoxy-,methylester	x	-	-	-
39. Benzenepropanoic acid,-methoxy-,methylester isomer	x	-	-	-
40. Benzeneacetic acid,-hydroxy-,methylester isomer	x	x	-	-
41. Benzenedicarboxylic acid,dimethylester isomer	x	x	-	x
42. Benzenedicarboxylic acid,dimethylester isomer	x	x	-	x
43. Benzenepropanoic acid,-methoxy-,methylester isomer	x	-	-	-
44. Benzenepropanoic acid,4-hydroxy-,methylester	-	x	-	-
45. Nonanedioic acid,dimethylester	x	x	-	x
46. Benzoic acid,3,4-dimethoxy-,methylester	x	-	-	x
47. 1,4-Benzenedicarboxylic acid,2-(acetyloxy)-,dimethylester	-	x	-	-
48. 1,2-Benzenedicarboxylic acid,4-methyl-,dimethylester	-	x	-	x
49. Decanedioic acid,dimethylester	x	-	-	-
50. Cyclohexanecarboxylic acid,4-(1,5-dimethyl-3-oxohexyl)-,methylester isomer	x	x	-	-
51. Cyclohexanecarboxylic acid,4-(1,5-dimethyl-3-oxohexyl)-,methylester isomer	x	x	-	-
52. Decanoic acid,8-methyl-,methylester	-	-	x	-
53. Heneiocsanoic acid,methylester	-	-	x	x
54. 1-Cyclohexene-1-carboxylic acid,4-(1,5-dimethyl-3-oxohexyl)-,methylester	x	-	-	-
55. 1-Phenanthrenecarboxylic acid,1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-,methylester	x	-	-	x

TABLE 12.—*Neutral organic compounds identified in a sample from Spirit Lake, April 30, 1981*
[RRT, relative retention time; FIT, mass-spectral-library fit]

Compound	RRT	FIT
1. Cyclopentanone,3-methyl-	0.28	949
2. Cyclopentane,1-ethyl-2-methyl,cis	.40	942
3. Trisulfide,dimethyl-	.42	937
4. 2-Cyclopenten-1-one,3-methyl-	.42	917
5. 2-Cyclopenten-1-one,2,3,4-trimethyl-	.56	971
6. Phenol,2,5-dimethyl-	.62	919
7. Ethanone,1-(methylphenyl)-	.74	991
8. 1-H-inden-1-one,2,3,-dihydro-	.87	972
9. 1-H-inden-1-one,2,3-dihydro-3-methyl-	.92	941

TABLE 13.—*Organic acids identified in a sample from Spirit Lake, April 30, 1981*
[RRT, relative retention time; FIT, mass-spectral-library fit]

Compound	RRT	FIT
1. Butanedioic acid,dimethylester	0.54	990
2. Butanedioic acid,-methyl-,dimethylester	.58	768
3. Benzoic acid,methylester	.63	936
4. Benzoic acid,-methyl-,methylester isomer	.80	794
5. Hexanedioic acid,dimethylester	.84	810
6. Benzoic acid,-dimethyl-,methylester isomer	.93	759
7. Benzoic acid,-(1-methylethyl)-,methylester isomer	.95	717
8. Benzoic acid,-(1-methylethyl)-,methylester isomer	1.07	947
9. 1,2-Benzenedicarboxylic acid,dimethylester	1.12	986
10. 1,3-Benzenedicarboxylic acid,dimethylester	1.17	917
11. Dodecanoic acid,methylester	1.20	899
12. Nonanedioic acid,dimethylester	1.23	727
13. Benzoic acid,3,4-dimethoxy-,methylester	1.28	769
14. Heneicosanoic acid,methylester	2.82	884

spring 1981 can be attributed to the tremendous inflow of rain and snowmelt to these lakes. For example, the volume of South Fork Castle Lake increased about 14 times during the same period that the DOC concentration decreased from 135 to 10 mg C/L. The apparent conservative nature of DOC in these lakes is explained by the fact that most of the DOC was aquatic fulvic acids, which are generally thought of as refractory end products of organic-material degradation.

Another important observation was that during the summer of 1981, the DOC concentrations were greater in the hypolimnion than in the epilimnion for Spirit Lake and South Fork Castle Lake, where hypolimnetic anoxic conditions developed from the decomposition of organic material in the lake-bottom volcanic deposits. This observation indicates that the anaerobic degradation of lake-bottom organic material is a source of dissolved organic material in these lakes. In Spirit Lake, where anoxic conditions were most severe, hydrophilic acids were more important than fulvic acids in hypolimnetic waters, whereas aquatic fulvic acids were the most important fraction in samples from the oxygenated epilimnion of Spirit Lake and from other lakes.

One of the unique characteristics of aquatic fulvic acids isolated from Spirit Lake and South Fork Castle Lake in the summer of 1980 was very high sulfur content: 4.31 percent by weight in Spirit Lake, and 2.14 percent in South Fork Castle Lake. In the spring and summer of 1981, the sulfur contents of the aquatic fulvic acids continued to be moderately high compared to other aquatic fulvic acids, but had decreased by about a factor of 2 to 2.35 percent in Spirit Lake fulvic acid and 1.09 percent in South Fork Castle Lake fulvic acid. Characterization of the chemical form of sulfur in these aquatic-fulvic acids may provide insight into interactions between sulfur and dissolved organic matter in aquatic environments.

In South Fork Castle Lake, many of the organic compounds found in September 1980 including terpenes, resin acids, and phenolic compounds, per-

TABLE 14.— *Organic acids identified in samples from Spirit Lake, September 11, 1980, and April 30, 1981, and in volcanic ash*

[x, present; -, absent]

Compound	Spirit Lake		
	September 11 1980	April 30 1981	Volcanic ash 1980
1. Butanedioic acid,dimethylester	x	x	x
2. Butanedioic acid,-methyl-,dimethylester	x	x	-
3. Benzoic acid,methylester	x	x	x
4. Pentanedioic acid,2-methyl-,dimethylester	x	-	-
5. Benzoic acid,-methyl-,methylester isomer	x	x	x
6. Hexaneodioic acid,dimethylester	x	x	x
7. Benzoic acid,-dimethyl-,methylester isomer	-	x	-
8. Benzoic acid,-(1-methylethyl)-,methylester isomer	x	x	-
9. Benzoic acid,3-methoxy-,methylester	x	-	x
10. Benzoic acid,-(1-methylethyl)-,methylester isomer	x	x	-
11. 1,2-Benzenedicarboxylic acid,dimethylester	-	x	x
12. Benzoic acid,4-methoxy-,methylester	x	-	x
13. Benzoic acid,3,4-dichloro-,methylester	x	-	x
14. 1,3-Benzenedicarboxylic acid,dimethylester	x	x	-
15. Dodecanoic acid,methylester	x	x	x*
16. Nonanedioic acid,dimethylester	-	x	x
17. Benzoic acid,3,4-dimethoxy-,methylester	x	x	x
18. Benzenepropanoic acid,-methoxy-,methylester isomer	x	-	-
20. Heneicosanoic acid,methylester	-	x	x

TABLE 15.—*Neutral organic compounds identified in a sample from Coldwater Lake, April 30, 1981*
[RRT, relative retention time; FIT, mass-spectral-library fit]

Compound	RRT	FIT
1. Cyclopentane,1-ethyl-3-methyl-	0.64	961
2. Disulfide,bis(1,1-dimethylethyl)-	.65	795
3. 2-cyclohexen-1-one,4-ethyl-3,4dimethyl-	.84	925

sisted in the lake at detectable concentrations until March 27, 1981, but were not detectable by May 1, 1981. Most of the organic compounds found in April 1981 in the blast-zone lakes (Spirit, South Fork Castle, and Coldwater Lakes) were fatty acids, dicarboxylic acids, and aromatic acids that had also been found in volcanic ash. The conclusion is reached that leaching by rain and snowmelt of the large quantities of volcanic ash deposited in the watersheds was a significant source of low molecular-weight organic compounds. Since the low molecular weight organic compounds were only a small percentage of the dissolved organic material, this conclusion is consistent with the other conclusion that the dissolved organic material behaved conservatively and that there were no major new sources of dissolved organic material. Only a few fatty acids and aromatic acids were identified in samples from the Toutle and Cowlitz Rivers, and without pre-eruption data, it is not known whether these organic acids are associated with the effects of the May 18 eruption of Mount St. Helens.

TABLE 16.—*Organic acids identified in a sample from Coldwater Lake, April 30, 1981, and comparison with organic material in volcanic ash*
[RRT, relative retention time; FIT, mass-spectral-library fit; x, present; -, absent]

Compound	RRT	FIT	Volcanic ash
1. Butanedioic acid,dimethylester	0.55	954	x
2. Benzoic acid,methylester	.61	960	x
3. Benzoic acid,3-methyl-,methylester	.78	812	x
4. Hexanedioic acid,dimethylester	.83	888	x
5. Benzoic acid,3,5-dimethyl-,methylester	.89	826	-
6. Benzoic acid,-(1-methylethyl)-,methylester isomer	1.02	951	-
7. Benzoic acid,-(1-methylethyl)-,methylester isomer	1.06	975	-
8. 1,2-Benzenedicarboxylic acid,dimethylester	1.07	961	x
9. Benzenedicarboxylic acid,dimethylester isomer	1.11	998	x
10. Benzenedicarboxylic acid,dimethylester isomer	1.18	924	x
11. Nonanedioic acid,dimethylester	1.22	977	x
12. Benzoic acid,3,4-dimethoxy-,methylester	1.27	893	x
13. Decanoic acid,8-methyl-,methylester	1.71	935	-
14. Heneicosanioc acid,methylester	1.80	970	x

TABLE 17.—*Organic acids identified in samples from the Toutle and Cowlitz Rivers, and in volcanic ash*
[RRT, relative retention time; FIT, mass-spectral-library fit; x, present; -, absent]

Compound	RRT	FIT	Volcanic ash
Toutle River			
1. Benzoic acid,methylester	0.62	949	x
2. Benzoic acid,3-methoxy-,methylester	1.00	852	x
3. 1,2-Benzenedicarboxylic acid,dimethylester	1.11	928	x
4. Benzenedicarboxylic acid,dimethylester isomer	1.16	902	x
5. Benzenedicarboxylic acid,dimethylester isomer	1.17	950	x
6. Nonanedioic acid,dimethylester	1.21	924	x
Cowlitz River			
1. Butanedioic acid,dimethylester	0.56	892	x
2. 1,2-Benzenedicarboxylic acid,dimethylester	1.11	791	x
3. Benzenedicarboxylic acid,dimethylester isomer	1.17	877	x
4. Heneicosanoic acid,methylester	1.79	912	x

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SUPPLEMENTARY DATA

On September 7, 1980, water samples were collected from several lakes and surface waters in the blast zone of Mount St. Helens and the dissolved organic material was characterized. Most of the results are discussed in McKnight and others (1982). This supplementary data section presents the organic compounds identified in five lakes in the ashfall and timber-blowndown area that had lesser DOC concentrations than Spirit Lake and South Fork Castle Lake. In Coldwater Lake several terpenes were identified (compounds 1, 2, 4, and 5); in the other four lakes, only one or two compounds were identified (table 18). These data are important for comparison with data from other lakes more severely impacted by the May 18, 1980, eruption of Mount St. Helens.

TABLE 18.—*Neutral organic compounds and organic acids identified in samples from several lakes in the blast zone of Mount St. Helens*

[RRT, relative retention time, FIT, mass-spectral-library fit]

Compound	RRT	FIT
Coldwater Lake		
1. 7-Oxabicyclo, 2.2.1 heptane,1-methyl-4-(1-methylethyl)-	0.51	936
2. 2-Oxabicyclo, 2.2.2 octane,1,3,3-trimethyl- (cineole)	.54	965
3. Ethanone, 1-phenyl-	.59	975
4. Bicyclo, 2.2.1 heptane-2-one-1,2,2-trimethyl- (fenchone)	.62	911
5. 3-Cyclohexen-1-ol,4-methyl-1-(1-methylethyl)- (terpinen-4-ol)	.75	908
6. Ethanone,1-(methylphenyl)-	.76	984
7. Phenol,5-methyl-2-(1-methylethyl)-	.90	903
St. Helens Lake		
1. Disulfide,bis(1,1-dimethylethyl)-	.67	895
Hanaford Lake		
1. Cyclohexane,(1,1-dimethylethyl)-	.39	945
Ryan Lake		
1. Butanedioic acid,dimethylester	.54	989
2. Benzoic acid,chloro-,methylester isomer	.87	923
Fawn Lake		
1. Cyclohexane(1,1-dimethylethyl)-	.39	941

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