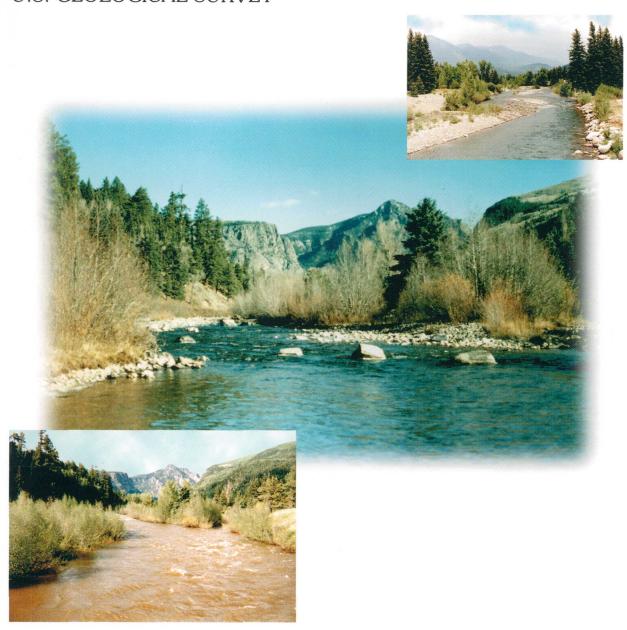


pecd
9/20/99

WATER QUALITY OF VALLECITO RESERVOIR AND ITS INFLOWS, SOUTHWESTERN COLORADO, 1996–97

U.S. GEOLOGICAL SURVEY



Water-Resources Investigations Report 99–4092

Prepared in cooperation with the PINE RIVER IRRIGATION DISTRICT

Cover Photographs

upper right - Vallecito Creek middle - Los Piños River in summer lower left - Los Piños River in spring

Water Quality of Vallecito Reservoir and Its Inflows, Southwestern Colorado, 1996–97

By Anthony J. Ranalli and Jonathan B. Evans

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 99-4092

Prepared in cooperation with the PINE RIVER IRRIGATION DISTRICT

U.S. DEPARTMENT OF THE INTERIOR BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY Charles G. Groat, Director

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

For additional information write to:

District Chief U.S. Geological Survey Box 25046, Mail Stop 415 Denver Federal Center Denver, CO 80225–0046 Copies of this report can be purchased from:

U.S. Geological Survey Information Services Box 25286 Federal Center Denver, CO 80225

CONTENTS

Abstr	ract	
Intro	ductionduction	•••••
	Purpose and Scope	3
	Acknowledgments	
Site I	Description	
	Geology	
	Soils	
	Vegetation and Land Use	
	Climate	
Meth	ods of Data Collection and Analysis	
	Stream Samples	
	Ground-Water Samples	
	Reservoir Samples	
	Laboratory Analysis	
Water	r Quality of Reservoir, Inflows, Ground Water, and Outflow	
	Trihalomethane Formation Potential and Dissolved Organic Carbon	
	Trophic State of Reservoir and Nutrients	
	Major Ions and Trace Metals	
Water	r-Quality Changes with Depth in Vallecito Reservoir	
	nary	
	rences Cited	
	ndix	
• •		
FIGI	JRES	
ı iac		
1.	Map showing study area and sampling sites	2
2.	Graph showing seasonal and spatial variability of total trihalomethane formation potential	9
3.	Sketch showing a simplified conceptual hydrologic model of the flow path of ground water to	
	streams and rivers from the surrounding watershed	10
4–9.	Graphs showing:	
	4. Seasonal and spatial variability of dissolved organic carbon concentrations	11
	5. Dissolved organic carbon concentration time series and hydrographs for A, Vallecito Creek and	
	B, Los Piños River, Colorado	12
	6. Seasonal and spatial variability of ultraviolet absorbance	13
	7. Seasonal and spatial variability of dissolved organic carbon composition at A, Vallecito Creek;	
	B, Los Piños River; C, well DH-MW-2; and D, Vallecito Reservoir, Colorado	14
	8. Seasonal and spatial variability of dissolved organic carbon concentration of surface sampling	
	sites at Vallecito Reservoir, Colorado	16
	9. Seasonal variability in trophic-state index of Vallecito Reservoir, Colorado	18
10.	Trilinear diagram showing average inorganic-ion composition of the five main sampling sites	19
11.	Graphs showing depth profiles of specific conductance, pH, water temperature, and dissolved-oxygen	
	concentration in the southern end of Vallecito Reservoir, Colorado, August 1996 through July 1997	24
12.	Graphs showing depth profiles of specific conductance, pH, water temperature, and dissolved-oxygen	
	concentration at the three sampling sites in Vallecito Reservoir, Colorado, August 1996 through June 1997	25
13.	Trilinear diagram showing inorganic-ion composition at all sampling sites in August 1996	
14.		

TABLES

1.	Trihalomethane formation potential data for Vallecito Reservoir, Colorado, and its inflows and outflows	8
2.	Instantaneous dissolved organic carbon loads of Vallecito Creek and Los Piños River, Colorado	16
3.	Median nutrient concentrations of Vallecito Reservoir, Colorado, and its inflows and outflow	18
4.	Molar ratio of bicarbonate to calcium for Vallecito Reservoir, Colorado, and its inflows and outflows	20
5.	Trace-metal data for Vallecito Reservoir, Colorado, and its inflows and outflows	22
6.	Discharge, dissolved organic carbon concentration, and ultraviolet absorbance data for Vallecito Creek	
	and Los Piños River, Colorado	31
7.	Water-level, dissolved organic carbon concentration, and ultraviolet absorbance data for well DH-MW-2	
	near Vallecito Reservoir, Colorado	31
8.	Dissolved organic carbon concentration and ultraviolet absorbance data for Vallecito Reservoir, Colorado	32
9.	Dissolved organic carbon concentration and ultraviolet absorbance data for Los Piños River, Colorado,	
	downstream from the dam	33
10.	Discharge and major-ion data for Vallecito Creek and Los Piños River, Colorado	33
11.	Water-level and major-ion data for well DH-MW-2 near Vallecito Reservoir, Colorado	34
12.	Major-ion data for Vallecito Reservoir, Colorado	34
13.	Major-ion data for Los Piños River, Colorado, downstream from the dam	36
14.	Nutrient data for all selected sites at Vallecito Reservoir, Colorado, and its inflows and outflow	36

Water Quality of Vallecito Reservoir and Its Inflows, Southwestern Colorado, 1996–97

By Anthony J. Ranalli and Jonathan B. Evans

Abstract

The water quality of the Vallecito Reservoir watershed in southwestern Colorado was studied by the U.S. Geological Survey from July 1996 to July 1997, in cooperation with the Pine River Irrigation District, to assess the suitability of the reservoir as a source of drinking water. This report presents the results of the study. A trihalomethane formation potential test indicated that the concentration of trihalomethanes can be greater than U.S. Environmental Protection Agency standards when water withdrawn from the reservoir at the peak of the spring snowmelt in June and July is chlorinated. The concentration of dissolved organic carbon varies little throughout the watershed for most of the year, but pronounced increases occur during peak runoff due to snowmelt in the spring. The composition of the dissolved organic carbon also changes during peak runoff. An increase in humic substances in the water during peak runoff could be the reason for any increases in the concentration of trihalomethanes that can form when the water is chlorinated. The concentration and composition of the dissolved organic carbon in Vallecito Reservoir are affected more by inflows from Los Piños River than by Vallecito Creek, especially during spring snowmelt.

Vallecito Reservoir is classified as oligotrophic, according to the Carlson trophic-state index, and the concentrations of trace metals, except for iron and manganese, are slightly greater than or at their respective detection limits. The dissolved inorganic ions throughout the watershed are dominated by calcium and bicarbonate. The abundance of calcium and dissolved bicarbonate and the presence of limestone in the bedrock and surficial deposits in the watershed indicate the weathering of limestone as the major source of dissolved inorganic ions. The dissolved inorganic chemistry of Vallecito Reservoir is a result of mixing of water from Vallecito Creek, Los Piños River, and possibly ground water.

INTRODUCTION

Vallecito Reservoir is located in La Plata County in southwestern Colorado (fig. 1). The reservoir was constructed by the Bureau of Reclamation in 1942 to provide flood control and water to irrigate about 18,500 acres of land on the Southern Ute Indian Reservation and about 45,000 acres of land outside the reservation. The reservoir is still owned by the Bureau of Reclamation, but the day-to-day operation of the reservoir is the responsibility of the Pine River Irrigation District. Recently, the Pine River Irrigation District announced its intention to use Vallecito Reservoir as a source of municipal drinking water for 6,000 homes in La Plata County. Although waterquality data have been collected at Vallecito Creek for more than 30 years as part of the U.S. Geological Survey Hydrologic Benchmark Program, waterquality data for Los Piños River, the reservoir, and ground water in the watershed are limited. The lack of water-quality data has caused the Pine River Irrigation District to express concern over how existing and proposed development in the watershed may affect water quality of the reservoir and, thus, potentially affect treatment costs. In July 1996, the U.S. Geological Survey began a study in cooperation with the Pine

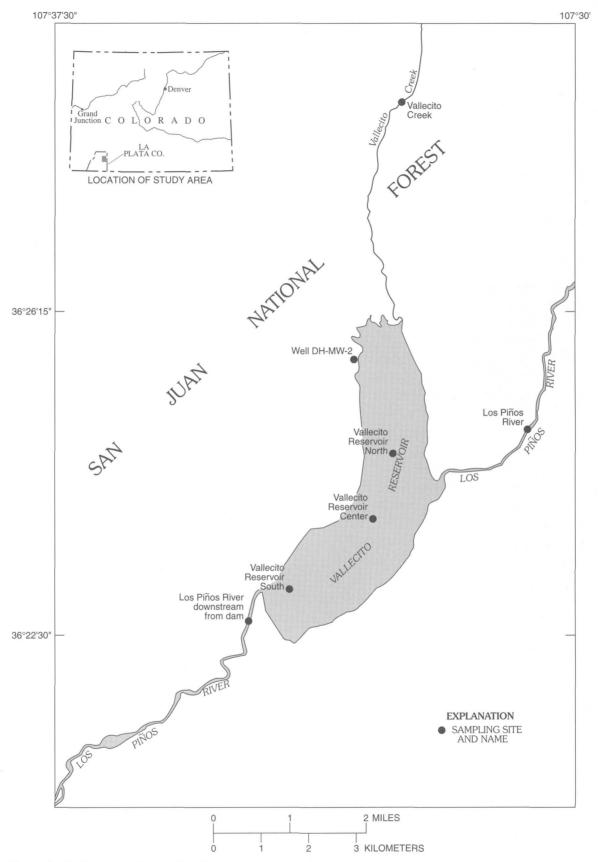


Figure 1. Study area and sampling sites.

2

River Irrigation District to assess the water quality of Vallecito Reservoir. The objectives of the study were to (1) determine the seasonal and spatial variability of the concentration and composition of dissolved organic carbon (DOC) in the Vallecito Reservoir watershed; (2) determine if trihalomethanes (THM's) can be at concentrations greater than the maximum contaminant level (MCL) for drinking water of 0.1 milligram per liter (mg/L) established by the U.S. Environmental Protection Agency (USEPA) (1994) if Vallecito Reservoir water were to be chlorinated; and (3) determine the trophic state of Vallecito Reservoir.

Purpose and Scope

This report summarizes the water-quality data collected in the Vallecito Reservoir watershed during July 1996–July 1997. Specifically, the report (1) relates the seasonal variability of the concentration and composition of DOC to the levels of THM's that can potentially form when water is chlorinated, (2) describes the trophic state of the reservoir, and (3) describes how surface- and ground-water inflow affects reservoir water quality (DOC, major inorganic ions, nutrients, and trace metals).

Acknowledgments

The authors thank the following people who contributed to the study: Keith Graham and Gene Roberts who allowed access to their land so that samples could be collected at Los Piños River; Phil Alcon and Stan Powers of the Bureau of Reclamation for their assistance with the ground-water sampling; Dr. Gary Amy of the University of Colorado at Boulder for the use of his laboratory in which the THM measurements were made; Shahnawaz Sinha, a graduate student of Dr. Amy's for his assistance with the THM formation potential measurements; Dr. George R. Aiken of the U.S. Geological Survey for the use of his laboratory in which all the DOC analyses were performed; David Clow, M. Alisa Mast, Fred Rossi, and Paul Schuster of the U.S. Geological Survey who performed the inorganic-ion analysis; and Jim Bennett and Ken Leib of the U.S. Geological Survey for their assistance with the high-flow discharge measurements.

SITE DESCRIPTION

The spillway at Vallecito Reservoir is at an elevation of 7,665 feet (ft). When full, the reservoir has about 2,720 surface acres of water. The reservoir has a maximum depth of 110 ft, drains an area of 270 square miles (mi²), and has two major inflows—Vallecito Creek, which drains an area of 72 mi² (upstream from the U.S. Geological Survey streamflow-gaging station), and Los Piños River, which drains an area of 130 mi² (upstream from the sampling site) (fig. 1).

Geology

Vallecito Reservoir is located at the southern edge of the San Juan Mountains. The bedrock adjacent to the reservoir is primarily of the Cutler Formation of Lower Permian age, which consists of predominantly arkosic sandstone, siltstone, and conglomerate (Tweto, 1979). Also adjacent to the reservoir are the Rico and Hermosa Formations of Pennsylvanian age, which consist of arkosic sandstone, conglomerate, shale, and limestone. Farther north, in the valleys of Vallecito Creek and Los Piños River, are several other rock formations. These formations include the Leadville Limestone of Upper Mississippian age; Ouray Limestone of Upper Devonian age; Elbert Formation of Upper Devonian age, which consists of shale and sandstone; Ignacio Quartzite of Upper Cambrian age; and various metamorphic and granitic rocks of Precambrian age.

The unconsolidated deposits overlying bedrock throughout the watershed are largely glacial sediments of Quaternary age. The valleys of Vallecito Creek and Los Piños River underwent extensive glaciation. Glaciers advancing down the valleys of both drainages converged and deposited vast quantities of clay, sand, gravel, and boulders. As the glaciers retreated, they left behind a terminal moraine about 200 ft thick in the vicinity of the Vallecito Reservoir dam and a lateral moraine along the eastern side of the valley between Los Piños River and the dam (EDAW, Inc., 1996). Meltwater streams from the retreat of the glaciers resulted in large alluvial gravel deposits throughout the reservoir area.

Soils

Soils in the area immediately surrounding Vallecito Reservoir, in the valley of Vallecito Creek from its mouth upstream to several yards downstream from the gaging station, and in the valley of Los Piños River from its mouth to several hundred yards upstream from the sampling site were mapped and described by Pannell (1988). The predominant soil type throughout the lower elevations of the watershed is the Leadville very stony sandy loam. The predominant soil type on the southwestern and southeastern sides of the reservoir at higher elevations is the Uinta loam. The Leadville very stony sandy loam has slopes of 15 to 55 percent and an organic-matter content of 0.5 to 1 percent, and the Uinta loam has slopes of 5 to 60 percent and an organic-matter content of 1 to 2 percent.

In the valley of Vallecito Creek, two predominant soil types were mapped by Pannell (1988). Of these, one is the Pescar fine sandy loam, which has slopes of 0 to 2 percent and an organic-matter content of less than 1 percent. The other is the Tefton loam, which has slopes of 1 to 3 percent and an organic-matter content of 1 to 2 percent.

In the valley of Los Piños River from its mouth to several yards downstream from the sampling site and all along the uplands throughout the valley, the predominant soil type is the Leadville very stony sandy loam. The valley of Los Piños River begins to widen and becomes flat several yards downstream from the sampling site and remains wide and flat as far upstream as the soils were mapped. This flat part of the valley upstream has three predominant soil types—the Pastorius cobbly loam, the Pescar fine sandy loam, and Fluvaquents. The Pastorius cobbly loam has slopes of 1 to 3 percent and an organicmatter content of 2 to 4 percent. The Pescar fine sandy loam has slopes of 0 to 2 percent and an organicmatter content of less than 1 percent. The Fluvaquents are sandy, are frequently flooded, are almost level, and have an organic-matter content of less than 1 percent.

Vegetation and Land Use

The watershed is almost entirely forested and has a few small patches of grasslands near the northern end of Vallecito Reservoir where Vallecito Creek flows into the reservoir. The forest has been classified as

mixed coniferous and consists of ponderosa pine, Douglas fir, white fir, and quaking aspen (EDAW, Inc., 1996). The grasslands species include golden hairy aster, common dandelion, white Dutch clover, salisfy, western yarrow, narrowleaf plantain, wild rye, bluegrass, smooth brome, and foxtail barley (EDAW, Inc., 1996).

The Vallecito Reservoir watershed is entirely in the boundary of the San Juan National Forest. However, some privately owned land along the southwestern end and at the northern end of the reservoir has been developed primarily into seasonal and year-round residences. The primary land use is recreation, such as boating, fishing, hiking, camping, and horse-back riding. Other development includes two marinas, several restaurants, general stores, small motels, several campgrounds, and a ranch.

Climate

The climate of the area is classified as semiarid to subhumid. The summers are dry, and the winters are characterized by heavy snowfall. Average annual air temperature, as determined from data collected at Vallecito Reservoir dam from 1951 through 1978, is 43 degrees Fahrenheit (°F) (Pannell, 1988). Average summer temperature is 62°F, and average winter temperature is 24°F. Average annual precipitation is 25 inches (in.), and average snowfall is 131 in. (Pannell, 1988). Most of the summer precipitation is associated with thunderstorms, which occur on about 45 days each summer.

METHODS OF DATA COLLECTION AND ANALYSIS

Water-quality samples were collected monthly at all sites during July 1996–97, except during January and April 1997. The samples were analyzed for DOC, ultraviolet (UV) absorbance at 254 nanometers (nm), THM formation potential (beginning in November), and DOC fractionation (except for samples from Los Piños River downstream from the dam). Additional samples were collected for inorganic constituents in August and October 1996 and in June and July 1997. These samples were analyzed for specific conductance; pH; alkalinity; dissolved major inorganic ions (calcium, magnesium, sodium, potassium, sulfate, and

chloride); nutrients (nitrogen and phosphorus); and trace metals. Samples from Vallecito Reservoir also were analyzed for chlorophyll-a. The stream samples were collected over the range in flow that occurred during the study period.

The DOC samples were collected in stainless-steel containers that were kept on ice until the samples were filtered in the U.S. Geological Survey laboratory in Durango, Colo. The samples were filtered through 0.45-micrometer (µm) silver filters into glass bottles that had been previously heated in an oven to 400 degrees Celsius (°C) for a minimum of 4 hours. The collection and processing of samples for inorganic analysis were done in accordance with methods described by Horowitz and others (1994). The collection and processing of samples for chlorophyll-a were done in accordance with methods described by Fishman and Friedman (1989).

Field measurements of specific conductance, pH, water temperature, and dissolved oxygen were made with a Hydrolab multiparameter water-quality probe. Calibration of specific conductance, pH, and dissolved oxygen was done in the field each day before sample collection, in accordance with the methods described by Hydrolab Corporation (1993).

Stream Samples

Water samples were collected at the U.S. Geological Survey gaging station on Vallecito Creek, upstream from a bridge on Los Piños River, and downstream from the dam on Los Piños River (fig. 1). On each sampling date, a discharge measurement was made at the Vallecito Creek and the upstream Los Piños River site in accordance with procedures described by Rantz and others (1982). Occasionally, a discharge value at Vallecito Creek was obtained from a rating curve. Because of the rapid velocity of the flow on Los Piños River downstream from the dam, discharge measurements were not made, and samples were collected from the bank only. Hydrolab readings were taken at 5 to 10 stations in a cross section across Vallecito Creek and the upstream Los Piños River site and from the streambank at Los Piños River downstream from the dam using the Hydrolab Scout 2 readout display.

Ground-Water Samples

Well DH-MW-2, which was installed by the Bureau of Reclamation in 1992 in a grassy field near the northwestern shore of Vallecito Reservoir, was sampled to assess the chemistry of ground water in the watershed (fig. 1). The well is 46 ft deep and was drilled through Quaternary alluvium that consists of sand- to gravel-size fragments of quartzite, pegmatite, gneiss, schist, granite, diorite, gabbro, and limestone (Bureau of Reclamation, 1995). The bottom 31 ft of the well is screened (0.038-in. slot size). The depth to bedrock was not established, but the Bureau of Reclamation (1995) did determine a transmissivity of 47,650 gallons per day per foot [(gal/d)/ft] based on a hydraulic conductivity of 635 gallons per day per square foot [(gal/d)/ft²] and an aquifer thickness of 75 ft. The water level in the well was measured during each sampling visit with an electric tape. Before water-quality samples were collected, three well volumes were pumped out of the well (Wilde and Radtke, 1997), using a GeoTech submersible pump that had a capacity of pumping 1 gallon per minute (gal/min) from a maximum depth of 50 ft. The pump was positioned a few feet above the bottom of the well within the screened layer. During the three-wellvolume purge and samplings of the well, readings were taken using a Hydrolab flowthrough chamber and recorded using a lap-top computer.

Reservoir Samples

During the warm weather when Vallecito Reservoir could be accessed by boat, water-quality samples were collected at three sites using a van Dorn sampler. Grab samples were collected from just below the surface; 3 ft above the bottom; and when the reservoir was stratified, at the top of the metalimnion. The north reservoir site is above the inflow of Los Piños River, the center reservoir site is below the inflow of Los Piños River, and the south reservoir site is at the deepest point in the reservoir and near the outflow from the reservoir (fig. 1). Samples collected in December 1996 and February and March 1997 were at the south site only and were done through a hole in the ice. Depth profiles of specific conductance, pH, water temperature, and dissolved oxygen were determined at the three sites using a Hydrolab. Readings were taken at 3- to 5-ft intervals. A Hydrolab dissolved-oxygen

stirrer with a flow rate of 1 foot per second (ft/s) was used for the measurement of dissolved oxygen. At each depth interval, readings were taken until the readings stabilized. Light penetration was measured with a 40-centimeter (cm)-diameter black and white Secchi disk.

Laboratory Analysis

The analyses for DOC concentration, UV absorbance at 254 nm, and DOC fractionation were performed in the U.S. Geological Survey laboratory in Boulder, Colo. The DOC measurements were made with an Oceanographic Instruments, Inc. (OI), model 700 total organic-carbon analyzer. The UV absorbance measurements were made with a Hewlett Packard 8453 spectrophotometer. The DOC fractionation (separation) into five operationally defined categories was accomplished using XAD-8 and XAD-4 resins. The operationally defined categories are hydrophobic acids (HPoA), hydrophobic neutrals (HPoN), hydrophilic acids (HPiA), hydrophilic neutrals (HPiN), and low-molecular-weight hydrophilic acids (LMW HPiA). A description of the physical and chemical properties of these resins is given by Aiken and others (1992). The fractionation procedure used in this study and the chemical composition of the operationally defined categories are described by Fujii and others (1998).

DOC fractionation is helpful in the investigation of the role of organic compounds in geochemical processes because the reactivity of an organic compound is determined by its structure. The DOC content of surface and ground water consists of thousands of individual compounds, each with its own unique structure. Structure refers to the molecular weight, shape of the molecule (for example, straight or branching chain or the presence of aromatic rings), and relative amount of functional groups (for example, carboxylic acid, ether, and amine). Because each compound has a unique structure and because many of these compounds are present in low concentrations, the fractionation and subsequent identification of all compounds individually are impractical. The ability to isolate compounds possessing similar structures greatly facilitates the study of THM formation. Because the compounds in each operationally defined category have similar structures and because the structures differ among categories, each category of organic

carbon reacts differently with chlorine. For example, Rook (1977) and Reckhow and others (1990) suggested that THM formation is a result of the reaction of chlorine with aromatic rings in humic substances. Humic substances are classified among the HPoA and are defined as an extremely complex and diverse group of poorly biodegradable decomposition products and byproducts of natural organic matter produced by plants and animals whose structure is not well defined (Snoeyink and Jenkins, 1980). By fractionating the part of DOC that is reactive with chlorine, the total DOC it comprises can be calculated, which results in a better understanding of the processes controlling the formation and seasonal variability of THM precursors in a given environment.

THM's were measured using the simulated distribution-system test that was designed to simulate the concentrations of THM's that could potentially form in a water-treatment plant under normal operating conditions. The samples were chlorinated with a dose of chlorine based on the inorganic and organic demand according to the formula by S.W. Krasner and M.J. Sclimenti (Metropolitan Water District of Southern California, written commun., 1996):(Cl₂) = (DOC) + [7.6x(NH₃)]. Samples were placed into a 42-milliliter (mL) serum vial and sealed using a Teflon-faced septum without leaving a headspace (to prevent volatilization of THM's). The chlorination solution (NaOCL) was injected through the septum with a syringe allowing the displaced volume to exit through a second syringe. The samples then were incubated for 24 hours at 20°C. The chlorination reaction was terminated by adding several drops of a 1.5-molar sodium sulfite solution. The extraction of the THM's from the aqueous phase and the quantification of the THM's are described by Fujii and others (1998).

Laboratory measurements of alkalinity, specific conductance, and pH were made by the U.S. Geological Survey in Lakewood, Colo. Alkalinity was determined from a Gran titration using a Radiometer Low Ionic Strength Titrator. Specific conductance was measured with a YSI model 32 conductance meter. The first measured value of pH during the Gran titration was used as the laboratory value of pH.

Cations were analyzed using two Perkin-Elmer Optima 3000 ICP-AES instruments at the Colorado School of Mines in Golden, Colo. The two instruments differ slightly in that the detection on one of them is oriented to view along the axis of the Argon plasma. A

conventional ICP-AES instrument views the plasma radially. The two instruments used similar software and methods; however, the elements analyzed by each method were different, and detection limits were lower on the axial instrument than on the conventional instrument. The axial instrument also analyzed for an additional wavelength of iron at 274 nm. Both instruments analyzed for scandium, which was used as an internal standard. The methods used by the two instruments to calculate calibration curves also differed. The conventional instrument was arbitrarily set for a twopoint calibration, and the axial instrument was set for a three-point calibration. Before analysis, samples were weighed on a balance by taring the scale with a small beaker holding a single sample vial that was rinsed once with some sample. Depending on which instrument was being used, 9.90 or 14.85 mL of sample then was poured into the vial and spiked with 0.10 or 0.15 mL of a 500-mg/L solution of scandium. The resultant 5-mg/L scandium spike in each sample was used as an internal standard. Samples generally were run in batches of 15 as follows: 2 quality-control check standards, 5 samples, 1 U.S. Geological Survey standard reference sample, 5 samples, and 2 qualitycontrol check samples. The quality-assurance/qualitycontrol samples were used to evaluate and correct the data produced by the instruments.

Anions were analyzed using a Dionex QIC analyzer Ion Chromatograph according to the method described by Fishman and Friedman (1989). Nutrient and chlorophyll-*a* analyses were performed at the U.S. Geological Survey central laboratory in Arvada, Colo., using the procedures described by Fishman and Friedman (1989).

WATER QUALITY OF RESERVOIR, INFLOWS, GROUND WATER, AND OUTFLOW

All of the data collected during the study, except for the THM data, are presented in tables 6 through 14 in the appendix at the back of the report. Except where indicated, any discussion of Vallecito Reservoir refers to the southern sampling site at the surface.

Trihalomethane Formation Potential and Dissolved Organic Carbon

DOC is operationally defined as the organic carbon passing through a 0.45-um silver filter (Thurman, 1985). The concentration and composition of the DOC in the Vallecito Reservoir watershed were a major focus of this study because, when water that is to be used as a municipal drinking-water source is chlorinated, certain types of organic molecules can react with chlorine to form THM's. THM's consist of trichloromethane (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl), and tribromomethane (CHBr₃) and are classified as carcinogens by the USEPA (U.S. Environmental Protection Agency, 1994). The USEPA has established an MCL for THM's of 100 micrograms per liter (µg/L). This level may become more stringent when stage 1 of the Disinfectant-Disinfection By Products rule, under which the MCL for THM's would be decreased to 80 µg/L, is implemented (originally scheduled for June 1998). Reckhow and others (1990) demonstrated that phenolic structures present in the humic substances are the main reactive site for THM formations. Other studies have reported that algae and plankton in lakes and reservoirs also can be THM precursors (Cooke and Carlson, 1989).

THM formation potential data are listed in table 1 and shown in figure 2. Trichloromethane was the predominate compound formed in all samples. For either of the two possible withdrawal points for a public supply system, Vallecito Reservoir or Los Piños River downstream from the dam, total THM's probably would exceed the proposed USEPA limits only during spring snowmelt in June and July (fig. 2). The concentrations of THM's that can potentially form in chlorinated water from the reservoir or Los Piños River downstream from the dam generally are either at the concentration of THM's from Los Piños River upstream from the reservoir or between the concentrations of THM's from the two inflows. This indicates that the reservoir is not a source of THM precursors, but that the concentrations of THM's that can form from reservoir water are a result of the mixing of THM precursors in the two inflows.

To understand the seasonal and spatial variability in the THM data, the causes of the seasonal and spatial variability in the concentration and composition of DOC need to be understood. DOC in streams and rivers is allochthonous, which means the DOC is

Table 1. Trihalomethane formation potential data for Vallecito Reservoir, Colorado, and its inflows and outflows

[Data presented are not concentrations of compounds measured in the reservoir, river water, or ground water, but are compounds formed in the laboratory test; $\mu g/L$, micrograms per liter; --, not detected]

Site	Date	Trichloro- methane (μg/L)	Bromo- dichloro- methane (μg/L)	Dibromo- chloro- methane (μg/L)	Tribromo- methane (μg/L)	Total trihalo- methanes (μg/L)
Vallecito Creek	11/21/96	43.7	2.4	0.2	0.5	46.8
Los Piños River	11/21/96	55.8	3.6	0.2	0.5	60.1
Well DH-MW-2	11/20/96	3.5	0.7			4.2
Vallecito Reservoir at surface	11/21/96	27.1	1.3		0.3	28.7
Vallecito Creek	12/12/96	24.0	2.0	0.9	3.7	30.6
Los Piños River	12/12/96	35.3	2.5	0.5	1.7	40.0
Well DH-MW-2	12/12/96	3.5	0.7			4.2
Vallecito Reservoir at surface	12/12/96	38.4	2.0	0.2	0.7	41.3
Los Piños River downstream from dam	12/12/96	36.7	2.0		0.3	39.0
Vallecito Creek	02/13/97	18.8	1.5			20.3
Los Piños River	02/13/97	25.4	1.8			27.2
Well DH-MW-2	02/14/97	5.4	1.5	0.4		7.3
Vallecito Reservoir at surface	02/12/97	25.4	1.4	0.1	0.3	27.2
Los Piños River downstream from dam	02/13/97	29.9	2.2	0.4	2.0	34.5
Vallecito Creek	03/28/97	68.8	3.0	0.1	0.5	72.4
Los Piños River	03/28/97	73.0	39.3	0.3	1.1	113.7
Los Piños River downstream from dam	03/28/97	30.1	1.9		1.1	33.1
Vallecito Creek	05/06/97	92.1	3.5	0.3	1.3	97.2
Los Piños River	05/06/97	133.3	4.4		0.7	138.4
Well DH-MW-2	05/06/97	2.5	0.5		0.4	3.4
Vallecito Reservoir at surface	05/06/97	64.4	2.8		0.6	67.8
Los Piños River downstream from dam	05/06/97	47.8	2.8	0.2	1.3	52.1
Vallecito Creek	06/02/97	80.8	2.3	0.1	0.7	83.9
Los Piños River	06/02/97	151.4	3.8		0.4	155.6
Well DH-MW-2	06/05/97	5.0	0.5		0.3	5.8
Vallecito Reservoir at surface	06/03/97	108.3	3.1		0.5	111.9
Los Piños River downstream from dam	06/04/97	92.1	3.2		0.5	95.8
Vallecito Creek	07/03/97	22.0	0.9		0.2	23.1
Los Piños River	06/30/97	89.0	2.4		0.4	91.8
Vallecito Reservoir at surface	07/01/97	92.6	1.7		0.6	94.9
Los Piños River downstream from dam	07/02/97	93.7	3.1	0.4	2.2	99.4

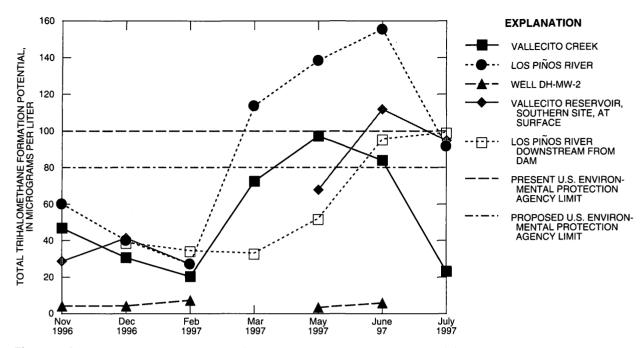


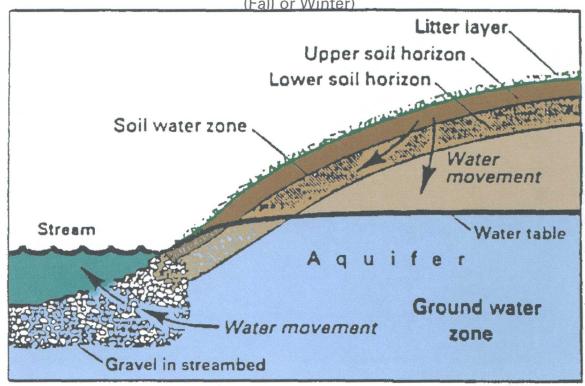
Figure 2. Seasonal and spatial variability of total trihalomethane formation potential.

derived from the vegetation of the surrounding watershed (Wetzel, 1983; Aiken and Cotsaris, 1995). The DOC can enter a stream by direct leaching of vegetation that has fallen into the stream from overhanging canopies, by being carried into the stream by storm runoff, or by being blown into the stream by the wind. Most DOC, however, originates from the leaching of organic detritus that is being microbially decomposed in the soils of the watershed and is transported in ground water to the stream. Thus, the flow path of water through a watershed is the main control on DOC concentration.

A simplified conceptual hydrologic model, which describes how ground water enters a stream or river, is shown in figure 3. Generally, the DOC concentration varies seasonally, with the lowest concentrations occurring in the fall or winter at the time of the low flows of the year, and the peak concentrations occurring in the spring at the time of snowmelt. This seasonal variability occurs because, during low flows when the water table is well below the land surface (fig. 3), the DOC that was initially dissolved in soil water decreases as the soil water migrates down to the water table because of microbial decomposition and sorption to clay particles. At the time of the spring snowmelt, when the ground becomes saturated and the water table moves up to the land surface, the water flows through the upper soil horizon (fig. 3). The DOC

in this water has a shorter residence time in the soil and is not subjected to the same decomposition processes as water that percolates down to the water table. The seasonal variability in flow path also could result in variability in the composition of the DOC in which humic substances become more prevalent in the spring than at any other time of the year. This variability in composition is of direct concern for THM formation because humic substances are the main THM precursors. In reservoirs, allochthonous DOC brought in by inflows is augmented by authorthonous DOC. Authorthonous DOC is produced within the reservoir from organisms, such as algae, bacteria, and macrophytes, that are capable of photosynthesis and from the release of organic compounds from these organisms at death.

The seasonal and spatial variability of DOC concentrations is shown in figure 4. At all sites except well DH-MW-2, a strong seasonal peak occurred in the spring at the peak of the snowmelt; a secondary peak occurred in late fall at Vallecito Creek and Los Piños River upstream from the reservoir. Vallecito Creek and Los Piños River had peak DOC concentrations in May 1997; Vallecito Reservoir and Los Piños River downstream from the dam had peak concentrations in June 1997. The peak DOC concentration of the reservoir and its outlet lagged behind the peak of the inflows because reservoirs do not respond as



HIGH FLOW (Spring)

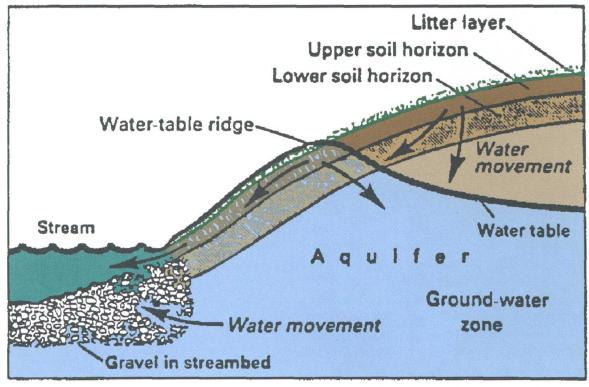


Figure 3. Simplified conceptual hydrologic model of the flow path of ground water to streams and rivers from the surrounding watershed (from Boyer and others, 1996).

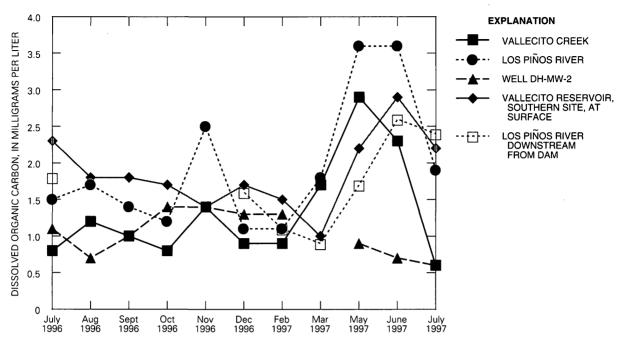


Figure 4. Seasonal and spatial variability of dissolved organic carbon concentrations.

quickly as streams to runoff-induced changes in DOC chemistry (Aiken and Cotsaris, 1995). Reservoirs tend to average out variations in DOC concentrations associated with increased stream discharge because most reservoirs are subject to various degrees of physical mixing that can result in spatially uniform DOC concentrations. Pulses of organic matter that enter Vallecito Reservoir are mixed with the existing organic matter, and the net effect is to dampen out the seasonal variability in DOC concentrations of the inflows. The DOC concentration of the reservoir is generally higher than the concentrations of the two inflows from the middle of summer and into the fall, but the concentration steadily decreases. The higher DOC concentrations in the reservoir during that time probably result from the presence of algae. The steady decrease during the mid-summer and fall results from the input into the reservoir of dilute DOC in water from the inflows.

The seasonal variability of DOC concentrations in Vallecito Creek and Los Piños River and the variability in discharge were similar (fig. 5). The higher DOC concentrations in Los Piños River all year probably result from differences in the organic-matter content of the soils in the two watersheds and differences in watershed geomorphology. Most of the soils in the Vallecito Reservoir watershed have organic-matter contents of less than 2 percent (Pannell, 1988).

However, Pannell (1988) mapped a soil group (Pastorius cobbly loam) in the valley of Los Piños River upstream from the reservoir that has an organic-matter content of 2 to 4 percent in the area of the sampling site and in several other patches upstream from the sampling site. The valley of Vallecito Creek at and upstream from the gaging station has steep valley walls and many bedrock outcrops and thin soils. The valley of Los Piños River at and upstream from the sampling site is flatter and wider and has thicker soils than the valley of Vallecito Creek. This difference in watershed geomorphology could allow ground water in the valley of Los Piños River to have a greater residence time in the soil organic layer before being discharged into the stream. The combination of soils of higher organic-matter content and a possible greater residence time of ground water in the soil organic layer probably causes the ground water in Los Piños River watershed to have higher DOC concentrations. Therefore, DOC concentrations are higher in Los Piños River because of the ground water discharging into the river. The peak DOC concentrations occur before the peak discharges in both streams because the initial meltwater infiltrates the soil and dissolves the readily available DOC. As more water is routed through the soil, the pool of available DOC decreases, and the DOC concentrations decrease. The DOC concentration of Los Piños River at peak flow in June

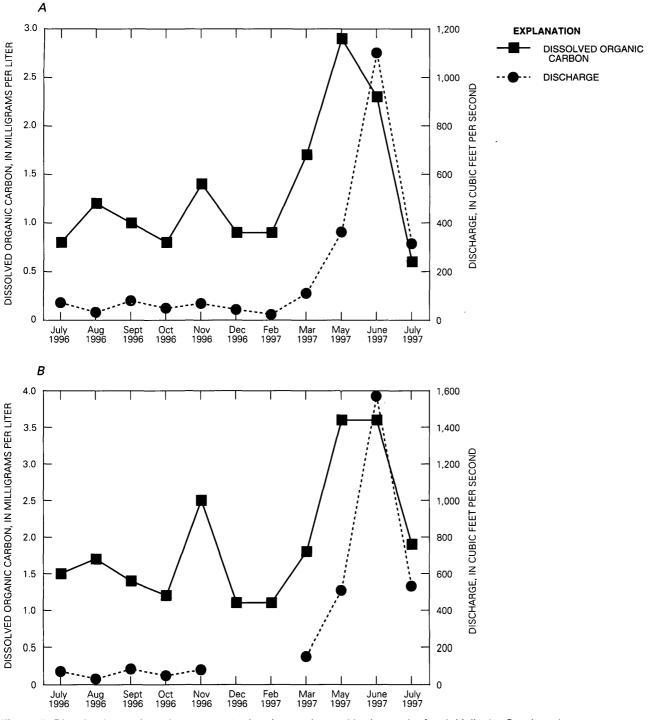


Figure 5. Dissolved organic carbon concentration time series and hydrographs for *A*, Vallecito Creek and *B*, Los Piños River, Colorado.

remained the same as in May, possibly because the thicker soils in that watershed, compared to the soils in the Vallecito Creek watershed, provided a larger reservoir of readily available DOC. The DOC concentrations of well DH-MW-2 varied during the study but were less than 1.5 mg/L all year (fig. 4 and table 7, which is in the appendix).

Seasonal and spatial variability also occurred in the composition of the DOC. Comparison of UV absorbance values at 254 nm indicate the relative aromaticity of the DOC (Aiken and Cotsaris, 1995). Los Piños River had the greatest UV absorbance values most of the year (fig. 6), and the seasonal pattern generally followed the pattern of DOC concen-

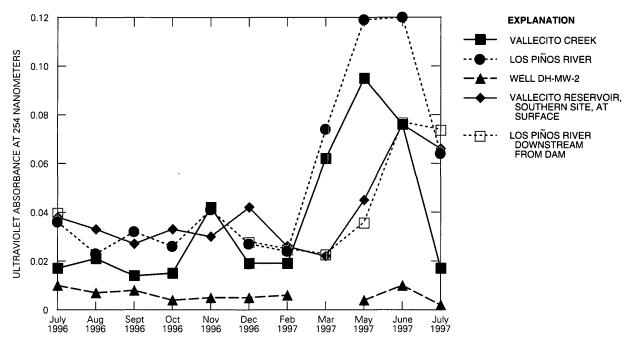


Figure 6. Seasonal and spatial variability of ultraviolet absorbance.

trations at all sites (fig. 4). This seasonal pattern indicates that Los Piños River had the largest amount of aromatic compounds, which can be THM precursors. During the spring snowmelt at all sites, except well DH-MW-2, the DOC concentration increased to about three times greater than in winter, whereas the UV abundance values increased to about four to five times greater than in winter. The greater increase in UV abundance values compared to DOC concentration indicates that the DOC was becoming more aromatic and that the DOC had a larger percentage of humic substances in the spring. The DOC fractionation data support this observation (fig. 7). For most of the year, Los Piños River has the greatest mass of the hydrophobic acids fraction. (The fractionation data are plotted as a percentage of the total DOC mass that each fraction contributes to the total DOC mass; the percentage of hydrophobic acids for Los Piños River is similar to the percentage for Vallecito Creek. The mass of this fraction is greater in Los Piños River because the DOC concentration of Los Piños River is greater than the DOC concentration of Vallecito Creek on every sampling date.) For most of the year at all sites, the hydrophobic acids fraction had less mass than the low-molecular-weight hydrophilic acids fraction, but at the spring snowmelt, the mass of the hydrophobic acids increased to equal the mass of the lowmolecular-weight hydrophilic acids, except well DH-MW-2. Thus, at the spring snowmelt, not only was

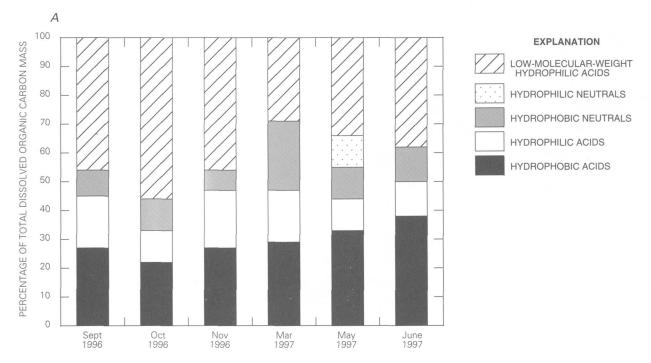
more DOC in the water, but there was more of the type of DOC that is THM precursors, especially in Los Piños River.

The seasonal and spatial variability of the concentration and composition of DOC in the Vallecito Reservoir watershed indicate that the concentration and composition of the DOC in Vallecito Reservoir is affected more by inflows from Los Piños River than by inflows from Vallecito Creek, primarily during snowmelt runoff. The effect of Los Piños River can be demonstrated by comparing the instantaneous DOC loads of Vallecito Creek with the loads of Los Piños River (table 2). The terms "load" and "loading" are defined here to be the amount (mass) of a compound or element that is added to a water body during a given period of time. Loads were calculated by multiplying the concentration of the substance of interest by the instantaneous discharge. On all sampling dates, Los Piños River contributed a greater load of DOC to the reservoir than did Vallecito Creek. The difference was especially great in June and July 1997 during the spring snowmelt when the DOC loads from Los Piños River were about 2 and 5 times as much as the loads from Vallecito Creek (table 2). The DOC concentration and the mass of the hydrophobic acids fraction of the water sampled from well DH-MW-2 remained consistently low during the study. The effect of ground-water inflows on the concentration and composition of the DOC in Vallecito Reservoir cannot be

determined because of the limited amount of data on ground-water quality and the lack of data on groundwater inflows to Vallecito Reservoir.

DOC concentrations at the surface for the north, center, and south reservoir sites in Vallecito Reservoir

during the study are shown in figure 8. Except during June 1997, differences between the sites were small, only about 0.1 to 0.2 mg/L, and the seasonal variability was about the same at each site. DOC concentrations at each site gradually decreased during the



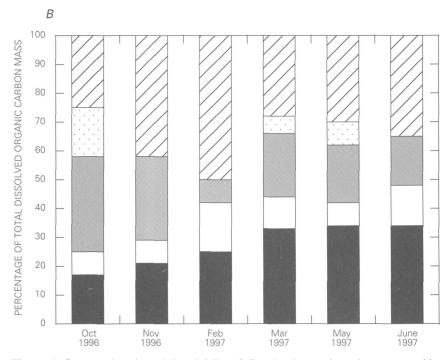
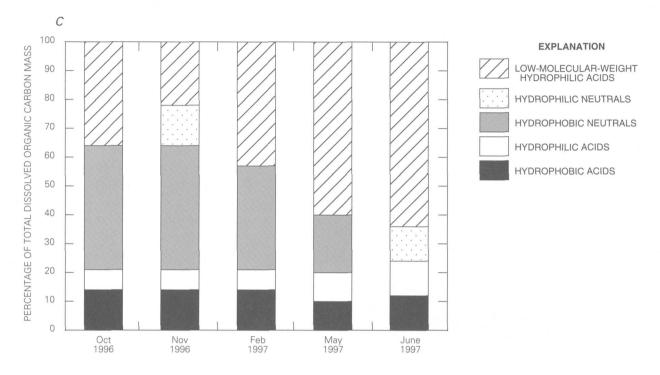


Figure 7. Seasonal and spatial variability of dissolved organic carbon composition at *A*, Vallecito Creek; *B*, Los Piños River; *C*, well DH-MW-2; and *D*, Vallecito Reservoir, Colorado.

summer, increased through the spring, and peaked in June 1997. The consistently higher DOC concentrations for the center reservoir site compared to the north reservoir site reflect the consistently higher DOC

concentrations in Los Piños River compared to those in Vallecito Creek. The DOC concentration at the south reservoir site was consistently higher than the concentrations at the other two sites until the spring



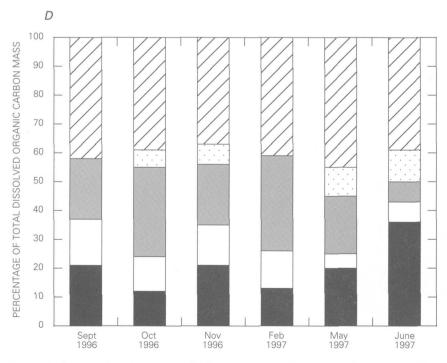


Figure 7. Seasonal and spatial variability of dissolved organic carbon composition at *A*, Vallecito Creek; *B*, Los Piños River; *C*, well DH-MW-2; and *D*, Vallecito Reservoir, Colorado—Continued.

Table 2. Instantaneous dissolved organic carbon loads of Vallecito Creek and Los Piños River, Colorado

Date		Dissolved organic carbon loads (grams per second)				
-	Vallecito Creek	Los Piños River				
July 1996	1.6	3.1				
August 1996	1.1	1.5				
September 1996	2.3	3.4				
October 1996	1.1	1.6				
November 1996	2.7	5.7				
March 1997	5.3	7.7				
May 1997	30	52				
June 1997	72	160				
July 1997	5.3	28				

snowmelt when DOC concentrations at the south reservoir site decreased slightly to a concentration between the concentrations for the other two sites. This decrease probably reflects the mixing of water from the two inflows. Differences in DOC concentrations and in UV absorbance values with depth (not shown) were about the same as differences in these parameters between the surface sites, indicating that the concentration of THM's that could form would be about the same regardless of where in the reservoir the water was obtained.

Trophic State of Reservoir and Nutrients

The water temperature, nutrient (nitrogen and phosphorus) concentration, dissolved-oxygen concentration, and dissolved and particulate organic carbon concentration are among the most important factors controlling the biological productivity of a reservoir. The nitrogen and phosphorus concentrations commonly limit the growth of algae in reservoirs (Wetzel, 1983). When the concentration of these nutrients is high, growth of algae may be so high that algal blooms occur, which may result in taste and odor problems for a water-treatment facility (Cooke and Carlson, 1989). In addition, some of the organisms, such as crytoposporidium, may be harmful to human health (Cooke and Carlson, 1989). The most important consequence of high growths of algae is that, when these organisms die, they decay and the metabolic activity of microorganisms that decompose the algae consume oxygen. This metabolic activity can deplete the dissolved oxygen in a reservoir and result in fish kills.

Water temperature is important because the density of water is directly related to temperature. Differences in water density throughout the year control the degree to which wind can mix the water column. As summer begins, the upper layers of the reservoir, which are penetrated by sunlight, absorb

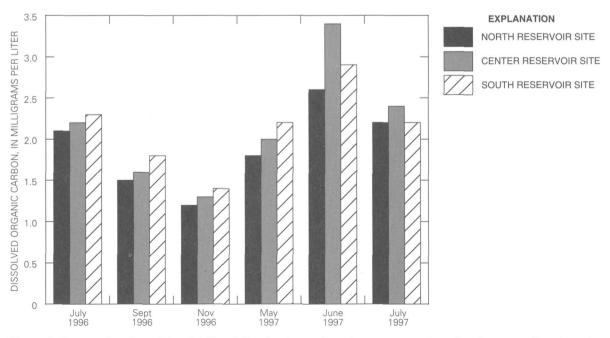


Figure 8. Seasonal and spatial variability of dissolved organic carbon concentration of surface sampling sites at Vallecito Reservoir, Colorado.

solar radiation and become warmer than the lower layers, which are not heated by solar radiation. This difference in temperature causes differences in density between the upper and lower layers of a reservoir and impedes mixing of the entire water column by the wind. Thus, a stratification or division of the reservoir into distinct layers occurs. These layers are referred to as the epilimnion, hypolimnion, and metalimnion. The epilimnion is the upper stratum of less dense and more or less uniformly warm and circulating water. The hypolimnion is the lower strata of more dense and cooler water below the epilimnion. The metalimnion is the transitional stratum of marked thermal change between the epilimnion and hypolimnion.

Stratification has a major effect on reservoirs. Because water in the hypolimnion is, in essence, cut off from exchange with the atmosphere during the summer, oxygen depletion can occur if oxygen consumption exceeds the amount of oxygen available at the start of the summer stratification. The amount of dissolved oxygen in a reservoir is of concern not only because little or no oxygen can result in fish kills but also because oxygen controls the solubility of certain elements. When oxygen is absent or present in very low concentrations, iron, manganese, and phosphorus concentrations in the hypolimnion increase (Wetzel, 1983).

In fall as the upper layers cool, a reservoir reaches a uniform temperature, and the entire water column is mixed by the wind because the density of the water is uniform throughout the reservoir. This mixing is known as fall turnover. In winter, the reservoir stratifies again as water at less than 4°C overlies water at 4°C in the bottom one-half of the reservoir (the density of water is greatest at 4°C, which is why, in winter, colder water can overlie warmer water.) In spring, the reservoir mixes again as the upper layers warm and reach the same temperature as the lower layers, permitting wind-driven mixing of the entire water column. This mixing is known as spring turnover.

All of these factors work together in complex dynamic ways to affect the biological productivity of a reservoir. Limnologists use the term "trophic state" to describe the degree of biological productivity and the terms "oligotrophic," "eutrophic," "mesotrophic," and "hypereutrophic" to describe the trophic state of a reservoir (Cooke and Carlson, 1989). Oligotrophic reservoirs have small nutrient concentrations and a low level of productivity. Eutrophic reservoirs have large nutrient concentrations and a high level of

productivity. Mesotrophic reservoirs are in transition between oligotrophic and eutrophic. Hypereutrophic reservoirs have extraordinarily large algal growth.

Characterizing a drinking-water reservoir by its trophic state provides many advantages to a drinking-water utility. Knowledge of the trophic state of a reservoir provides a quantitative assessment of the condition of the reservoir and can be used by water-treatment-plant operators to anticipate the types of water-quality problems likely to occur. This knowledge also allows for a quantitative assessment of the effect of future land-use and water-use practices in the watershed on water quality.

Many methods have been used to assign a trophic-state classification to a lake or reservoir; however, the trophic-state index (TSI) developed by Carlson (1977) has been widely used and is the method used in this report to determine the trophic state of Vallecito Reservoir. In this method, the trophic-state classification of a reservoir is assigned on the basis of values of chlorophyll-a concentration (CHL), surface values of total phosphorous concentration (TP), and Secchi-disk depth (SD). These values are substituted into separate equations, which produce a number that ranges from 0 to 100. A reservoir with a TSI value of less than 30 is classified as oligotrophic, and one with a TSI value greater than 70 is classified as hypereutrophic. TSI values between 30 and 70 represent transitional states (Cooke and Carlson, 1989). Each TSI variable gives a separate estimate of trophic state, although the equations are designed to give approximately the same TSI value. The chlorophyll-a TSI value is given priority for classification because it is a biological variable indicating the amount of algae in the water.

The seasonal variability in the TSI variables in Vallecito Reservoir is shown in figure 9. CHL and TP TSI values range from 20 to 32. The similarity in these values indicates that phosphorus probably controls the amount of algae in Vallecito Reservoir (Cooke and Carlson, 1989). SD TSI values, however, are higher than the other two values and are much higher in June 1997 at peak snowmelt.

Secchi-disk transparency is a measure of turbidity. If the turbidity is caused by algae cells, then the SD TSI value would correspond well with the CHL TSI value. If the turbidity is caused by sediment, the SD TSI value would be higher than the CHL TSI value.

The values of the TSI variables indicate that Vallecito Reservoir can be classified as an oligotrophic

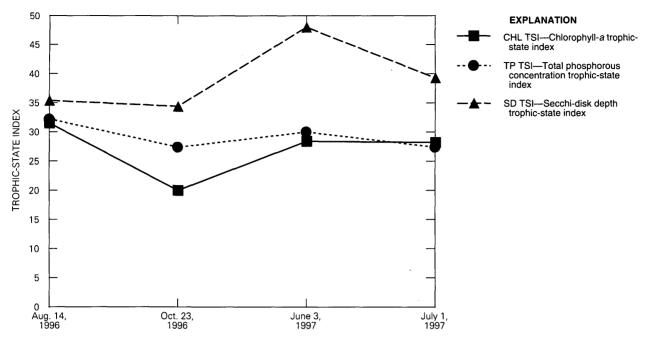


Figure 9. Seasonal variability in trophic-state index of Vallecito Reservoir, Colorado.

reservoir. The turbidity present in the reservoir probably results more from sediment brought in by surface runoff and wave erosion of the shoreline than from algal growth. The major reason for the reservoir being oligotrophic is the low nutrient concentration in water entering the reservoir (table 3).

Major Ions and Trace Metals

In pristine streams and lakes, the main source of dissolved inorganic constituents is from the weathering of rocks in the watershed. Weathering refers to the chemical reaction between rocks and carbonic acid dissolved in rain and snowmelt that results in the disintegration of the rock. Carbonic acid forms when carbon dioxide in the atmosphere dissolves in water droplets. As these droplets coalesce and fall to earth as rain and snow, water infiltrates the ground and chemical reactions occur that remove ions from the rock; these ions are transported with the runoff into streams and lakes.

The average inorganic-ion composition of water at the sampling sites is shown on a trilinear diagram, also known as a Piper diagram, in figure 10. The percentage of the total milliequivalents per liter for

Table 3. Median nutrient concentrations of Vallecito Reservoir, Colorado, and its inflows and outflow

[mg/L, milligrams per liter; N, nitrogen; P, phosphorus, <, less than]

Site	Ammonia (mg/L as N)	Nitrite (mg/L as N)	Ammonia plus organic, dissolved (mg/L as N)	Ammonia plus organic, total (mg/L as N)	Nitrite plus nitrate (mg/L as N)	Phos- phorus, total (mg/L as P)	Phos- phorus, dissolved (mg/L)	Ortho- phos- phorus (mg/L as P)
Vallecito Creek	<0.002	0.001	<0.2	<0.2	0.080	0.002	0.002	<0.001
Los Piños River	< 0.002	0.001	<0.2	<0.2	0.014	0.009	0.004	0.002
Well DH-MW-2	0.002	0.001	< 0.2	<0.2	0.178	0.002	0.002	0.001
Vallecito Reservoir	< 0.002	0.001	< 0.2	<0.2	0.006	0.006	0.002	0.001
Los Piños River down- stream from dam	0.005	0.001	<0.2	<0.2	0.022	0.005	0.003	<0.001

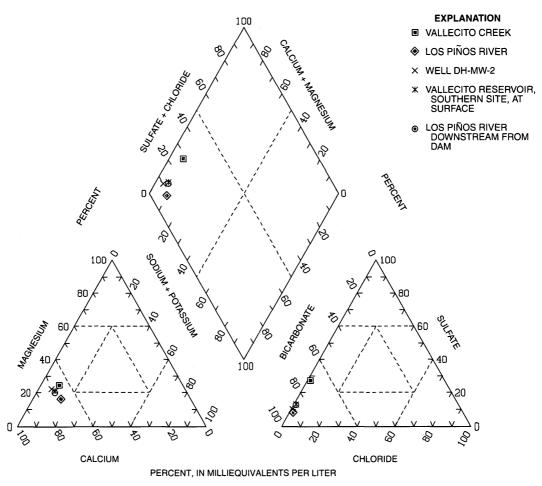


Figure 10. Average inorganic-ion composition at the five main sampling sites.

each ion in a sample also is shown in figure 10. The water in the Vallecito Reservoir watershed is dominated by calcium and bicarbonate ions, indicating that the weathering of limestone is the major source of the inorganic ions. The ratio of the concentrations of various ions can sometimes indicate the predominant weathering reaction that is occurring. The equation for the weathering of limestone is calcite + carbonic acid = calcium ion + bicarbonate ion ($CaCO_3 + H_2CO_3 =$ $Ca^{++} + 2 HCO_3^-$). Thus, if limestone is the source of the inorganic ions, the molar ratio of bicarbonate to calcium would be 2:1. As indicated in table 4, this molar ratio is slightly greater than 2:1 for almost all sites. Thus, the concentration of bicarbonate dissolved in the surface and ground waters of the Vallecito Reservoir watershed is slightly greater than expected from the weathering of limestone. A possible explanation for the additional bicarbonate ions is the weathering of another mineral which yields bicarbonate ions but no calcium ions. An example of such a reaction is

albite (sodium feldspar) weathering to kaolinite (a clay mineral):

$$2NaAlSi_{3}O_{8} + 11H_{2}O + 2CO_{2} =$$

$$Al_{2}Si_{2}O_{5}(OH)_{4} +$$

$$2Na^{+} + 2HCO_{3}^{-} + 4H_{4}SiO_{4}$$

That limestone weathering is the predominant weathering reaction occurring in the Vallecito Reservoir watershed is made more plausible by the fact that limestone has been mapped in the bedrock and in glacial deposits in the watershed (as described in the "Site Description" section), and limestone weathers more rapidly than most rocks.

Trilinear diagrams also can be used to determine if a water is the result of mixing of water from other sources. The compositions of water in Vallecito Reservoir and in Los Piños River downstream from the dam plot in the triangle defined by the compositions of water in Vallecito Creek and in Los Piños River and by

Table 4. Molar ratio of bicarbonate to calcium for Vallecito Reservoir, Colorado, and its inflows and outflows [µmol/L, micromoles per liter; ft, feet]

Site	Date	Calcium (µmol/L)	Bicarbonate (μmol/L)	Molar ratio of bicarbonate to calcium
Vallecito Creek	08/13/96	209.6	421.3	2.0
Los Piños River	08/13/96	349.3	865.3	2.5
Well DH-MW-2	08/13/96	1,586.8	2,392.9	1.5
North reservoir site at surface	08/15/96	267.0	657.5	2.5
Center reservoir site at surface	08/15/96	257.0	642.6	2.5
Center reservoir site at 22 ft	08/15/96	274.5	638.0	2.3
South reservoir site at surface	08/14/96	242.0	617.3	2.6
South reservoir site at 39 ft	08/14/96	264.5	610.8	2.3
South reservoir site at 55 ft	08/14/96	247.0	581.6	2.4
Los Piños River downstream from dam	08/16/96	269.5	614.9	2.3
Vallecito Creek	10/21/96	197.1	395.3	2.0
Los Piños River	10/22/96	272.0	656.9	2.4
Well DH-MW-2	10/22/96	1,482.0	2,940.0	2.0
North reservoir site at surface	10/23/96	269.5	716.5	2.7
Center reservoir site at surface	10/23/96	331.8	706.0	2.1
South reservoir site at surface	10/23/96	304.4	702.1	2.3
South reservoir site at 58 ft	10/23/96	272.0	664.7	2.4
Los Piños River downstream from dam	10/21/96	306.9	701.9	2.3
Vallecito Creek	06/02/97	159.7	316.3	2.0
Los Piños River	06/02/97	177.1	396.7	2.2
Well DH-MW-2	06/05/97	1,482.0	3,556.6	2.4
North reservoir site at surface	06/04/97	262.0	634.7	2.4
North reservoir site at 45 ft	06/04/97	239.5	556.4	2.3
Center reservoir site at surface	06/03/97	272.0	648.2	2.4
Center reservoir site at 56 ft	06/03/97	247.0	579.7	2.3
South reservoir site at surface	06/03/97	276.9	640.9	2.3
South reservoir site at 25 ft	06/03/97	276.9	651.7	2.4
South reservoir site at 90 ft	06/03/97	289.4	691.3	2.4
Los Piños River downstream from dam	06/04/97	272.0	657.9	2.4
Vallecito Creek	07/03/97	112.3	208.5	1.9
Los Piños River	06/30/97	162.2	383.3	2.4
Well DH-MW-2	06/30/97	1,464.6	3,425.5	2.3
North reservoir site at surface	07/01/97	219.6	514.9	2.3
North reservoir site at 45 ft	07/01/97	202.1	460.7	2.3
Center reservoir site at surface	07/01/97	234.5	512.7	2.2
Center reservoir site at 45 ft	07/01/97	217.1	497.7	2.3
South reservoir site at surface	07/01/97	222.1	517.3	2.3
South reservoir site at 25 ft	07/01/97	214.6	506.8	2.4
South reservoir site at 90 ft	07/01/97	229.5	531.3	2.3
Los Piños River downstream from dam	07/02/97	224.6	492.4	2.2

the composition of ground water (fig. 10-central diamond figure). For a three-source mixing, the compositions of the three sources form a triangle on the trilinear diagram, and all possible mixtures plot in that triangle (Briel, 1993). The composition of water in the reservoir and its outlet results from the mixing of these three sources. However, another possible explanation exists for the similarity in water quality between well DH-MW-2 and the reservoir. The well could contain water that moves from the reservoir into ground water as reservoir stage rises, especially during spring. This phenomenon is known as bank storage. Water-quality data from other wells around the reservoir, as well as ground-water and reservoir-head data, are needed to determine if the inorganic composition of the reservoir results from the mixing of ground water with water from the inflows.

Trace-metal data are presented in table 5. Iron and manganese concentrations were consistently greater than their respective detection limits. Manganese concentrations near the bottom of Vallecito Reservoir at the south reservoir site had the largest seasonal variability and ranged from 3.4 micrograms per liter (μ g/L) in July 1997 to 278 μ g/L in August 1996.

Water-Quality Changes with Depth in Vallecito Reservoir

Depth profiles for Vallecito Reservoir show that the reservoir was stratified on August 14, 1996, and had gone through fall turnover by October 24, 1996 (fig. 11). A weak stratification developed by June 3, 1997, and the reservoir was stratified again by July 1, 1997. Dissolved-oxygen concentrations approached zero in the hypolimnion on August 14, 1996. Because the relations among the TSI variables demonstrate that turbidity in the reservoir is caused more by sediment than by algae, this depletion of oxygen probably resulted from the decomposition of organic matter as sediment was brought in by Vallecito Creek and Los Piños River during peak snowmelt. Large amounts of organic matter (branches, leaves, grasses, pine needles, and flowers), which was washed in by tributary inflow, were observed in the reservoir in June and July 1997. The seasonal variability in the dissolvedoxygen profiles shown in figure 11 probably results from this influx of particulate organic matter. Dissolved-oxygen concentrations remained constant

in June and July 1997 although the reservoir was thermally stratified in July. Dissolved-oxygen concentrations remained unchanged in the early summer because the organic matter was still at the surface, but by August, this material probably settled out of the water column, was deposited in the sediments, and was being decomposed by microorganisms along with other particulate matter that had been washed in over the years and settled to the bottom of the reservoir.

Specific-conductance and pH measurements also are useful in any water-quality study. Specific conductance is a measure of the ability of water to conduct an electrical current that results from ions dissolved in water. As the concentration of dissolved ions increases, specific conductance increases. Because of this relation, concentrations of the individual major chemical constituents may be estimated from specific conductance. Measured differences in specific-conductance profiles help distinguish differences in dissolved-ion concentration with depth and time.

The pH value is a measure of the hydrogen-ion concentration of the water. The pH affects the solubility of many chemical constituents and is affected by the metabolic processes of planktonic organisms, such as algae. When these organisms photosynthesize during daytime, they produce oxygen and consume carbon dioxide. When they respire at night, they consume oxygen and produce carbon dioxide. When the carbon dioxide concentration decreases, pH increases; and when the carbon dioxide concentration increases, pH decreases.

Specific-conductance data indicate that the amount of dissolved solids in Vallecito Reservoir was not large (fig. 11). Specific conductance was not uniform with depth, but variations with depth were not large. Specific conductance was smallest in the reservoir in July 1997, probably because of dilution following spring runoff.

Values of pH in Vallecito Reservoir were circumneutral and varied within a 1.5-pH-unit range. Values of pH decreased with depth in August 1996 and in June and July 1997 (fig. 11), probably because photosynthesis declines as light is scattered and absorbed as it passes through the water column. This decline in photosynthesis means that carbon dioxide production by respiration is not balanced by carbon dioxide removal by photosynthesis; thus, the concentration of carbon dioxide increases. As the concentra-

Table 5. Trace-metal data for Vallecito Reservoir, Colorado, and its inflows and outflows

Ę
fe
ft,
Ë,
tha
SS
<u>e</u>
V
ter;
•
re in micrograms per l
SI
a
50
<u>5</u>
Έ
Ξ.
are
us
ō
rat
ä
ĕ
Ŕ
\simeq

Site	Date Time	0				Trace metals (micrograms per liter)	Trace metals rograms per lit	er)				
		Aluminum	Cadmium	Chromium	Cobalt	Copper	Iron	Lead	Lithium	Manganese	Nickel	Zinc
Vallecito Creek	08/13/96 1130	0 <11.0	<0.7	<3.0	<2.3	<0.4	2.1	<9.1	<1.5	0.7	2.6	<0.5
Los Piños River	08/13/96 1520	0 <11.0	<0.7	<3.0	<2.3	<0.4	10.4	<9.1	<1.5	6.5	<2.5	<0.5
Well DH-MW-2	08/13/96 0930	0 <11.0	<0.7	<3.0	<2.3	<0.4	<2.1	<9.1	<1.5	0.2	<2.5	<0.5
North reservoir site at surface	08/15/96 1245	5 <11.0	<0.7	<3.0	<2.3	<0.4	13.5	<9.1	<1.5	3.0	<2.5	<0.5
Center reservoir site at surface	08/15/96 1045	5 <11.0	<0.7	<3.0	<2.3	<0.4	19.6	<9.1	<1.5	5.3	2.5	3.7
Center reservoir site at 22 ft	08/15/96 1115	5 <11.0	<0.7	<3.0	<2.3	<0.4	18.0	<9.1	<1.5	5.2	<2.5	<0.5
South reservoir site at surface	08/14/96 1115	5 22.3	<0.7	<2.0	9.0	6.0	11.7	<9.1	1.9	0.7	<2.0	9:0>
South reservoir site at 39 ft	08/14/96 1200	0 <11.0	<0.7	<3.0	<2.3	<0.4	2.7	<9.1	<1.5	6.4	<2.5	<0.5
South reservoir site at 55 ft	08/14/96 1245	5 <11.0	<0.7	<3.0	<2.3	<0.4	31.3	<9.1	<1.5	278.4	<2.5	8.0
Los Piños River downstream from dam	08/16/96 0915	5 <11.0	<0.7	<3.0	<2.3	<0.4	8.4	<9.1	1.8	23.8	<2.5	<0.5
Vallecito Creek	10/21/96 1200	0 <11.0	<0.7	<3.0	<2.3	<0.4	<2.1	<9.1	1.9	7.3	<2.5	<0.5
Los Piños River	10/22/96 0950	0 <11.0	<0.7	<3.0	<2.3	1.1	13.0	<9.1	<1.5	2.5	<2.5	<0.5
Well DH-MW-2	10/22/96 1250	0 <11.0	<0.7	<3.0	<2.3	<0.4	<2.1	<9.1	<1.5	<0.2	<2.5	<0.5
North reservoir site at surface	10/23/96 1225	5 <11.0	<0.7	<3.0	<2.3	<0.4	24.4	<9.1	<1.5	66.4	<2.5	<0.5
Center reservoir site at surface	10/23/96 1155	5 <11.0	<0.7	<3.0	5.2	<0.4	2.1	<9.1	<1.5	74.4	2.7	<0.5
South reservoir site at surface	10/23/96 1035	5 <11.0	<0.7	<3.0	<2.3	<0.4	17.0	<9.1	5.5	78.5	<2.5	<0.5
South reservoir site at 58 ft	10/23/96 1115	5 <11.0	<0.7	<3.0	<2.3	<0.4	70.8	<9.1	<1.5	100.5	<2.5	<0.5
Los Piños River downstream from dam	10/21/96 1530	0 <11.0	<0.7	<3.0	<2.3	<0.4	15.3	<9.1	2.1	62.7	<2.5	<0.5
Vallecito Creek	06/02/97 1030	0 15.3	<0.4	<2.0	1.0	1.7	16.6	<4.0	1.0	15.7	<2.0	9.0>
Los Piños River	06/02/97 1525	5 26.9	<0.4	<2.0	0.5	4.3	25.3	<4.0	8.0	4.0	<2.0	9.0>
Well DH-MW-2	06/05/97 1110	0 <27.0	<0.4	<2.0	<0.4	<1.0	<4.0	<4.0	<0.1	<0.3	<2.0	<0.6

Table 5. Trace-metal data for Vallecito Reservoir, Colorado, and its inflows and outflows—Continued

[Concentrations are in micrograms per liter; <, less than; ft, feet]

Site	Date	Time					Trace metals (micrograms per liter)	Trace metals rograms per lit	er)				
		l	Aluminum	Cadmium	Chromium	Cobalt	Copper	Iron	Lead	Lithium	Manganese	Nickel	Zinc
North reservoir site at surface	060/4/97 1000	0001	<27.0	<0.4	<2.0	9.0	2.8	10.6	<4.0	8.0	<0.3	<2.0	<0.6
North reservoir site at 45 ft	06/04/97 1005	1005	<27.0	<0.4	<2.0	9.0	3.1	29.0	<4.0	1.3	2.1	<2.0	9.0>
Center reservoir site at surface	06/03/97 1525	1525	27.0	<0.4	<2.0	0.4	4.2	7.0	<4.0	1.0	<0.3	<2.0	9.0>
Center reservoir site at 56 ft	06/03/97 1555	1555	<27.0	0.4	<2.0	9.0	1.6	23.1	<4.0	0.7	1.0	<2.0	9.0>
South reservoir site at surface	06/03/97 1100	1100	<27.0	<0.4	<2.0	0.4	4.4	8.9	<4.0	6.0	<0.3	<2.0	9.0>
South reservoir site at 25 ft	06/03/97 1230	1230	<27.0	<0.4	<2.0	0.4	4.2	7.1	<4.0	1.0	<0.3	<2.0	<0.6
South reservoir site at 90 ft	06/03/97 1330	1330	<27.0	<0.4	<2.0	9.0	2.6	15.0	<4.0	1.1	42.1	<2.0	<0.6
Los Piños River downstream from dam	06/04/97 1335	1335	<27.0	<0.4	<2.0	<0.4	4.1	14.6	<4.0	6.0	<0.3	<2.0	<0.6
Vallecito Creek	07/03/97 1110	1110	<27.0	4.0>	<2.0	1.2	2.9	<4.0	<4.0	1.6	13.7	2.3	9.0>
Los Piños River	06/30/97 1500	1500	<27.0	0.4	<2.0	0.7	1.3	23.4	<4.0	0.7	2.7	<2.0	9.0>
Well DH-MW-2	06/30/97 1120	1120	<27.0	<0.4	<2.0	<0.4	<1.0	<4.0	<4.0	<0.1	<0.3	<2.0	9.0>
North reservoir site at surface	07/01/97 1530	1530	<27.0	<0.4	<2.0	9.0	2.2	8.9	<4.0	6.0	1.4	<2.0	<0.6
North reservoir site at 45 ft	07/01/97 1545	1545	<27.0	<0.4	<2.0	6.0	1.4	91.3	<4.0	1.2	79.4	<2.0	9.0>
Center reservoir site at surface	07/01/97 1330	1330	9.99	<0.4	<2.0	0.4	5.5	8.2	<4.0	6.0	1.6	2.0	9:0>
Center reservoir site at 45 ft	07/01/97 1415	1415	<27.0	<0.4	<2.0	9.0	2.0	12.9	<4.0	8.0	2.4	<2.0	9:0>
South reservoir site at surface	07/01/97 1050	1050	<27.0	0.4	<2.0	9.0	2.1	8.7	<4.0	6.0	1.0	<2.0	9:0>
South reservoir site at 25 ft	07/01/97 1150	1150	38.8	<0.4	<2.0	<0.4	3.8	7.0	<4.0	6.0	0.7	<2.0	9.0>
South reservoir site at 90 ft	07/01/97 1215	1215	<27.0	<0.4	<2.0	0.7	1.6	18.0	<4.0	1.0	3.4	<2.0	9:0>
Los Piños River downstream from dam	07/02/97 0910	0160	30.1	<0.4	<2.0	0.4	4.5	10.8	<4.0	6.0	1.5	<2.0	<0.6

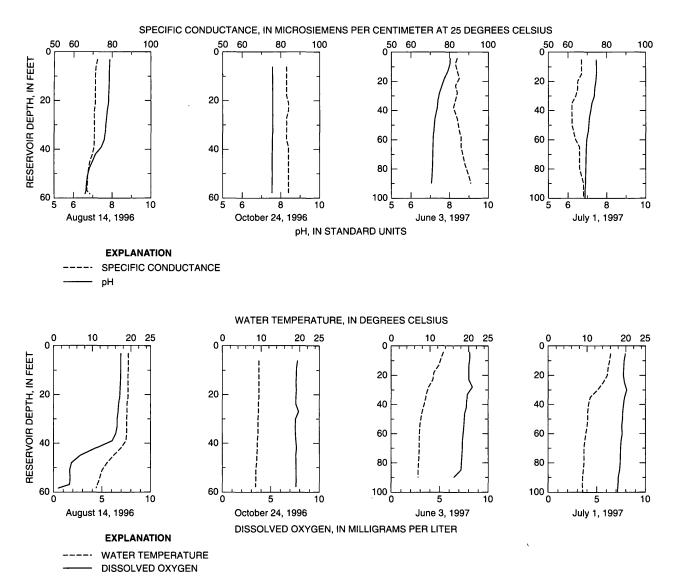


Figure 11. Depth profiles of specific conductance, pH, water temperature, and dissolved-oxygen concentration in the southern end of Vallecito Reservoir, Colorado, August 1996 through July 1997.

tion of carbon dioxide increases, pH decreases. Values of pH remained the same throughout the water column in October 1996 because water in the reservoir had turned over, and the water column had mixed uniformly.

Depth profiles indicate specific conductance, pH, water temperature, and dissolved oxygen at the sampling sites for Vallecito Reservoir also were uniformly distributed both seasonally and spatially (fig. 12). The plots of dissolved oxygen and water temperature show that stratification of the water column in the summer and turnover in the fall happened at the same time throughout the reservoir and that the values of these two constituents varied

slightly between sites. Values of pH between the sites remained constant throughout the study period but decreased with depth in August 1996 and June 1997. Values of pH at the center reservoir site did not decrease with depth in August. The Secchi-disk depth in August was 12 ft, and the bottom of the reservoir at the center reservoir site was 24 ft. Photosynthesis can occur down to light levels of about 1 percent surface light intensity. The depth of 1 percent light intensity can be estimated as twice the Secchi-disk depth (Cooke and Carlson, 1989). Thus, the reservoir was shallow enough at the center reservoir site to allow light penetration to the bottom. Specific-conductance

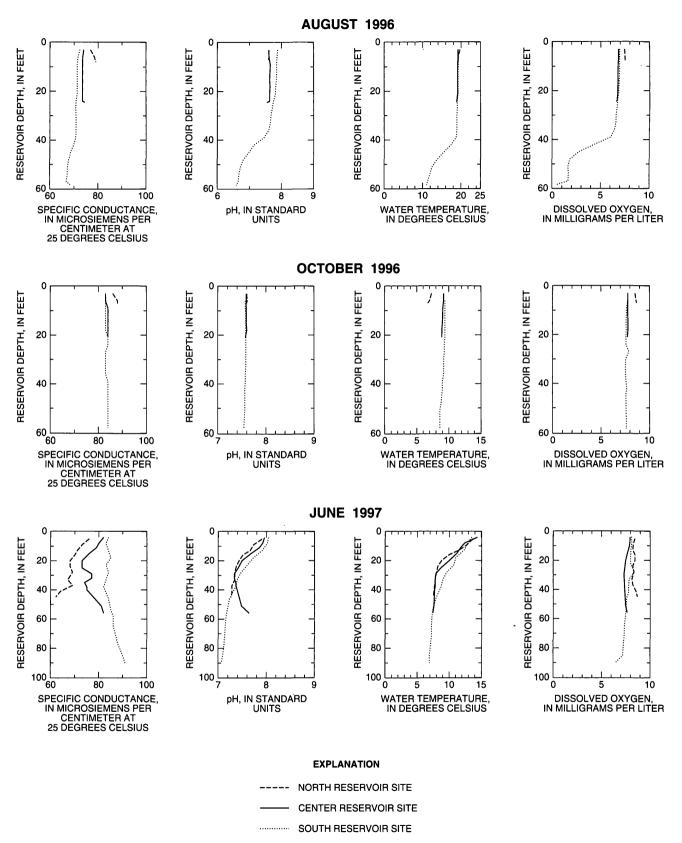


Figure 12. Depth profiles of specific conductance, pH, water temperature, and dissolved-oxygen concentration at the three sampling sites in Vallecito Reservoir, Colorado, August 1996 through June 1997.

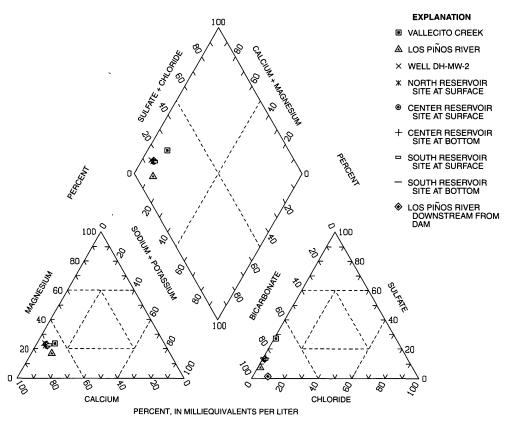


Figure 13. Inorganic-ion composition at all sampling sites in August 1996.

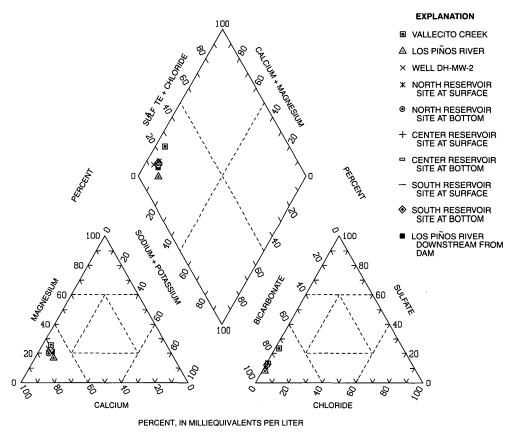


Figure 14. Inorganic-ion composition at all sampling sites in June 1997.

values were similar for each site, and each site had similar seasonal variability.

The major-ion and nutrient data indicate that inorganic-ion constituents were distributed uniformly throughout Vallecito Reservoir (tables 12 and 14 and figs. 13 and 14). The composition of the water for the reservoir on two sampling dates, one in August 1996, which represents a low-flow sampling, and the other in June 1997, which represents a high-flow sampling, is shown in figures 13 and 14. On both sampling dates, the inorganic-ion compositions of the samples plot in the same pattern.

SUMMARY

Water-quality samples were collected from Vallecito Reservoir, its two main inflows, its outlet, and a ground-water well at monthly intervals from July 1996 to July 1997. These samples were analyzed for dissolved organic carbon, ultraviolet absorbance at 254 nanometers, trihalomethane formation potential, dissolved organic carbon fractionation, specific conductance, pH, alkalinity, major inorganic ions and nutrients, and trace metals. The trophic state of the reservoir also was determined. This report presents the results of the sampling.

The chlorination of water withdrawn from Vallecito Reservoir or Los Piños River downstream from the dam forms trihalomethanes in excess of U.S. Environmental Protection Agency MCL's only during spring snowmelt. The seasonal variability of trihalomethane formation potential was related to the seasonal variability in the concentration and composition of dissolved organic carbon in the watershed, which in turn, probably was related to the seasonal variability in the flow path that ground water follows before discharging into surface-water bodies. The trihalomethanes form as a result of chlorine reacting with humic substances dissolved in water. During low flows, the concentration of humic substances, as well as dissolved organic carbon in general, that are dissolved in ground water probably is low because of microbial decomposition and sorption to clay particles. During high flows, the concentration probably increases because the dissolved organic carbon has a shorter residence time in the soil and is not subject to the same decompositional processes. Los Piños River had the higher dissolved organic carbon concentration all year than Vallecito Creek probably because of the

higher organic-matter content of the soils in its watershed and because of its wide, flat valley, which may increase the residence time of ground water in the soil organic layer compared to the residence time in the valley of Vallecito Creek. Thus, the concentration and composition of dissolved organic carbon in Vallecito Reservoir were most heavily affected by inflows from Los Piños River, primarily during spring snowmelt.

Vallecito Reservoir was classified as oligotrophic. The major reason for the reservoir being oligotrophic is the low nutrient concentration in its inflows. The turbidity present in the reservoir probably results more from sediment brought in by surface runoff and wave erosion of the shoreline than from algal growth. Dissolved-oxygen concentrations approached zero in the hypolimnion on August 14, 1996. This depletion of oxygen probably resulted from the decomposition of large amounts of particulate organic matter brought into the reservoir during peak snowmelt that settled to the bottom of the reservoir by late summer and from the decomposition of organic matter deposited in the bottom sediments in previous years. This oxygen depletion caused increased levels of iron and manganese at the bottom of the reservoir. but surface levels of these trace metals remained low.

Water in the Vallecito Reservoir watershed is dominated by calcium and bicarbonate ions. The abundance of these two dissolved species and the presence of limestone in the bedrock and surficial deposits in the watershed indicate that limestone weathering is the major source of dissolved inorganic ions. The composition of water in Vallecito Reservoir and downstream in Los Piños River results from a mixing of water from Vallecito Creek, Los Piños River, and possibly ground water.

REFERENCES CITED

Aiken, G.R., McKnight, D.M., Thorn, K.A., and Thurman, E.M., 1992, Isolation of hydrophilic organic acids from water using nonionic macroporous resins: Organic Geochemistry, v. 18, no. 4, p. 567–573.

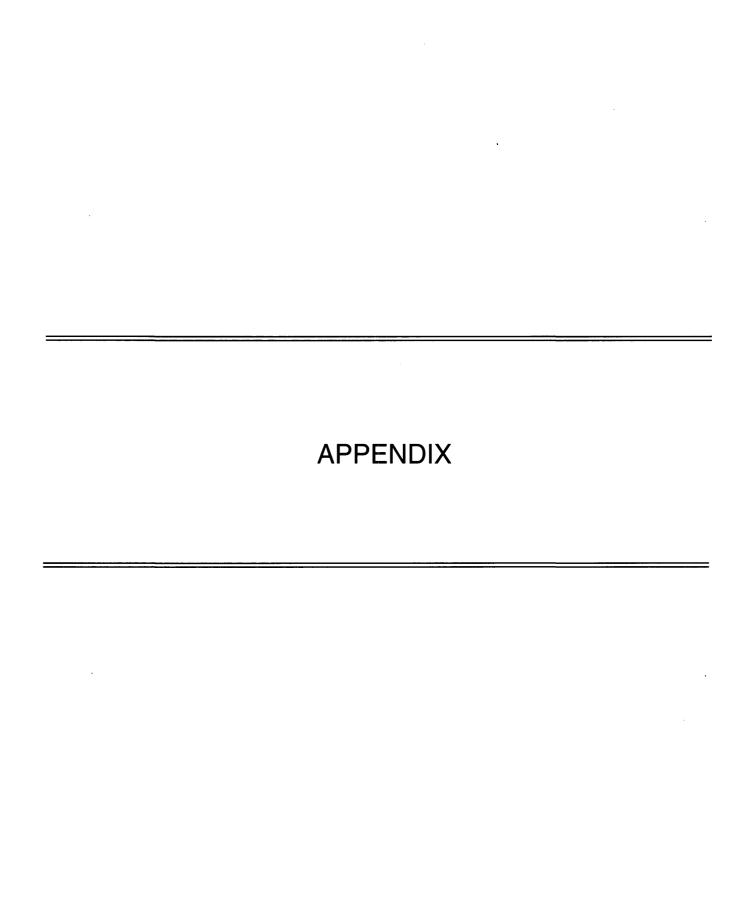
Aiken, G.R., and Cotsaris, E., 1995, Soil and hydrology—Their effect on NOM: Journal of the American Water Works Association, January 1995, p. 36–45.

Boyer, E.W., Hornberger, G., Bencala, K.E., and McKnight, D.M, 1996, Overview of a simple model describing variation of dissolved organic carbon in an upland catchment: Ecological Modelling, v. 86, p. 183–188.

- Briel, L.I., 1993, Documentation of a multiple-technique computer program for plotting major-ion composition of natural waters: U.S. Geological Survey Open-File Report 93–74, 88 p.
- Bureau of Reclamation, 1995, Vallecito Lake area waterquality study, Pine River Project, Vallecito Reservoir, technical assistance to State of Colorado: Durango, Colo., 15 p.
- Carlson, R.E., 1977, A trophic state index for lakes: Limnology and Oceanography, v. 22, no. 2, p. 361–369.
- Cooke, G.D., and Carlson, R.E., 1989, Reservoir management for water quality and THM precursor control:

 American Water Works Association Research Foundation and the American Water Works Association,
 387 p.
- EDAW, Inc., 1996, Vallecito Reservoir resource management plan: variously paged. [Prepared for the Bureau of Reclamation]
- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
- Fujii, Roger, Ranalli, A.J., Aiken, G.R., and Bergamaschi, B.A., 1998, Dissolved organic carbon concentrations and compositions, and trihalomethane formation potentials in waters from agricultural peat soils, Sacramento-San Joaquin Delta, California—Implications for drinking-water quality: U.S. Geological Survey Water-Resources Investigations Report 98–4147, 75 p.
- Hydrolab Corporation, 1993, Technical manual: Austin, Tex., 130 p.

- Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surfacewater samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94–539, 57 p.
- Pannell, J.P., 1988, Soil survey of La Plata County area, Colorado: U.S. Department of Agriculture Soil Conservation Service (now known as Natural Resources Conservation Service), 238 p.
- Rantz, S.E., and others, 1982, Measurement and computation of streamflow—v. 1, Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 284 p.
- Reckhow, D.A., Singer, P.C., and Malcolm, R.L., 1990, Chlorination of humic materials—Byproduct formation and chemical interpretations: Environmental Science and Technology, v. 24, no. 11, p. 1655–1664.
- Rook, J.R., 1977, Chlorination reactions of fulvic acids in natural waters: Environmental Science and Technology, v. 11, no. 5, p. 478–482.
- Snoeyink, V.L., and Jenkins, D., 1980, Water chemistry: New York, Wiley, 463 p.
- Thurman, E.M., 1985, Organic geochemistry of natural waters: Boston, Martinus Nijhoff/Dr W. Junk Publishers, 497 p.
- Tweto, Ogden, 1979, Geologic map of Colorado: U.S. Geological Survey Map, 2 sheets, scale 1:500,000.
- U.S. Environmental Protection Agency, 1994, Information collection rule: Federal Register, v. 59, no. 28, February 10, 1994, p. 6332–6444.
- Wetzel, R.G., 1983, Limnology (2d ed.): San Francisco, Saunders College Publishing, 767 p.
- Wilde, F.D., and Radtke, D.F., 1997, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, variously paged.



•		

Table 6. Discharge, dissolved organic carbon concentration, and ultraviolet absorbance data for Vallecito Creek and Los Piños River, Colorado

[DOC, dissolved organic carbon; --, no data]

Date	Time	Discharge (cubic feet per second)	DOC (milligrams per liter)	Ultraviolet absorbance
		Val	llecito Creek	
07/17/96	0945	72.1	0.8	0.017
08/13/96	1130	32	1.2	0.021
09/25/96	1424	80	1.0	0.014
10/21/96	1200	49.2	0.8	0.015
11/21/96	1245	68.3	1.4	0.042
12/12/96	1310	43	0.9	0.019
02/13/97	1525	23	0.9	0.019
03/28/97	1230	110	1.7	0.062
05/06/97	0930	362	2.9	0.095
06/02/97	1030	1,101	2.3	0.076
06/05/97	1300		1.8	0.060
07/03/97	1110	314	0.6	0.017
		Los	s Piños River	
07/17/96	1820	69.8	1.5	0.036
08/13/96	1520	31.2	1.7	0.023
09/25/96	1710	85.2	1.4	0.032
10/22/96	0950	48.8	1.2	0.026
11/21/96	1345	80.5	2.5	0.041
12/12/96	1135		1.1	0.027
02/13/97	1030		1.1	0.024
03/28/97	0955	152	1.8	0.074
05/07/97		508	3.6	0.119
06/02/97	1525	1,570	3.6	0.120
06/05/97	1335		3.0	0.116
06/30/97	1500	531	1.9	0.064

Table 7. Water-level, dissolved organic carbon concentration, and ultraviolet absorbance data for well DH-MW-2 near Vallecito Reservoir, Colorado

[DOC, dissolved organic carbon; --, no data]

Date	Time	Water level (feet below land surface)	DOC (milligrams per liter)	Ultraviolet absorbance
07/17/96	1030	18.9	1.1	0.010
08/13/96	0930	18.5	0.7	0.007
09/25/96		18.8	1.0	0.008
10/22/96	1250	18.9	1.4	0.004
11/20/96	1600	19	1.4	0.005
12/12/96	1505	21.5	1.3	0.005
02/14/97	1020	21.3	1.3	0.006
05/06/97	1605	20.8	0.9	0.004
06/05/97	1110	3.5	0.7	0.010
06/30/97	1120	0	0.6	0.002

Table 8. Dissolved organic carbon concentration and ultraviolet absorbance data for Vallecito Reservoir, Colorado [DOC, dissolved organic carbon; --, no data; ft, feet]

Site	Date	Time	DOC (milligrams per liter)	Ultraviolet absorbance
North reservoir site at surface	07/17/96		2.1	0.043
Center reservoir site at surface	07/17/96		2.2	0.041
South reservoir site at surface	07/17/96		2.3	0.038
South reservoir site at 35 ft	07/17/96		1.7	0.038
South reservoir site at 65 ft	07/17/96		1.6	0.045
South reservoir site at surface	08/13/96		1.8	0.033
South reservoir site at 55 ft	08/13/96		2.0	0.038
North reservoir site at surface	09/25/96	1040	1.5	0.026
Center reservoir site at surface	09/25/96	1015	1.6	0.028
Center reservoir site at 20 ft	09/25/96	1020	1.5	0.029
South reservoir site at surface	09/25/96	0942	1.8	0.027
South reservoir site at 45 ft	09/25/96	0950	1.5	0.028
South reservoir site at surface	10/24/96	0949	1.7	0.033
South reservoir site at 48 ft	10/24/96	1024	1.6	0.030
North reservoir site at surface	11/21/96	1013	1.2	0.026
Center reservoir site at surface	11/21/96	0951	1.3	0.029
South reservoir site at surface	11/21/96	0914	1.4	0.030
South reservoir site at 56 ft	11/21/96	0927	1.2	0.028
North reservoir site at surface	12/12/96	1345	1.5	0.027
South reservoir site at surface	12/12/96	0855	1.7	0.042
South reservoir site at surface	02/12/97	1530	1.5	0.026
South reservoir site at surface	03/28/97	1420	1.0	0.022
North reservoir site at surface	05/06/97	1215	1.8	0.045
Center reservoir site at surface	05/06/97	1150	2.0	0.044
South reservoir site at surface	05/06/97	1115	2.2	0.045
North reservoir site at surface	06/04/97	1000	2.6	0.075
Center reservoir site at surface	06/03/97	1525	3.4	0.074
Center reservoir site at 56 ft	06/03/97	1555	2.9	0.089
South reservoir site at surface	06/03/97	1100	2.9	0.076
South reservoir site at 25 ft	06/03/97	1230	2.3	0.078
South reservoir site at 90 ft	06/03/97	1330	2.4	0.068
South reservoir site at surface	06/05/97		2.6	0.077
South reservoir site at 90 ft	06/05/97		2.2	0.064
North reservoir site at surface	07/01/97	1505	2.2	0.064
North reservoir site at 48 ft	07/01/97		2.3	0.071
Center reservoir site at surface	07/01/97	1313	2.4	0.064
Center reservoir site at 50 ft	07/01/97		2.4	0.076
South reservoir site at surface	07/01/97	1004	2.2	0.066
South reservoir site at 20 ft	07/01/97		2.2	0.068
South reservoir site at 100 ft	07/01/97	1029	2.5	0.080

Table 9. Dissolved organic carbon concentration and ultraviolet absorbance data for Los Piños River, Colorado, downstream from the Vallecito Reservoir dam

[DOC, dissolved organic carbon]

400	i i	DOC	Ultraviolet
Date	<u> </u>	(milligrams per liter)	absorbance
07/17/96	1135	1.8	0.040
12/12/96	0942	1.6	0.028
02/13/97	1630	1.1	0.025
03/28/97	1435	6.0	0.023
05/06/97	1540	1.7	0.036
06/04/97	1335	2.6	0.077
07/02/97	0160	2.4	0.074

Table 10. Discharge and major-ion data for Vallecito Creek and Los Piños River, Colorado

[ft³/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; µeq/L, microequivalents per liter]

Percent charge balance		3.4	2.2	1.9	2.5		1.3	3.3	4.7	4.4
Sum F anions L		290	578	443	331		362	744	447	426
Sum		632	604	460	348		986	794	491	465
Nitrate (μeq/L)		5.5	8.9	9.1	6.2		<1.6	<1.6	2.5	<1.6
Chloride (μeq/L)		5.5	9.4	8.4	2.5		11.7	12.8	4.6	4.5
Sulfate (μeq/L)		158	166	109	114		84.6	74.6	43.6	38.4
Potas- sium (μeq/L)		12.8	10.2	7.7	7.7		28.1	28.1	15.3	15.3
Sodium (µeq/L)		52.2	43.5	17.4	17.4		87	82.7	39.2	43.5
Magne- sium (μeq/L)	Creek	148	156	115	7.86	s River	173	140	82.3	82.3
Calcium (μeq/L)	Vallecito Creek	419	394	319	225	Los Piños River	669	544	354	324
Alka- linity (μeq/L)		421	395	316	208		865	657	397	383
Labora- tory pH (units)		7.90	7.74	7.62	7.47		8.06	7.95	7.69	7.62
Field pH (units)		7.33	7.22	7.46	6.73		7.76	7.22	7.35	7.24
Labora- tory specific conduc- tance (μS/cm)		67.2	64.4	50.5	38.6		102	77.5	50.6	47.5
Field specific conduc- tance (µS/cm)		65	63	45	42		8.98	75	43	51
Discharge (ft³/s)		32	49.2	1,101	314		31.2	48.8	1,570	531
Time		1130	1200	1030	1110		1520	060	1525	1500
Date		08/13/96 1130	10/21/96	06/02/97	07/03/97		08/13/96 1520	10/22/96 0950	06/02/97 1525	06/30/97 1500

👺 Table 11. Water-level and major-ion data for well DH-MW-2 near Vallecito Reservoir, Colorado

Percent charge oalance	23.5	11.2	1:1	2.7
Sum	2,796	3,351	4,026	3,853
Sum	4,511	4,196	4,116	4,069
Nitrate (μeq/L)	21.2	17.4	8.7	9.6
Chloride (μeq/L)	292	20.4	18.2	20
Sulfate (μeq/L)	336	373	442	398
Potas- sium (μeq/L)	48.6	43.5	48.6	48.6
Sodium (µeq/L)	252	226	165	170
Magne- sium (μeq/L)	1,036	362	938	921
Calcium (µeq/L)	3,174	2,964	2,964	2,929
Alkalinity (μeq/L)	2,393	2,940	3,557	3,426
Labora- tory pH (units)		;	;	;
Field pH (units)	6.74	7.21	7.30	7.06
Labora- tory specific conduc- tance (µS/cm)	370	398	1	;
Field specific conduc- tance tance (μS/cm)	430	367	378	379
Water level (feet below land surface)	18.5	18.9	3.5	0
Time I	0630	1250	11110	1120
Date	08/13/96 0930	10/22/96 1250	06/05/97	06/30/97

Date	08/13/96	10/22/96	06/05/97	06/30/97	Fable 12. ft³/s, cubic f	Site	North reservoir site at surface	Center reservoir site at surface	Center reservoir site at 22 ft	South reservoir site at surface	South reservoir site at 39 ft	South reservoir site at 55 ft	North reservoir site at surface	Center reservoir site at surface	South reservoir site at surface	
Time	0630	1250	1110	1120	Major-ic		voir	rvoir ırface	rvoir 2 ft	voir ırface	voir) ft	voir 5 ft	voir ırface	rvoir ırface	voir ırface	
Water level (feet below land surface)	18.5	18.9	3.5	0	Table 12. Major-ion data for Vallecito Reservoir, Colorado [ft ³ /s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 of	Date	08/12/96	08/15/96 1045	08/15/96	08/14/96	08/14/96 1200	08/14/96	10/23/96	10/23/96	10/23/96 1035	
		.,	. ,	. •	Valleci ı, microsi	Time	1245	1045	1115	1115	1200	1245	1225	1155	1035	
Field Specific Sconduc- Cottance tance (µS/cm) (µ	430	367	378	379	to Rese	Field specific conduc- tance (µS/cm)	75.9	74.2	73.5	74.1	70.7	67.2	87.0	83.0	83.0	
Labora- tory specific conduc- tance (µS/cm)	370	398	1	:	ervoir, Co	Labora- tory c specific c- conduc- tance (u.S/cm)	83.4	82.1	81.3	77.5	78.3	75.0	89.5	87.9	85.3	
Field pH (units)	6.74	7.21	7.30	7.06	olorado er at 25 de	a- fic Field ic pH ic- (units) e	7.88	7.61	7.63	7.90	7.45	6.67	7.60	7.59	7.56	
Labora- tory pH (units)	1	;	;	:	grees Celk	Labora- tory pH s) (units)	3 7.74	7.9	7.7	7.82	7.94	7.31	7.85	8.00	7.89	
Alkalinity (μeq/L)	2,393	2,940	3,557	3,426	ius; µeq/L,	ra- Alka- / linity s) (µeq/L)	t 658	643	638	617	t 611	582	717	902 (702	
O -	3,174	2,964	2,964	2,929	microequi	Calcium V (µeq/L)	534	514	549	484	529	494	539	664	609	
	1,036	362	938	921	/alents per	Magne- sium -) (μeq/L)	156	156	164	156	148	148	156	197	173	
Sodium (µeq/L)	252	226	165	170) degrees Celsius; μeq/L, microequivalents per liter; ft, feet]	e- Sodium	52.2	47.9	47.9	43.5	6.09	47.9	9.99	74.0	52.2	
Potas- sium (μeq/L)	48.6	43.5	48.6	48.6	=	Potas- sium (μeq/L)	7.7	12.8	17.9	15.3	17.9	15.3	17.9	20.5	23.0	
Sulfate (μeq/L)	336	373	442	398		Sulfate (µeq/L)	103	104	102	103	9.66	97.2	123	116	118	
Chloride (μeq/L)	26.2	20.4	18.2	20		Chloride (μeq/L)	7.2	7.1	15.4	9.7	8.0	2 7.9	8.6	9.5	10.5	
Nitrate (μeq/L)	21.2	17.4	8.7	9.6		e Nitrate (μeq/L)	<1.6	<1.6	<1.6	<1.6	<1.6	5.5	<1.6	<1.6	<1.6	
Sum cations	4,511	4,196	4,116	4,069		Sum	750	731	611	669	756	705	770	926	857	
Sum anions	2,796	3,351	4,026	3,853		Sum	292	753	755	728	718	692	849	831	831	
Percent charge balance	23.5	11.2	1.1	2.7		Percent charge balance	-1.2	-1.5	1.5	-2.0	2.5	0.0	4.9	6.9	1.5	

[ft³/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; µeq/L, microequivalents per liter; ft, feet] Table 12. Major-ion data for Vallecito Reservoir, Colorado—Continued

				l ahora.													
Site	Date	Time	Field specific conduc- tance (μS/cm)	tory specific conduc- tance tance	Field pH (units)	Labora- tory pH (units)	Alka- linity (μeq/L)	Calcium (μeq/L)	Magne- sium (μeq/L)	Sodium (µeq/L)	Potas- sium (μeq/L)	Sulfate (μeq/L)	Chloride (μeq/L)	Nitrate (μeq/L)	Sum	Sum anions	Percent charge balance
North reservoir	06/04/97 1000	1000	76.0	80.3	7.96	7.96	635	524	156	39.2	15.3	105	7.0	1.0	735	747	-0.8
site at surface	9	1	;	i	!	1	1	!	;		•	;	1		,		(
North reservoir site at 45 ft	06/04/97 1005	1005	62.0	71.1	7.27	7.78	556	479	132	34.8	15.3	83.9	5.8	3.4	661	650	6:0
Center reservoir site at Surface	06/03/97 1525	1525	82.0	81.8	7.99	7.86	648	544	164	43.5	15.3	101	7.5	0.7	191	758	9.0
Center reservoir site at 56 ft	06/03/97 1555	1555	82.0	73.9	7.64	7.85	280	494	140	43.5	15.3	87.4	8.9	3.2	693	212	1.1
South reservoir site at surface	06/03/97 1100	1100	84.0	81.5	8.07	7.73	641	554	164	43.5	15.3	101	8.3	0.7	777	751	1.7
South reservoir site at 25 ft	06/03/97 1230	1230	83	82.0	7.60	7.81	652	554	156	43.5	15.3	101	7.2	1.2	692	761	0.5
South reservoir site at 90 ft	06/03/97 1330	1330	91	87.9	7.06	7.81	691	579	173	39.2	15.3	111	8.4	4.3	908	815	9.0-
North reservoir site at surface	07/01/97 1530	1530	99	67.0	7.52	7.70	515	439	140	34.8	12.8	84.4	5.0	0.4	979	909	1.8
North reservoir site at 45 ft	07/01/97 1545	1545	61	61.4	7.18	7.6	461	404	123	39.2	15.3	74.4	5.0	3.0	582	543	3.5
Center reservoir site at surface	07/01/97 1330	1330	99	9:99	7.54	7.74	513	469	148	39.2	15.3	79.7	5.0	0.4	672	298	5.8
Center reservoir site at 45 ft	07/01/97 1415	1415	09	9:59	7.15	7.45	498	434	132	39.2	12.8	75.2	5.7	3.4	618	582	3.0
South reservoir site at surface	07/01/97 1050	1050	<i>L</i> 9	6.99	7.43	7.84	517	444	140	34.8	15.3	83.7	5.7	0.5	634	209	2.2
South reservoir site at 25 ft	07/01/97	1150	65	65.2	7.38	7.65	507	429	140	34.8	12.8	75.6	5.4	6:0	617	589	2.3
South reservoir site at 90 ft	07/01/97 1215	1215	89	68.5	6.9	7.69	531	459	140	39.2	15.3	75.1	5.9	3.6	653	616	3.0

Table 13. Major-ion data for Los Piños River, Colorado, downstream from Vallecito Reservoir dam

[ft³/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; µeq/L, microequivalents per liter]

Date	Time	Field specific conduc- tance (µS/cm)	Field Labora- specific tory Field conduc- conduc- tance tance (µS/cm) (µS/cm)	Field pH (units)	Labora- tory pH (units)	Alka- linity (μeq/L)	Calcium (μeq/L)	Magne- sium (μeq/L)	Sodium (μeq/L)	Potas- sium (µeq/L)	Sulfate (μeq/L)	Chloride (μeq/L)	Nitrate (μeq/L)	Sum cations	Sum anions	Percent charge balance
08/16/96	0915	73.8	83.4	7.16	7.74	615	539	156	47.9	17.9	101	8	<1.6	761	724	2.5
10/21/96	1530		87.4	7.61	7.94	702	614	173	9.69	15.3	119	10	<1.6	871	831	2.4
06/04/97	1335		78.0 83.7	7.36	7.97	859	544	156	43.5	15.3	86	8.2	3.3	759	89/	9.0-
07/02/97	0160	65.0 64.1	64.1	7.10	7.72	492	449	132	39.2	12.8	72	5	2.8	633	572	5.0

Table 14. Nutrient data for all selected sites at Vallecito Reservoir, Colorado, and its inflows and outflow

[mg/L, milligrams per liter; ft, feet]

Site	Date	Time	Ammonia (mg/L as N)	Nitrite (mg/L as N)	Ammonia plus organic, dissolved (mg/L as N)	Ammonia plus organic, total (mg/L as N)	Nitrite plus nitrate (mg/L as N)	Phosphorus, total (mg/L as P)	Phosphorus, dissolved (mg/L)	Ortho- phosphorus (mg/L as P)
Vallecito Creek	08/13/96	1130	<0.002	< 0.001	<0.2	<0.2	0.078	<0.001	0.003	<0.001
Los Piños River	08/13/96	1520	<0.002	<0.001	<0.2	<0.2	0.018	0.008	0.005	<0.001
Well DH-MW-2	08/13/96	0660	<0.002	<0.001	<0.2	<0.2	0.300	0.003	0.004	<0.001
North reservoir site at surface	08/12/96	1245	<0.002	<0.001	<0.2	<0.2	0.007	0.008	0.003	<0.001
Center reservoir site at surface 08/15/96	08/12/96	1045	<0.002	<0.001	<0.2	<0.2	<0.005	0.009	0.004	<0.001
Center reservoir site at 22 ft	08/12/96	1115	<0.002	<0.001	<0.2	<0.2	9000	0.010	0.005	<0.001
South reservoir site at surface	08/14/96	1115	<0.002	<0.001	<0.2	<0.2	900.0	0.007	0.002	<0.001
South reservoir site at 39 ft	08/14/96	1200	<0.002	<0.001	<0.2	<0.2	0.009	0.008	0.004	<0.001
South reservoir site at 55 ft	08/14/96	1245	<0.002	<0.001	<0.2	<0.2	0.074	0.019	0.009	<0.001
Los Piños River downstream from dam	08/16/96	0915	<0.002	<0.001	<0.2	<0.2	0.007	0.007	0.005	<0.001
Vallecito Creek	10/21/96	1200	<0.002	<0.001	<0.2	<0.2	0.071	<0.001	0.002	<0.001
Los Piños River	10/22/96	060	<0.002	<0.001	<0.2	<0.2	<0.005	0.004	0.023	<0.001
Well DH-MW-2	10/22/96	1250	0.002	<0.001	<0.2	<0.2	0.220	0.002	0.002	<0.001
North reservoir site at surface 10/23/96	10/23/96	1225	0.01	0.001	<0.2	<0.2	<0.005	0.005	0.001	<0.001
Center reservoir site at surface 10/23/96	10/23/96	1155	0.009	<0.001	<0.2	<0.2	<0.005	0.003	0.002	<0.001

Table 14. Nutrient data for all selected sites at Vallecito Reservoir, Colorado, and its inflows and outflow

[mg/L, milligrams per liter; ft, feet]

Site	Date	Time	Ammonia (mg/L as N)	Nitrite (mg/L as N)	Ammonia plus organic, dissolved (mg/L as N)	Ammonia plus organic, total (mg/L as N)	Nitrite plus nitrate (mg/L as N)	Phosphorus, total (mg/L as P)	Phosphorus, dissolved (mg/L)	Ortho- phosphorus (mg/L as P)
South reservoir site at surface	10/23/96	1035	0.014	<0.001	<0.2	<0.2	<0.005	0.005	0.002	<0.001
South reservoir site at 58 ft	10/23/96	1115	0.016	<0.001	<0.2	0.2	<0.005	0.027	0.004	<0.001
Los Piños River downstream from dam	10/21/96	1530	0.010	<0.001	<0.2	<0.2	<0.005	0.005	0.004	<0.001
Vallecito Creek	06/02/97	1030	0.099	0.009	<0.2	<0.2	0.142	0.011	0.003	<0.001
Los Piños River	06/02/97	1525	<0.002	0.002	<0.2	<0.2	0.035	0.051	0.004	0.004
Well DH-MW-2	06/05/97	1110	0.003	0.001	<0.2	<0.2	0.132	0.002	0.002	0.002
North reservoir site at surface	06/04/97	1000	<0.002	0.002	<0.2	<0.2	0.017	0.005	0.001	0.001
North reservoir site at 45 ft	06/04/97	1005	<0.002	0.002	<0.2	<0.2	0.044	0.008	0.003	<0.001
Center reservoir site at surface	06/03/97	1525	<0.002	0.002	<0.2	<0.2	0.012	0.008	0.002	<0.001
Center reservoir site at 56 ft	06/03/97	1555	<0.002	0.001	<0.2	<0.2	0.045	0.012	0.002	0.001
South reservoir site at surface	06/03/97	1100	<0.002	0.001	<0.2	<0.2	0.063	900'0	0.001	0.004
South reservoir site at 25 ft	06/03/97	1230	0.026	0.002	<0.2	<0.2	0.030	0.009	0.002	<0.001
South reservoir site at 90 ft	06/03/97	1330	0.011	0.001	<0.2	<0.2	0.059	0.080	0.003	0.002
Los Piños River below dam	06/04/97	1335	0.002	0.002	<0.2	<0.2	0.053	0.004	0.001	<0.001
Vallecito Creek	07/03/97	1110	<0.002	0.001	<0.2	<0.2	0.081	0.002	<0.001	0.002
Los Piños River	06/30/97	1500	<0.002	0.001	<0.2	<0.2	0.009	0.010	0.004	0.004
Well DH-MW-2	26/30/90	1120	<0.002	0.001	<0.2	<0.2	0.136	0.003	0.002	0.003
North reservoir site at surface	07/01/97	1530	<0.002	0.001	<0.2	<0.2	0.007	0.005	0.002	0.001
North reservoir site at 45 ft	07/01/97	1545	0.023	0.002	0.2	2.4	0.037	0.797	0.003	0.002
Center reservoir site at surface	07/01/97	1330	<0.002	0.001	<0.2	<0.2	0.007	0.005	0.002	0.002
Center reservoir site at 45 ft	07/01/97	1415	0.010	0.002	<0.2	<0.2	0.041	800.0	0.002	0.002
South reservoir site at surface	07/01/97	1050	<0.002	0.001	<0.2	<0.2	0.007	0.005	0.002	0.001
South reservoir site at 25 ft	07/01/97	1150	<0.002	0.001	0.2	<0.2	0.010	0.005	0.003	0.001
South reservoir site at 90 ft	07/01/97	1215	0.010	0.001	<0.2	0.2	0.045	0.012	0.001	0.001
Los Piños River downstream from dam	07/02/97	0160	0.008	0.001	0.2	<0.2	0.037	0.005	0.002	0.002