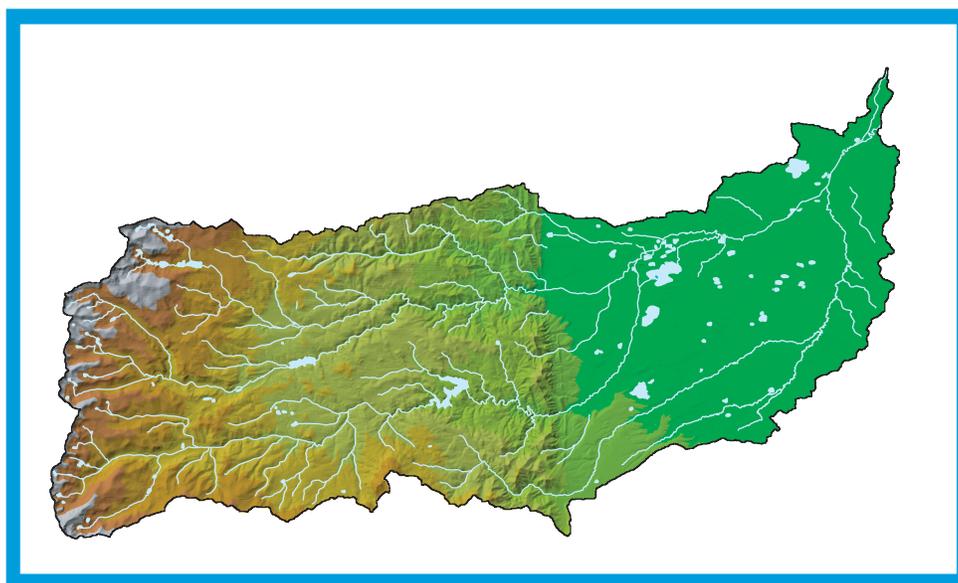
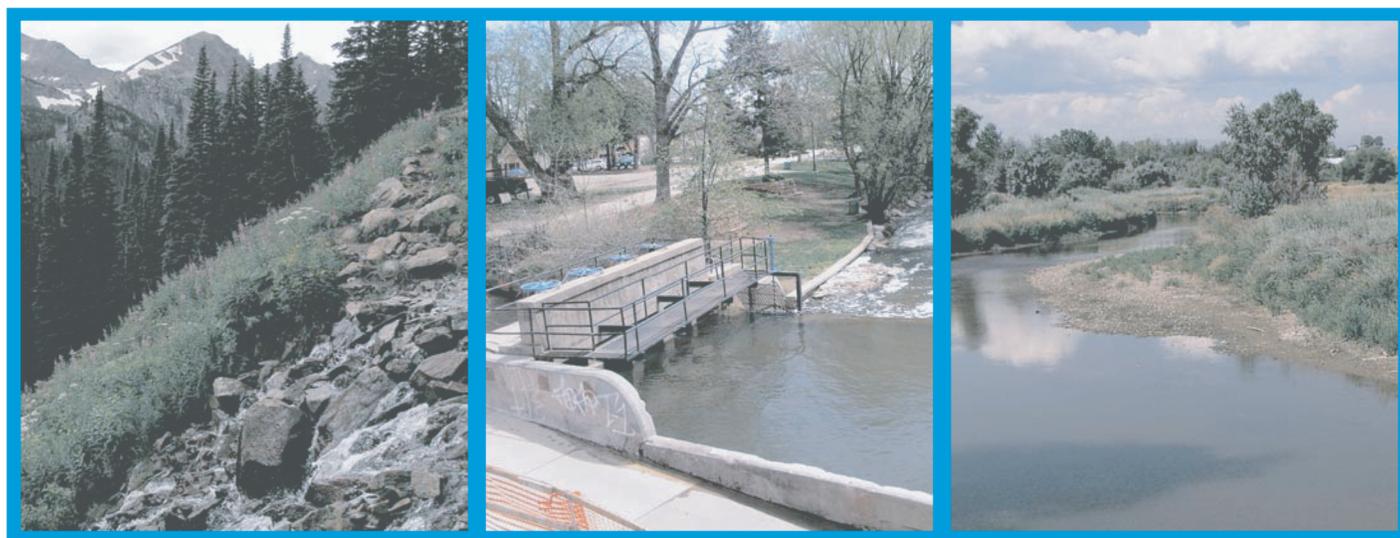


Comprehensive Water Quality of the Boulder Creek Watershed, Colorado, During High-Flow and Low-Flow Conditions, 2000

Water-Resources Investigations Report 03-4045



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Sheila F. Murphy, Philip L. Verplanck, and Larry B. Barber, editors

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FOREWORD

A watershed is a feature of a natural landscape within which we can study the movement of water through the environment. The watershed delimits the river basin. In nature, if it were not for loss of water through evaporation to the atmosphere, transpiration by plants, or seepage into ground water, all water that falls within a watershed would flow downhill to accumulate in streams and eventually flow into a single stream or river. The volume of water moving through the single channel, the discharge, is one of easier watershed characteristics to measure. If we also measure the concentrations of dissolved and solid constituents in the water, we can calculate the mass flux (or load) of these constituents. For more than a century researchers have been measuring discharge and analyzing constituents to assess phenomena that may be influencing the water composition upstream. Today, we also do this to estimate rates of erosion, examine the introduction of contaminants, and judge the health of a river.

In the last three decades, a revolution has taken place in the study of river-borne material. With the rapid growth of computer-controlled instrumentation and sophisticated new technologies for detecting chemicals, elements, and isotopes, we can now measure a great variety of chemical constituents at very low levels, such as parts per billion (micrograms per liter) or even parts per trillion (nanograms per liter). We can now measure not only traditional water quality variables such as nutrients and trace metals, but also many of the pharmaceuticals and chemicals that we consume and excrete, the pesticides that we use, and compounds we use for cleaning our households.

This revolution in chemical analysis has been accompanied by a quieter revolution in water sampling and processing. The containers in which we collect water, filter out particles, and store the samples must all be clean. In the

last few decades researchers have learned advanced techniques of cleaning and careful sample collection and processing. Many of the approaches and ideas were introduced, in the 1970's, from the world of oceanography, where the research focused on estimating the input of materials to the ocean by rivers.

The U.S. Geological Survey (USGS) Water Resources Discipline has been at the forefront in developing both the more sophisticated analytical techniques and the clean-sampling methodologies. Research and development centers in two programs: the National Research Program and the National Water Quality Laboratory. Many of the researchers collaborate with university scientists, other public agencies, and international groups in these efforts.

The Boulder Creek Watershed in Colorado was chosen for one such collaborative effort by the USGS and the City of Boulder, with additional funding from the U.S. Environmental Protection Agency. This study was initiated through discussions at the Boulder Creek Watershed Forum, a monthly gathering of watershed residents, USGS scientists (located in Boulder and Lakewood, Colorado), city of Boulder personnel, and University of Colorado researchers. A need for a comprehensive water-quality investigation of Boulder Creek was identified. The study was then facilitated by the Boulder Area Sustainability Information Network (BASIN), a local collaboration that provides public access to environmental information in Boulder (www.basin.org). Scientists working for the National Science Foundation Long-Term Ecological Research Site in Green Lakes Valley and on Niwot Ridge contributed additional data for the headwaters of Boulder Creek.

Boulder Creek has features that make it ideal for assessing our ability to study natural and human-contributed constituents in water. The headwaters of the Creek include a protected

watershed from which all but a few researchers are excluded. The Creek then flows through a progressively more urbanized region and finally a dominantly agricultural landscape until it discharges into Saint Vrain Creek.

Boulder Creek has another feature that is typical of many western rivers but quite unlike many rivers in the eastern United States that have been the focus of contaminant studies. In Boulder Creek, some of the water is transferred through pipes and tunnels from other watersheds, some on the other side of the Continental Divide. Moreover, in the dry climate of the Colorado Front Range, much of the water in Boulder Creek is diverted for municipal and agricultural uses. Little of the agricultural water returns to the Creek, while much of the municipal water returns after having been processed through the toilets, showers, sinks, washing machines, and small industries of the city of Boulder. The discharge of Boulder Creek after all the diversions is a fraction of its former volume. During dry parts of the year, most of the water in lower Boulder Creek has passed through a wastewater treatment plant. Groundwater inflows and storm water runoff from agricultural lands contribute more chemicals.

Such is the theme for water as it crosses the vast Mississippi River system, which Boulder Creek is a part of – intensive use with repeated passage through water-treatment facilities and growing agricultural contributions. Chemicals that are introduced into the municipal stream and which survive wastewater treatment and subsequent river transport will be part of the drinking water for those who live downstream. Little is known about what many of these chemicals do to humans or wildlife in small concentrations. Studies such as this one help us better understand which chemicals enter and persist in streams. This information is crucial to guiding future research on health and ecological effects of man-made chemicals. Effective management and protection of our nation's rivers depends on accurate data. This study is an example of USGS efforts to improve knowledge of our nation's natural resources to guide the stewardship of those resources.

Robert M. Hirsch
Associate Director for Water
U.S. Geological Survey

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CONVERSION FACTORS, DATUM, ABBREVIATIONS, AND DEFINITIONS

Multiply	By	To obtain
<i>Length</i>		
centimeter (cm)	0.3937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6215	mile (ft)
<i>Area</i>		
square meter (m ²)	10.76	square feet (ft ²)
square meter (m ²)	2.471	acre
square kilometer (km ²)	0.3861	square mile (mi ²)
<i>Volume</i>		
liter (L)	0.2642	gallon (gal)
cubic meter (m ³)	1.308	cubic yard (yd ³)
cubic meter (m ³)	0.000811	acre-feet
<i>Mass</i>		
gram (g)	0.03527	ounce avoirdupois (oz)
kilogram (kg)	2.205	pounds (lb)
<i>Discharge</i>		
meter per second (m/s)	3.281	foot per second (ft/s)
cubic meter per second (m ³ /s)	35.31	cubic feet per second (ft ³ /s)
cubic meter per second (m ³ /s)	22.82	million gallons per day (mgd)

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32$$

DATUM

Vertical datum: Vertical coordinate information is referenced to the North American Vertical Datum of 1929 (NAVD 29).

Horizontal datum: Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

ADDITIONAL ABBREVIATIONS AND ACRONYMS

Å	angstrom
a.i.	active ingredient
amu	atomic mass units
ANC	acid neutralizing capacity
APHA	American Public Health Association
BASIN	Boulder Area Sustainability Information Network
CDPHE	Colorado Department of Public Health and Environment
CLLE	continuous liquid-liquid extraction
cols/100 mL	colonies per 100 milliliters
DBP	disinfection byproducts
DEM	Digital Elevation Model
DO	dissolved oxygen
DOC	dissolved organic carbon

DON	dissolved organic nitrogen
E	estimated
GC/MS	gas chromatograph with mass spectrophotometer
GFF	glass fiber filter
GIS	Geographic Information Systems
HPLC	high-performance liquid chromatography
IC	ion chromatography
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectroscopy
INSTAAR	Institute of Arctic and Alpine Research
kg ha ⁻¹ yr ⁻¹	kilogram per hectare per year
kPa	kilopascals
kV	kilovolt
LRL	laboratory-reporting level
ln(<i>a/tanβ</i>)	topographic index
MCL	maximum contaminant level
m/km	meter per kilometer
MDL	method detection limit
μg/L	micrograms per liter
μm	micrometer
μS/cm	microSiemens per centimeter
mA	milliamp
mg/L	milligrams per liter
mL	milliliter
mm	millimeter
nm	nanometer
NAPAP	National Acid Precipitation Assessment Program
NAWQA	National Water-Quality Assessment
ng/L	nanogram per liter
NIST	National Institute of Standards and Technology
NLCD	National Land Cover Dataset
NOM	natural organic matter
NTU	nephelometric turbidity units
NWQL	National Water Quality Laboratory
PRISM	Parameter-elevation Regressions Independent Slopes Model
QA	quality assurance
QA/QC	quality assurance/quality control
REE	rare earth elements
SA	specific UV absorbance
SC	specific conductance
SPE	solid-phase extraction
SRWS	standard reference water samples
STATSGO	States Geographic Soil Database
TOC	total organic carbon
TOX	total organic halogens
TDS	total dissolved solids

TSS	total suspended solids
THM	trihalomethane
USDA	U.S. Department of Agriculture
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
v/v	volume per volume
WWTP	Wastewater Treatment Plant
XRD	X-ray diffraction

DEFINITIONS

Water Year in U.S. Geological Survey reports is the 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months.

Executive Summary

The Boulder Creek Watershed, Colorado, is 1160 square kilometers in area and ranges in elevation from 1480 to 4120 meters above sea level. Streamflow originates primarily as snowmelt near the Continental Divide, and thus discharge varies seasonally and annually (Chapter 1). Most of the water in Boulder Creek is diverted for domestic, agricultural, and industrial use. Some diverted water is returned to the creek as wastewater effluent and by ditch returns, and additional water enters as groundwater and by transbasin diversions. These diversions and returns lead to complex temporal and spatial variations in discharge. The variations in discharge, along with natural factors such as geology and climate, and anthropogenic factors such as wastewater treatment, agriculture, mining, and urbanization, can affect water chemistry. As with many watersheds in the American West, dependable water quality and sufficient water supply are issues facing local water managers and users.

Detailed water-quality and sediment sampling allows the identification of sources and sinks of chemical constituents and an understanding of the processes at work in a river system. This study, the most comprehensive water-quality analysis performed for Boulder Creek to date, was a cooperative effort of the U.S. Geological Survey (USGS) and the city of Boulder. Geographic information systems and modeling programs were used to delineate watershed boundaries, land cover, and geology (Chapter 2). During high-flow (June 2000) and low-flow (October 2000) conditions, researchers evaluated 226 water-quality variables, including basic water-quality indicators (Chapter 3), major ions and trace elements (Chapter 4), wastewater-derived organic compounds (Chapter 5), and pesticides (Chapter 6). Discharge (Chapter 1) and bed-sediment particle size and mineralogy (Chapter 7) were also evaluated. This cooperative study was facilitated by the Boulder Area

Sustainability Information Network (BASIN), which provides public access to environmental information about the Boulder Creek Watershed on a website, www.basin.org. In addition to the USGS and city of Boulder data, researchers at the Institute of Arctic and Alpine Research at the University of Colorado provided water chemistry data for the headwaters of North Boulder Creek, upstream of the reach of the USGS/city of Boulder sampling sites (Chapter 8).

Snowmelt produces high flows in Boulder Creek in late spring to early summer (Chapter 1). Because precipitation falling in the headwaters is very dilute (specific conductance about 5 microsiemens per centimeter), most chemical constituents are present in lower concentrations during high flows (Chapters 3, 4, 5, 6, and 8). However, concentrations of some constituents, such as total suspended solids (Chapter 3) and organic carbon (Chapter 5), increase during the spring snowmelt flush.

The upper basin, which consists of alpine, subalpine, montane, and foothills regions west of the mouth of Boulder Canyon, is underlain by Precambrian igneous and metamorphic rocks (Chapter 1). Major dissolved inorganic constituents in headwater sites were found to be enriched by factors of 10 to 20 relative to precipitation; this is consistent with minor weathering of the local crystalline bedrock (Chapter 4). Some anthropogenic input is observed in the headwaters; precipitation introduces nitrogen derived from fossil fuel combustion and agricultural activities (Chapter 8).

The lower basin, which consists of the plains region east of the mouth of Boulder Canyon, is underlain by Mesozoic sedimentary rock and Quaternary alluvium, and has substantially more anthropogenic sources. Concentrations of most dissolved inorganic constituents increased in the lower basin. Differentiation between natural and anthropogenic sources of some dissolved constituents is difficult because both sources contribute to the water composition in this region. The increase of most major constituents

List of chemical and physical variables analyzed in this study

Field parameters and basic water quality variables	Major elements and anions	Trace elements	Wastewater-derived organic compounds
temperature- water	aluminum	antimony	ethylenediaminetetraacetic acid
temperature- air	calcium	arsenic	nitrilotriacetic acid
pH	iron (total)	barium	4-nonylphenolmonoethoxycarboxylate
specific conductance	iron (II)	beryllium	4-nonylphenoldiethoxycarboxylate
dissolved oxygen	magnesium	bismuth	4-nonylphenoltriethoxycarboxylate
alkalinity	manganese	boron	4-nonylphenoltetraethoxycarboxylate
hardness	potassium	cadmium	bisphenol A
turbidity	silica	cerium	4- <i>tert</i> -butylphenol
fecal coliform	sodium	cesium	2[3]- <i>tert</i> -butyl-4-methoxyphenol
total dissolved solids		chromium	2,6-di- <i>tert</i> -butyl-1,4-benzoquinone
total suspended solids	sulfate	cobalt	2,6-di- <i>tert</i> -butyl-4-methylphenol
nitrogen- nitrate	chloride	copper	2,6-di- <i>tert</i> -butylphenol
nitrogen- nitrite	bromide	dysprosium	1,2-dichlorobenzene
nitrogen- ammonia	fluoride	erbium	1,3-dichlorobenzene
nitrogen- organic		europium	1,4-dichlorobenzene
orthophosphate		gadolinium	4-ethylphenol
phosphorus- total		holmium	4-methylphenol
carbon- organic		lanthanum	4-nonylphenol
ultraviolet light absorption		lead	4-nonylphenolmonoethoxylate
		lithium	4-nonylphenoldiethoxylate
		lutetium	4-nonylphenoltriethoxylate
		mercury	4-nonylphenoltetraethoxylate
		molybdenum	4- <i>normal</i> -octylphenol
		neodymium	4- <i>tert</i> -octylphenol
		nickel	4- <i>tert</i> -octylphenolmonoethoxylate
		praseodymium	4- <i>tert</i> -octylphenoldiethoxylate
		rhenium	4- <i>tert</i> -octylphenoltriethoxylate
		rubidium	4- <i>tert</i> -octylphenoltetraethoxylate
		samarium	4- <i>tert</i> -octylphenolpentaethoxylate
		selenium	4- <i>tert</i> -pentylphenol
		strontium	4-propylphenol
		tellurium	triclosan
		terbium	<i>cis</i> -androsterone
		thallium	cholesterol
		thorium	coprostanol
		thulium	equilenin
		uranium	equilin
		vanadium	17- α -estradiol
		ytterbium	17- β -estradiol
		yttrium	estriol
		zirconium	estrone
		zinc	17- α -ethynylestradiol
			mestranol
			19-norethisterone
			progesterone
			testosterone

Pharmaceutical compounds	Pesticides	Pesticides (continued)
acetaminophen	acetochlor	methiocarb
albuterol	acifluoren	methomyl
caffeine	alachlor	metolachlor
cimetidine	aldicarb	metribuzin
codeine	aldicarb sulfone	molinate
cotinine	aldicarb sulfoxide	napropamide
dehydronifedipine	atrazine	neburon
digoxigenin	azinphos-methyl	norflurazon
digoxin	benfluralin	oryzalin
diltiazem	bentazon	oxamyl
1,7-dimethylxanthine	bromacil	p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE)
diphenhydramine	bromoxynil	parathion
enalaprilat	butylate	methyl parathion
fluoxetine	carbaryl	pebulate
gemfibrozil	carbofuran	pendimethalin
ibuprofen	chloramben, methyl ester	cis-permethrin
metformin	chlorothalonil	phorate
paroxetine metabolite	chlorpyrifos	picloram
ranitidine	clopyralid	prometon
sulfamethoxazole	cyanazine	propachlor
trimethoprim	dacthal (DCPA)	propanil
warfarin	dacthal monoacid	propargite
	desethylatrazine	propham
	diazinon	propoxur
	dicamba	propyzamide
	dichlobenil	simazine
	dichloroprop	tebuthiuron
	dieldrin	terbacil
	dinoseb	terbufos
	disulfoton	thiobencarb
	diuron	tri-allate
	s-ethyl dipropylthiocarbamate (EPTC)	triclopyr
	ethalfluralin	trifluralin
	ethoprophos	2,4-dichlorophenoxyacetic acid (2,4-D)
	fenuron	4-(2,4-dichlorophenoxy)butyric acid (2,4-DB)
	fluometuron	2,4,5-trichlorophenoxyacetic acid (2,4,5-T)
	fonofos	2-(2,4,5-trichlorophenoxy) propionic acid (2,4,5-TP)
	glyphosate	2,6-diethylaniline
	alpha-hexachlorocyclohexane (alpha-HCH)	2-methyl-4-chlorophenoxyacetic acid (MCPA)
	gamma-hexachlorocyclohexane (lindane)	4-(2-methyl-4-chlorophenoxy) butyric acid (MCPB)
	linuron	3-hydroxycarbofuran
	malathion	4,6-dinitro-2-methylphenol

(bicarbonate, calcium, chloride, magnesium, sodium, and sulfate) is consistent with weathering of the underlying sedimentary bedrock (Chapter 4). It is likely that anthropogenic loading of constituents in this reach occurs during storm events. Fecal coliform concentrations were variable and in some cases exceeded state standards, primarily during low-flow conditions (Chapter 3).

Effluent from Boulder's 75th Street Wastewater Treatment Plant (WWTP) has a substantial impact on the water chemistry of lower Boulder Creek. The WWTP increases the concentrations of nutrients such as nitrogen and phosphorus (Chapter 3), major ions and trace metals (Chapter 4), and organic carbon (Chapter 5) in Boulder Creek. The effluent contained a spike in gadolinium, a rare earth element that is ingested for magnetic resonance imaging as a contrasting agent and then excreted to the urban wastewater system. The effluent also contained trace organic compounds such as surfactants, pharmaceuticals, hormones (Chapter 5), and pesticides (Chapter 6), which also were detected at downstream Boulder Creek sites. Water chemistry of Boulder Creek downstream of the WWTP is largely controlled by the degree of dilution of the wastewater effluent, which varies depending on the baseflow of Boulder Creek, the volume of wastewater effluent, and depletion by agricultural diversions. Coal Creek, a tributary of Boulder Creek, contains wastewater effluent from four additional WWTPs, and increases the load of many constituents in Boulder Creek. In addition to the impact from wastewater effluent, lower Boulder

Creek is affected by agricultural land use. Eleven of 84 analyzed pesticides were detected in Boulder Creek or its inflows, primarily in the eastern section of the watershed (Chapter 6).

This collaborative study provides an in-depth evaluation of the hydrology, water chemistry, and sediment mineralogy of North Boulder Creek, Middle Boulder Creek, Boulder Creek, and major inflows. The detailed sampling and analysis in this report provide a baseline for future reference, as well as information on the effect of land use and geology on water chemistry.

Acknowledgements

Administrative, field and laboratory assistance was provided by F. Bebler, R. Dingeman, S. Duren, S. Gillespie, V. Jones, K. Keilbach, C. Rudkin, B. Segal, and E. Solek (city of Boulder); R.C. Antweiler, J.W. Ball, J.L. Flynn, P.A. LaTour, P.H. Leinweber, D.M. Mixon, J.A. Moody, D.K. Nordstrom, T.I. Plowman, R.F. Stallard, and H.E. Taylor (USGS); G. Andrews and C. Youngberg (city of Longmont); M. McCaffrey and J. Waterman (BASIN); E. Gardner, K.A. Grasmic, and M. Miller (University of Colorado); and L.T. Rozaklis of Hydrosphere Resource Consultants. Partial funding was provided by the city of Boulder and by a grant to BASIN from the U.S. Environmental Protection Agency's Environmental Monitoring, Public Access, and Community Tracking (EMPACT) program.

Chapter 1 - Environmental Setting and Hydrology of the Boulder Creek Watershed, Colorado

By Sheila F. Murphy, Larry B. Barber, Philip L. Verplanck, and David A. Kinner

Abstract

The Boulder Creek Watershed, Colorado, is 1160 square kilometers in area and ranges in elevation from 1480 to 4120 meters above sea level. The watershed consists of two regions that differ substantially in geology, climate, and land use. The upper basin consists primarily of Precambrian metamorphic and granitic bedrock with alpine, subalpine, montane, and foothills climatic/ecological zones. It is sparsely populated, and forest is the dominant land cover. The lower basin consists primarily of Paleozoic and Mesozoic sedimentary rocks with a plains climatic/ecological zone. The majority of the population in the watershed lives in the lower basin, where dominant land covers are grassland, agricultural land, and urbanized land.

Streamflow in the Boulder Creek Watershed originates primarily as snowmelt at and near the Continental Divide, and thus discharge shows great seasonal and annual variation. Most of the water in Boulder Creek is diverted for domestic, agricultural, and industrial use. Some diverted water is returned as wastewater effluent and groundwater contributions to baseflow. Non-native water is brought into the watershed by transbasin diversions. These diversions and returns lead to complex temporal and spatial variations in discharge.

The differing geology, climate, land use, and water use produce variations in water quality within the watershed. Boulder Creek can be further divided into five reaches based on hydrology and water quality: headwater, mountain, urban, wastewater-dominated, and wastewater/agricultural/aggregate-mining dominated reaches.

The issues affecting the Boulder Creek Watershed are typical for many river systems in the American West. Accordingly, the Boulder Creek Watershed offers an excellent opportunity to evaluate the potential effects of natural and anthropogenic processes on a small river system. Boulder Creek and its tributaries were sampled during high-flow and low-flow conditions in the year 2000. The study was a cooperative effort of the U.S. Geological Survey, the city of Boulder, and the University of Colorado, and included measurements of discharge, basic water quality variables, major ions, trace metals, wastewater-derived organic compounds, and pesticides. In addition, geographic information systems were used to delineate geology, land use, and watershed boundaries. This chapter briefly describes the physiography, climate, geology, vegetation, land use, and hydrology of the Boulder Creek Watershed and the natural and anthropogenic factors that can potentially affect water quantity and quality.

INTRODUCTION

Conditions such as climate and geology affect the natural water chemistry of a stream, while anthropogenic factors such as land and water use also can have considerable influence on water quality. In order to effectively evaluate water quality of a stream, the environmental setting and hydrology of its basin must be well characterized.

Purpose and Scope

This chapter briefly describes the physiography, climate, geology, vegetation, land

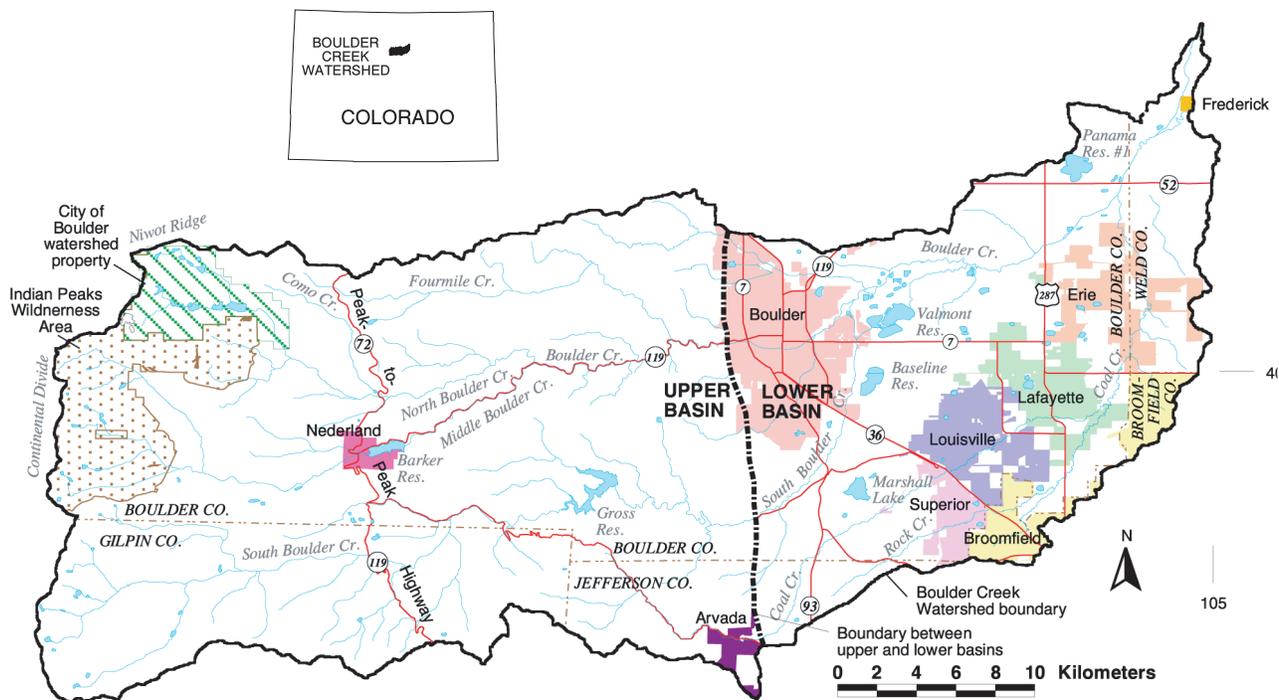


Figure 1.1. Map of the Boulder Creek Watershed showing location of study area, political boundaries, and major transportation routes. (County boundaries from National Weather Service, 2002; municipal boundaries from Colorado Department of Local Affairs, 2002; roads from Colorado Department of Transportation, 2002; surface waters from U.S. Geological Survey, 2002a; Indian Peaks Wilderness boundary from U.S. Department of Agriculture Forest Service, 2002; City of Boulder watershed property boundary courtesy City of Boulder)

use, and hydrology of the Boulder Creek Watershed and the potential solute sources that can affect water chemistry. A flow balance of the Middle Boulder Creek/Boulder Creek profile during high-flow and low-flow conditions is calculated. This chapter also provides background information about the U.S. Geological Survey/City of Boulder cooperative study.

The study was designed to capture a detailed profile of water quality during high-flow and low-flow conditions of Boulder Creek. Sampling occurred over three days in June 2000, which represented high-flow conditions, and over three days in October 2000, which represented low-flow conditions. The discharge of Boulder Creek downstream of the confluence of North Boulder Creek and Middle Boulder Creek reached its maximum value for the year 2000 two days before sampling began in June. While discharge in Boulder Creek dropped slightly after the October sampling, later sampling was not feasible

due to short periods of daylight and limited accessibility to some sample sites.

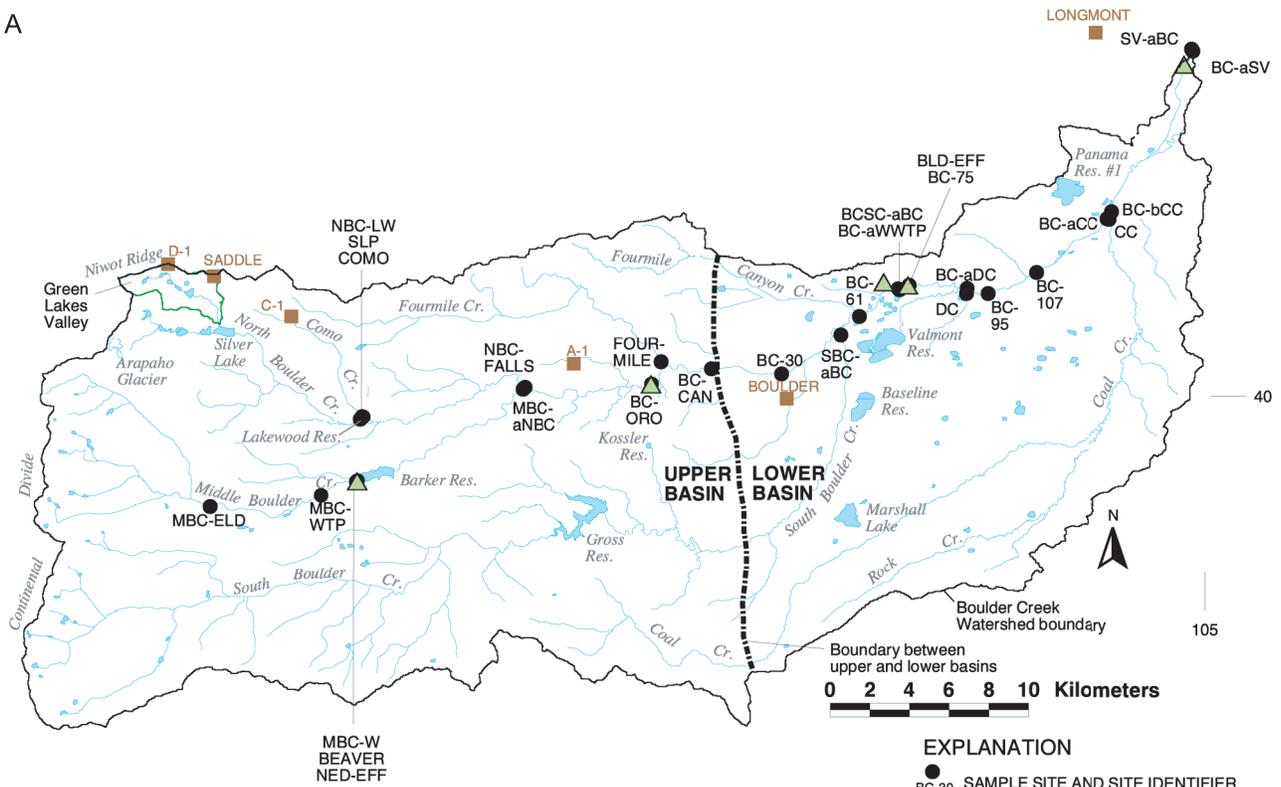
Water-quality samples were collected from 29 sites along a 70-km reach, including 16 sites on the mainstem of Middle Boulder Creek/Boulder Creek, seven tributaries, wastewater effluent from the town of Nederland and the city of Boulder, the Silver Lake Pipeline, the Boulder Creek Supply Canal, and Saint Vrain Creek upstream of the confluence of Boulder Creek (figs. 1.1 and 1.2, table 1.1). A complete list of water quality variables evaluated is provided in the executive summary of this report.

SITE DESCRIPTION

Physiography

The Boulder Creek Watershed is approximately 1160 km² (447 mi²) in area and is located in the Front Range of the Colorado Rocky

A



B

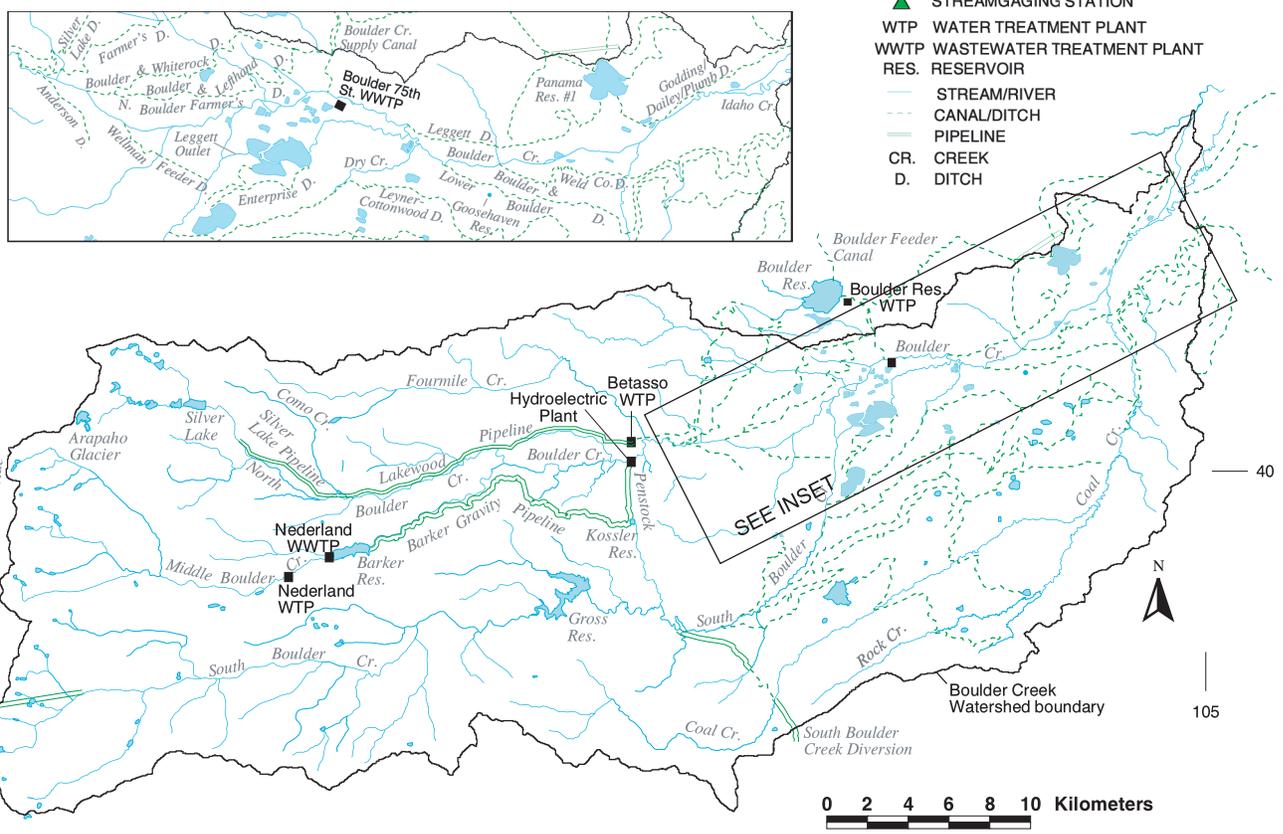


Figure 1.2. Maps of the Boulder Creek Watershed showing (A) sample sites and (B) major diversions. (Descriptions of sample sites provided in table 1.1; surface water data from U.S. Geological Survey, 2002a)

Table 1.1. Descriptions of sampling sites

[Distance, distance upstream from Saint Vrain Creek confluence; M., Middle; WTP, Water Treatment Plant; N., North; St., Street; WWTP, Wastewater Treatment Plant; S., South]

Site	Site description	Distance (meters)	Elevation (meters)	Latitude	Longitude
Middle Boulder Creek/Boulder Creek					
MBC-ELD	M. Boulder Creek upstream of town of Eldora	69590	2722	39.949722	-105.590833
MBC-WTP	M. Boulder Creek at Nederland WTP intake	62970	2560	39.955278	-105.525000
MBC-W	M. Boulder Creek at weir upstream of Barker Reservoir	60920	2496	39.961389	-105.504444
MBC-aNBC	M. Boulder Creek upstream of N. Boulder Creek	49440	2121	40.003889	-105.406389
BC-ORO	Boulder Creek at Orodell gaging station	41520	1775	40.006389	-105.330000
BC-CAN	Boulder Creek at Eben G. Fine Park (Boulder Canyon mouth)	36710	1646	40.013333	-105.294722
BC-30	Boulder Creek downstream of 30th St. bridge	32990	1603	40.011111	-105.252778
BC-61	Boulder Creek upstream of 61st St. bridge	27320	1567	40.037222	-105.206944
BC-aWWTP	Boulder Creek upstream of the Boulder 75th St. WWTP	24440	1562	40.050000	-105.183889
BC-75	Boulder Creek under 75 th St. bridge	23850	1556	40.051667	-105.177778
BC-aDC	Boulder Creek upstream of Dry Creek	20180	1542	40.050278	-105.143333
BC-95	Boulder Creek downstream of 95th St. bridge	18790	1539	40.047778	-105.130833
BC-107	Boulder Creek upstream of 107th St. (Highway 287) bridge	16320	1530	40.058889	-105.101944
BC-aCC	Boulder Creek upstream of Coal Creek	10970	1513	40.081944	-105.059722
BC-bCC	Boulder Creek downstream of Coal Creek	10540	1512	40.085000	-105.057222
BC-aSV	Boulder Creek upstream of Saint Vrain Creek	110	1478	40.158056	-105.009444
Inflows/other flows					
COMO	Como Creek upstream of N. Boulder Creek	59340	2495	39.990833	-105.501111
NBC-LW	N. Boulder Creek upstream of Lakewood Reservoir	59370	2502	39.989722	-105.502500
SLP	Silver Lake Pipeline	59340	2495	39.991111	-105.500833
BEAVER	N. Beaver Creek upstream of M. Boulder Creek	60910	2495	39.961667	-105.504167
NED-EFF	Nederland WWTP effluent	60880	2497	39.961944	-105.503889
NBC-FALLS	N. Boulder Creek upstream of M. Boulder Creek	49420	2103	40.004722	-105.405556
FOURMILE	Fourmile Creek upstream of Boulder Creek	40120	1753	40.016389	-105.324444
SBC-aBC	S. Boulder Creek upstream of Boulder Creek	29070	1573	40.028889	-105.217778
BCSC-aBC	Boulder Creek Supply Canal upstream of Boulder Creek	24680	1567	40.500000	-105.190000
BLD-EFF	Boulder 75th St. WWTP effluent	24380	1559	40.049722	-105.183333
DC	Dry Creek upstream of Boulder Creek	20040	1542	40.047778	-105.143611
CC	Coal Creek upstream of Boulder Creek	10970	1512	40.081667	-105.058889
SV-aBC	Saint Vrain Creek upstream of Boulder Creek	90	1478	40.158889	-105.010000

Mountains, east of the Continental Divide (fig. 1.1). The watershed is located within two physiographic provinces (Worcester, 1960): the upper basin, defined on the west by the Continental Divide, is part of the Southern Rocky Mountain Province and is characterized by steeply sloping valleys; the lower basin, defined on the west by the foothills of the Rocky Mountains, is part of the Colorado Piedmont Section of the Great Plains Province, and slopes gently to the northeast.

Elevations in the watershed range from 4120 m at the Continental Divide to 1480 m at the

confluence of Boulder Creek and Saint Vrain Creek. The most upstream site sampled for this study was located on Middle Boulder Creek upstream of the town of Eldora, at an elevation of approximately 2720 m (table 1.1). The elevations of sampling sites drop steeply as Middle Boulder Creek flows downstream through the town of Nederland and Boulder Canyon (fig. 1.3). The slope is much less steep when Boulder Creek reaches the plains at the mouth of Boulder Canyon. The most downstream site in the study was located on Boulder Creek approximately 110 m upstream from the confluence with Saint Vrain

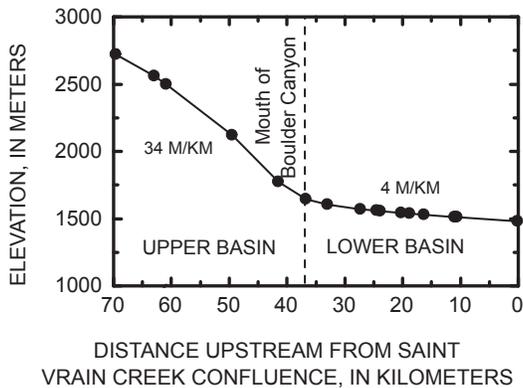


Figure 1.3. Graph showing elevation versus distance for Middle Boulder Creek/Boulder Creek sample sites.

Creek, at an elevation of 1478 m. Saint Vrain Creek discharges into the South Platte River a short distance downstream from the confluence.

Climate

The large variation in topography leads to different climatic zones in the watershed, including alpine, subalpine, montane, foothills, and plains (Rodeck, 1964; Weber, 1995). Temperatures vary widely across the climatic zones. In general, as elevation decreases, temperature increases, and the difference between daily minimum and maximum temperatures increases. In the year 2000, average daily minimum temperatures at three monitoring stations in the alpine (D-1 and Saddle) and subalpine (C-1) zones (fig. 1.2a) were -6°C , -5°C , and -3°C ; average daily maximum temperatures were 1°C , 3°C , and 10°C (fig. 1.4). A monitoring station in the foothills zone (A-1) recorded average daily minimum and maximum temperatures of 3°C and 16°C , while stations in the plains zone recorded average daily minimum and maximum temperatures of 3°C and 19°C (Boulder) and 0°C and 20°C (Longmont). The majority of precipitation in the watershed falls as snow in the upper basin (fig. 1.5).

Geology

The upper basin of the watershed is composed primarily of Precambrian siliceous metamorphic and granitic rocks (fig. 1.6a). These rocks consist of gneisses and schists (1800 million years old) that were intruded by the Boulder Creek Granodiorite (1700 million years old) and the Silver Plume Granite (1400 million years old). In addition, early- and middle-Tertiary (30 to 60 million years old) deposits of metallic ores associated with intrusive dikes and sills are found in the upper basin. Deposits of gold, silver, tungsten, copper, lead, zinc, tin, and uranium were mined in the upper watershed beginning in 1859 (Lovering and Goddard, 1950; Bilodeau and others, 1987).

The lower basin is underlain by Paleozoic and Mesozoic sedimentary rocks that are progressively younger as they trend eastward. Shale, sandstone, limestone, and conglomerate formations that were deposited between 75 and 300 million years ago (Fountain, Lyons, Lykins, Ralston Creek, Morrison, Dakota, Benton, Niobrara, and Pierre formations, in order of oldest to youngest and west to east) were steeply tilted during mountain-building events, forming the easterly-dipping hogbacks, ridges, and valleys found at the edge of the mountain front just west of the city of Boulder (fig. 1.6a). Most of the city of Boulder is underlain by the Pierre Shale. Sandstone, shale, and coal-bearing formations that were deposited between 65 and 75 million years ago (Fox Hills and Laramie formations) overlay the Pierre Shale and dominate the geology east of the city of Boulder. Quaternary alluvium covers most of the flood plain of Boulder Creek and its tributaries (Runnells, 1976; Bilodeau and others, 1987).

Vegetation and Land Use

The upper and lower basins of the Boulder Creek Watershed differ markedly in vegetation and land use. The upper basin, which includes the

TEMPERATURE, IN DEGREES CELSIUS

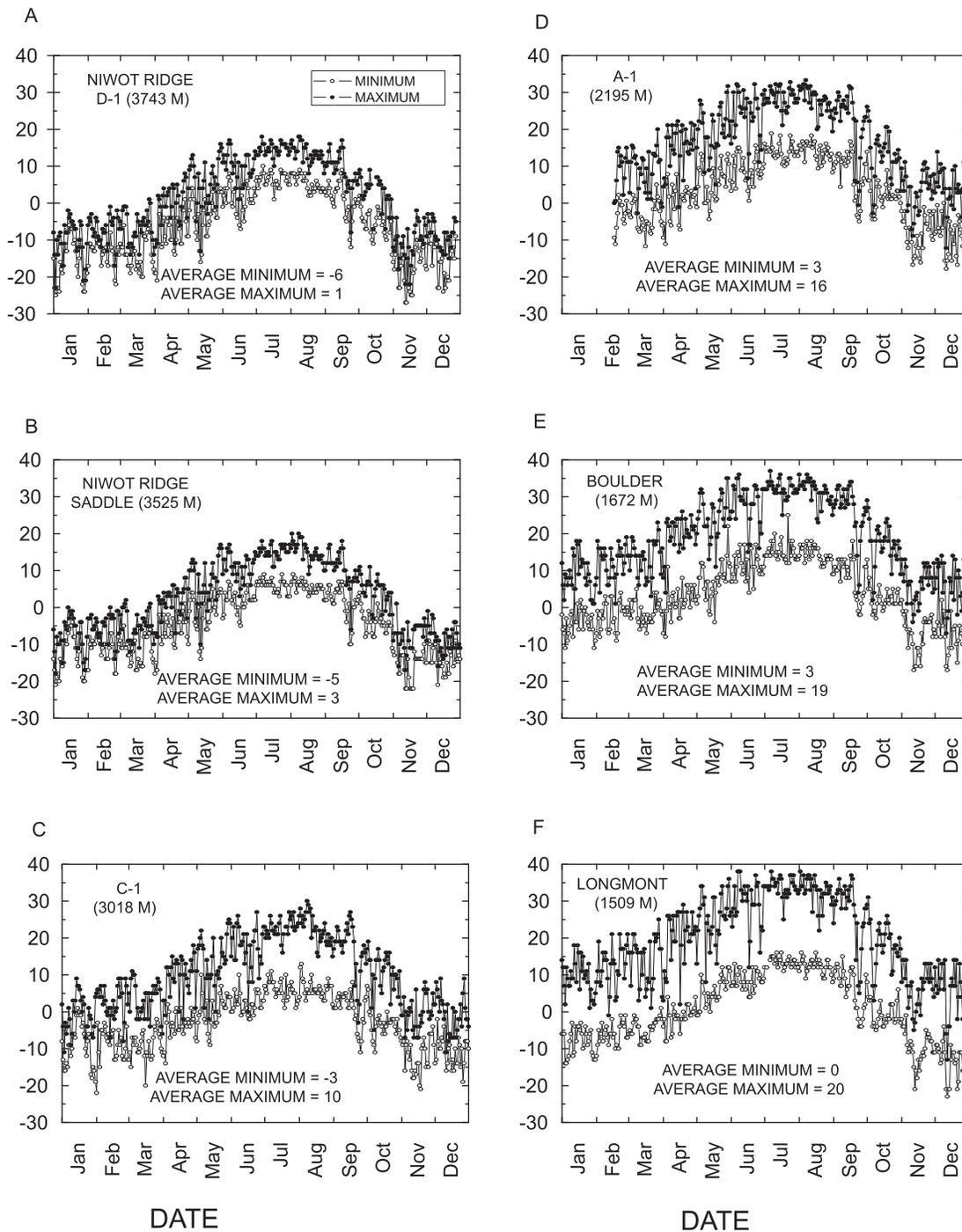


Figure 1.4. Graphs showing minimum and maximum daily air temperatures for sites in or near the Boulder Creek Watershed during 2000: (A) Niwot Ridge site D-1, (B) Niwot Ridge Saddle, (C) site C-1, (D) site A-1, (E) Boulder, (F) Longmont. (Site locations shown in fig. 1.2a. Data not available for site A-1 for January 1-February 17. Data for A-D obtained from Niwot Ridge Long-Term Ecological Research Program, 2002; data for E-F obtained from National Oceanic and Atmospheric Administration, 2002)

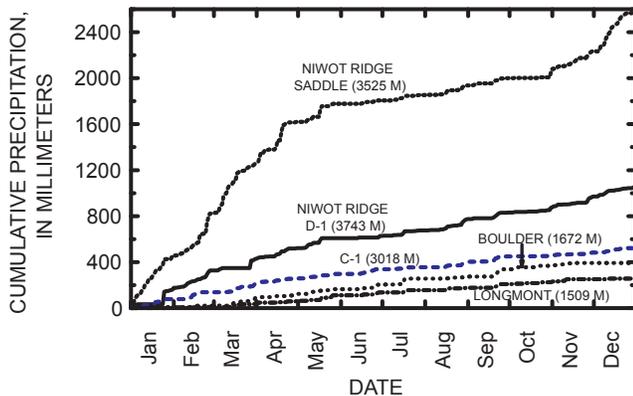


Figure 1.5. Graph showing cumulative precipitation for sites in the Boulder Creek Watershed for the year 2000. (Site locations shown in fig. 1.2a; data for Niwot Ridge sites obtained from Niwot Ridge Long-Term Ecological Research Program, 2002; data for Boulder and Longmont sites obtained from National Oceanic and Atmospheric Administration, 2002)

alpine, subalpine, montane, and foothills climatic zones, consists primarily of forests, shrubs, and ice (USGS, 2003; fig. 1.6b). The alpine tundra (elevations above 3500 m) is above tree line and is sparsely vegetated with lichen and low-growing herbaceous plants. The subalpine zone (3500 to 2700 m) primarily contains Engelmann spruce (*Picea engelmannii*) and subalpine fir (*Abies lasiocarpa*) forests, meadows, willow carrs, and peat fens. The montane zone (2700 to 2400 m) is dominated by lodgepole pine (*Pinus contorta*), quaking aspen (*Populus tremuloides*), and douglas-fir (*Pseudotsuga menziesii*). The foothills zone (2400 to 1800 m) contains ponderosa pine (*Pinus ponderosa*), douglas-fir, grasses, and flowering herbaceous plants (Rodeck, 1964; Weber, 1995). The upper basin is sparsely populated; the largest community is Nederland, with a year 2000 population of 1394 (U.S. Census Bureau, 2001).

The lower basin, which includes the plains climatic zone (1800 to 1500 m), consists of grassland, agricultural land, and residential/industrial/commercial land (fig. 1.6b). Grasslands consist of short-grass prairie, cactus, yucca (*Yucca glauca*), and flowering herbs (Rodeck, 1964; Weber, 1995). Boulder County agricultural lands are primarily comprised of

pasture, alfalfa, wheat, corn, and barley (U.S. Department of Agriculture, 1999). Urbanized areas in the Boulder Creek Watershed include the cities and towns of Boulder (population 94,673 in 2000; U.S. Census Bureau, 2001), Louisville (18,937), Lafayette (23,197), Erie (6,291), Superior (9,011), and part of Broomfield (total population 38,272; fig. 1.1).

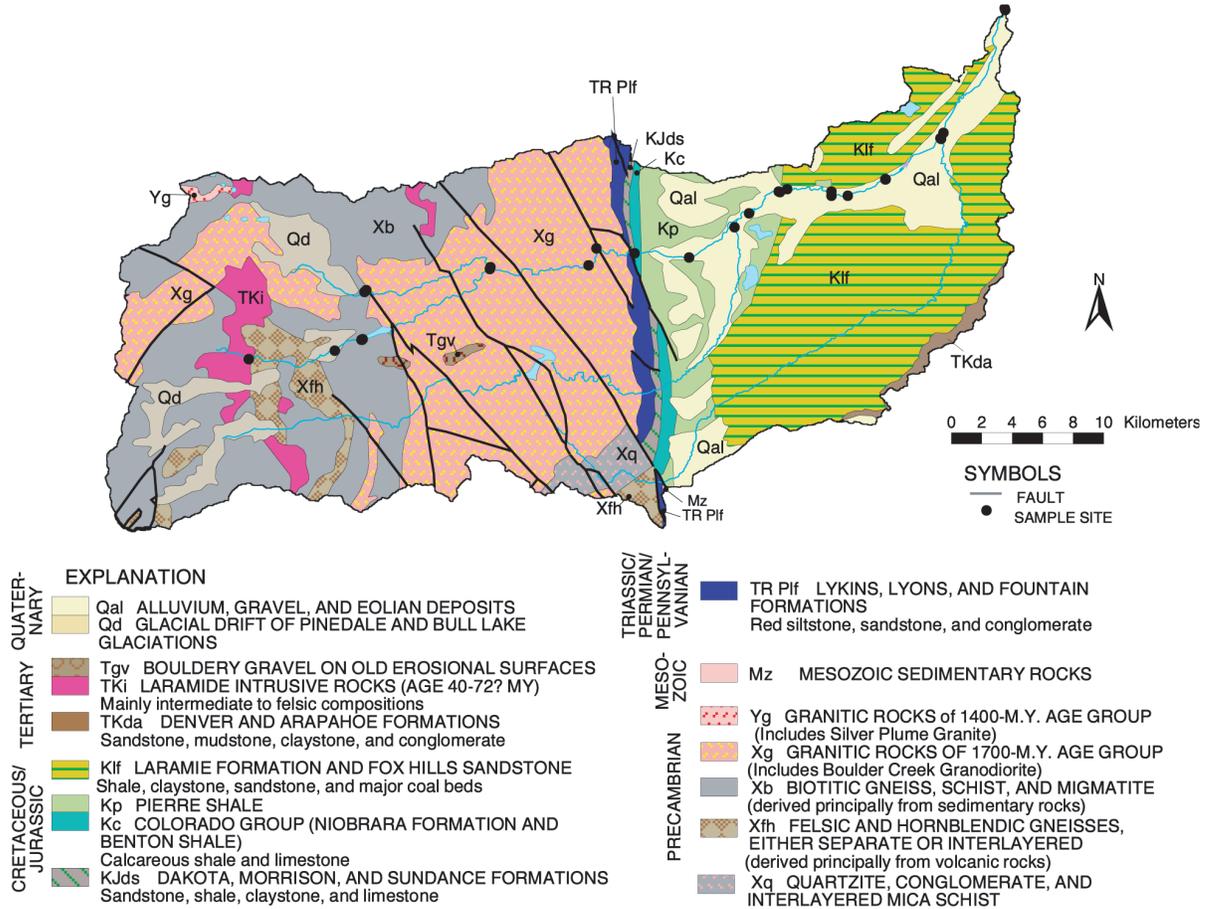
REACHES OF BOULDER CREEK

As Boulder Creek and its tributaries flow from the mountains to the plains, they are subjected to a complex water management system. Differences in geology, climate, land use, and solute sources produce variations in water quality within the watershed. Boulder Creek can be divided into five reaches based on hydrology, geology, topography, and potential sources of pollution: (1) headwater region, (2) mountain corridor, (3) urban corridor, (4) wastewater-dominated reach, and (5) wastewater/agricultural/aggregate-mining region.

Headwater Region

The headwater region is considered the area upstream of population centers and most paved roads, and is defined here as the region from the Continental Divide to the Peak-to-Peak Highway (Highways 72 and 119; fig. 1.1). Streamflow primarily originates from snowpack stored within the watershed. In order to provide year-round water availability, water is stored and augmented. On North Boulder Creek, up to 8,600,000 cubic meters (m³), or 7000 acre-feet of water can be stored in seven reservoirs owned by the city of Boulder (WBLA Inc., 1988). A pipeline diverts water from North Boulder Creek two kilometers downstream of Silver Lake Reservoir to Lakewood Reservoir (fig. 1.2b). Portions of Como Creek and North Boulder Creek are also diverted to Lakewood Reservoir during part of the year. Water in Lakewood

A



B

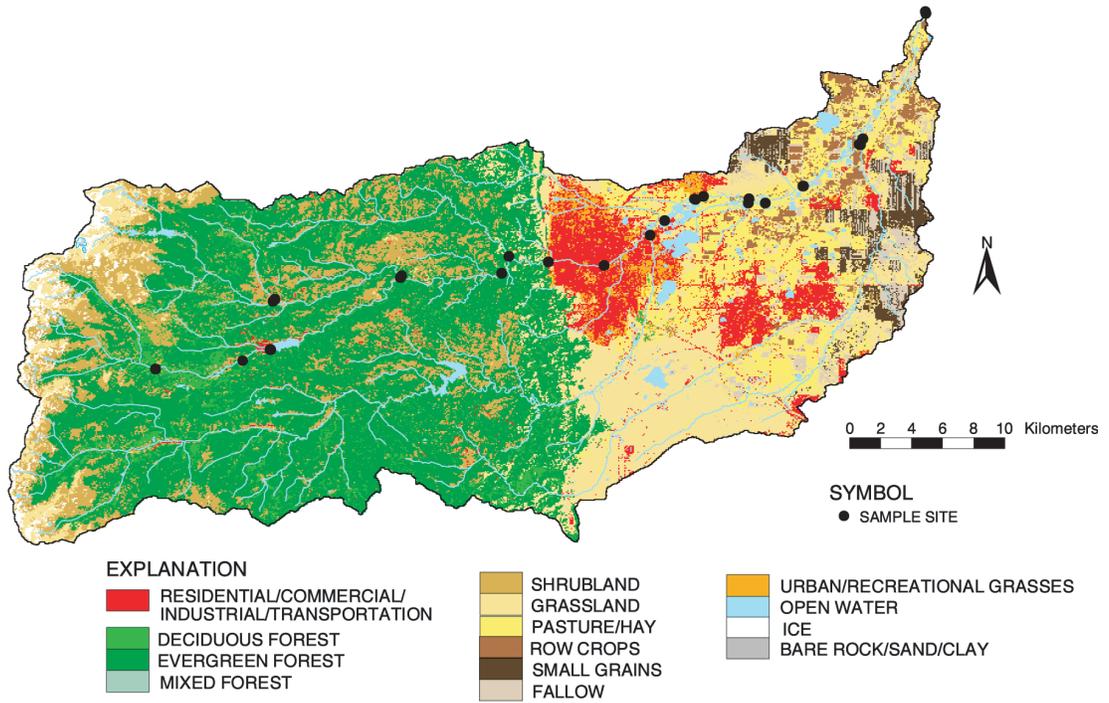


Figure 1.6. Maps showing (A) geology and (B) land cover in the Boulder Creek Watershed. (Geology modified from Tweto, 1979, and Green, 1992; land cover from U.S. Geological Survey, 2003).

Reservoir is diverted to the city of Boulder's Betasso Water Treatment Plant via the Lakewood Pipeline. The Silver Lake/Lakewood Reservoir watershed provides about 40 percent of the city of Boulder's water supply (City of Boulder, 2001). In contrast to North Boulder Creek, only a few small diversions, including the town of Nederland's water supply intake, affect the discharge of Middle Boulder Creek upstream of Barker Reservoir. South Boulder Creek receives transbasin water diverted from Denver Water's collection systems in the Fraser and Williams Fork basins via the Moffat Tunnel (fig. 1.2b). The headwater region is sparsely populated, but can be affected by recreation, air pollution, historical mining activity, road runoff, and mountain cabins. A 32-km² area of the North Boulder Creek watershed, including Arapaho Glacier and the Green Lakes Valley, is owned by the city of Boulder (fig. 1.1); public entry is prohibited. Most of the remaining headwater region lies within the Roosevelt National Forest; the headwaters of Middle Boulder Creek are located in the Indian Peaks Wilderness Area. While neither motorized vehicles nor mountain bikes are permitted, Indian Peaks is one of the most frequently visited wilderness areas in the state of Colorado (City of Boulder, 2002a). Numerous cabins, three developed U.S. Forest Service campgrounds, and the Eldora Mountain Ski Resort are located within the Middle Boulder Creek Watershed. The headwater region is represented in this study by sample sites on Middle Boulder Creek upstream of the town of Eldora (MBC-ELD) and at the Nederland Water Treatment Plant Intake (MBC-WTP), Como Creek (COMO), the Silver Lake Pipeline (SLP), and North Boulder Creek upstream of Lakewood Reservoir (NBC-LW; table 1.1 and fig. 1.2a).

Mountain Corridor

The Mountain Corridor is roughly considered the reaches of North Boulder Creek, Middle Boulder Creek, and the mainstem of Boulder

Creek from the Peak-to-Peak Highway to the mountains/plains interface (fig. 1.1). Several paved roads traverse the region, including Highway 119, which runs alongside Middle Boulder Creek and Boulder Creek in Boulder Canyon. Road runoff can carry sediment, leaked automobile fluids, road salts, and debris. Population of the corridor has increased rapidly in recent years. Middle Boulder Creek flows through Nederland, a community whose population increased by 27 percent to 1394 from 1990 to 2000 (U.S. Census Bureau, 2001). Nederland's Wastewater Treatment Plant (WWTP) operates an aerated lagoon treatment process and discharges up to 0.008 m³/s into Barker Reservoir when the reservoir is full, or into Middle Boulder Creek upstream of Barker Reservoir when the reservoir is low (City of Boulder, 2002a; U.S. Environmental Protection Agency, 2003). Barker Reservoir has a storage capacity of 14,426,000 m³ (11,700 acre-feet) and provides up to 40 percent of the city of Boulder's drinking water supply (City of Boulder, 2002a). Water is released from the reservoir via the Barker Dam outlet works, which deliver water to the Barker Gravity Pipeline or to Middle Boulder Creek below the dam (fig. 1.2b). During times of high flow (as in June 2000), Barker Reservoir and the Barker Gravity Pipeline reach maximum capacity, and water spills over the dam into Middle Boulder Creek. During times of low flow (including October 2000), Middle Boulder Creek below Barker Dam has historically been virtually dry from October to April because all released water was diverted to the pipeline. Water in North Boulder Creek that is not diverted to Lakewood Reservoir flows 10 km, receiving some discharge from snowmelt and a few streams, before converging with Middle Boulder Creek below Boulder Falls (fig. 1.2b).

The Boulder Canyon Hydroelectric Plant, located 8 km downstream of the confluence of North and Middle Boulder Creeks, uses water diverted from Barker Reservoir via the Barker Gravity Pipeline, Kossler Reservoir, and the Boulder Canyon Hydroelectric Penstock (fig.

1.2b) to produce electricity, and discharges the water directly to Boulder Creek. The Orodell streamgaging station is located just downstream of the hydroelectric plant.

Boulder Creek receives flow from Fourmile Creek, minor tributaries, a small amount of treated wastewater from a restaurant, and possibly groundwater, and loses water to three diversion ditches before reaching the mouth of Boulder Canyon (fig. 1.2b). Fourmile Creek drains several historical mining districts and has the potential to contribute trace metals to Boulder Creek. Septic systems in the region have the potential to contribute bacteria, nutrients, and consumer products to groundwater.

The mountain corridor is represented by sample sites on Middle Boulder Creek in Nederland (MBC-W) and upstream of the confluence with North Boulder Creek (MBC-aNBC), North Beaver Creek in Nederland (BEAVER), North Boulder Creek upstream of the confluence with Middle Boulder Creek below Boulder Falls (NBC-FALLS), Boulder Creek at the Orodell streamgaging station (BC-ORO), Boulder Creek at the mouth of Boulder Canyon (BC-CAN), and Fourmile Creek (FOURMILE; table 1.1, fig. 1.2a). Nederland's wastewater effluent (NED-EFF) also was sampled.

Urban Corridor

At the mouth of Boulder Canyon, bedrock geology transitions from igneous and metamorphic rocks to much younger sedimentary rocks (fig. 1.6a), and Boulder Creek enters the main urban corridor of the city of Boulder (fig. 1.1). The population of Boulder was 94,673 in the year 2000, an increase of 13 percent since 1990 (U.S. Census Bureau, 2001). In the urban corridor, Boulder Creek gains water from minor tributaries, storm drains, treated wastewater from a mobile home park, and groundwater, but loses much of its water to irrigation ditches from May through September, and to off-channel reservoirs from October through April. South Boulder Creek

enters Boulder Creek east of the city of Boulder; however, it usually contributes little discharge to the mainstem because most of the water in South Boulder Creek is diverted for domestic, industrial, and agricultural use.

Downstream from the South Boulder Creek confluence, Boulder Creek periodically receives water from the Colorado-Big Thompson Project. This water is conveyed from Lake Granby west of the Continental Divide via pipelines and canals to Carter Lake, and then via the Boulder Feeder Canal to Boulder Reservoir or the Boulder Creek Supply Canal (fig. 1.2b). Boulder Reservoir sources provide about 20 percent of the city of Boulder's water supply (City of Boulder, 2001). Water that is not diverted to the Boulder Reservoir Water Treatment Plant is conveyed to Boulder Creek via the Boulder Creek Supply Canal. Discharge in the canal varies depending on downstream delivery requests.

Human impact on Boulder Creek water quality increases in the urban corridor. Storm drains carry runoff from roads and lawns that may contain nutrients, pesticides, metals, and bacteria, particularly during storm events. Recreational activities, including swimming, wading, kayaking, and dog walking, can contribute suspended sediments, bacteria, and personal care products. The urban corridor is represented by sample sites on Boulder Creek at 30th Street (BC-30), at 61st Street (BC-61), and upstream of the Boulder 75th Street Wastewater Treatment Plant (BC-aWWTP), and South Boulder Creek upstream of Boulder Creek (SBC-aBC; table 1.1, fig. 1.2). The Boulder Creek Supply Canal (BCSC-aBC) also was sampled.

Wastewater-Dominated Reach

The Boulder 75th Street WWTP discharges to Boulder Creek downstream of the Boulder Creek Supply Canal (during the study, the discharge point was 300 m downstream of the canal; in March 2003, the discharge point was moved about 500 m downstream). The WWTP receives

wastewater that originates from several sources (including Lakewood, Barker, and Boulder Reservoirs) and has undergone drinking-water treatment and residential, commercial, and industrial use. The wastewater is treated using a trickling filter/solids contact and nitrification process (City of Boulder, 2002b). The average discharge of raw sewage entering the WWTP, recorded with an ultrasonic meter, is about 0.74 m³/s (26 ft³/s). This rate varies diurnally depending on water usage within the city of Boulder.

The downstream impact of the WWTP is variable, depending on the baseflow of Boulder Creek, the volume of wastewater effluent, and depletion by agricultural diversions. In addition, Dry Creek, which carries water diverted from South Boulder Creek and released from Baseline Reservoir, discharges a varying amount of water to Boulder Creek about 4 km downstream from the WWTP (fig. 1.2b). The downstream boundary of the wastewater-dominated reach is therefore difficult to define. Boulder Creek at 75th Street (BC-75), upstream of Dry Creek (BC-aDC), at 95th Street (BC-95), and at 107th Street (BC-107; table 1.1, fig. 1.2a) are considered to be within the wastewater-dominated reach, with impact from the WWTP decreasing downstream (Murphy and others, 2003). Boulder 75th Street WWTP effluent (BLD-EFF) and Dry Creek (DC) also were sampled.

Wastewater/Agricultural/ Aggregate-Mining Region

Downstream of the Boulder 75th Street WWTP, Boulder Creek flows through agricultural fields, pastures, and open space. Panama Reservoir #1 and Goosehaven Reservoir (fig. 1.2b) release water to Boulder Creek during part of the year. Several aggregate mines operate along lower Boulder Creek, and small-scale oil wells are located in this area. Diversion ditches remove large amounts of water; some water is returned by agricultural return ditches and

groundwater contributions to baseflow. Coal Creek discharges to Boulder Creek just upstream of the Boulder/Weld County line (fig. 1.1). Coal Creek receives effluent from the Erie, Lafayette, Louisville, and Superior WWTPs, which are permitted to discharge a total of 0.36 m³/s (8.2 million gallons per day) into Coal Creek or its tributary Rock Creek (USEPA, 2003).

The water quality of the creek in the wastewater/agricultural/aggregate-mining region can be affected by agricultural runoff, road runoff, wastewater effluent, and interaction with groundwater. Due to less topographic variation and riparian vegetation than the mountain and urban reaches, Boulder Creek is much less shaded in this region than in the upper basin. Water temperatures approach 30°C in summer months, and the direct sunlight, shallow water, and high temperatures, along with nutrients provided by wastewater effluent and agricultural runoff, lead to extensive algal growth in the creek. This algal growth in turn causes dissolved oxygen and pH levels to oscillate from nighttime lows to daytime highs (TetraTech, Inc., 1993). The population of the lower Coal Creek watershed has grown substantially in recent years; the combined populations of Superior, Louisville, Lafayette, and Erie grew 102 percent to 57,436 from 1990 to 2000 (U.S. Census Bureau, 2001), increasing urban pressures on this tributary. The wastewater/agricultural/aggregate-mining region is represented by sampling sites on Boulder Creek above and below Coal Creek (BC-aCC and BC-bCC) and above Saint Vrain Creek (BC-aSV), Coal Creek (CC), and Saint Vrain Creek above Boulder Creek (SV-aBC; table 1.1, fig. 1.2a).

DISCHARGE OF BOULDER CREEK

Because the majority of precipitation in the Boulder Creek Watershed falls as snow (fig. 1.5), snowmelt controls discharge in Boulder Creek, leading to large seasonal fluctuations. Low-flow conditions occur from October through March, with discharge between 0.14 and 1.1 cubic

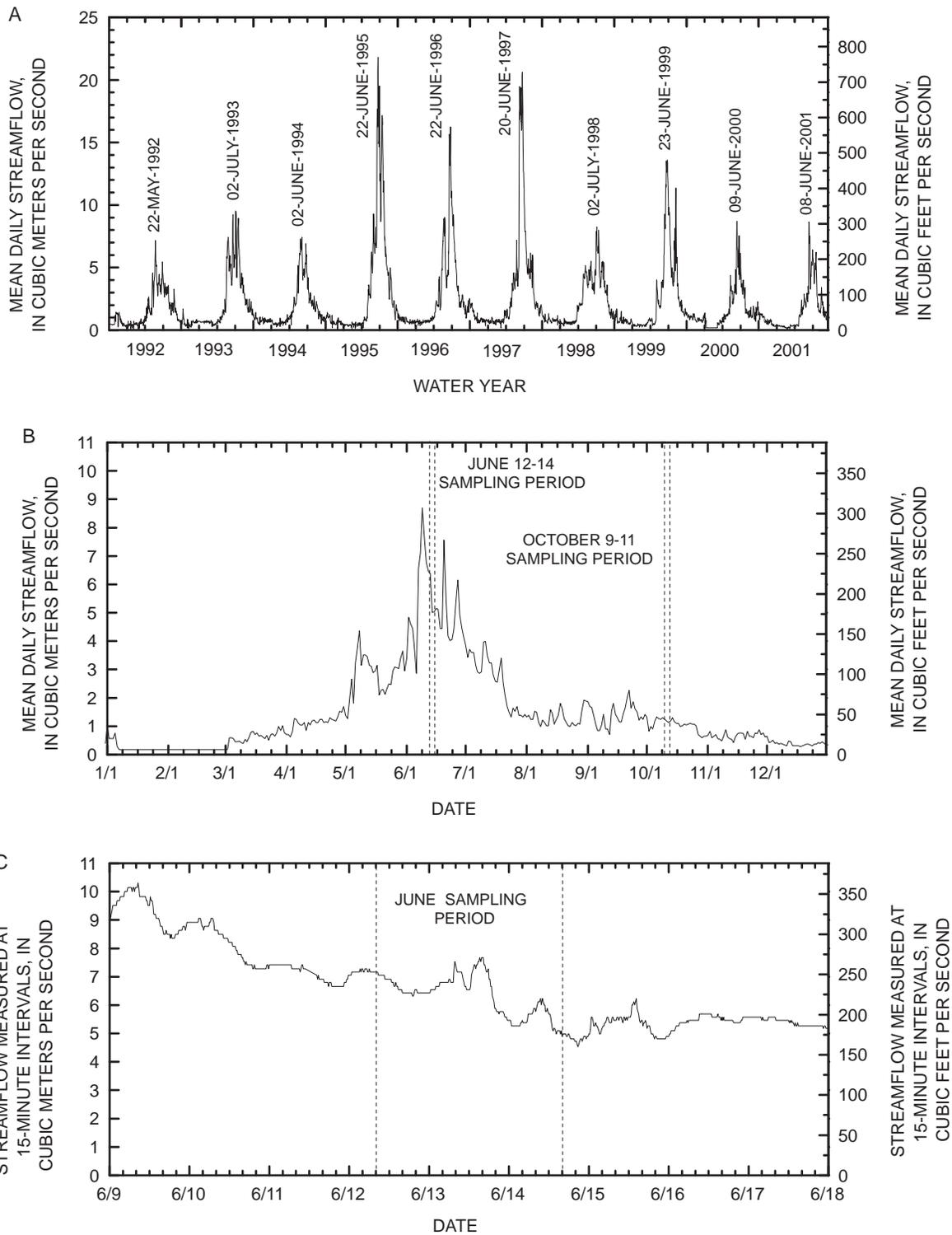


Figure 1.7. Hydrographs of Boulder Creek at the Orodell streamgaging station, (A) Water years 1992 to 2001 (water years begin October 1); dates of maximum annual discharge shown; (B) January 1 to December 31, 2000; (C) June 9 to June 18, 2000. (Data from U.S. Geological Survey, 2002b)

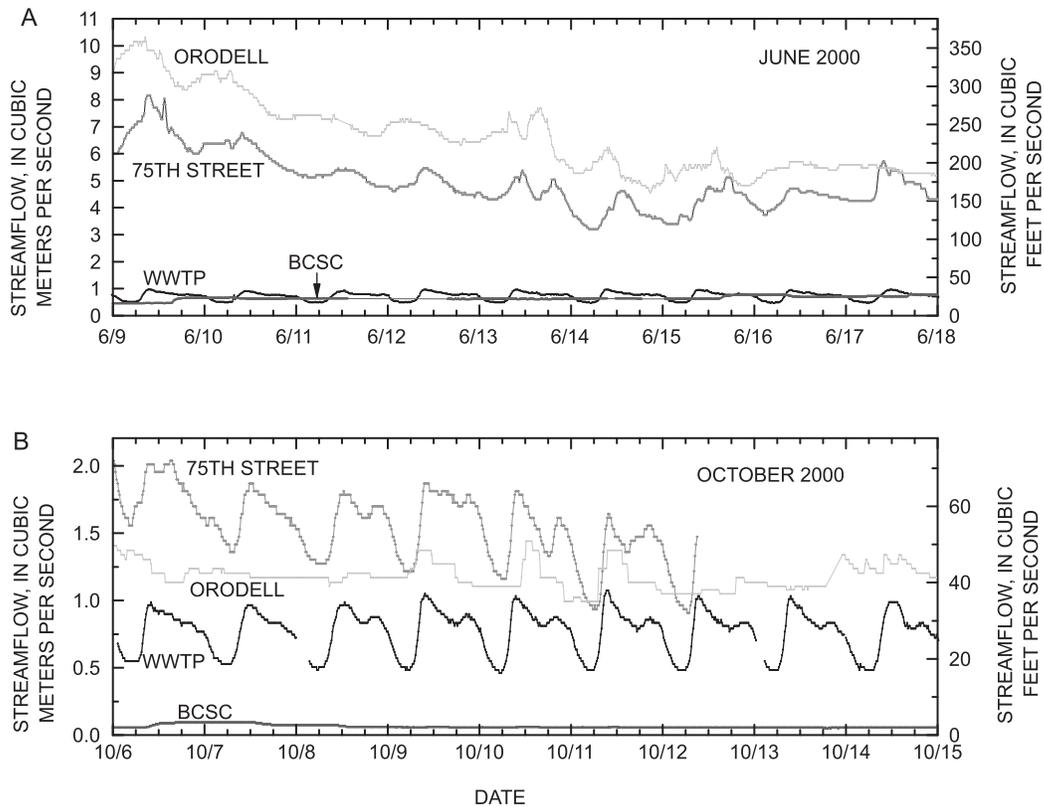


Figure 1.8. Hydrographs of Boulder Creek at the Orodell streamgaging station (Orodell), Boulder Creek at the 75th Street streamgaging station (75th Street), Boulder 75th Street Wastewater Treatment Plant inflow (WWTP), and Boulder Creek Supply Canal (BCSC) in (A) June 2000 and (B) October 2000. (Discharge measured at 15-minute intervals; data from U.S. Geological Survey, 2002b, Colorado Water Conservation Board and Colorado Division of Water Resources, 2002, and F. Bebler, City of Boulder, written commun., 2002)

meters per second (m^3/s), or 5 and 40 cubic feet per second (ft^3/s) measured at the Orodell streamgaging station from 1992 to 2001 (fig. 1.7a). High-flow conditions typically occur from May to July and peak in June, depending on snowpack depth and air temperature. Maximum average daily discharge between 1992 and 2001 ranged from 7 to 23 m^3/s (250 to 800 ft^3/s). During June 2000, the discharge at the Orodell streamgaging station reached its annual maximum average daily value of 9 m^3/s (307 ft^3/s) two days prior to the beginning of sampling (fig. 1.7b). The daily cycle of solar heating and subsequent snow melt produces a diurnal variation in discharge (fig. 1.7c; Caine, 1989).

The Boulder 75th Street WWTP also imparts a diurnal signal on the discharge of lower Boulder Creek. During the study, the rate of raw sewage

entering the WWTP was lowest (0.45 to 0.51 m^3/s ; 16 to 18 ft^3/s) between 3 and 7 AM, and then rose rapidly to maximum daily values (0.88 to 1.1 m^3/s ; 31 to 38 ft^3/s) between 8 and 10 AM on weekdays and between 11 AM and 12 noon on Saturdays and Sundays (fig. 1.8). Discharge at the 75th Street streamgauge, located about 500 m downstream of the WWTP discharge point in 2000, typically peaked within 0.5 to 1 hours of the WWTP influent peak, but the timing of the peak varies depending on the residence time in the WWTP and the discharge of the creek. This variation complicates the calculation of effluent contribution to discharge in Boulder Creek at the 75th Street streamgauge; however, a range can be estimated by comparing discharge of raw sewage entering the Boulder 75th Street WWTP to discharge measured 0.5 to 1 hours later at the 75th

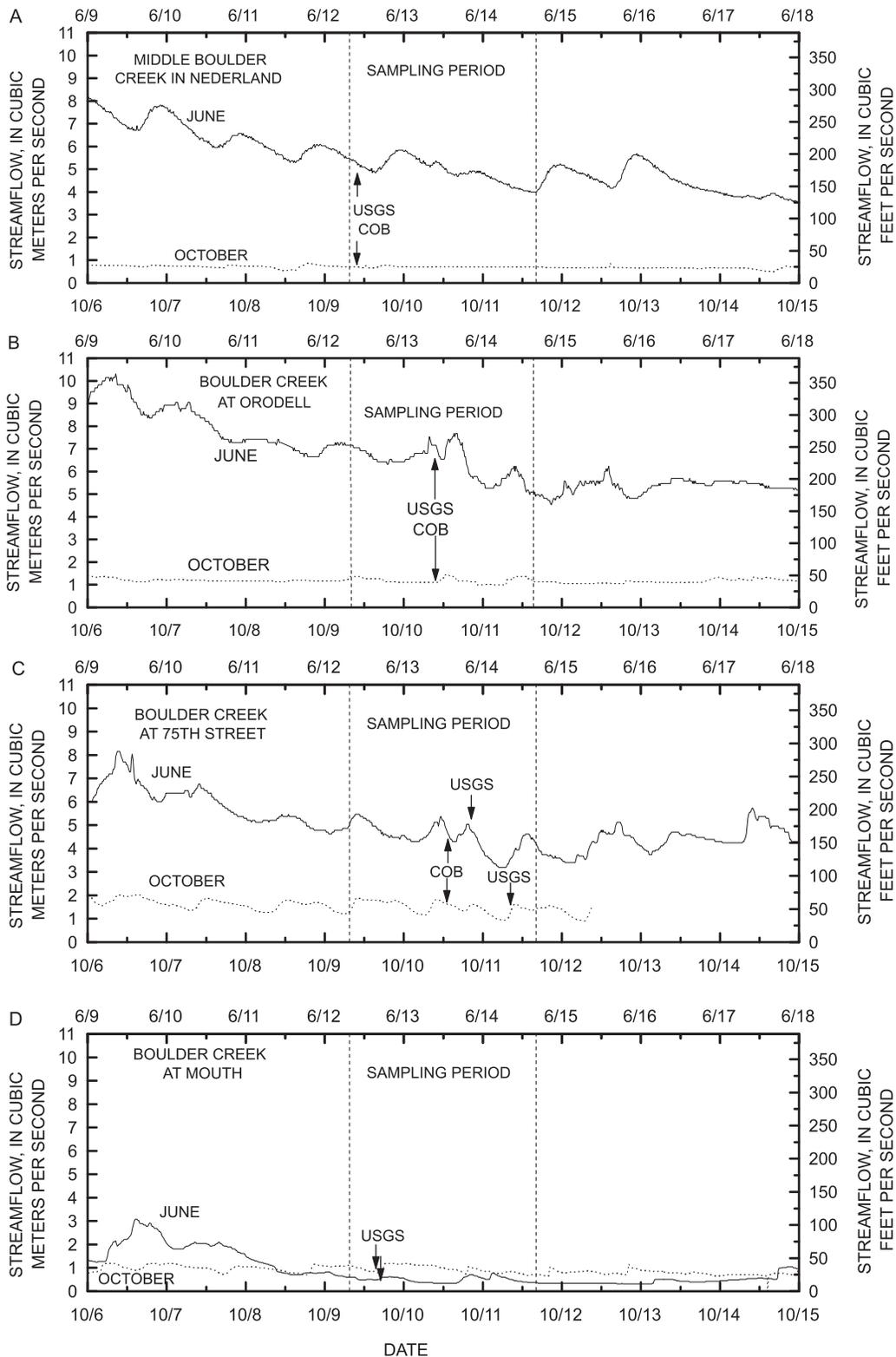


Figure 1.9. Hydrographs of streamgaging stations along Middle Boulder Creek and Boulder Creek, June and October 2000: (A) Middle Boulder Creek in Nederland, (B) Boulder Creek at Orodell, (C) Boulder Creek at 75th Street, and (D) Boulder Creek at mouth. (Arrows indicate times of sampling by U.S. Geological Survey (USGS) and City of Boulder (COB); discharge measured at 15-minute intervals; data from U.S. Geological Survey, 2002b)

Street streamgage. This calculation suggests that WWTP effluent contributed between 15 and 20 percent of the discharge measured at 75th Street during high-flow sampling and between 50 and 65 percent during low-flow sampling. Chemical mass-balance calculations imply that the effluent contributed between 37 and 49 percent to the discharge at 75th Street at the time of high-flow sampling, and between 69 and 77 percent at low flow (Barber and others, 2003; Murphy and others, 2003; Verplanck and others, 2003).

Because of the many diversions removing water during high flow, discharge at the mouth of Boulder Creek was substantially lower than at upstream streamgages (fig. 1.9). During the June sampling, discharge at the streamgage at the mouth of Boulder Creek was as little as 5 percent of that at the Orodell streamgage. Discharge at the mouth of Boulder Creek was actually higher in October than in June.

The velocity at which water travels down Boulder Creek varies depending on discharge and stream gradient. Previous studies on travel time in Boulder Creek have focused on the hydroelectric plant in the upper basin and WWTP releases in the lower basin. Prior to the year 2001, the Boulder Canyon Hydroelectric Plant released about 4.2 m³/s (150 ft³/s) of water to Boulder Creek for about three hours (between 6 and 9 pm) from November to March (City of Boulder, 2002a). This resulted in a wave of water estimated to have a speed of 1.1 m/s (J.A. Moody, USGS, written commun., 1999). At that speed, water would travel from the Orodell streamgage to the mouth of Boulder Creek in about 11 hours. Hydrosphere Resource Consultants (written commun., 1997) found that at a discharge of 1.7 m³/s (60 ft³/s), water traveled from 75th Street to 95th Street in 206 minutes, a speed of about 0.4 m/s. At this speed, water would travel from the 75th Street streamgage to the confluence of Boulder Creek and Saint Vrain Creek in about 17 hours. However, inputs and outputs along Boulder Creek would change the flow and thus the travel time. During the 2000 study, similar discharge peaks occurred on June 13 at 7:45 am

at the Orodell streamgage, at 11:30 am at the 75th Street streamgage, and at 8:30 pm at the streamgage at the mouth of Boulder Creek (fig. 1.9). Discharge varies along the reach, complicating the calculation of speed.

A discharge profile along Middle Boulder Creek/Boulder Creek was estimated for one day in June and October based on discharge recorded at streamgages (fig. 1.9), measured by city of Boulder personnel (tables 1.2 and 1.3), and obtained from the Colorado Water Conservation Board and Colorado Division of Water Resources (2002; table 1.4), the town of Nederland, the city of Boulder, and the Public Service Company. The second day of sampling (Tuesday) was selected for the calculation because this was the day during which most discharge measurements were made. For sites with continuous discharge measurements (streamgaging stations and Boulder 75th Street WWTP influent), discharge recorded near the sampling times of nearby sites were used (table 1.5). The discharge passing through diversion structures were estimated by assuming constant discharge during the day (table 1.4).

The estimated discharge along the Middle Boulder Creek/Boulder Creek profile on June 13 and October 10, 2000 are shown in figure 1.10. In June, discharge of Middle Boulder Creek above Barker Reservoir increased downstream as it received snowmelt and tributary inflow. Water was flowing over Barker Dam into Middle Boulder Creek. Below the reservoir, the discharge of Middle Boulder Creek increased downstream, receiving inflows from snowmelt, leakage from the Barker Gravity Pipeline (which loses about 10 percent of the water it carries to leaks; City of Boulder, 2002a), and groundwater. Downstream of the confluence of Middle and North Boulder Creeks, the creek received water from the hydroelectric plant and Fourmile Creek and reached the maximum discharge along the Middle Boulder Creek/Boulder Creek profile, about 7.8 m³/s (276 ft³/s). Discharge was reduced by two-thirds over the next 4 km after diversions removed about 4.8 m³/s (170 ft³/s) from the

Table 1.2. Discharge measurements at sampling sites, June and October 2000

[COB group, city of Boulder group that measured discharge; ID, identification number; m³/s, cubic meters per second; ft³/s, cubic feet per second; meter, Marsh-McBirney Flo-Mate 2000 portable flow meter, following USGS midsection methods (Rantz and others, 1982); Storm, Stormwater; --, not measured; Source, Sourcewater; WWTP, Wastewater Treatment Plant; data for gages 06725500, 06727000, and BCSCBCCO from Colorado Water Conservation Board and Colorado Division of Water Resources, 2002; data for gages 06730200 and 06730500 from U.S. Geological Survey (USGS), 2002b; when sampling times by USGS and city of Boulder differ, discharge at both times is given, if available; if discharge was determined by both meter and gage, both values are given]

Site	Method (COB group or station ID)	June				October			
		Date	Time	Discharge (m ³ /s) (ft ³ /s)		Date	Time	Discharge (m ³ /s) (ft ³ /s)	
Middle Boulder Creek/Boulder Creek									
MBC-ELD	meter (Storm)	6/12/00	0820	3.7	130	10/9/00	0848	0.40	14
MBC-WTP	--	--	--	--	--	--	--	--	--
MBC-W	gage (06725500)	6/12/00	1315	5.0	176	10/9/00	1300	0.34	12
MBC-aNBC	--	--	--	--	--	--	--	--	--
BC-ORO	meter (Storm)	6/13/00	0900	6.5	231	10/10/00	1000	1.3	46
BC-ORO	gage (06727000)	6/13/00	1000	7.1	249	10/10/00	1000	1.1	39
BC-CAN	meter (Storm)	--	--	--	--	10/10/00	1045	1.0	35
BC-30	meter (Storm)	6/13/00	1445	2.3	81	10/11/00	--	0.37	13
BC-61	meter (Storm)	6/13/00	1110	3.2	113	10/10/00	1120	0.54	19
BC-aWWTP	meter (Storm)	--	--	--	--	10/10/00	1355	0.34	12
BC-75	gage (06730200)	6/13/00	1400	4.5	158	10/10/00	1330	1.6	57
BC-75	gage (06730200)	6/13/00	2000	4.9	172	10/11/00	0900	1.5	54
BC-aDC	meter (Storm)	6/13/00	1525	3.3	116	10/10/00	1355	1.1	37
BC-95	meter (Storm)	--	--	--	--	10/10/00	1435	0.99	35
BC-107	meter (Storm)	--	--	--	--	10/10/00	1510	0.68	24
BC-aCC	meter (Storm)	6/13/00	1645	1.1	38	10/10/00	1545	0.88	31
BC-bCC	meter (Storm)	6/13/00	1655	1.4	51	10/10/00	1610	1.2	43
BC-aSV	meter (Storm)	6/13/00	1740	0.45	16	10/9/00	1600	0.48	17
BC-aSV ¹	gage (06730500)	6/13/00	1800	0.57	20	10/9/00	1600	0.79	28
Inflows/other flows									
COMO	flume (Source)	6/12/00	1012	0.14	5.2	10/9/00	1023	0.03	1.0
NBC-LW	flume (Source)	6/12/00	1023	1.7	59	10/9/00	1040	0.17	6.0
SLP	Lakewood plant	--	--	--	--	10/9/00	1058	0.17	5.7
BEAVER	meter (Source)	6/12/00	1249	0.09	3.2	10/9/00	1230	0.01	0.48
NED-EFF	Nederland WWTP	6/12/00	1323	0.005	0.17	10/9/00	1317	0.003	0.10
NBC-FALLS	--	--	--	--	--	--	--	--	--
FOURMILE	meter (Storm)	6/13/00	0908	0.11	3.9	10/9/00	1005	0.02	0.66
SBC-aBC	²	6/13/00	ave.	0.02	0.72	10/9/00	ave.	0.01	0.5
BCSC-aBC	gage (BCSCBCCO)	6/11/00	1030	0.62	22	10/9/00	1740	0.06	1.9
BLD-EFF	Boulder WWTP	6/13/00	1345	0.86	30	10/10/00	1315	0.90	32
BLD-EFF	Boulder WWTP	6/13/00	2000	0.79	28	10/11/00	0830	1.0	34
DC	³	6/13/00	ave.	0.37	13	10/9/00	1344	0.03	0.9
CC	meter (Storm)	6/13/00	1650	0.31	11	10/10/00	1555	0.34	12
SV-aBC	meter (Storm)	6/13/00	1750	3.3	116	10/9/00	1545	1.9	68

¹Gage located 1000 m upstream of sampling site.

²June discharge estimated from data for Leggett Outlet release (R. Rhodes, Xcel Energy, oral commun., 2003); October discharge visually estimated.

³June discharge estimated from Colorado Water Conservation Board and Colorado Division of Water Resources (2002) data for Baseline Reservoir replacement-to-river discharge minus Cottonwood Ditch #2 discharge; October discharge measured with meter by Stormwater group.

Table 1.3. Discharge measurements of ditches and minor tributaries of Boulder Creek, June and October 2000

[Discharge measured by city of Boulder Stormwater group; m³/s, cubic meters per second; ft³/s, cubic feet per second; --, not measured; <, less than]

Tributary/Ditch	June					October				
	Method	Date	Time	Discharge (m ³ /s) (ft ³ /s)		Method	Date	Time	Discharge (m ³ /s) (ft ⁶ /s)	
Tributaries										
Bear Canyon Creek	--	--	--	--	--	visual	10/9/00	1114	<0.1	<5
Goose Cr.	meter	6/13/00	1040	0.01	0.5	meter	10/9/00	1120	0.02	0.8
Fourmile Canyon Creek	meter	6/13/00	1130	0.14	5.0	visual	10/9/00	--	<0.06	<2
Ditches										
Silver Lake	--	--	--	--	--	visual	10/9/00	1034	0	0
Anderson	meter	6/13/00	0920	0.04	1.4	meter	10/9/00	1015	0.001	0.02
Farmers	meter	6/13/00	0938	0.68	24	visual	10/9/00	1027	0	0
12 th Street Diversion ¹	meter	6/13/00	0955	3.0	107	meter	10/9/00	1043	0.96	34
Wellman Feeder	--	--	--	--	--	visual	10/9/00	1105	0	0
Butte Mill	meter	6/13/00	1050	0.06	2.1	visual	10/9/00	1130	0	0
Green	flume	6/13/00	1145	0.08	3	flume	10/9/00	1135	0.0003	0.01
Leggett	--	--	--	--	--	meter	10/9/00	1420	0.23	8.1
Lower Boulder	--	--	--	--	--	meter	10/9/00	1435	0.39	14
Boulder and Weld County	--	--	--	--	--	meter	10/9/00	1520	0.02	0.6

¹ Includes Boulder and White Rock, North Boulder Farmer's, Boulder and Left Hand, and McCarty Ditches.

Table 1.4. Discharge through major diversion structures on Boulder Creek, June and October 2000

[Data from Colorado Water Conservation Board and Colorado Division of Water Resources (2002) unless noted; distance, distance upstream from SaintVrain Creek confluence; m³/s, cubic meters per second; ft³/s, cubic feet per second; Co., County]

Diversion	Distance (meters)	Discharge ¹											
		6/12		6/13		6/14		10/9		10/10		10/11	
		(m ³ /s)	(ft ³ /s)	(m ³ /s)	(ft ³ /s)	(m ³ /s)	(ft ³ /s)	(m ³ /s)	(ft ³ /s)	(m ³ /s)	(ft ³ /s)	(m ³ /s)	(ft ³ /s)
Silver Lake	38660	0.14	4.9	0.14	5.1	0.13	4.6	0	0	0	0	0	0
Anderson	37300	0.13	4.5	0.12	4.3	0.13	4.5	0	0	0.08	2.9	0.11	3.8
Farmers	36860	0.76	27	0.79	28	0.74	26	0	0	0	0	0	0
12th Street ²	35290	3.5	124	3.7	129	3.1	110	1.0	36	0.96	34	0.93	33
Smith-Goss	35290	0.11	4.0	0.11	4.0	0.11	4.0	0.11	4.0	0.11	4.0	0.11	4.0
Wellman Feeder ³	33420	0	0	0	0	0	0	0	0	0	0	0	0
Butte Mill	29500	0.17	5.9	0.14	4.8	0.11	4.0	0	0	0	0	0	0
Green	27010	0.16	5.5	0.17	6.0	0.22	7.7	0	0	0	0	0	0
Leggett	21140	1.0	36	0.91	32	0.91	32	0.25	8.9	0.28	10	0.26	9.2
Lower Boulder	18550	2.3	81	2.3	80	2.5	87	0.51	18	0.48	17	0.48	17
Boulder and Weld Co.	16320	0.42	15	0.45	16	0.37	13	0	0	0	0	0	0
Howell	10320	0.06	2	0.06	2	0.06	2.0	0	0	0	0	0	0
Godding Dailey Plumb	9610	0.40	14	0.40	14	0.42	15	0.09	3.2	0.09	3.2	0.09	3.2
Idaho Creek ⁴	6550	1.3	46	1.3	45	1.3	45	0.14	5.0	0.08	3.0	0.08	3.0
Rural	4560	0.74	26	0.54	19	0.54	19	0	0	0	0	0	0

¹ Estimated from cubic feet per second per day by assuming discharge was constant over 24 hours.

² Includes Boulder and Whiterock, Boulder and Lefthand, and North Boulder Farmer's Ditches.

³ Data from R. Rhodes, Xcel Energy, oral commun., 2003.

⁴ Includes Houck #2, Carr-Tyler, Highland South Side, Smith-Emmons, and Delehant Ditches.

Table 1.5. Estimated discharge of Middle Boulder Creek/Boulder Creek, June 13 and October 10, 2000

[Mainstem sites shown in bold; inflows and outflows indented; m³/s, cubic meters per second; --, not applicable; WTP, water treatment plant; plant; PSCo, Public Service Company records obtained by the city of Boulder; NR, not recorded; USEPA, U.S. Environmental Protection Agency (2003);

Site	Discharge obtained from	June discharge (m ³ /s)					
		Date	Time	Measured	Inflow	Outflow	Calculated ¹
MBC-ELD	meter	6/12/00	0820	3.7	--	--	--
Nederland WTP diversion	CWCB/CDWR	6/12/00	ave.	--	--	0.010	--
North Beaver Creek	meter	6/12/00	1249	--	0.09	--	--
MBC-W	gage	6/12/00	1300	5.0	--	--	3.8
Nederland WWTP effluent	Nederland WWTP	6/12/00	1323	--	0.005	--	--
MBC below Barker Reservoir	PSCo	6/13/00	NR	4.3	--	--	--
North Boulder Creek ²	meter	6/12/00	1023	--	1.7	--	--
Hydroelectric plant discharge	PSCo	6/13/00	NR	--	0.51	--	--
BC-ORO	gage	6/13/00	1000	7.1	--	--	6.5
Red Lion Inn	USEPA	5/31/00	NR	--	0.0002	--	--
Fourmile Creek	meter	6/13/00	0908	--	0.11	--	--
Silver Lake Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.14	--
Anderson Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.12	--
Farmers Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.79	--
BC-CAN	meter	--	--	--	--	--	6.2
12th Street Diversion	CWCB/CDWR	6/13/00	ave.	--	--	3.7	--
Smith-Goss Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.11	--
Wellman Feeder Ditch	Xcel	6/13/00	--	--	--	0	--
BC-30	meter	6/13/00	1445	2.3	--	--	2.4
Bear Canyon Creek	visual	--	--	--	--	--	--
Butte Mill Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.14	--
San Lazaro WWTP	USEPA	5/31/00	NR	--	0.005	--	--
South Boulder Creek ³		6/13/00	ave.	--	0.02	--	--
BC-61	meter	6/13/00	1110	3.2	--	--	2.2
Fourmile Canyon Creek	meter	6/13/00	1130	--	0.14	--	--
Green Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.17	--
Boulder Creek Supply Canal	gage	6/13/00	1310	--	0.62	--	--
BC-aWWTP	meter	--	--	--	--	--	3.8
Boulder WWTP effluent	Boulder WWTP	6/13/00	1245	--	0.86	--	--
BC-75	gage	6/13/00	1315	4.7	--	--	4.7
Leggett Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.91	--
BC-aDC	meter	6/13/00	1525	3.3	--	--	3.6
Dry Creek ⁴		6/13/00	--	--	0.28	--	--
BC-95	meter	--	--	--	--	--	3.6
Lower Boulder Ditch	CWCB/CDWR	6/13/00	ave.	--	--	2.3	--
Boulder and Weld Co. Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.45	--
BC-107	meter	--	--	--	--	--	0.85
Goosehaven Reservoir release	CWCB/CDWR	6/13/00	ave.	--	0	--	--
BC-aCC	meter	6/13/00	1645	1.1	--	--	0.85
Coal Creek	meter	6/13/00	1650	--	0.31	--	--
BC-bCC	meter	6/13/00	1655	1.4	--	--	1.4
Howell Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.06	--
Panama Reservoir #1 release	CWCB/CDWR	6/13/00	ave.	--	0.59	--	--
Godding Dailey Plumb Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.40	--
Idaho Creek ditches	CWCB/CDWR	6/13/00	ave.	--	--	1.3	--
Rural Ditch	CWCB/CDWR	6/13/00	ave.	--	--	0.54	--
Boulder Creek above mouth	gage	6/13/00	1800	0.57	--	--	-0.31

¹ Estimated by adding inflows to and subtracting outflows from the last measured discharge of upstream site; negative values indicate additional source (such

² Measured at Lakewood Reservoir.

³ Estimated in June from Valmont Reservoir release (R. Rhodes, Xcel Energy, oral commun., 2003); visually estimated in October.

⁴ June discharge estimated from Colorado Water Conservation Board and Colorado Division of Water Resources (2002) data for Baseline Reservoir

CWCB/CDWR, Colorado Water Conservation Board and Colorado Division of Water Resources (2002); ave., daily average; WWTP, wastewater treatment Xcel, oral commun. from R. Rhodes, Xcel Energy, 2003; Co., County]

Site	October discharge (m ³ /s)						Other possible inflows and outflows
	Date	Time	Measured	Inflow	Outflow	Calculated ¹	
MBC-ELD	10/9/00	0848	0.40	--	--	--	
	10/9/00	ave.	--	--	0.007	--	
	10/9/00	1230	--	0.01	--	--	
MBC-W	10/9/00	1300	0.34	--	--	0.40	lakes, wetlands, snowmelt
	10/9/00	1317	--	0.003	--	--	
	10/10/00	NR	0	--	--	--	
BC-ORO	10/9/00	1040	--	0.17	--	--	
	10/10/00	NR	--	1.0	--	--	
	10/10/00	1000	1.1	--	--	1.2	pipeline leakage, snowmelt, gulches
	9/30/00	NR	--	0.0003	--	--	
	10/9/00	1005	--	0.02	--	--	
BC-CAN	10/10/00	ave.	--	--	0	--	
	10/10/00	ave.	--	--	0.08	--	
	10/10/00	ave.	--	--	0	--	
	10/10/00	1045	1.0	--	--	1.0	storm sewers, gulches
	10/10/00	ave.	--	--	0.96	--	
BC-30	10/10/00	ave.	--	--	0.11	--	
	10/10/00	NR	--	--	0	--	
	10/11/00	NR	0.37	--	--	-0.07	storm sewers, groundwater
	10/9/00	1114	--	0.03	--	--	
BC-61	10/10/00	ave.	--	--	0	--	
	9/31/00	NR	--	0.003	--	--	
	10/9/00	ave.	--	0.01	--	--	
	10/10/00	1120	0.54	--	--	0.41	storm sewers, ponds
BC-aWWTP	10/9/00	NR	--	0.03	--	--	
	10/10/00	ave.	--	--	0	--	
	10/10/00	1330	--	0.06	--	--	
BC-75	10/10/00	1355	0.34	--	--	0.63	ponds
	10/10/00	1230	--	0.94	--	--	
BC-aDC	10/10/00	1330	1.6	--	--	1.3	groundwater from WWTP, ditch returns
	10/10/00	ave.	--	--	0.28	--	
BC-95	10/10/00	1355	1.1	--	--	1.3	ditch return, ponds
	10/9/00	1344	--	0.03	--	--	
BC-107	10/10/00	1435	0.99	--	--	1.1	ponds
	10/10/00	ave.	--	--	0.48	--	
	10/10/00	ave.	--	--	0	--	
BC-aCC	10/10/00	1510	0.68	--	--	0.51	
	10/10/00	ave.	--	--	0	--	
BC-bCC	10/10/00	1545	0.88	--	--	0.68	ponds, ditch returns
	10/10/00	1555	--	0.34	--	--	
BC-mouth	10/10/00	1610	1.2	--	--	1.2	
	10/10/00	ave.	--	--	0	--	
	10/10/00	ave.	--	0	--	--	
	10/10/00	ave.	--	--	0.09	--	
	10/10/00	ave.	--	--	0.08	--	
	10/10/00	ave.	--	--	0	--	
	10/10/00	2100	1.0	--	--	1.0	ponds, groundwater, ditch returns

as ground water) required to produce measured discharge.

replacement-to-river discharge minus Cottonwood Ditch #2 discharge; October discharge measured with meter by Stormwater group.

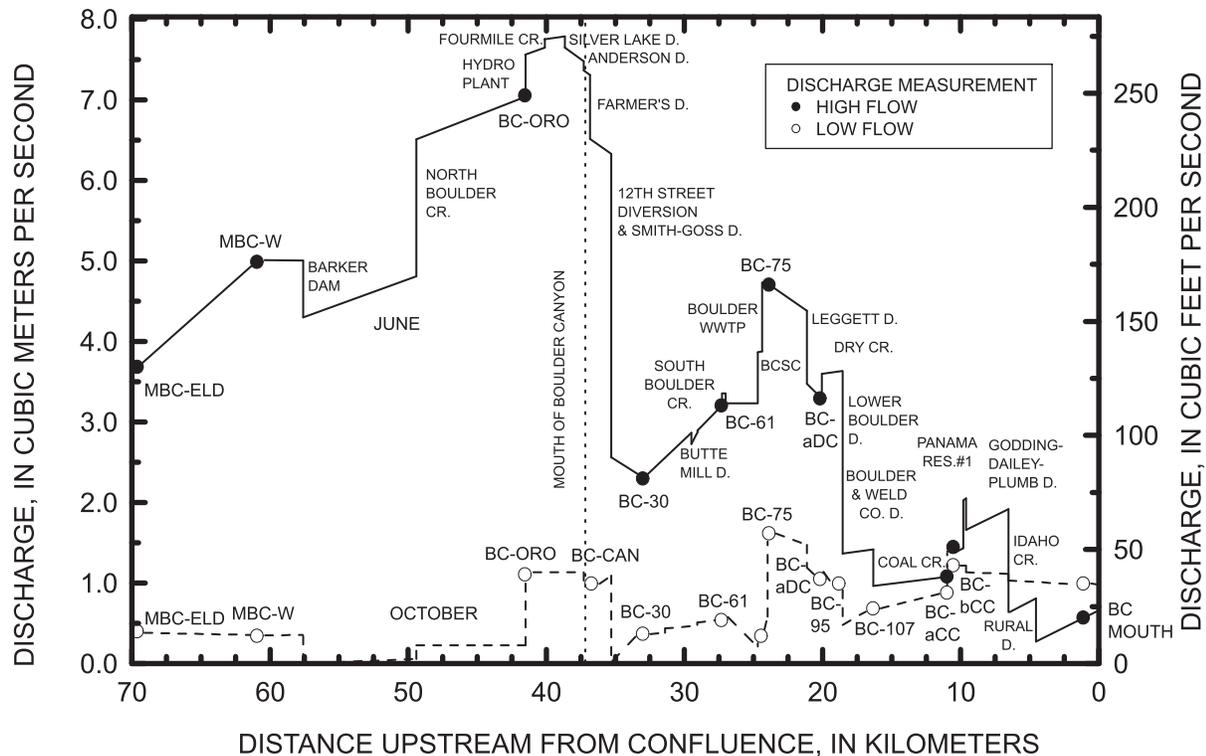


Figure 1.10. Estimated discharge along Middle Boulder Creek/Boulder Creek, June 12-13 and October 9-10, 2000. (Based on table 1.5; D., Ditch; Cr., Creek; WWTP, Wastewater Treatment Plant; BCSC, Boulder Creek Supply Canal)

creek. Boulder Creek regained about $1.8 \text{ m}^3/\text{s}$ ($62 \text{ ft}^3/\text{s}$) from South Boulder Creek, Fourmile Canyon Creek, the Boulder Creek Supply Canal, and Boulder 75th Street WWTP effluent, reaching a discharge of about $4.5 \text{ m}^3/\text{s}$ ($160 \text{ ft}^3/\text{s}$) at the 75th Street streamgage. From 75th Street to the mouth of Boulder Creek (a distance of approximately 25 km), a total of almost $5.9 \text{ m}^3/\text{s}$ ($210 \text{ ft}^3/\text{s}$) of water was diverted from the creek. The creek gained about $1.2 \text{ m}^3/\text{s}$ ($42 \text{ ft}^3/\text{s}$) from Dry Creek, Coal Creek, and Panama Reservoir #1, and some additional discharge from groundwater and agricultural returns. At the mouth of Boulder Creek, the discharge was $0.57 \text{ m}^3/\text{s}$ ($20 \text{ ft}^3/\text{s}$), less than 8 percent of the maximum discharge in Boulder Canyon.

In October 2000, discharge in most of Middle Boulder Creek and Boulder Creek was much lower than in June (fig. 1.10, table 1.5). The discharge was fairly constant from MBC-ELD to Barker Reservoir. Below Barker Dam,

Middle Boulder Creek was dry for some distance, regaining a small amount of water from groundwater and the leaking pipeline. North Boulder Creek contributed some discharge, but a majority of the discharge recorded at the Orodell streamgaging station was due to releases from the hydroelectric plant. Downstream of the Orodell streamgage, fewer diversions were removing less water from Boulder Creek in October than in June (table 1.4), but the diversions in operation still removed a large fraction of the discharge. The 12th Street Diversion removed $0.96 \text{ m}^3/\text{s}$ ($34 \text{ ft}^3/\text{s}$), leaving less than $0.14 \text{ m}^3/\text{s}$ ($5 \text{ ft}^3/\text{s}$) in Boulder Creek. While the creek gained discharge from tributaries and groundwater inflow, the most significant contributor of water in the lower basin in October was the Boulder 75th Street WWTP. Discharge in Boulder Creek reached its maximum value of $1.6 \text{ m}^3/\text{s}$ ($57 \text{ ft}^3/\text{s}$) at the 75th Street streamgage. Downstream of 75th Street, Boulder Creek lost about $0.93 \text{ m}^3/\text{s}$ ($33 \text{ ft}^3/\text{s}$) to diversions,

and gained about 0.37 m³/s (13 ft³/s) from Dry Creek and Coal Creek, with additional flow added by groundwater and agricultural returns. The discharge at the streamgage upstream of the mouth of Boulder Creek was 1.0 m³/s (35 ft³/s), roughly 90 percent of the discharge measured at the Orodell streamgaging station, and was higher in October than in June.

SUMMARY

The Boulder Creek Watershed is 1160 square kilometers in area and ranges in elevation from 1480 to 4120 meters above sea level. The upper and lower basins differ drastically in climate, geology, and land use. The upper basin consists primarily of metamorphic and granitic bedrock with alpine, subalpine, montane, and foothills climatic/ecological zones, with forest being the dominant land cover. The lower basin consists primarily of sedimentary bedrock with a plains climatic/ecological zone, with grassland, agricultural land, and urbanized land being the dominant land covers. The majority of the population lives in the lower basin.

Discharge varies annually and seasonally due to the snowmelt-dominated flow regime. Discharge also is affected by extensive water management. Boulder Creek gains water from wastewater effluent, transbasin diversions, and groundwater, and loses water to domestic, agricultural, and industrial diversions. Much of the diverted water is not returned immediately to the watershed, resulting in up to a 92 percent reduction in discharge from Boulder Canyon to the confluence with Saint Vrain Creek during high flow.

Variations in climate, geology, land cover, and hydrology affect water chemistry both spatially and temporally. Information presented in this chapter will assist in the evaluation of the effect of natural and anthropogenic factors on water quality of the Boulder Creek Watershed.

REFERENCES CITED

- Barber, L.B., Furlong, E.T., Keefe, S.H., Brown, G.K., and Cahill, J.D., 2003, Natural and contaminant organic compounds in the Boulder Creek Watershed, Colorado during high-flow and low-flow conditions, 2000– Chapter 5 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 103-144.
- Bilodeau, S.W., Van Buskirk, D., and Bilodeau, W.L., 1987, Geology of Boulder, Colorado, United States of America: Bulletin of the Association of Engineering Geologists, v. 24, no. 3, p. 289-332.
- Caine, Nel, 1989, Diurnal variations in the organic solute content of water draining from an alpine snowpatch: Catena, v. 16, p. 153-162.
- City of Boulder, 2001, Drinking water quality report no. 3: Boulder, Colo., Boulder Public Works Department, accessed May 10, 2002, at http://www.ci.boulder.co.us/publicworks/depts/utilities/water_quality/drinking/report01/index.htm
- _____, 2002a, Middle Boulder Creek water source management plan, Boulder, Colo., version 1: Boulder, Colo., Boulder Public Works Department, accessed May 10, 2002, at <http://www.ci.boulder.co.us/publicworks/depts/utilities/projects/barker-res/pdf/draftreport.pdf>
- _____, 2002b, Water and wastewater treatment– Boulder’s wastewater treatment plant: Boulder, Colo., Boulder Public Works Department, accessed May 10, 2002, at http://www.ci.boulder.co.us/publicworks/depts/utilities/water_treatment/plants/wastepant.htm
- Colorado Department of Local Affairs, 2002, Census 2000 Tiger GIS data: accessed June 13, 2002, at <http://www.dola.state.co.us/oem/cartography/Tiger2000.htm>
- Colorado Department of Transportation, 2002, Statistics and data: accessed May 10, 2002, at http://www.dot.state.co.us/app_dtd_dataaccess/index.cfm
- Colorado Water Conservation Board and Colorado Division of Water Resources, 2002, Colorado Decision Support Systems website, accessed August 30, 2002, at <http://cdss.state.co.us>
- Green, G.N., 1992, The digital geologic map of Colorado in ARC/INFO format: U.S. Geological Survey Open-File Report 92-0507, accessed May 10, 2002 at <http://geology.cr.usgs.gov/pub/open-file-reports/ofr-92-0507>
- Lovering, T.S., and Goddard, E.N., 1950, Geology and ore deposits of the Front Range, Colorado: U.S. Geological Survey Professional Paper 223, 319 p., 30 plates.

- Murphy, S.F., Shelley, J.J., Stout, J.A., and Mead, E.P., 2003, Basic water quality in the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000– Chapter 3 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 41-70.
- National Oceanic and Atmospheric Administration, 2002, National Oceanic and Atmospheric Administration Climate Diagnostics Center web page: accessed May 10, 2002, at <http://www.cdc.noaa.gov>
- National Weather Service, 2002, Advanced Weather Interactive Processing System (AWIPS) map database: accessed May 10, 2002, at <http://www.awips.noaa.gov/mapdata/newcat/>
- Niwot Ridge Long-Term Ecological Research Program, 2002, Niwot Ridge (Colorado) Long-Term Ecological Research web page: accessed June 10, 2002, at <http://culter.colorado.edu:1030/>
- Rodeck, H.G., ed., 1964, Natural history of the Boulder area: Boulder, Colo., University of Colorado Museum, leaflet no. 13, 100 p.
- Rantz, S.E., and others, 1982, Measurement and computation of streamflow: U.S. Geological Survey Water-Supply Paper 2175, 2 v., 631 p.
- Runnells, D.D., 1976, Boulder– A sight to behold– guidebook: Boulder, Colo., Estey Printing Co., 93 p.
- TetraTech, Inc., 1993, Boulder Creek, Colorado– TMDL Case Study: Denver, Colo., U.S. Environmental Protection Agency, Office of Water, EPA number EPA/841/F-93/006, no. 8, 8 p., accessed May 10, 2002, at <http://www.epa.gov/OWOW/TMDL/cs8/cs8.htm>
- Tweto, O.L., 1979, Geologic Map of Colorado: U.S. Geological Survey, Special Geologic Map.
- U.S. Census Bureau, 2001, Census 2000 Summary File 1: accessed May 10, 2002, at <http://www.census.gov/>
- U.S. Department of Agriculture, 1999, 1997 Census of Agriculture– Colorado: U.S. Department of Agriculture, National Agricultural Statistics Service, accessed March 28, 2003 at <http://www.nass.usda.gov/co/>
- U.S. Department of Agriculture Forest Service, 2002, Roadless area conservation– GIS coverages: U.S. Department of Agriculture Forest Service, Geospatial Service and Technology Center, accessed May 14, 2002 at <http://roadless.fs.fed.us/documents/feis/data/gis/coverages/>
- U.S. Environmental Protection Agency, 2003, Permit Compliance System database: accessed April 15, 2003, at <http://www.epa.gov/enviro/html/pcs/index.html>
- U.S. Geological Survey, 2002a, National hydrography dataset: accessed May 10, 2002, at <http://nhd.usgs.gov/>
- _____, 2002b, Water resources of the United States web site: accessed May 10, 2002, at <http://water.usgs.gov/>
- _____, 2003, National land cover data set, accessed January 22, 2003, at <http://landcover.usgs.gov/natl/landcover.html>
- Verplanck, P.L., McCleskey, R.B., and Roth, D.A., 2003, Inorganic water chemistry of the Boulder Creek watershed, Colorado, during high-flow and low-flow conditions, 2000– Chapter 4 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 71-102.
- WBLA Inc., 1988, City of Boulder raw water master plan: Boulder, Colo., prepared for the City of Boulder, Colo.
- Weber, W.A., 1995, Checklist of vascular plants of Boulder County, Colorado: Boulder, Colo., University of Colorado Museum, Natural history inventory of Colorado series, no. 16, p. 1-66.
- Worcester, P.G., 1960, A guide to the geology of the Boulder region, Boulder, Colorado: Boulder, Colo., Boulder Chamber of Commerce, 16 p.

Chapter 2 - Delineation and Characterization of the Boulder Creek Watershed and its Sub-Watersheds

By David A. Kinner

Abstract

The 1160-km² Boulder Creek Watershed was delineated from Digital Elevation Model data using automated techniques. The resulting watershed boundary compares favorably to previous watershed maps and contributing areas estimated for U.S. Geological Survey streamgaging stations. The automation of watershed delineation allows for easy replication.

The Boulder Creek Watershed was divided into eight sub-watersheds for a more detailed accounting of the watershed's topography, land cover, soils, and precipitation. The four steeper mountain sub-watersheds are primarily forested with shallow soils, while the four foothill/plains sub-watersheds have grassland, urban, and agricultural land cover with deeper soils. Topography, as measured by mean slope and topographic index, $\ln(a/\tan\beta)$, is more highly variable among foothills/plains sub-watersheds than among mountain sub-watersheds. Estimated precipitation varies from over 1000 mm near the Continental Divide to 330 mm near the watershed outlet.

INTRODUCTION

Purpose and Scope

In this chapter, the Boulder Creek Watershed is delineated from the surrounding landscape using a digital extraction method. This watershed delineation is fundamental in distinguishing between areas that contribute solutes and water to Boulder Creek and those that contribute constituents to neighboring drainages. Consequently, watershed boundaries are critical in understanding the development of water chemistry. Fundamental watershed properties

such as basin area and relief are defined for Boulder Creek and each of its major tributaries.

The watershed boundaries are also used to characterize the topographic, soil, land cover, and precipitation for each Boulder Creek sub-watershed. These data can be used to interpret the chemical effects of non-point sources. They also could guide future sampling or experimental design by defining topographic, soil, and land use end-members.

Basics of Automated Watershed Delineation

Delineation of the Boulder Creek Watershed was completed with the computer program RiverToolsTM (Peckham, 1998; Rivix Limited Liability Co., 2001). The use of an automated method and readily-available topographic data allows the procedure to be easily replicated. RiverToolsTM uses Digital Elevation Model (DEM) data to predict water flow paths and determine the location of drainage basin boundaries. Digital Elevation Models are gridded representations of the earth's surface with each grid cell assigned an elevation, and have the advantage of being continuous, regular surfaces, so quantities like surface slope and aspect can be readily calculated. Digital Elevation Models are available at several scales; the DEM of the Boulder area displayed in figure 2.1 is a 1:24,000 scale grid with 900-m² cells. This is the finest resolution that is publicly available for both the Boulder Creek Watershed and the entire United States.

With a tunnel and canal transporting water into the Boulder Creek Watershed, the actual watershed contributing area extends beyond the topographic boundaries demarcated here. Defining the actual watershed would involve

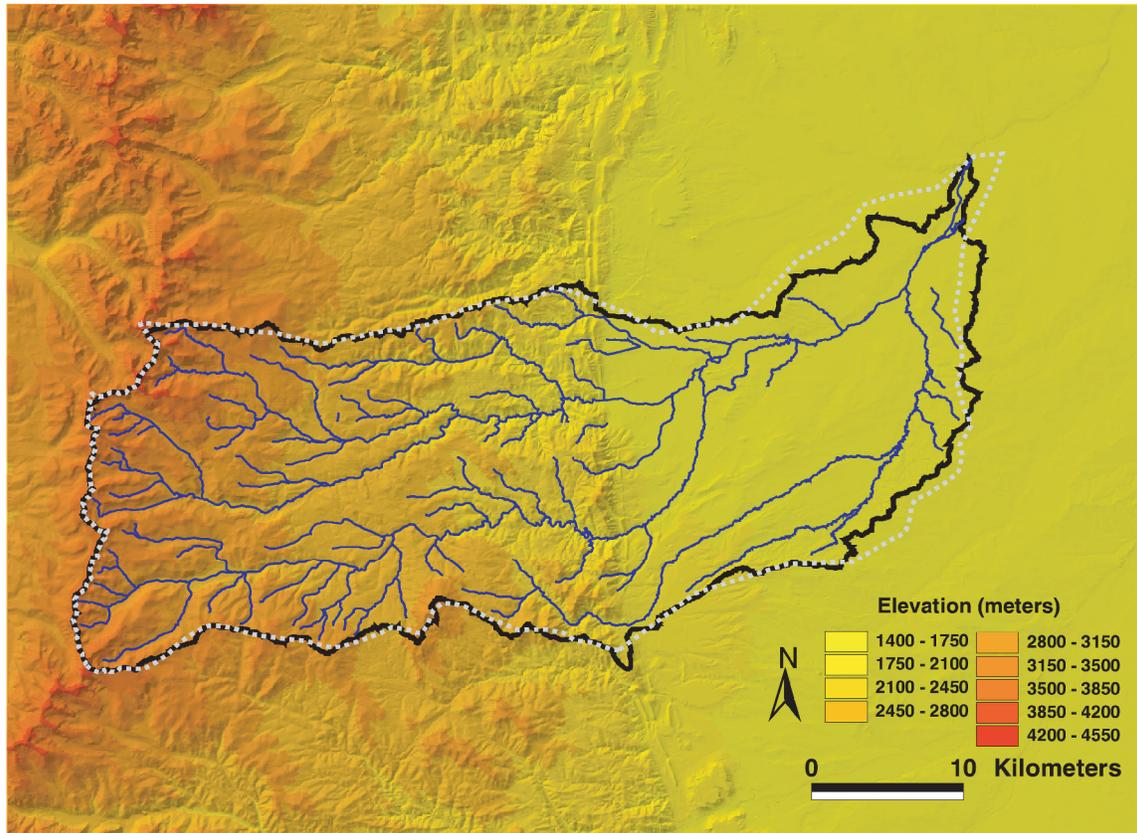


Figure 2.1. Digital elevation model of the Boulder Creek Watershed and surrounding area. (Watershed boundary determined by this study is shown by solid black line; boundary given by the Colorado Division of Water Resources, 2002, is shown by white dashed line; surface waters from U.S. Geological Survey, 2002)

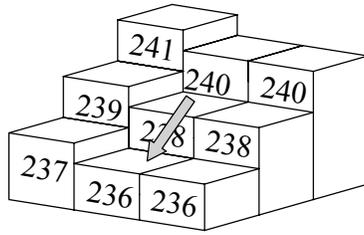
defining the contributing areas for the imported waters and is beyond the scope of this study. This analysis is restricted to the natural topographic boundary of the watershed.

Defining watershed boundaries strictly by topography has disadvantages. Because the boundaries are based on the surficial expression of the landscape, groundwater flow paths or drainage ditches that are inconsistent with topography may be misrepresented. Further, in areas where topography is subtle, it may be difficult to calculate the direction of flow because of limited resolution in the DEM. The method of topographic extraction used in RiverTools™ is most accurate in areas where the DEM properly resolves the topographic gradient, basically in regions where topography is steep.

The key assumption in using DEM data to extract the watershed boundary is that water falling as precipitation flows downhill, along the topographic gradient. The flow direction algorithm employed here checks the eight surrounding cells for the steepest slope between cell centers. As the flow direction is into only one of the surrounding cells, this algorithm is known as the single-direction or D-8 algorithm (Jenson and Domingue, 1988). Because of its simplicity and effectiveness, the D-8 algorithm is applied in most DEM analysis software packages.

Figure 2.2 shows how the D-8 algorithm works. The block diagram on the left of the figure shows the relative elevations of a theoretical nine-cell DEM neighborhood. The plan-view to the right shows the calculated slopes from the center cells, assuming that each DEM cell has an area of

A



B

2.1	2.0	1.4
1.0	↓	0.0
-0.7	-2.0	-1.4

Figure 2.2. Diagram showing the principle behind the single-direction or D-8 flow algorithm of Jenson and Domingue (1988): (A) Theoretical eight-cell neighborhood (numbers indicate elevation of cell); (B) Computed slopes between center cell and each of the surrounding eight cells. Water follows the largest negative (downhill) slope to the south.

1 m². As the highest negative (downhill) slope is in the south direction, water “flows” south.

The D-8 algorithm (fig. 2.2) assumes that there are elevation differences between adjacent cells. However, DEMs typically have flat regions (known as flats) where a neighborhood of cells has the identical elevation. For these situations, the imposed gradient method of Garbrecht and Martz (1997) was used. This method builds up artificial topography over flats that direct flow away from surrounding higher topography to the lowest cell adjacent to the flat region. The imposed gradient method tends to create a single channel centered in broad flat valleys. This algorithm has been implemented and improved upon in RiverTools™ as the flat resolution method called “imposed gradient plus” (Rivix Limited Liability Co., 2001).

After the flow direction is defined for every cell in a DEM, the watershed outlet is selected. For Boulder Creek, this point has been defined as the confluence of Saint Vrain Creek and Boulder Creek. RiverTools™ then determines all of the cells that “flow” into the outlet cell. This routine is continued recursively until all of the cells in a watershed have been identified. The watershed boundary is then defined as the interface between cells that are included in the watershed and adjacent cells that are not.

Characterization of Morphologic Parameters

Given a watershed boundary, a wide range of basin variables can be defined from topography. In the present case, three parameters of interest are slope, aspect, and the topographic index, $\ln(a/\tan\beta)$ (Beven and Kirkby, 1979; Wolock, 1993; Quinn and others, 1995).

The concept of $\ln(a/\tan\beta)$ is illustrated in figure 2.3, which it adapted from Wolock (1993). A represents the upslope area that contributes water to the calculation point. The calculation point is a specific grid cell. The contributing area, A , (in units of length²) is divided by the grid cell contour length, c , to get a normalized area, a , which has units of length. For $\ln(a/\tan\beta)$ calculations using the D-8 algorithm, c can have one of two values. If water flows to a cell that is in a cardinal direction (north, south, east, or west), then the contour length is the length of the grid cell, or in the case of 900-m² cells, 30 m. If water flows diagonally, then the contour length is the length of the grid cell multiplied by the square root of two. This contour-length convention allows for topographic convergence due to diagonal flow to be represented in the index. $\tan\beta$ represents the local slope gradient. For a complete derivation of the $\ln(a/\tan\beta)$ index the reader is referred to Beven and Kirkby (1979) and Wolock (1993).

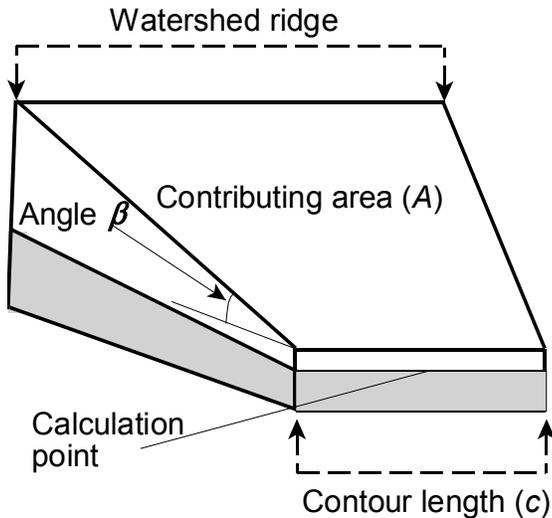


Figure 2.3. Diagram illustrating the concept of $\ln(a/\tan\beta)$, after Wolock (1993).

As the distance from a ridgeline increases, the source area increases in size, and there is more groundwater flowing through a given grid cell. If the slope is large, then water in the subsurface moves more rapidly. Conversely, areas that have a low slope serve as areas where flow is limited. If these two concepts are enjoined, the landscape is partitioned between areas near ridges with high gradients and low contributing areas (low $\ln(a/\tan\beta)$ regions) and areas in valleys with low gradients and high contributing areas (high $\ln(a/\tan\beta)$ regions). Given similar soil types throughout the landscape, high $\ln(a/\tan\beta)$ cells are likely to be inundated because there is a large volume of water moving through them at low velocities. Conversely, areas near ridges are often dry.

The topographic index is a relative measure of the proximity of the water table to the surface and has been used to predict the relative interaction of water with the shallow nutrient and mineral soil (Robson and others, 1992). The acid neutralizing capacity of watersheds also has been positively correlated with the mean value of $\ln(a/\tan\beta)$ in watersheds in the northeast United States (Wolock and others, 1989, 1990).

Other characteristics that may be important to chemical analysis include stream network

properties such as drainage density, stream length, and stream order. Automatically defining these properties over an entire river basin requires channel DEM cells to be distinguished from other DEM cells in the watershed. One method for differentiating stream channels is to define a minimum contributing area for channel formation, and all cells with contributing areas greater than that threshold are labeled “stream” cells. In Boulder Creek, there is such diversity in lithology, climate, and soils that there are likely different thresholds for different regions of the watershed. Because the scope of this characterization is limited, there was no attempt to define channel network thresholds or examine stream network properties. Mapped channels from the 1:24,000 topographic maps and part of the U.S. Geological Survey (USGS) National Hydrography Dataset (USGS, 2002) are included in figure 2.1 for the reader’s benefit. These mapped channels represent larger perennial streams. Smaller-scale, ephemeral channels are often omitted from the mapped network.

Extracting Environmental Parameters

Three additional data sources were used to establish environmental conditions throughout the basin. For characterizing soil type, the States Geographic Soil Database (STATSGO) was queried. The STATSGO database is a digital summary of all of the U.S. Department of Agriculture (USDA) field soil surveys aggregated into soil association units. The STATSGO attributes that were queried are organic matter, calcium carbonate, and soil pH. A description of how to develop soil attribute maps from the STATSGO database is included in USDA (1994) and Bliss and Reybold (1989).

The second data source is the National Land Cover Data Set (NLCD; Vogelmann and others, 2001). This work summarizes the land use characterized by the LANDSAT satellite imagery. Land cover classes are defined by examining both winter (leaves-off) and summer

(leaves-on) images. For Boulder County, the data set is based on satellite images over the period 1989-1994. These data provide a detailed (900-m² grid cell) analysis of land cover. Much of the basin, particularly the mountain regions, has similar land cover today to what is recorded in the NLCD. However, rampant growth and development east of the mountains make the data set less applicable in these areas.

The third data source is the PRISM (Parameter-elevation Regressions Independent Slopes Model) mean annual precipitation dataset that has been produced by the Oregon State Climate Center (Daly and others, 1994). This unique dataset interpolates between individual rain gages to create a gridded map of precipitation for the United States. One focus of PRISM is the estimation of rainfall variation in mountainous or hilly areas. This is achieved by using linear regression to interpolate between gages at different mountain elevations. These interpolations are done locally, so, for example, rainfall on the leeward and windward sides of a mountain range is distinguished.

These three data sets do not represent the only available data that could be used for analysis. Given a watershed boundary, other datasets produced by the USGS or other agencies or individuals could be queried and utilized to interpret chemical data. These datasets could include current and future land cover or higher-resolution soil coverages.

METHODS

The first step in this analysis was to piece together the requisite DEMs to delineate the Boulder Creek Watershed. To make sure the Boulder Creek Watershed could be fully defined, twenty 7.5-minute, 30-m cell DEMs were joined (table 2.1). DEMs were read into the Geographic Information System (GIS) Arc-InfoTM and merged. The key Arc-Info commands for joining the DEMs were “Merge” which joins the DEMs and “Nibble” which fills in gaps between the

Table 2.1. List of digital elevation models used in deriving figure 2.1

Quadrangles completely or partially in Boulder Creek Watershed	
Boulder	Longmont
Black Hawk	Louisville
Central City	Monarch Lake
East Portal	Nederland
Eldorado Springs	Niwot
Empire	Ralston Buttes
Erie	Tungsten
Gold Hill	Ward
Lafayette	
Additional quadrangles included in figure 2.1	
Allenspark	Gowanda
Arvada	Hygiene
Commerce City	Isolation Peak
Eastlake	Lyons
Golden	Raymond

joined grids. Gaps between adjacent DEMs are fairly common at the 7.5-minute resolution. Nibble uses linear interpolation to fill in topography between joined DEM sheets.

The aggregate DEM was imported as a binary grid into RiverToolsTM for basin delineation. RiverToolsTM was selected because it offers several algorithms for flow direction calculation. After the flow directions were defined, the basin outlet was chosen at the confluence of Boulder Creek and Saint Vrain Creek and the automated watershed delineation tool was applied. Aspect, slope and $\ln(a/\tan\beta)$ were also computed using RiverToolsTM. The basin boundary was exported to Arc-InfoTM to “clip” the soil, land cover, and precipitation grids. After the polygons representing the soils were truncated at the basin boundary, derivative maps were created.

To examine variability in watershed characteristics, nine sub-watersheds were delineated (fig. 2.4, table 2.2): South Boulder Creek above Gross Reservoir; Middle Boulder Creek; North Boulder Creek; Fourmile Creek; South Boulder Creek below and including Gross Reservoir; Boulder Creek between the North and Middle Boulder Creek confluence and Coal Creek; Coal Creek; Rock Creek; and Boulder

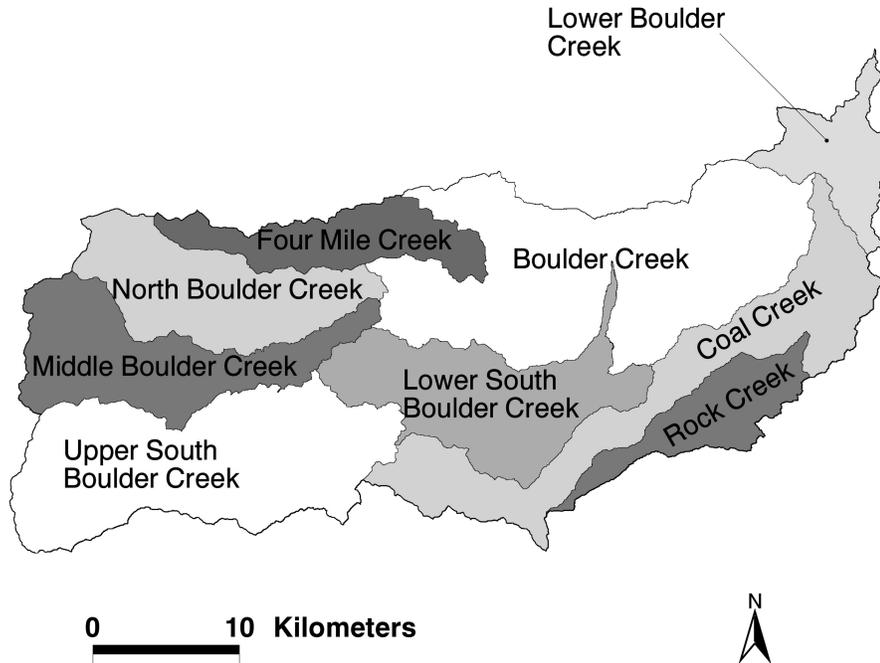


Figure 2.4. Map of sub-watersheds in the Boulder Creek Watershed.

Creek from its confluence with Coal Creek to the watershed outlet. The first four sub-watersheds listed are primarily mountain watersheds; the last five are foothills/plains watersheds. Because South Boulder Creek includes both mountain and plains areas, the watershed was divided to examine the differences between these two physiographic regions. All topographic and environmental data were clipped to these boundaries to determine the properties of different regions within the Boulder Creek Watershed.

RESULTS AND DISCUSSION

Basin Area and Relief

The Boulder Creek Watershed has a computed area of 1160 km² (447 mi²) if the outlet point is defined at the confluence of Boulder Creek and Saint Vrain Creek (fig. 2.1). The watershed relief as measured from the highest point to the basin outlet is 2275 m. Thus, as one might expect with a mountain river basin, there is

a dramatic change of relief over a relatively short river distance.

Validation of the RiverToolsTM-derived watershed boundary is difficult because there is no definitive map of the Boulder Creek Watershed boundary. One indication that the map is relatively accurate is that the stream network from the National Hydrography Dataset shown in figure 2.1 does not cross any derived watershed boundaries. The derived boundary does appear similar to other boundaries displayed in earlier reports (Muller Engineering Company, 1983; Naropa Institute, 1996) and is similar to the boundary of Boulder Creek Basin (Water Division 1, District 6) given by the Colorado Division of Water Resources (2002), shown as a white dashed line in figure 2.1. The Water District 6 boundary was originally mapped at a scale of 1:2,000,000, and has a watershed area of 1190.4 km². The fact that the two boundaries were mapped at different scales likely accounts for the disparity in the boundary shape near the watershed outlet. Because topography is subtle near the outlet on the eastern boundary, errors are

Table 2.2. List of characteristics for sub-watersheds of the Boulder Creek Watershed

[km², square kilometers; km, kilometers; mm, millimeters; kg, kilograms; standard deviations are in parentheses; Confl., confluence; N., North; Cr., Creek; M., Middle; S., South; organic matter from U.S. Department of Agriculture, 1994]

Sub-watershed	Watershed	outlet	Drainage area (km ²)	Relief (km)	Mean elevation (km)	Precipitation (mm)	Mean slope (degrees)	Mean ln(a/tan)	Percent north-facing aspect	Organic matter (kg)
Boulder Cr. (entire)	Basin outlet		1160	2.63	2.29 (0.63)	526.2 (153.0)	11.1 (10.0)	7.1 (2.3)	56.1	15.4 (1.4)
Fourmile Cr.	Confl. with Boulder Cr.		68	1.81	2.49 (0.39)	533.0 (116.3)	17.9 (8.7)	6.1 (1.9)	39.6	14.9 (1.3)
N. Boulder Cr.	Confl. with M. Boulder Cr.		112	1.99	2.99 (0.40)	682.5 (174.6)	15.2 (9.5)	6.5 (1.9)	44.8	13.8 (1.2)
M. Boulder Cr.	Confl. with N. Boulder Cr.		115	1.93	3.04 (0.39)	697.8 (152.8)	16.8 (9.6)	6.4 (1.9)	48.4	13.8 (1.3)
S. Boulder Cr.	Confl. with Boulder Cr.		338	2.47	2.62 (0.48)	582.9 (120.8)	14.2 (9.1)	6.5 (2.1)	57.0	15.0 (1.3)
Lower S. Boulder Cr.	Confl. with Boulder Cr.		130	0.64	2.15 (0.30)	494.0 (356.7)	13.9 (10.3)	6.6 (2.3)	55.7	16.1 (0.3)
Upper S. Boulder Cr.	Inlet of Gross Reservoir		208	1.83	2.92 (0.30)	637.9 (122.8)	14.4 (8.3)	6.5 (1.9)	57.9	14.3 (1.2)
Coal Cr. (entire)	Confl. with Boulder Cr.		208	1.69	1.83 (0.36)	419.5 (71.8)	6.3 (7.8)	7.8 (2.3)	60.0	16.4 (0.4)
Coal Cr. (except Rock Cr.)	Confl. with Boulder Cr.		151	1.69	1.89 (0.40)	431.8 (79.7)	7.3 (8.8)	7.6 (2.4)	57.7	16.3 (0.4)
Rock Cr.	Confl. with Coal Cr.		57	0.56	1.69 (0.09)	387.0 (236.4)	3.7 (3.4)	8.2 (2.3)	65.1	16.6 (0.1)
Lower Boulder Cr.	Basin outlet		320	1.24	1.72 (0.02)	423.5 (54.7)	6.7 (9.3)	8.0 (2.5)	64.3	16.5 (0.2)
Lower Boulder Cr. above Coal Cr.	Confl. with Coal Cr.		269	1.20	1.76 (0.25)	437.8 (47.8)	7.6 (9.8)	7.7 (2.5)	63.6	16.4 (0.2)
Lower Boulder Cr. below Coal Cr.	Basin outlet		51	0.14	1.52 (0.20)	348.1 (4.9)	1.2 (1.1)	9.0 (1.9)	67.9	16.6 (0.1)

Table 2.3. Contributing areas calculated by this study and reported by the U.S. Geological Survey (USGS) for streamgaging stations (USGS, 2002)

[ID#, identification number; km², square kilometers; percent difference is expressed as (Area_{study}-Area_{USGS})/Area_{study}.]

Streamgaging station (station ID#)	Area- this study (km ²)	Area- USGS reported (km ²)	Percent difference
Boulder Creek at mouth near Longmont, CO (06730500)	1160	1137	2.0
Boulder Creek at N 75 th St NR Boulder, CO (06730200)	799	787	1.5
South Boulder Creek near Eldorado Springs, CO (06729500)	288	282	2.0
Boulder Creek at Orodell, CO (06727000)	260	264	-1.5
South Boulder Creek at Pinecliffe, CO (06729300)	193	188	2.6
South Boulder Creek near Rollinsville, CO (06729000)	113	111	1.8
Middle Boulder Creek at Nederland, CO (06725500)	95	94	1.1
Coal Creek near Louisville, CO (06730400)	84	71	15
Fourmile Creek at Orodell, CO (06727500)	67	62	7.5
Coal Creek near Plainview, CO (06730300)	39	39	0
North Boulder Creek at Silver Lake, CO (06726000)	23	23	0

possible in this region; this area might merit further analysis.

A second method for validating the method is comparing RiverToolsTM-derived area estimates to the contributing areas reported for USGS streamgaging stations. The USGS calculated contributing areas by measuring the areas directly from river basin maps of Colorado (Crowfoot and others, 2000). To compare the RiverToolsTM-derived areas with these values, we used coordinates provided by the USGS (USGS, 2002) to locate streamgaging station locations on the Boulder Creek Watershed DEM. The streamgage locations did not always lie exactly on the DEM-derived streams. In that case, the nearest stream point was selected as the streamgage location.

A comparison of derived and reported contributing areas for streamgaging stations is given in table 2.3. Most of the errors are below 3 percent, but two locations, Fourmile Creek at Orodell and Coal Creek at Louisville, have larger errors (7.5 and 15 percent, respectively). To examine whether our method or the USGS historical method was responsible for the discrepancy, we examined topographic maps of the watersheds. It appears that that the boundaries of these two watersheds derived from the DEM follow ridges on 1:24,000 topographic maps, indicating that the DEM-derived estimates are reliable.

The comparison between areas derived by DEM analysis and through other methods provides some verification of the DEM analysis algorithms. However, errors in the DEM-derived estimates are not necessarily due to algorithm choice but could be due to DEM construction. Mixon (2002) identified two types of DEM errors in the 1:24,000 DEMs, which he labeled “granularity” and “seams.” Seams are created when adjacent DEMs are joined and there are vertical discontinuities at the boundaries between the two DEMs. Granularity occurs when visible, east-west bands occur in the DEM data. Both types of errors occur in the DEM shown in figure 2.1. They do not appear to affect the position of the watershed boundary, but these errors may cause subtle differences in watershed delineation.

Variability in Topographic Parameters

Slope decreases markedly with the transition from mountains to plains. This decrease in slope is manifested as an increase in $\ln(a/\tan\beta)$. The lower-elevation sub-watersheds have larger variability in $\ln(a/\tan\beta)$ (table 2.2). This occurs because the lower sub-watersheds, with the exception of Rock Creek, straddle topographically distinct foothills and plains. These sub-watersheds have terrace features (for

example, Table Mesa and Rocky Flats) which are extremely flat but have steep slopes at their boundaries.

Another important observation can be made by comparing the mean and standard deviations of $\ln(a/\tan\beta)$ for three mountain sub-watersheds: North Boulder Creek, South Boulder Creek above Gross Reservoir, and Middle Boulder Creek. The mean value is approximately 6.5 m with a standard deviation of approximately 1.9 m. As $\ln(a/\tan\beta)$ is a good measure of the landscape structure (Woods and Sivapalan, 1997), this correlation indicates that the topography in these three sub-watersheds is remarkably similar.

There is variability in the percentage of north-facing (slopes with an aspect of 270 to 90 degrees) and south-facing slopes in the various sub-watersheds in the Boulder Creek Watershed. Generally, sub-watersheds in the south are bending north and therefore have up to 65 percent north-facing slopes. Sub-watersheds in the north are bending slightly south and therefore have less than 50 percent north-facing slopes. These differences in aspect may affect the soil moisture status of the sub-watersheds, as north-facing slopes tend to remain moister because they receive less solar radiation. Aspect also influences the local composition of the vegetation community.

Variability in Land Cover, Soil Chemistry and Mean Precipitation

Land cover varies with topography (table 2.4, fig. 2.5a). The land cover of the mountain sub-watersheds typically consists of ice, evergreen forests, and shrubs (vegetation below 1.8 m feet tall). Foothills/plains sub-watersheds have a high percentage of grasslands. Superimposed on the natural grassland vegetation are the anthropogenic land covers: agriculture and urban development. Due to rapid urban development, especially on Rock Creek, anthropogenic land uses in the lower-elevation sub-watersheds may already be outdated from when it was mapped in the early 1990s. An updated land cover

characterization, which is imminent, will likely show the differences in land cover between the early 1990s and the present.

A map of soil organic matter (fig. 2.5b) indicates that there is higher soil organic matter associated with the grassland and agricultural ecosystems of the plains than the mountain ecosystems. Total organic matter has been calculated by examining 1-m wide, 1-m long columns of soil with variable depths. The organic matter mass is calculated for each soil horizon and then summed over the entire soil column (table 2.2). Much of the difference in organic matter inventories on the plains is due to deeper soils in this area.

Additional soil attributes (soil pH and calcium carbonate content) were queried in STATSGO, but showed little variability within the Boulder Creek Watershed and therefore are not reported. This lack of variability is not consistent with field observations of soil profile chemistry in the watershed, which shows considerable variability in pH and calcium carbonate content along an altitudinal gradient (P.M. Birkeland, University of Colorado, written commun., 2002). Therefore, STATSGO data may not provide an accurate picture of soil chemistry for the watershed. A finer-scale soil map might contribute to a greater understanding of this variability. Digital county-level soil maps are currently only available for the region of the Boulder Creek Watershed east of the foothills.

Using the PRISM dataset, the elevation-weighted mean annual precipitation in the Boulder Creek watershed is 526 mm/yr (20.7 in/yr). There is tremendous variability within individual sub-watersheds and also among the various sub-watersheds (table 2.2, fig. 2.6). Mean precipitation in sub-watersheds that border the Continental Divide (North, South and Middle Boulder Creeks) exceeds 600 mm/yr. Foothills and plains sub-watersheds generally have mean precipitation values below 450 mm/yr.

Table 2.4. Land cover in the Boulder Creek Watershed and sub-watersheds

[Data from Vogelmann and others (2001) for period 1989 to 1994; km², square kilometers; water, exposed surface of water, reservoirs and wide streams; ice, perennial ice or snow; developed, high- and low-intensity residential (30-100 percent construction) and urban area; grass, herbaceous grasslands; deciduous, over 75 percent deciduous plants; evergreen, over 75 percent evergreen plants; shrub, 25-100 percent of cover less than 1.8 m tall; agriculture, includes pasture, row crop, small grain crops and fallow land; barren, rock outcrop or quarried land; Cr., Creek; N., North; M., Middle, S. South]

Stream	Area (km ²)	Percent									
		water	ice	developed	grass	deciduous	evergreen	shrub	agriculture	barren	
Boulder Cr. (entire)	1160	1.9	1.5	6.5	18.4	7.3	36.5	12.4	15.5	0.0	
Fourmile Cr.	68	0.2	0.1	0.4	2.1	7.7	65.1	24.3	0.1	0.0	
N. Boulder Cr.	112	1.1	5.8	0.7	8.3	12.7	45.0	26.3	0.0	0.1	
M. Boulder Cr.	115	1.1	7.2	1.0	8.2	15.0	41.1	26.3	0.0	0.1	
S. Boulder Cr.	338	1.6	1.2	1.0	11.3	11.0	57.7	15.2	1.0	0.0	
Lower S. Boulder Cr.	130	3.1	0.0	1.7	22.4	7.8	47.4	14.9	2.7	0.0	
Upper S. Boulder Cr.	208	0.7	2.0	0.4	4.3	13.0	64.2	15.4	0.0	0.0	
Coal Cr. (entire)	208	0.9	0.0	10.2	41.6	3.3	13.4	2.3	28.3	0.0	
Coal Cr. (except Rock Cr.)	151	0.9	0.0	11.8	35.6	4.5	18.4	3.1	25.7	0.0	
Rock Cr.	57	0.9	0.0	5.7	57.8	0.0	0.0	0.1	35.5	0.0	
Lower Boulder Cr.	320	3.9	0.0	14.0	21.8	2.1	17.4	3.5	37.3	0.0	
Lower Boulder Cr. above Coal Cr.	269	3.6	0.0	16.4	22.4	2.5	20.7	4.2	30.2	0.0	
Lower Boulder Cr. below Coal Cr.	51	5.5	0.0	1.5	18.3	0.0	0.0	0.0	74.7	0.0	

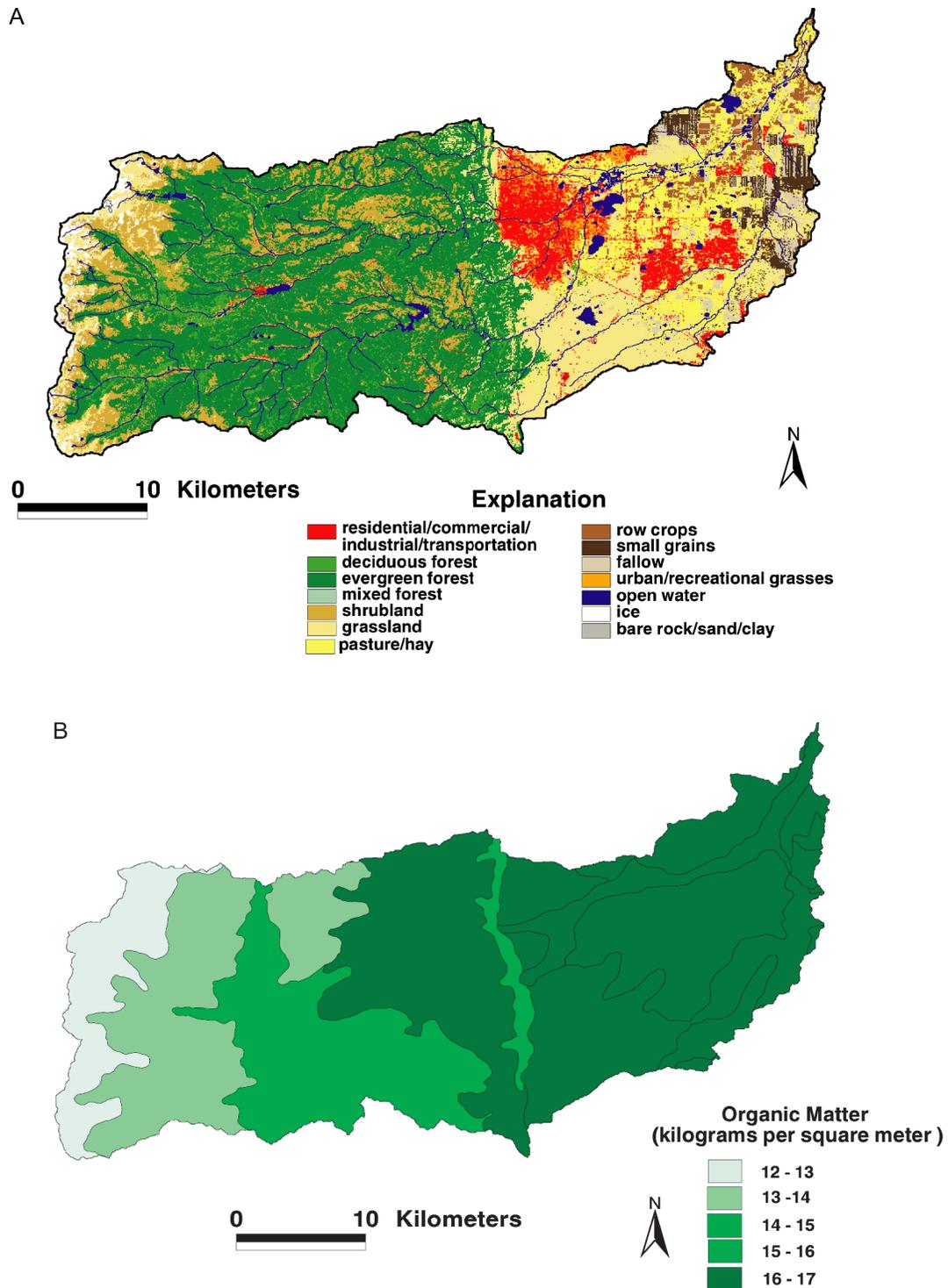


Figure 2.5. Maps showing (A) land cover (using National Land Cover Data Set of Vogelmann and others, 2001) and (B) soil organic matter (using STATSGO database of U.S. Department of Agriculture, 1994) in the Boulder Creek Watershed.

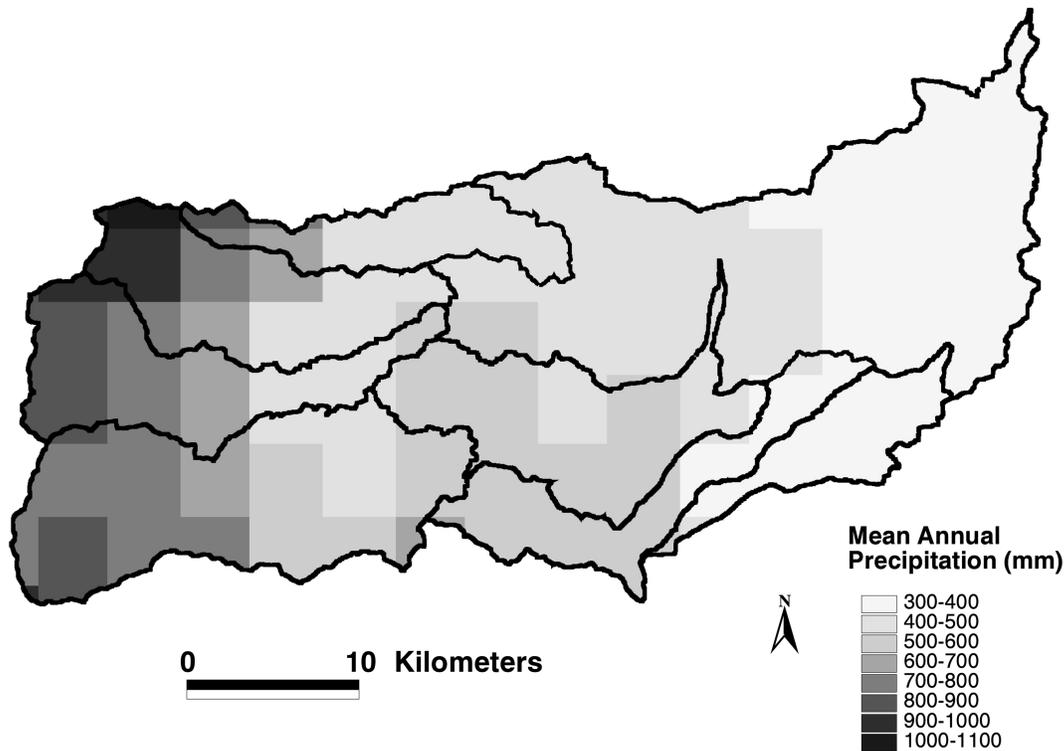


Figure 2.6. Map of precipitation in the Boulder Creek Watershed derived from the PRISM precipitation dataset (Daly and others, 1994).

SUMMARY

This work delineates and synthesizes landscape properties for the 1160-km² Boulder Creek Watershed. The boundary was computed with an automated procedure using digital data and represents an estimate of the watershed boundary determined with the best available Digital Elevation Model (DEM)-analysis algorithms. When the DEM-derived watershed areas are compared with USGS-reported contributing areas for streamgaging stations, most agreed within 3 percent error. The sub-watersheds with the largest discrepancies, Fourmile Creek and Coal Creek, appear to be correctly delineated on a topographic map. The location of the Boulder Creek Watershed boundary may change in flat regions near the Boulder Creek and Saint Vrain Creek confluence with the development of better flat-resolution algorithms or finer-resolution DEM data.

Not surprisingly, the variables identified—topography, land cover, soils and precipitation—are not independent, but can be easily grouped into environmental-physiographic regions. From the sub-watershed analysis, there are clear topographic and land cover differences between mountain and foothills/plains sub-watersheds.

This work is only the first step in providing a Geographic Information System (GIS) framework for studying chemical variability in Boulder Creek. The environmental data sets described here were used for illustrative purposes, and this comparison was not exhaustive. A GIS framework, like the one exhibited here, provides an efficient method for integrating diverse data sources into a single framework. Finer resolution soil and updated land cover data may be necessary to aid in the interpretation of variability.

REFERENCES CITED

- Beven, K.J. and Kirkby, M.J., 1979, A physically-based variable contributing area model of basin hydrology: *Hydrological Sciences Bulletin*, v. 24, no. 1, p. 43-69.
- Bliss, N. B. and Reybold, W.U., 1989, Small-scale digital soil maps for interpreting national resources: *Journal of Soil and Water Conservation*, v. 44, p. 30-34.
- Colorado Division of Water Resources, 2002, GIS information for the Office of the State Engineer: Denver, Colo., Colorado Division of Water Resources, accessed May 18, 2002 at <http://water.state.co.us/pubs/gis.asp>
- Crowfoot, R.M., Unruh, J.W., Steger, R.D., and O'Neill, G.B., 2000, Water resources data, Colorado, water year 2000— Volume 1. Missouri River Basin, Arkansas River Basin, and Rio Grande River Basin, U.S. Geological Survey, Water-Data Report, CO-00-1, 498 p., 2 figs.
- Daly, C., Neilson, R.P., and Phillips D.L., 1994, A statistical-topographic model for mapping climatological precipitation over mountainous terrain: *Journal of Applied Meteorology*, v. 33, p. 140-158.
- Garbrecht, J. and Martz, L.W., 1997, The assignment of drainage directions over flat surfaces in raster digital elevation models: *Journal of Hydrology*, v. 193, p. 204-213.
- Jenson, S.K. and Domingue, J.O., 1988, Extracting topographic structure from digital elevation data for geographic information system analysis: *Photogrammetric Engineering and Remote Sensing*, v. 54, p. 1593-1600.
- Mixon, D.M., 2002, Automatic watershed location and characterization with GIS for an analysis of reservoir sedimentation patterns: Boulder, University of Colorado, Master's Thesis, 170 p., 23 figs.
- Muller Engineering Company, Inc., 1983, Flood hazard area delineation, Boulder Creek: Denver, Colo., Prepared for City of Boulder, Urban Drainage and Flood Control District, 65 p.
- Naropa Institute, 1996, The many voices of the Boulder Creek Watershed: Boulder, Colo., Naropa Institute, 35 p.
- Peckham, S.D., 1998, Efficient extraction of river networks and hydrologic measurements from digital elevation data, in Barndorff-Nielsen, O.E., Gupta, V.K., Perez-Abreu, V., and Waymire, E., eds., *Stochastic Methods in Hydrology— Rain, Landforms and Floods*: Singapore, Advanced series on statistical science and applied probability, World Scientific, p. 173-203.
- Quinn, P.F., Beven, K.J., and Lamb, R., 1995, The $\ln(A/\tan\beta)$ index— How to calculate it and how to use it within the TOPMODEL framework: *Hydrological Processes*, v. 9, p. 161-182.
- Rivix Limited Liability Company, 2001, RiverTools™ User's Guide release 2001: Boulder, Colo., Research Systems, Inc., 202 p.
- Robson, A., Beven, K.J. and Neal, C., 1992, Towards identifying sources of subsurface flow— a comparison of components identified by a physically based runoff model and those determined by chemical mixing techniques: *Hydrological Processes*, v. 6, p. 199-214.
- U.S. Department of Agriculture, 1994, State Soil Geographic data base: (STATSGO) data use information: Soil Conservation Service, Miscellaneous Publication Number 1492, 113 p.
- U.S. Geological Survey, 2002, National water information system web site, accessed May 19, 2002, at <http://water.usgs.gov>
- Vogelmann, J.E., Howard, S.M., Yang, L., Larson, C.R., Wylie, B.K., and Van Driel, N., 2001, Completion of the 1990s National Land Cover Data Set for the conterminous United States from Landsat Thematic Mapper data and ancillary data sources: *Photogrammetric Engineering and Remote Sensing*, v. 67, p. 650-652.
- Wolock, D.M., 1993, Simulating the variable source area concept of streamflow generation with the watershed model TOPMODEL: U.S. Geological Survey Open-File Report 93-4124, 33 p.
- Wolock, D.M., Hornberger, G.M., Beven, K.J., and Campbell, W.G., 1989, The relationship of catchment topography and soil hydraulic characteristics to lake alkalinity in the northeastern United States: *Water Resources Research*, v. 25, p. 829-837.
- Wolock, D.M., Hornberger, G.M., and Musgrove, T.J., 1990, Topographic effects of flow path and surface-water chemistry of the Llyn-Brianne catchments in Wales: *Journal of Hydrology*, v. 115, p. 243-259.
- Woods, R.A. and Sivapalan, M., 1997, A connection between topographically driven runoff generation and channel network structure: *Water Resources Research*, v. 33, p. 2939-2950.

Chapter 3 - Basic Water Quality in the Boulder Creek Watershed, Colorado, During High-Flow and Low-Flow Conditions, 2000

By Sheila F. Murphy, James J. Shelley*, James A. Stout*, and Edward P. Mead*

Abstract

The city of Boulder collaborated with the U.S. Geological Survey to provide a detailed examination of the water quality of Boulder Creek, Colorado, during high-flow and low-flow conditions in the year 2000. The city measured alkalinity, ammonia, dissolved oxygen, fecal coliform, hardness, nitrate, nitrite, organic nitrogen, orthophosphate, pH, specific conductance, temperature, total dissolved solids, total phosphorus, total suspended solids, and turbidity. Dissolved constituents were typically higher during low-flow conditions, when less water was available for dilution. Total suspended solids and turbidity were higher during high-flow conditions, when spring runoff occurs. Most constituent concentrations were higher in the lower watershed (urban, wastewater-dominated, and agricultural regions, with sedimentary bedrock) than in the upper watershed (headwater and mountain regions, with crystalline bedrock). Concentrations of several constituents in Boulder Creek increased after the creek received wastewater effluent.

INTRODUCTION

Two programs within the city of Boulder's Water Quality and Environmental Services group collect samples from Boulder Creek, reservoirs, and inflows throughout the year. The Sourcewater program conducts monthly sampling and water-quality characterization of city of Boulder drinking water sources, including North Boulder Creek, Middle Boulder Creek, Barker Reservoir, Boulder Reservoir, and their inflows (fig. 3.1). This characterization includes assessing seasonal trends and impacts to water treatment, analyzing

for possible contaminants, and identifying the source of contaminants. The Stormwater program monitors the impacts of point and non-point source pollutants as Boulder Creek flows through the urban corridor. The program collects monthly water-quality samples of Boulder Creek and its inflows from the confluence of North Boulder Creek and Middle Boulder Creek to the confluence of Boulder Creek and Coal Creek (fig. 3.1). Historical data for Sourcewater and Stormwater programs are available on the Boulder Area Sustainability Information Network (BASIN) website, www.basin.org (Murphy and Waterman, 2003; U.S. Environmental Protection Agency [USEPA], 2001).

For this collaborative study with the U.S. Geological Survey (USGS), the two city of Boulder programs performed monthly sampling at their regular sites, and also analyzed samples collected from additional sites during the USGS sampling. City personnel attempted to sample at or near the same time as the USGS sampling. However, due to time constraints, sampling times and days occasionally differ from those of the USGS (Verplanck and others, 2003).

METHODS

The Sourcewater and Stormwater programs have different goals and collect different types of samples, so their analytical methods and detection limits differ for some constituents. The Stormwater program samples waters that contain higher levels of dissolved and suspended constituents, so it uses methods developed for higher concentrations, and these methods usually have higher detection limits. Typically, Sourcewater samples are analyzed at the city of Boulder's Drinking Water Laboratory, and

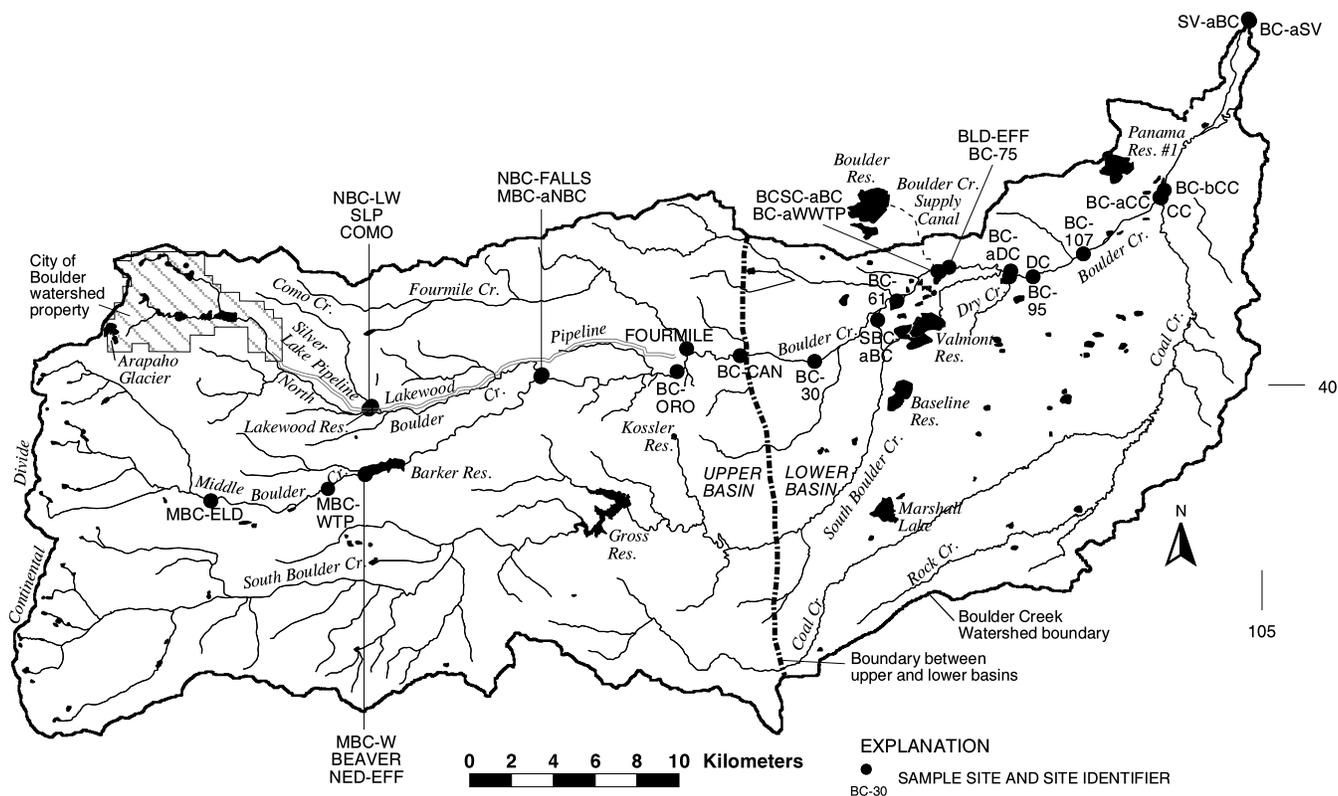


Figure 3.1. Map of Boulder Creek Watershed and sampling sites.

Stormwater samples are analyzed at the city’s Wastewater and Environmental Laboratory. For this study, extensive cooperation between the two laboratories was required to include the analysis of all constituents. The laboratory at which each sample was analyzed is given in tables 3.1 and 3.2.

Sampling

The Sourcewater program collected water-quality samples from North Boulder Creek upstream of Lakewood Reservoir (NBC-LW); Middle Boulder Creek at the Nederland Water Treatment Plant Intake (MBC-WTP) and at the weir upstream of Barker Reservoir (MBC-W); Como Creek upstream of the confluence with North Boulder Creek (COMO); North Beaver Creek upstream of the confluence with Middle Boulder Creek (BEAVER); the Silver Lake

Pipeline (SLP); and Nederland Wastewater Treatment Plant (WWTP) effluent (NED-EFF; fig. 3.1, tables 3.1 and 3.2). Stream samples were vertically- and horizontally-composited using hydrochloric acid washed sample churns. Grab samples were collected for SLP and NED-EFF. All sample bottles were filled from the same aliquot of water. One replicate sample was collected for each sampling event. Field blanks were collected using deionized water. Samples were packed in plastic bags, stored on ice, transported to the Drinking Water Laboratory, and refrigerated until analysis.

The Stormwater program collected water-quality samples from North Boulder Creek upstream of the confluence with Middle Boulder Creek (NBC-FALLS); Middle Boulder Creek upstream of the confluence with North Boulder Creek (MBC-aNBC); Boulder Creek at the Orodell streamgaging station (BC-ORO), at the

mouth of Boulder Canyon (BC-CAN), at 30th Street (BC-30), at 61st Street (BC-61), upstream of the Boulder 75th Street WWTP (BC-aWWTP), at 75th Street (BC-75), upstream of the confluence with Dry Creek (BC-aDC), at 95th Street (BC-95), at 107th Street (BC-107), and upstream and downstream of the confluence with Coal Creek (BC-aCC and BC-bCC); from Coal Creek upstream of the Boulder Creek confluence (CC); and from the Boulder 75th Street WWTP effluent (BLD-EFF; fig. 3.1, tables 3.1 and 3.2). Grab samples were taken from mid-channel or the area in the channel which best represented the discharge. Sample bottles were submerged to approximately 60 percent of the water depth, filled, capped, and shaken. One to two inches of air space was left in the bottle (unless sample analysis required that no air space be left). Replicate samples were collected for each sampling event. Field blanks were collected using deionized water. Samples were stored on ice and transported to the Wastewater and Environmental Laboratory.

Samples at additional sites (Middle Boulder Creek upstream of the town of Eldora, MBC-ELD; Fourmile Creek, FOURMILE; South Boulder Creek, SBC-aBC; Boulder Creek Supply Canal, BCSC-aBC; Dry Creek, DC; Boulder Creek upstream of the confluence with Saint Vrain Creek, BC-aSV; and Saint Vrain Creek upstream of the confluence with Boulder Creek, SV-aBC) were collected during the USGS sampling in June and October for analysis of some parameters (ammonia, fecal coliform, hardness, orthophosphate, total dissolved solids, total phosphorus, total suspended solids, and turbidity) at the Drinking Water Laboratory or the Wastewater and Environmental Laboratory (tables 3.1 and 3.2).

The Sourcewater program also samples water in Barker Reservoir on a monthly basis. In June and October 2000, these samples were collected one week after the cooperative USGS/city of Boulder sampling event. Water samples were collected from the top and bottom of the reservoir, at a distance of 91 m from the middle

of Barker Dam. Composite samples were collected from the photic zone; grab samples were collected from 0.5 m above the bottom of the reservoir using a Van Dorn Water Sampler (J.J. Shelley, unpub. data, 2000).

Field Parameters

The Sourcewater program used a YSI 600XL multi-probe to analyze water temperature, dissolved oxygen (DO), specific conductance (SC), and pH. Calibrations of DO were conducted in the field at the sample site with a moist-air saturated bottle. Specific conductance was calibrated in the laboratory the day of sampling using a potassium chloride (KCl) solution of 1412 microSiemens/centimeter ($\mu\text{S}/\text{cm}$) at 25°C. Calibration of pH was performed in the laboratory the day of sampling with pH 7.00 and 10.01 buffers.

The Stormwater program used an Orion Model 1230 ion-selective probe to measure pH and DO. Calibration of pH was performed in the laboratory the day of sampling using pH 7.00 and 10.01 buffers. An Orion Model 130 conductivity meter was used to measure SC and water temperature. The probe was calibrated in the laboratory the day of sampling with a KCl solution of 1412 $\mu\text{S}/\text{cm}$ at 25°C. A thermometer was used to measure air temperature. Meter failure prevented the measurement of DO for several sites in June 2000 and measurement of SC for several sites in October 2000.

Laboratory Analyses

The Wastewater and Environmental Laboratory measured total dissolved solids (TDS) using Standard Method 2540B of the American Public Health Association (APHA) and others (1998). A 50-mL aliquot of sample was passed through a 1.5- μm filter, and the filtrate was evaporated in a tared dish at 103 to 105°C to a constant weight. Laboratory blanks and field replicates were analyzed for each sampling event (tables 3.1 and 3.2). The detection limit was

Table 3.1. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000

[Units are milligrams per liter unless otherwise indicated; alkalinity and hardness reported as CaCO₃; distance, distance from Boulder Creek/Saint Vrain degrees Celsius; DO, dissolved oxygen; %, percent; SC, specific conductance; μS/cm, microsiemens per centimeter; TDS, total dissolved solids; TSS, total nitrite as N; NH₃-N, ammonia as N; Org-N, organic nitrogen as N; P, phosphorus as P; ortho PO₄-P, orthophosphate as phosphorus; --, not measured; <, less

Site	Distance (meters)	Discharge (m ³ /s)	Sample date	Sample time	Lab	T _{air} (°C)	T _{water} (°C)	DO	DO saturation ¹ (%)	SC (μS/cm)	pH (units)	TDS
Middle Boulder Creek/Boulder Creek												
MBC-ELD	69590	3.7	--	--	³	--	--	--	--	--	--	--
MBC-WTP	62970	--	6/12/00	1216	DW	--	8.2	8.5	100	25	7.57	15 ⁴
MBC-W	60920	4.9	6/12/00	1309	DW	--	9.4	9.9	120	23	7.55	14 ⁴
MBC-aNBC	49440	--	6/13/00	805	WW	14	11	--	--	27	7.68	14
BC-ORO	41520	6.5	6/13/00	900	WW	15	11	--	--	26	7.62	20
BC-CAN	36710	--	6/13/00	925	WW	20	12	--	--	28	7.49	16
BC-30	32990	2.3	--	--	³	--	--	--	--	--	--	--
BC-61	27320	3.2	6/13/00	1110	WW	22	15	--	--	56	7.57	<1
BC-aWWTP	24440	2.5	6/13/00	1320	WW	27	18	10	130	94	8.36	26
BC-75	23850	5.1	6/13/00	1405	WW	24	19	7.9	100	330	7.36	190
BC-aDC	20180	3.3	6/13/00	1525	WW	27	20	9.3	120	210	8.49	34
BC-95	18790	--	6/13/00	1600	WW	26	21	9.9	140	230	8.92	110
BC-107	16320	--	6/13/00	1615	WW	26	22	9.2	130	250	9.19	120
BC-aCC	10970	1.1	6/13/00	1645	WW	19	23	9.7	140	280	9.79	122
BC-bCC	10540	1.4	6/13/00	1655	WW	19	23	13	180	340	9.63	220
BC-aSV	110	0.45	--	--	³	--	--	--	--	--	--	--
Inflows/other flows												
COMO	59340	0.15	6/12/00	1012	DW	--	9.5	8.1	100	34	7.56	21 ⁴
NBC-LW	59370	1.7	6/12/00	1023	DW	--	9.1	8.1	100	23	7.57	14 ⁴
SLP	59340	--	6/12/00	1050	DW	--	11	8.0	100	20	7.57	12 ⁴
BEAVER	60910	0.09	6/12/00	1249	DW	--	11	9.5	120	95	7.91	58 ⁴
NED-EFF	60880	0.005	6/12/00	1323	DW	--	15	0.89	10	580	7.10	350 ⁴
NBC-FALLS	49420	--	6/13/00	825	WW	14	9.9	--	--	20	7.56	10
FOURMILE	40120	0.11	--	--	³	--	--	--	--	--	--	--
SBC-aBC	29070	--	--	--	³	--	--	--	--	--	--	--
BCSC-aBC	24680	0.63	--	--	³	--	--	--	--	--	--	--
BLD-EFF	24380	0.88	6/13/00	1345	WW	25	20	6.9	90	600	7.07	400
DC	20040	--	--	--	³	--	--	--	--	--	--	--
CC	10970	0.30	6/13/00	1650	WW	19	22	10	140	870	9.22	580
SV-aBC	90	3.28	--	--	³	--	--	--	--	--	--	--
Quality assurance/quality control- Drinking Water Laboratory												
Field blank			6/12/00	1245	DW	--	--	--	--	--	--	--
Laboratory blank			--	--	DW	--	--	--	--	--	--	--
BEAVER field replicate			6/12/00	1255	DW	--	--	--	--	--	--	--
Standard reference percent recovery			--	--	--	--	--	--	--	--	--	--
Quality assurance/quality control- Wastewater Laboratory												
Laboratory blank			--	--	WW	--	--	--	--	--	--	<1
BC-aDC field replicate			6/13/00	1525	WW	--	--	--	--	--	--	10
NBC-FALLS lab duplicate			6/13/00	825	WW	--	--	--	--	--	--	--
Standard reference percent recovery			--	--	--	--	--	--	--	--	--	--

¹ Calculated from dissolved oxygen, temperature, and elevation.

² All turbidity measurements analyzed by DW.

³ Samples for these sites were collected during USGS sampling and analyzed for hardness, total phosphate, and orthophosphate by WW, and for fecal

⁴ Estimated from specific conductance.

Creek confluence; m³/s, cubic meters per second; Lab, city of Boulder laboratory that analyzed sample; T_{air}, air temperature; T_{water}, water temperature; °C, suspended solids; NTU, nephelometric turbidity units; cols/100 mL, number of colonies per 100 milliliters; NO₂+NO₃-N, nitrite plus nitrate as N; NO₂, than; DW, Drinking Water Laboratory; WW, Wastewater and Environmental Laboratory; discharge from Murphy and others, 2003]

Site	Alka- linity	Hard- ness	TSS	Turbidity ² (NTU)	Fecal coliform (cols/100 mL)	NO ₂ + NO ₃ -N	NO ₂ -N	NH ₃ -N	Org-N	P (total)	ortho PO ₄ -P
MBC-ELD	--	40	--	0.56	2	--	--	--	--	0.03	<0.03
MBC-WTP	10	12	2	1.0	<1	0.08	--	--	--	0.01	--
MBC-W	11	11	2	0.83	<1	0.07	--	--	--	0.01	--
MBC-aNBC	13	15	7	2.5	<20	<0.1	<0.001	<0.1	0.2	0.03	<0.03
BC-ORO	13	15	10	2.5	20	<0.1	<0.001	<0.1	0.3	0.05	<0.03
BC-CAN	14	15	9	3.0	20	<0.1	<0.001	0.1	0.3	0.03	<0.03
BC-30	--	90	--	3.1	170	--	--	--	--	<0.02	0.06
BC-61	23	30	13	2.6	170	<0.1	<0.001	<0.1	0.4	<0.02	<0.03
BC-aWWTP	33	60	13	10	140	<0.1	<0.001	<0.1	0.2	0.03	<0.03
BC-75	59	260	8	4.7	170	4.9	0.255	2.1	0.9	0.90	0.85
BC-aDC	45	90	7	8.6	80	3.0	0.203	0.7	0.9	0.43	0.46
BC-95	52	90	10	11	20	2.7	0.218	0.5	0.9	0.44	0.42
BC-107	55	90	7	2.1	130	2.9	0.259	0.4	0.8	0.47	0.46
BC-aCC	71	110	8	5.6	40	1.0	0.035	<0.1	0.6	0.29	0.29
BC-bCC	93	120	19	9.4	110	1.2	0.031	<0.1	0.7	0.33	0.33
BC-aSV	--	20	--	3.9	<10	--	--	--	--	0.22	0.35
COMO	2	14	6	4.6	6	<0.01	--	--	--	0.02	--
NBC-LW	9	9	5	1.6	2	<0.01	--	--	--	0.01	--
SLP	8	9	2	1.3	<1	0.01	--	--	--	0.01	--
BEAVER	41	45	4	2.4	1	<0.01	--	--	--	0.01	--
NED-EFF	160	79	69	55	1300	<0.01	--	24	10.5	5.25	--
NBC-FALLS	11	10	5	1.6	<20	<0.1	<0.001	<0.1	0.1	0.05	<0.03
FOURMILE	--	50	--	1.6	80	--	--	--	--	0.04	<0.03
SBC-aBC	--	140	--	2.3	--	--	--	--	--	--	<0.03
BCSC-aBC	--	80	--	28	--	--	--	--	--	0.02	0.06
BLD-EFF	95	370	5	3.3	<20	10.2	0.540	5.0	1.7	1.95	2.67
DC	--	160	--	5.4	80	--	--	--	--	0.12	0.05
CC	250	240	77	29	230	1.8	0.026	<0.1	1.2	0.66	0.65
SV-aBC	--	230	--	23	210	--	--	--	--	0.55	0.58
	1.3	<1	--	0.05	--	<0.01	--	--	--	0.0009	--
	--	--	--	--	--	--	--	--	--	0.0006	--
	41	45	--	2.5	--	<0.01	--	--	--	0.01	--
	--	--	--	--	--	133%	--	--	--	107-110%	--
	1.1	--	<1	--	<20	--	0.003	<0.1	--	<0.003	<0.003
	54	--	4	--	--	--	0.260	0.4	--	0.43	0.46
	11	--	--	--	--	--	0.202	--	--	--	--
	--	99-102%	--	--	--	97-111%	99-101%	--	--	93-101%	98-101%

coliform and turbidity by DW.

Table 3.2. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000

[Units are milligrams per liter unless otherwise indicated; alkalinity and hardness reported as CaCO₃; distance, distance from Boulder Creek/Saint Vrain degrees Celsius; DO, dissolved oxygen; %, percent; SC, specific conductance; μS/cm, microsiemens per centimeter; TDS, total dissolved solids; TSS, total nitrite as N; NH₃-N, ammonia as N; Org-N, organic nitrogen as N; P, phosphorus as P; ortho PO₄-P, orthophosphate as phosphorus; --, not measured; <, less

Site	Distance (meters)	Discharge (m ³ /s)	Sample date	Sample time	Lab	T _{air} (°C)	T _{water} (°C)	DO	DO Saturation (%)	SC (μS/cm)	pH (units)	TDS
Middle Boulder Creek/Boulder Creek												
MBC-ELD	69590	0.40	--	--	²	--	--	--	--	--	--	8 ³
MBC-WTP	62970	--	10/9/00	1204	DW	--	4.0	9.7	100	48	7.48	29 ⁴
MBC-W	60920	0.33	10/9/00	1257	DW	--	5.6	9.3	100	48	7.54	29 ⁴
MBC-aNBC	49440	--	10/10/00	900	WW	8	4.2	9.8	94	89	7.62	84
BC-ORO	41520	1.3	10/10/00	1000	WW	10	8.0	9.4	96	54	7.59	60
BC-CAN	36710	1.0	10/10/00	1045	WW	11	8.2	9.3	96	62	7.64	56
BC-30	32990	0.38	--	--	²	--	--	--	--	--	--	68 ³
BC-61	27320	0.53	10/10/00	1120	WW	25	10	10	110	188	8.95	168
BC-aWWTP	24440	0.35	10/10/00	1355	WW	18	12	9.1	100	221	8.90	--
BC-75	23850	1.6	10/10/00	1325	WW	17	18	11	140	572	7.80	368
BC-aDC	20180	1.1	10/10/00	1355	WW	18	17	13	160	527	7.82	332
BC-95	18790	1.0	10/10/00	1435	WW	22	18	14	180	543	8.46	374
BC-107	16320	0.69	10/10/00	1510	WW	22	17	13	160	--	8.62	296
BC-aCC	10970	0.87	10/10/00	1545	WW	22	16	13	150	--	9.32	374
BC-bCC	10540	1.2	10/10/00	1610	WW	21	15	12	150	--	8.59	432
BC-aSV	110	0.49	--	--	²	--	--	--	--	--	--	450 ³
Inflows/other flows												
COMO	59340	0.03	10/9/00	1023	DW	--	3.8	9.8	100	67	7.57	41 ⁴
NBC-LW	59370	0.17	10/9/00	1040	DW	--	2.8	10	100	32	7.34	20 ⁴
SLP	59340	0.16	10/9/00	1058	DW	--	5.2	8.5	91	22	7.72	13 ⁴
BEAVER	60910	0.01	10/9/00	1230	DW	--	6.1	9.1	99	180	8.04	110 ⁴
NED-EFF	60880	0.003	10/9/00	1317	DW	--	7.3	3.0	30	579	7.07	350 ⁴
NBC-FALLS	49420	--	10/10/00	920	WW	--	3.3	9.7	92	75	7.47	82
FOURMILE	40120	0.02	--	--	²	--	--	--	--	--	--	184
SBC-aBC	29070	0.01	--	--	²	--	--	--	--	--	--	192 ³
BCSC-aBC	24680	0.05	--	--	²	--	--	--	--	--	--	110 ³
BLD-EFF	24380	0.91	10/10/00	1310	WW	20	20	6.1	83	682	7.37	396
DC	20040	0.03	10/10/00	--	²	--	--	--	--	--	--	712 ³
CC	10970	0.34	10/10/00	1555	WW	22	15	12	120	--	8.50	668
SV-aBC	90	1.9	--	--	²	--	--	--	--	--	--	904 ³
Quality assurance/quality control- Drinking Water Laboratory												
Field blank			10/9/00	1225	DW	--	--	--	--	--	--	--
BEAVER field replicate			10/9/00	1235	DW	--	--	--	--	--	--	--
Standard reference percent recovery			--	--	--	--	--	--	--	--	--	--
Quality assurance/quality control- Wastewater Laboratory												
Laboratory blank			--	--	DW	--	--	--	--	--	--	6
BC-CAN field replicate			10/10/00	1045	WW	--	--	--	--	--	--	48
Standard reference percent recovery			--	--	--	--	--	--	--	--	--	--

¹ All turbidity measurements analyzed by DW.

² Samples for these sites were collected during USGS sampling and analyzed for TDS, TSS, hardness, ammonia, total phosphate, and orthophosphate by

³ Analyzed 22 days after holding time.

⁴ Estimated from specific conductance.

Creek confluence; m³/s, cubic meters per second; Lab, city of Boulder laboratory that analyzed sample; T_{air}, air temperature; T_{water}, water temperature; °C, suspended solids; NTU, nephelometric turbidity units; cols/100 mL, number of colonies per 100 milliliters; NO₂+NO₃-N, nitrite plus nitrate as N; NO₂, than; DW, Drinking Water Laboratory; WW, Wastewater and Environmental Laboratory; discharge measurements from Murphy and others, 2003]

Site	Alka- linity	Hard- ness	TSS	Turbidity ¹ (NTU)	Fecal coliform (cols/100 mL)	NO ₂ + NO ₃ -N	NO ₂ -N	NH ₃ -N	Org-N	P (total)	ortho PO ₄ -P
MBC-ELD	--	40	2 ³	0.22	1	--	--	<0.1	<0.1	<0.02	<0.03
MBC-WTP	17	19	4	0.66	<1	0.09	--	--	--	0.01	--
MBC-W	17	20	2	0.51	<1	--	--	--	--	0.01	--
MBC-aNBC	22	50	1	0.38	50	<0.1	<0.001	<0.1	<0.1	0.07	<0.03
BC-ORO	17	--	3	3.0	20	<0.1	<0.001	0.1	0.2	0.06	<0.03
BC-CAN	18	50	1	1.7	20	<0.1	<0.001	<0.1	0.1	0.04	<0.03
BC-30	--	190	6 ³	2.8	690	--	--	<0.1	--	<0.02	0.09
BC-61	58	260	1	2.3	130	<0.1	<0.001	<0.1	1.7	0.04	<0.03
BC-aWWTP	68	120	4	5.3	80	<0.1	<0.001	<0.1	0.1	0.11	<0.03
BC-75	112	210	4	3.8	330	6.7	0.408	7.8	1.4	1.73	1.49
BC-aDC	111	200	5	4.1	230	6.2	0.152	6.8	1.5	1.44	1.26
BC-95	123	200	3	3.0	80	5.9	0.104	6.2	1.4	1.34	1.18
BC-107	109	190	4	2.1	80	2.9	0.026	3.6	0.9	0.99	0.87
BC-aCC	139	260	3	2.2	220	3.2	0.007	1.6	0.1	0.82	0.75
BC-bCC	164	300	14	9.2	130	3.1	0.025	1.2	1.1	0.78	0.64
BC-aSV	--	330	10 ³	3.1	2	--	--	<0.1	--	0.48	0.50
COMO	31	27	4	2.4	85	<0.01	--	--	--	0.02	--
NBC-LW	14	13	2	0.95	<1	<0.01	--	--	--	0.01	--
SLP	10	9	1	1.3	<1	<0.01	--	--	--	0.01	--
BEAVER	69	82	2	2.3	1	--	--	--	--	0.01	--
NED-EFF	123	88	50	43	30	--	--	--	--	5.45	--
NBC-FALLS	27	80	1	1.3	<20	<0.1	<0.001	<0.1	0.7	0.04	<0.03
FOURMILE	--	180	<1	0.38	17	--	--	--	--	0.02	0.14
SBC-aBC	--	290	18 ³	6.6	5	--	--	--	--	<0.02	0.06
BCSC-aBC	--	80	6 ³	32	6	--	--	--	--	<0.02	0.02
BLD-EFF	125	350	6	2.4	790	7.7	0.490	9.9	0.2	2.29	3.64
DC	--	510	6 ³	1.1	1560	--	--	--	--	0.02	0.01
CC	255	320	39	--	330	2.7	0.093	<0.1	0.9	0.51	0.45
SV-aBC	--	560	6 ³	4.7	240	--	--	--	--	0.71	0.75
	1.2	<1	--	0.038	--	<0.01	--	--	--	0.0006	--
	69	82	--	2.35	--	--	--	--	--	0.0140	--
	--	--	--	--	--	125%	--	--	--	104-145%	--
	--	<1	<1	--	--	<0.1	<0.001	--	--	0.07	<0.03
	19	50	2	--	--	<0.1	0.003	<0.1	--	--	--
	--	100%	--	--	--	96-112%	99-102%	--	--	99-108%	96-106%

WW, and for fecal coliform and turbidity by DW.

1 mg/L. The Drinking Water Laboratory estimated TDS from SC by multiplying SC by 0.61, based on the laboratory's previous studies of the correlation between TDS and SC for samples from the same sites.

Alkalinity was measured at both laboratories using Standard Method 2320 (APHA and others, 1998). A 200-mL aliquot of unfiltered sample was stirred and titrated to a pH of 4.5 with 0.02N sulfuric acid. This method assumes that alkalinity consists of bicarbonate, carbonate, and/or hydroxide. The Drinking Water Laboratory analyzed field blanks and field replicates for each sampling event. The Wastewater and Environmental Laboratory analyzed laboratory blanks and field replicates for each sampling event (tables 3.1 and 3.2). The detection limit was 1 mg/L as calcium carbonate (CaCO_3).

Hardness was measured at both laboratories using Standard Method 2340 (APHA and others, 1998). A buffered indicator solution was added to a 100-mL aliquot of unfiltered sample to bring the pH to 10. The sample turned red if calcium and magnesium were present. The sample was then titrated with ethylenediaminetetraacetic acid (EDTA) until it turned blue, indicating that all calcium and magnesium had complexed with EDTA. The amount of EDTA added represented the hardness (from calcium and magnesium) of the sample. The Drinking Water Laboratory analyzed field blanks and field replicates for each sampling event. The Wastewater and Environmental Laboratory analyzed laboratory blanks and field replicates for each sampling event (tables 3.1 and 3.2), and also analyzed standard reference samples (percent recoveries ranged from 99 to 102 percent). The detection limit was 1 mg/L as CaCO_3 .

Both laboratories measured Total Suspended Solids (TSS) using Standard Method 2540D (APHA and others, 1998). A 100-mL aliquot of sample was passed through a 1.5- μm filter, and the filter with residue was dried at 103 to 105°C to a constant weight. The Drinking Water Laboratory analyzed laboratory blanks and field

replicates for each sampling event (tables 3.1 and 3.2). The detection limit was 1 mg/L.

Turbidity values of all samples were measured with a nephelometer at the Drinking Water Laboratory using Standard Method 2130B (APHA and others, 1998). Field blanks and field replicates for each sampling event were analyzed. The detection limit for this method was 0.03 nephelometric turbidity units (NTU).

The Drinking Water Laboratory measured fecal coliform using Standard Method 9222D (membrane filter method; APHA and others, 1998). The water sample was filtered through a sterile membrane filter. The filter was transferred to a sterile petri dish and placed on a nutrient pad saturated with a fecal coliform-specific broth. The plates were inverted, placed in watertight plastic bags, and incubated in a water bath at 44.5°C for 24 hours. Colonies produced by fecal coliform bacteria were counted using a microscope or magnifying lens. The fecal coliform density was recorded as the number of colonies per 100 mL (cols/100 mL) of sample; the detection limit was 1 cols/100 mL. The Wastewater and Environmental Laboratory measured fecal coliform using a modified version of Standard Method 9221E (most probable number method; APHA and others, 1998). A "presumptive test" was first performed, in which a series of fermentation tubes containing lauryl tryptose broth were inoculated with varying dilutions of water samples and incubated for 24 hours at 35.6°C. The fermentation tubes contained an inverted tube to trap gases produced by the coliform bacteria. The fermentation tubes were examined for gas production after 24 and 48 hours. If gas production was observed by the end of 48 hours, the presumptive test was positive and coliform bacteria were present in the sample. A "confirmed test" was then performed to determine if fecal coliform bacteria were present. A portion of the content of the fermentation tube was transferred with a sterile loop to a fermentation tube containing a fecal coliform-specific broth. The sample was incubated in a water bath at 44.5°C for 24 hours. Gas production

in the fermentation tube after 24 hours indicated fecal coliform. Based on which dilutions showed positive for coliform and/or fecal coliform, a table of most probable numbers was used to estimate the coliform content of the sample. The results were reported as most probable number of coliform per 100 mL. The detection limit for this method was 20 cols/100 mL.

Both laboratories measured and reported nitrite and nitrate together (designated nitrite+nitrate, NO_2+NO_3). The Drinking Water Laboratory used Hach Method 8192 (low-range cadmium reduction) on a filtered sample, while the Wastewater and Environmental Laboratory used Hach Method 8039 (high-range cadmium reduction; Hach Company, 2001) on an unfiltered sample. Both methods involved the reduction of nitrate to nitrite with cadmium, followed by the addition of sulfanilic acid to form an intermediate diazonium salt. In Method 8192, the diazonium salt coupled with chromotropic acid, and the pink-colored product was analyzed with a spectrophotometer at a wavelength of 507 nanometers (nm). In Method 8039, the diazonium salt coupled with gentisic acid, and the amber-colored product was analyzed at 500 nm. The Drinking Water Laboratory corrected NO_2+NO_3 sample concentrations by subtracting a reagent blank. The Drinking Water Laboratory analyzed field blanks and standard reference samples (133 percent recovery in June and 125 percent recovery in October) for each sampling event (tables 3.1 and 3.2). The Wastewater and Environmental Laboratory analyzed standard reference samples (between 96 and 112 percent recovery). A correction factor was then obtained by averaging the two analyses, subtracting the reagent blank from the average, and then dividing the actual standard concentration by this number. The correction factor was then subtracted from each analytic result. Field replicates were also analyzed (tables 3.1 and 3.2). The detection limits for Methods 8192 and 8039 were approximately 0.01 mg/L as N and 0.1 mg/L as N, respectively. The Wastewater and Environmental Laboratory also measured nitrite separately using Hach

Method 8507 (low range) and a Hach DR4000 spectrophotometer. This method is similar to Method 8192, described above, without the cadmium reduction. Nitrite (NO_2) concentrations were corrected in the same manner as NO_2+NO_3 . Field replicates were also analyzed (tables 3.1 and 3.2). The detection limit for NO_2 was approximately 0.001 mg/L as N.

All ammonia (NH_3) and organic nitrogen (organic N) analyses were performed at the Wastewater and Environmental Laboratory, using Standard Methods 4500-NH₃ B and 4500-NH₃ C (APHA and others, 1998) on an unfiltered sample. Both the ammonium ion (NH_4^+) and unionized ammonia (NH_3) were included in the ammonia measurement. Sodium borate buffer was added to the sample, and the pH of the sample was adjusted to 9.5 with sodium hydroxide. Ammonia was separated from organic N by distilling the sample into a flask containing a boric acid/color indicator solution. Sample concentrations were corrected by subtracting the concentration in a reagent blank. The detection limit for both NH_3 and organic N was 0.1 mg/L as N.

For determination of total phosphorus (total P), both laboratories first prepared an unfiltered sample with a persulfate digestion; the Drinking Water Laboratory used Standard Method 4500-P B.5 (APHA and others, 1998) while the Wastewater and Environmental Laboratory used Hach Method 8190 (Hach Company, 2001), which is based on Standard Method 4500-P B.5. In the persulfate digestion, condensed and organic phosphorus were converted to orthophosphate by adding sulfuric acid, ammonium persulfate, and phenolphthalein indicator and boiling the sample. After boiling, the sample was cooled and additional phenolphthalein indicator was added. The sample was then neutralized to a faint pink color with sodium hydroxide. The sample was then analyzed for orthophosphate. The Drinking Water Laboratory analyzed the converted orthophosphate using Standard Method 4500-P E (ascorbic acid method), in which phenolphthalein indicator, sulfuric acid, potassium antimonyl

tartrate, ammonium molybdate, and ascorbic acid were added to the sample. Potassium antimonyl tartrate and ammonium molybdate formed phosphomolybdic acid, which was then reduced by ascorbic acid. The blue-colored product was analyzed with a spectrophotometer at a wavelength of 430 nm. The Drinking Water Laboratory analyzed field blanks, laboratory blanks, and field replicates for each sampling event, and also analyzed standard reference samples (percent recoveries ranged from 107 to 145 percent). The detection limit for this method was approximately 0.002 mg/L as P. The Wastewater and Environmental Laboratory analyzed the converted orthophosphate using Hach Method 8114 (Hach Company, 2001), which is based on Standard Method 4500-P C (vanadomolybdophosphoric acid method; APHA and others, 1998). In this method, molybdovanadate reagent was added to the sample, forming vanadomolybdophosphoric acid. The yellow-colored product was analyzed with a spectrophotometer at a wavelength of 430 nm. The Wastewater and Environmental Laboratory analyzed laboratory blanks and field replicates for each sampling event (tables 3.1 and 3.2), and also analyzed standard reference samples (percent recoveries ranged from 96 to 106 percent). The detection limit for this method was 0.05 mg/L as phosphate (PO_4); values were converted to mg/L as P by dividing by 3.07.

Orthophosphate was measured only by the Wastewater and Environmental Laboratory using an unfiltered sample and Hach Method 8114 as discussed above, without persulfate digestion. The Wastewater and Environmental Laboratory analyzed laboratory blanks and field replicates for each sampling event (tables 3.1 and 3.2), and also analyzed standard reference samples (percent recoveries ranged from 93 to 108 percent). The detection limit was approximately 0.05 mg/L as PO_4 ; values provided in tables 3.1 and 3.2 were converted to mg/L as P by dividing by 3.07.

RESULTS

Analytical results for the June and October sampling events are provided in tables 3.1 and 3.2. Sample sites are listed in downstream order starting with the most upstream Middle Boulder Creek site (MBC-ELD). Sites not located on the mainstem of Middle Boulder Creek/Boulder Creek are listed below the mainstem sites in downstream order of flow into Boulder Creek. Sampling sites are shown in figure 3.1 and described in Murphy and others (2003).

Lateral profiles for the physical and chemical measurements of Middle Boulder Creek/Boulder Creek and sampled inflows are shown in figures 3.2 through 3.7. Data collected from Barker Reservoir one week after the sampling event (J.J. Shelley, unpub. data, 2000) are included in these figures. Seasonal and longitudinal trends in water quality are presented in this section; the trends will be discussed in more depth in the Discussion section. Most water-quality variables had higher concentrations during low-flow conditions (October) than during high-flow conditions (June), and were typically higher in the lower watershed (downstream of site BC-CAN) than in the upper watershed.

Temperature

Water temperatures at Boulder Creek sampling sites were higher in June than in October (tables 3.1 and 3.2, fig. 3.2a). During both sampling events, water temperatures increased down the Middle Boulder Creek/Boulder Creek profile from MBC-WTP (8.2°C in June and 4.0°C in October) to the site upstream of the Boulder 75th Street WWTP (BC-aWWTP; 18°C and 12°C). The WWTP effluent (BLD-EFF), which was about 20°C during both sampling events, caused temperatures in Boulder Creek to increase; at the site downstream of the WWTP (BC-75), temperatures were 19°C in June and 18°C in October. In June, water temperatures continued to increase downstream of BC-75, reaching 23°C at the site downstream of Coal

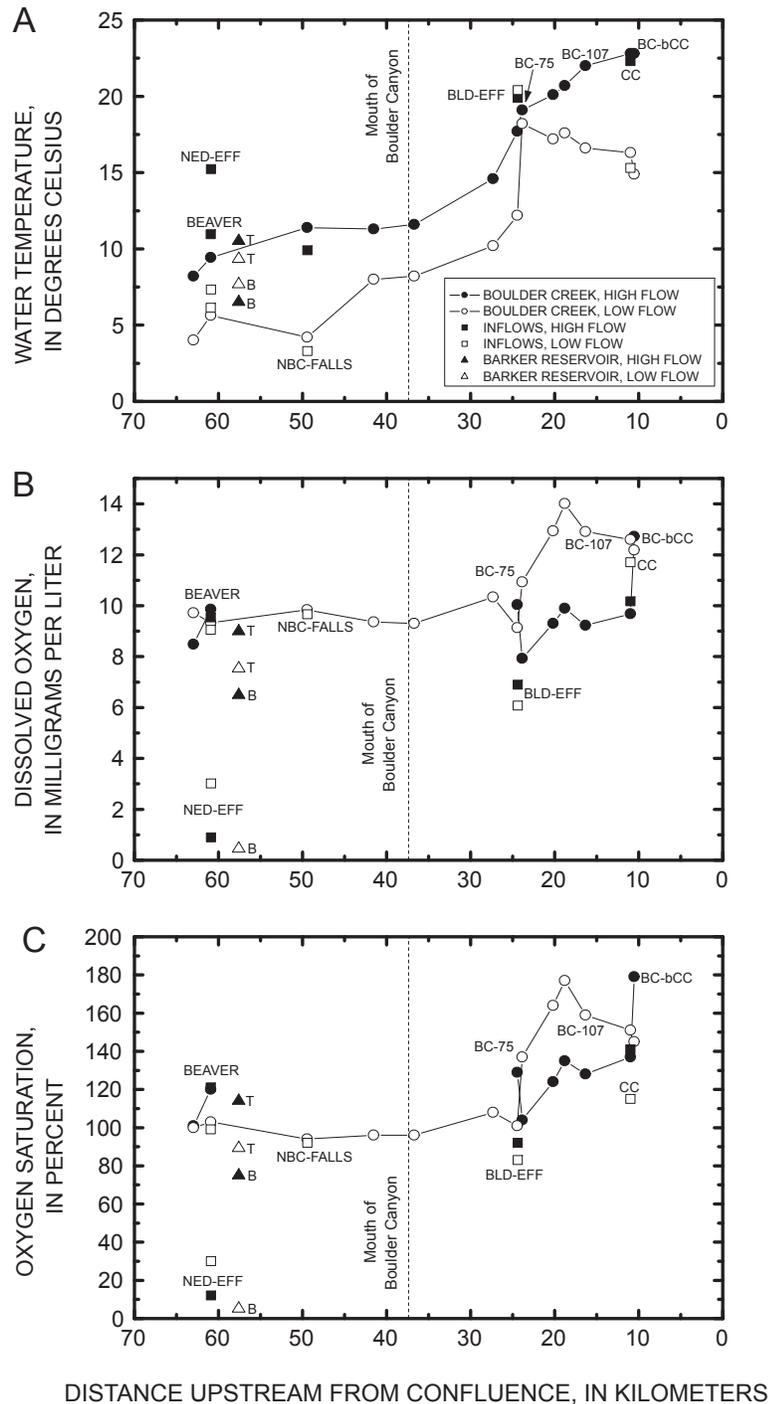


Figure 3.2. Graphs showing downstream variation in (A) water temperatures, (B) dissolved oxygen concentrations, and (C) oxygen saturation values for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence; B, sample collected at bottom of Barker Reservoir; T, sample collected from top of Barker Reservoir)

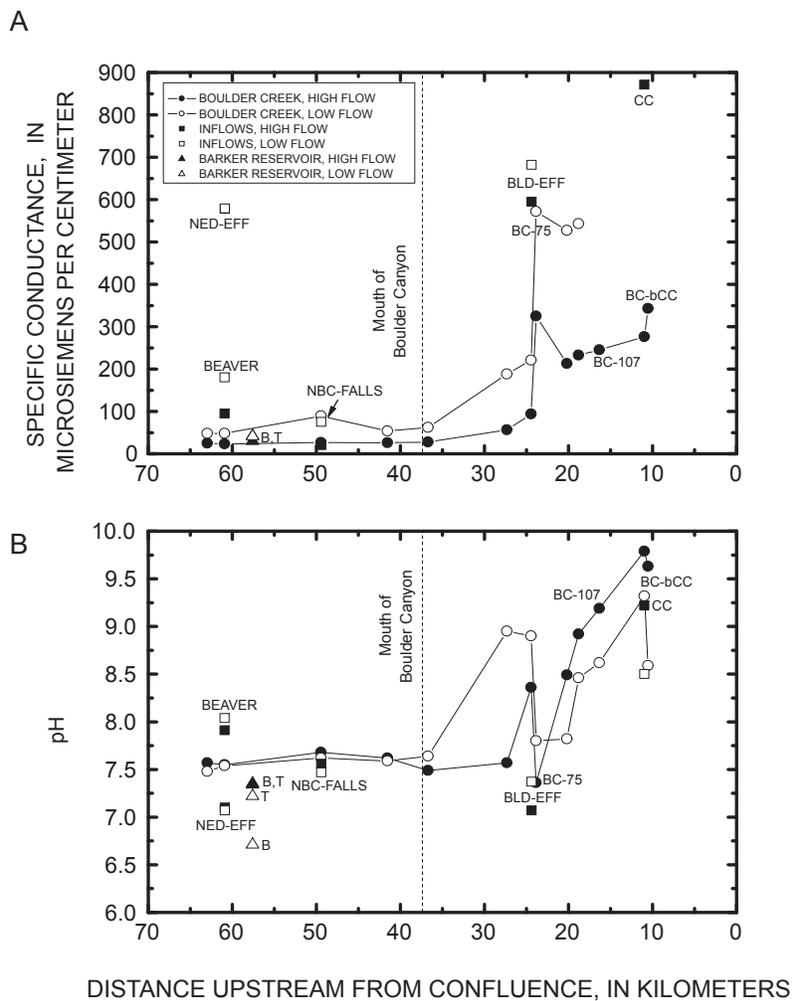


Figure 3.3. Graphs showing downstream variation in (A) specific conductance and (B) pH values for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence; B, sample collected at bottom of Barker Reservoir; T, sample collected from top of Barker Reservoir)

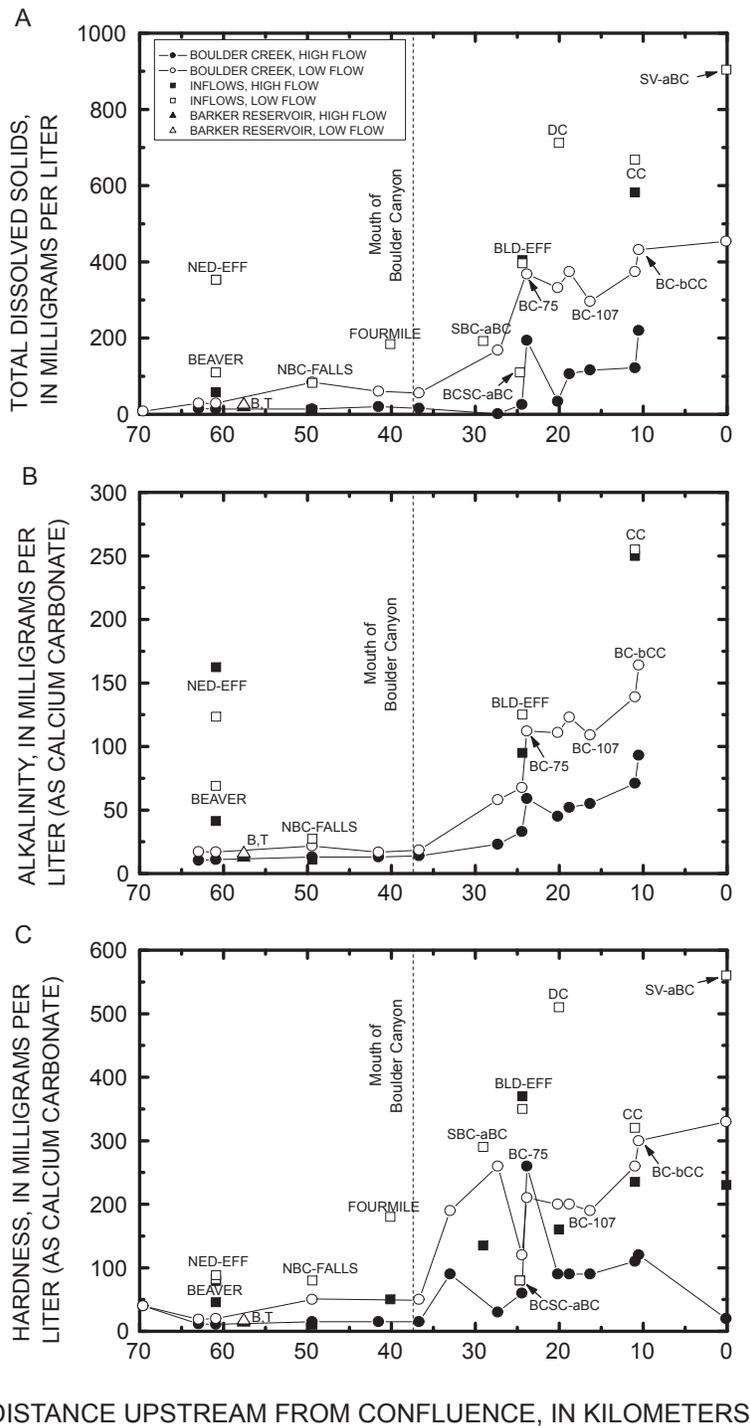


Figure 3.4. Graphs showing downstream variation in (A) total dissolved solids, (B) hardness, and (C) alkalinity values for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence; B, sample collected at bottom of Barker Reservoir; T, sample collected from top of Barker Reservoir)

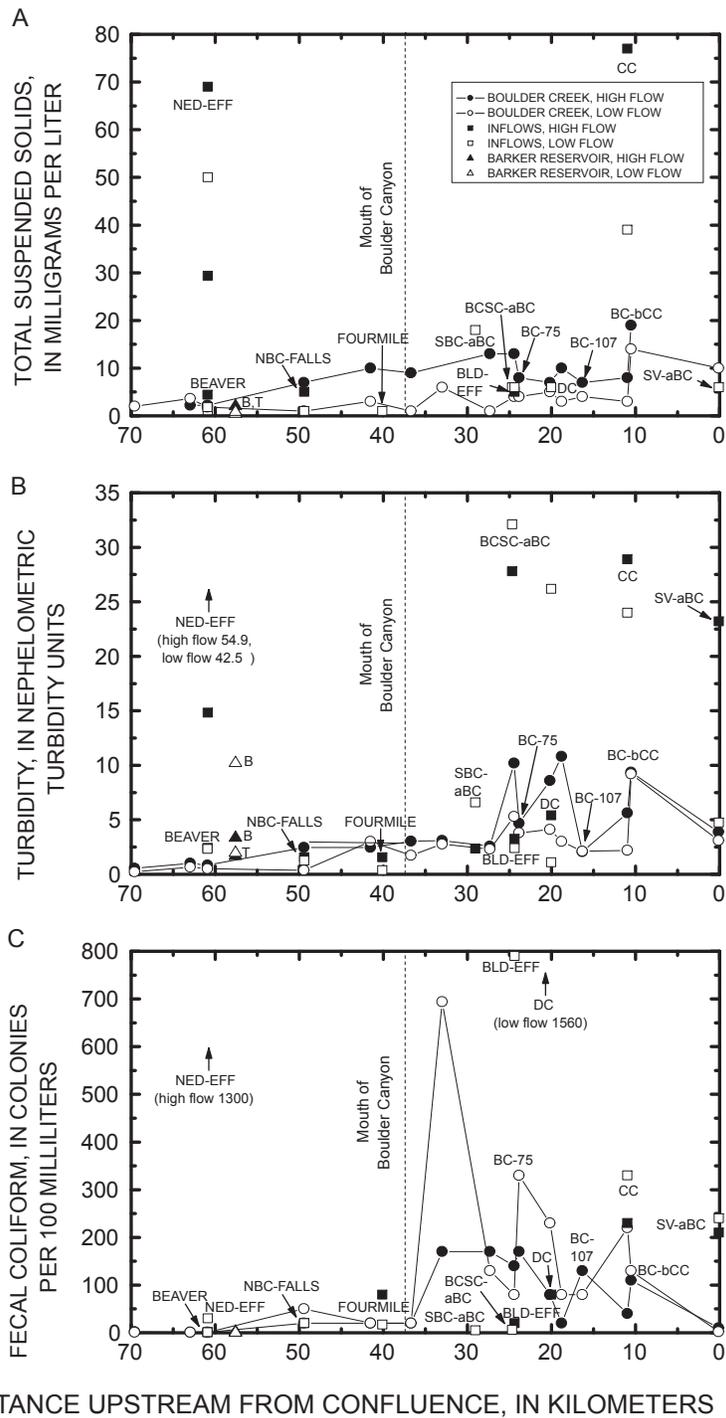


Figure 3.5. Graphs showing downstream variation in (A) total suspended solids, (B) turbidity, and (C) fecal coliform for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence; B, sample collected at bottom of Barker Reservoir; T, sample collected from top of Barker Reservoir)

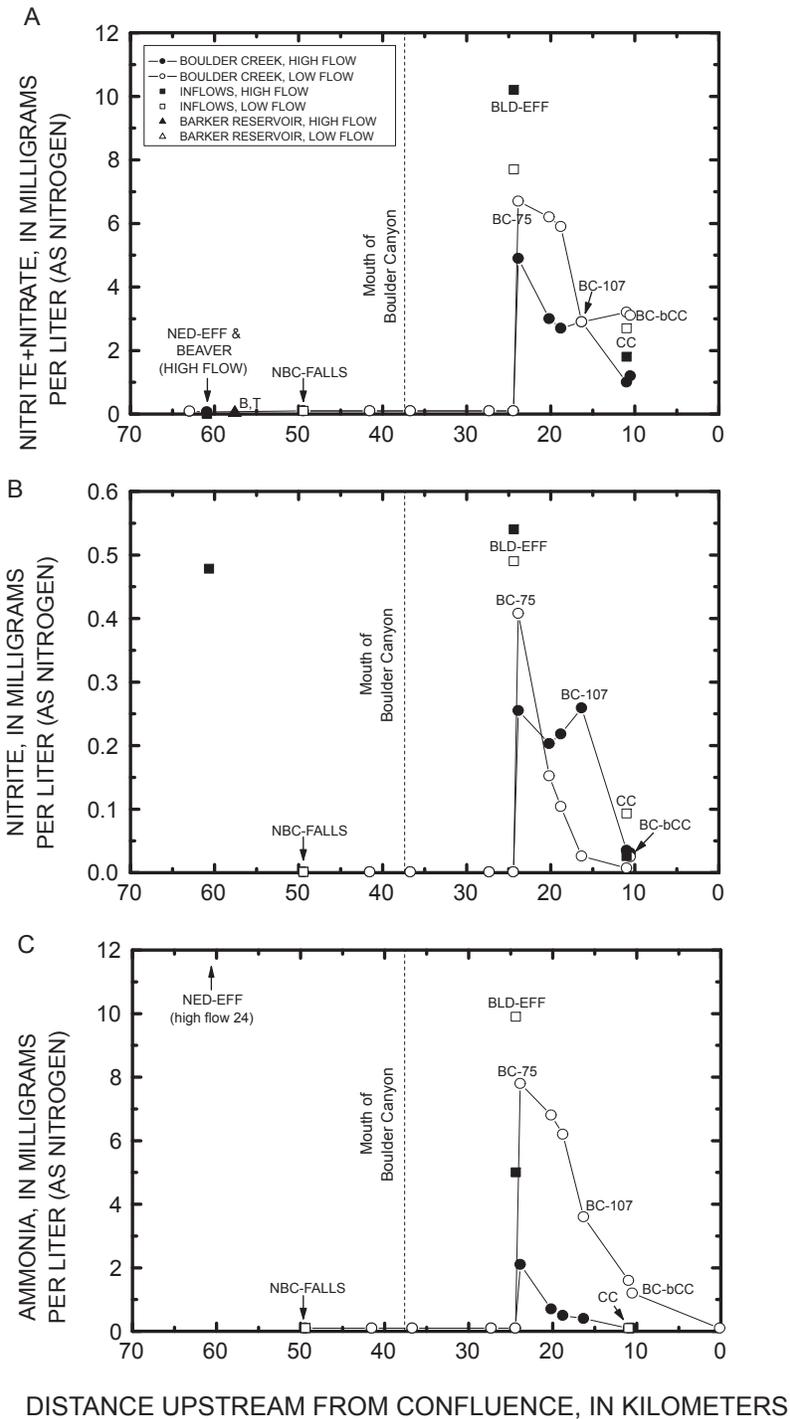


Figure 3.6. Graphs showing downstream variation in (A) nitrite+nitrate, (B) nitrite, and (C) ammonia concentrations or Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence; B, sample collected at bottom of Barker Reservoir; T, sample collected from top of Barker Reservoir)

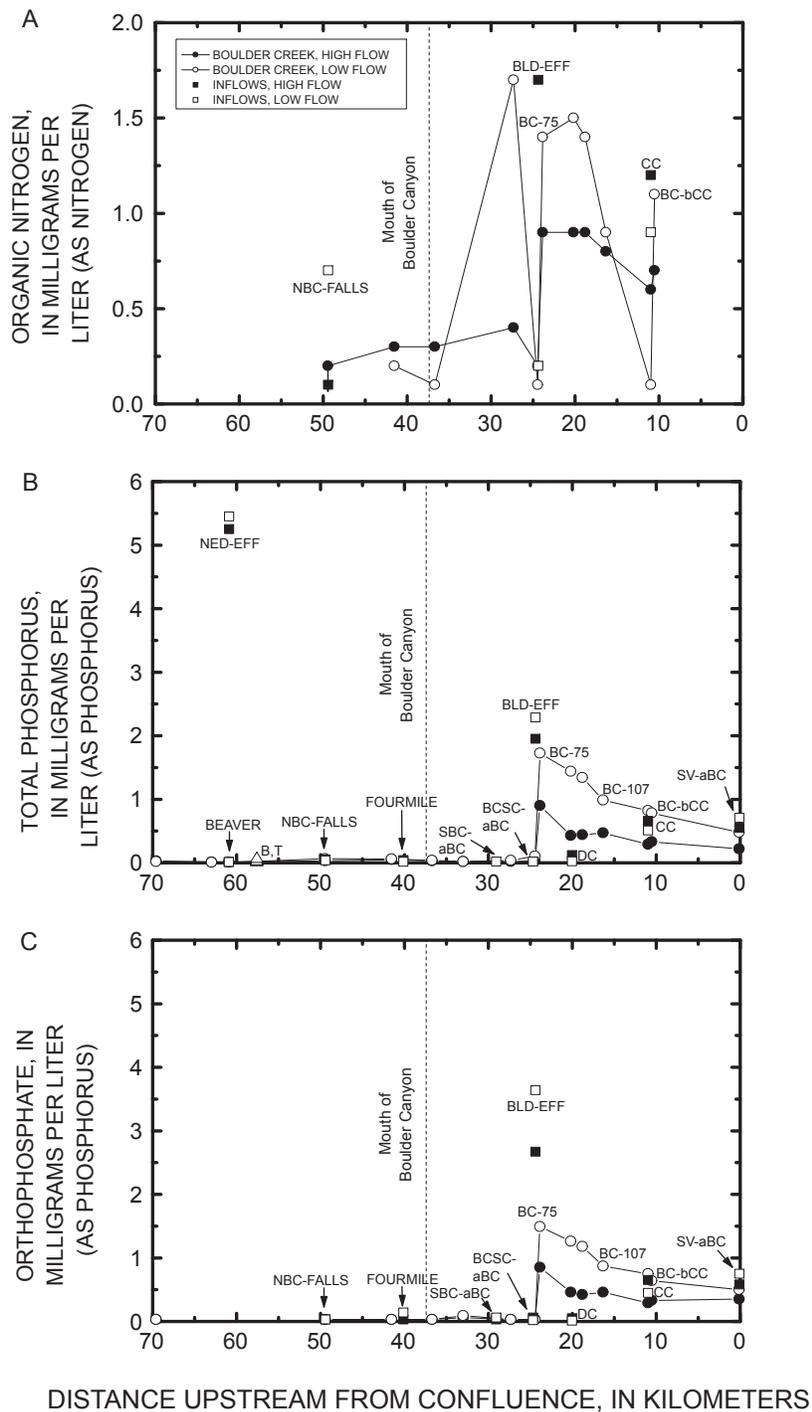


Figure 3.7. Graphs showing downstream variation in (A) organic nitrogen, (B) total phosphorus, and (C) orthophosphate concentrations for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence; B, sample collected at bottom of Barker Reservoir; T, sample collected from top of Barker Reservoir)

Creek (BC-bCC). In October, water temperatures decreased downstream to 15°C at BC-bCC.

Dissolved Oxygen

It is difficult to compare DO concentrations among the sampling sites because of the variations in temperature and atmospheric pressure in the watershed. Therefore, it is best to compare the percent oxygen saturation. While DO was measured both as concentration and percent saturation in October, only concentration was measured in June (tables 3.1 and 3.2, fig. 3.2b). However, percent oxygen saturation can be estimated from measured oxygen concentration, temperature, atmospheric pressure, and SC (APHA and others, 1998). Comparisons of calculated percent oxygen saturation to measured percent oxygen saturation for October samples showed good agreement; therefore, percent oxygen saturation values were calculated for June samples.

Sample sites along the Middle Boulder Creek/Boulder Creek profile were at or near 100 percent oxygen saturation from site MBC-WTP through site BC-aWWTP (tables 3.1 and 3.2, fig. 3.2c; due to meter malfunction, DO values were not available for several sites in June). The BLD-EFF sample was 92 and 83 percent saturated with oxygen in June and October, respectively. Downstream of the WWTP, all sample sites were saturated or supersaturated with oxygen. In June, oxygen saturation increased downstream to 180 percent at BC-bCC. In October, oxygen saturation increased to a maximum of 180 percent at BC-95, then decreased to 150 percent at BC-bCC. Most sites downstream of the WWTP had higher oxygen saturation values in October than in June.

Oxygen saturation values of samples from the surface of Barker Reservoir were 114 and 89 percent in June and October, respectively. Samples from the bottom of the reservoir had oxygen saturation values of 75 and 5 percent in June and October, respectively.

Specific Conductance

Specific conductance values were higher in October than in June, and were much higher in the lower watershed (below the mouth of Boulder Canyon) than in the upper watershed (tables 3.1 and 3.2, fig. 3.3a). Specific conductance values in the upper watershed were below 30 $\mu\text{S}/\text{cm}$ in June and below 90 $\mu\text{S}/\text{cm}$ in October at all sites except BEAVER and NED-EFF, with no obvious downstream trend. In the lower watershed, SC values of Boulder Creek increased from 28 $\mu\text{S}/\text{cm}$ at the mouth of Boulder Canyon (BC-CAN) to 94 $\mu\text{S}/\text{cm}$ at BC-aWWTP in June, and from 62 $\mu\text{S}/\text{cm}$ to 220 $\mu\text{S}/\text{cm}$ at the same sites in October. Site BLD-EFF had SC values of 595 and 682 $\mu\text{S}/\text{cm}$ in June and October, respectively, leading to increases in SC at BC-75 (325 $\mu\text{S}/\text{cm}$ in June and 572 $\mu\text{S}/\text{cm}$ in October). In both June and October, SC values decreased at the next site, but then increased downstream. In June, SC was 343 $\mu\text{S}/\text{cm}$ at BC-bCC. Due to a meter malfunction, SC values were not obtained at most downstream sites in October; SC at site BC-95 was 543 $\mu\text{S}/\text{cm}$.

pH

Most sites in the upper watershed had pH values between 7 and 8, with little seasonal or spatial variation (tables 3.1 and 3.2, fig. 3.3b). In the lower watershed, however, pH values varied seasonally and spatially. Upstream of the Boulder 75th Street WWTP, pH values were higher during low-flow sampling; pH at BC-aWWTP was 8.36 in June and 8.90 in October. After input of BLD-EFF, pH values decreased to 7.36 in June and 7.80 in October at BC-75. Downstream of BC-75, pH values of Boulder Creek were higher during high-flow sampling, and increased downstream to 9.79 in June and 9.32 in October at the site upstream of Coal Creek (BC-aCC). Downstream of Coal Creek, pH decreased in both June and October.

Total Dissolved Solids

Concentrations of TDS were higher in October than in June, and were higher in the lower watershed than in the upper watershed (tables 3.1 and 3.2, fig. 3.4a). In the upper watershed, TDS values were generally low and fairly constant from MBC-ELD to BC-CAN, with values between 14 and 20 mg/L in June and between 8 and 84 mg/L in October. In the lower watershed, TDS remained low at the sites from BC-CAN to BC-aWWTP in June, but increased to 168 mg/L at BC-61 in October. BLD-EFF had TDS concentrations of about 400 mg/L in both June and October, leading to an increase in TDS at BC-75 to values of 190 mg/L in June and 368 mg/L in October. Downstream of BC-75, TDS values decreased at the next site, then increased downstream to 220 mg/L in June and 432 mg/L in October at BC-bCC; TDS concentration at BC-aSV in October was 454 mg/L. Coal Creek and Dry Creek contributed a large amount of dissolved constituents to Boulder Creek; these tributaries had TDS concentrations between 580 and 712 mg/L.

Hardness

Hardness values were higher in October than in June, and were higher in the lower watershed than in the upper watershed (tables 3.1 and 3.2, fig. 3.4b). Hardness was fairly constant from MBC-ELD to BC-CAN, with values between 11 and 40 mg/L as CaCO₃ in June and between 19 and 50 mg/L in October. Downstream of BC-CAN, hardness values were erratic but showed an overall increase downstream, with hardness values of 60 mg/L in June and 120 mg/L in October measured at BC-aWWTP. After input of BLD-EFF, which had hardness values of 370 mg/L in June and 350 mg/L in October, hardness increased to 260 mg/L in June and 210 mg/L in October at BC-75. Hardness decreased at the next site, but showed an overall increase downstream, reaching 120 mg/L in June and 300 mg/L in October at BC-bCC.

Alkalinity

Alkalinity values were higher in October than in June, and were higher in the lower watershed than in the upper watershed (tables 3.1 and 3.2, fig. 3.4c). Alkalinity was fairly constant from MBC-WTP to BC-CAN, with values between 10 and 14 mg/L as CaCO₃ in June and between 17 and 22 mg/L in October. Downstream of BC-CAN, alkalinity increased to 33 mg/L in June and 68 mg/L in October at BC-aWWTP. After input of BLD-EFF, which had alkalinity values of 95 mg/L in June and 125 mg/L in October, alkalinity increased to 59 mg/L in June and 112 mg/L in October at BC-75. Alkalinity decreased slightly at the next site but showed an overall increase downstream, reaching 93 mg/L in June and 164 mg/L in October at BC-bCC.

Total Suspended Solids

In contrast to most parameters, TSS concentrations in the watershed were generally higher in June than in October, and were not substantially higher in the lower watershed than in the upper watershed (tables 3.1 and 3.2, fig. 3.5a). In June, TSS concentrations in Middle Boulder Creek/Boulder Creek increased downstream from MBC-WTP (2 mg/L) to BC-aWWTP (13 mg/L), then decreased to 8 mg/L at BC-75 after receiving BLD-EFF (5 mg/L). Between BC-75 and BC-aCC, TSS concentrations in June were between 7 and 10 mg/L. In October, most TSS concentrations in both the upper and lower watersheds were between 0 and 7 mg/L. Coal Creek, which had TSS concentrations of 77 mg/L in June and 39 mg/L in October, caused increases in TSS at BC-bCC to 19 mg/L in June and 14 mg/L in October.

Turbidity

Turbidity values at most Boulder Creek sampling sites, similarly to TSS concentrations, were higher in June than in October (tables 3.1 and 3.2, fig. 3.5b). During both sampling events,

turbidity showed an overall increase from MBC-ELD (0.56 NTU in June and 0.22 NTU in October) to BC-61 (2.6 and 2.3 NTU). The Boulder Creek Supply Canal site (BCSC-aBC), which had turbidity values of about 30 NTU in both June and October, caused turbidity to increase to 10 NTU in June and 5.3 NTU in October at the next Boulder Creek site, BC-aWWTP. Turbidity values then decreased to 4.7 NTU in June and 3.8 NTU in October at BC-75 after receiving BLD-EFF (3.3 and 2.4 NTU). Below BC-75, turbidity values of Boulder Creek were between 2 and 11 NTU in June and October; Coal Creek had high turbidity values (29 NTU in June and 24 NTU in October).

Fecal Coliform

Fecal coliform concentrations in the watershed were variable. Differing detection limits for the methods used by the two city laboratories (1 cols/100 mL for samples analyzed by the Drinking Water Laboratory, 20 cols/100 mL for those analyzed by the Wastewater and Environmental Laboratory) complicated comparisons. The only obvious trend observed was that concentrations were higher in the lower watershed than in the upper watershed (tables 3.1 and 3.2, fig. 3.5c). Most Middle Boulder Creek/Boulder Creek sites in the upper watershed had concentrations of 20 cols/100 mL or less. In the lower watershed, fecal coliform concentrations of Boulder Creek ranged from less than 10 to 170 cols/100 mL in June and from 2 to 700 cols/100 mL in October. Several tributaries had higher fecal coliform concentrations; the highest fecal coliform concentration (1560 cols/100 mL) observed during either sampling event was found in Dry Creek in October.

Nitrogen

Nitrite+nitrate, nitrite, and ammonia concentrations were much higher in the lower watershed than the upper watershed, and were higher in October than in June (tables 3.1 and 3.2,

fig. 3.6). Middle Boulder Creek/Boulder Creek sites upstream of the Boulder 75th Street WWTP had NO_2+NO_3 concentrations at or below 0.1 mg/L as N, NO_2 concentrations below 0.001 mg/L as N, and NH_3 concentrations below 0.1 mg/L as N. Concentrations of NO_2+NO_3 , NO_2 , and NH_3 increased downstream of the Boulder 75th Street WWTP. BLD-EFF, which had NO_2+NO_3 concentrations of 10.2 mg/L as N in June and 7.7 mg/L in October, caused concentrations in Boulder Creek to increase to 4.9 mg/L in June and 6.7 mg/L in October at BC-75. NO_2+NO_3 concentrations then decreased downstream, with concentrations of 1.2 mg/L in June and 3.1 mg/L in October at BC-bCC. Nitrite and NH_3 behaved similarly; NO_2 concentrations at BC-75 were 0.255 mg/L in June and 0.408 mg/L in October, and declined to 0.031 mg/L in June and 0.025 mg/L in October at BC-bCC; NH_3 concentrations were 2.1 mg/L in June and 7.8 mg/L in October at BC-75, and declined to less than 0.1 mg/L in June and 1.2 mg/L in October at BC-bCC.

Organic nitrogen concentrations were erratic, with values ranging from less than 0.1 mg/L to 1.7 mg/L in stream samples (fig. 3.7a). In the upper watershed, concentrations were higher during high flow; in the lower watershed, concentrations were usually higher during low flow.

Phosphorus

Total P and orthophosphate concentrations were much higher in the lower watershed than the upper watershed, and were higher in October than in June (tables 3.1 and 3.2, figs. 3.7b and c). Middle Boulder Creek/Boulder Creek sites upstream of the Boulder 75th Street WWTP had total P concentrations that ranged from 0.01 mg/L as P in June to 0.11 mg/L in October. Orthophosphate concentrations were similar, indicating that most of the phosphorus is orthophosphate.

Concentrations of total P and orthophosphate species increased substantially downstream of the

Boulder 75th Street WWTP. BLD-EFF, which had total P concentrations of 1.95 mg/L in June and 2.29 mg/L in October, caused total P concentrations to increase to 0.9 mg/L in June and 1.73 mg/L in October at BC-75. Total P concentrations then decreased as Boulder Creek flowed downstream, reaching concentrations of 0.22 mg/L in June and 0.48 mg/L in October at BC-aSV. Orthophosphate concentration profiles were similar. Higher concentrations of orthophosphate than total P are likely due to laboratory error.

DISCUSSION

Streamflow in the Boulder Creek Watershed originates primarily as snowmelt; therefore, discharge varies seasonally (Murphy and others, 2003). The much higher discharge during spring runoff (June) provides dilution for dissolved constituents, producing lower values of SC, TDS, alkalinity, hardness, nitrogen, and phosphorus than during low-flow conditions (October). Total suspended solids and turbidity were generally higher in June, when water with higher discharge can carry more suspended particles.

In addition to seasonal patterns, chemical variations were observed from upstream to downstream. These variations are caused by natural factors, such as climate and geology, and by anthropogenic factors, such as wastewater treatment, agriculture, and urbanization. This section will discuss water chemistry as it moves downstream through the headwater, mountain, urban, wastewater-dominated, and wastewater/agricultural/aggregate-mining regions. A more detailed description of the environmental setting of these regions is provided in Murphy and others (2003).

Headwater and Mountain Regions

Stream sites in the headwater and mountain regions of the watershed are snowmelt-dominated waters that have had little reaction time with the

metamorphic and igneous bedrock of the region. Potential anthropogenic sources of solutes are relatively few, and include atmospheric deposition (Williams and others, 2003), historical hardrock mining (Verplanck and others, 2003), and effects from small communities, recreation, and road runoff. Sampling sites on North, Middle, and mainstem Boulder Creeks in the headwater and mountain regions were found to be relatively dilute in both June and October, with low values of SC, TDS, alkalinity, hardness, turbidity, fecal coliform, nitrogen, and phosphorus (figs. 3.3 to 3.7). Most sites had circumneutral pH values (fig. 3.3), with oxygen at or near saturation (fig. 3.2). Elevated levels of SC, pH, TDS, alkalinity, and hardness were observed in North Beaver Creek (BEAVER); this stream and its tributaries flow through the town of Nederland and historical and operating mining districts. Elevated values of most constituents were observed in the Nederland WWTP effluent (NED-EFF). The Nederland WWTP operates an aerated lagoon treatment process, and discharged about 0.003 to 0.005 m³/s of water into Middle Boulder Creek immediately upstream of Barker Reservoir during the sampling events (Murphy and others, 2003). The volume of water discharged by the Nederland WWTP is less than 1% of the total flow to Barker Reservoir (City of Boulder, 2002) and does not appear to have a substantial effect on water quality of the reservoir or the next site on Middle Boulder Creek (MBC-aNBC) during the sampling event (figs. 3.2 to 3.7). However, oxygen saturation values at the bottom of Barker Reservoir were low, particularly during October (fig. 3.2), when waters in the reservoir are stratified (City of Boulder, 2002). Nutrient loading from NED-EFF may contribute to eutrophication of the reservoir.

Urban Corridor

Between the mouth of Boulder Canyon and the Boulder 75th Street WWTP, increases in temperature, SC, pH, alkalinity, and hardness were observed (table 3.1 and 3.2, figs. 3.2, 3.3,

and 3.4). These increases are likely caused by both natural and anthropogenic factors. As Boulder Creek leaves Boulder Canyon and flows onto the plains, the underlying geology transitions from igneous and metamorphic rocks to more easily eroded sedimentary rocks (Murphy and others, 2003). Potential anthropogenic sources, such as instream recreational activities and road and lawn runoff, increase as the creek flows through the city of Boulder. Much of the water in Boulder Creek is diverted in this reach, leaving less water for dilution. There were no storm events during either sampling period; previous studies have suggested that the loading of many constituents to urban streams occur during storm events (USEPA, 1983, 2000; Paulson, 1994). Nitrogen and phosphorus species remained low or below detection in the urban reach. However, fecal coliform concentrations increased, with one particularly high value measured during low flow in the sample from site BC-30 (table 3.2, fig. 3.5). This site is located downstream of a city park, the main campus of the University of Colorado, and a shopping center.

Wastewater-Dominated Reach

A substantial change in water quality occurs downstream of the Boulder 75th Street WWTP. Increases in SC, TDS, alkalinity, hardness, NO₂+NO₃, NO₂, NH₃, total P, and orthophosphate were observed at site BC-75 (figs. 3.3, 3.4, 3.6, and 3.7), while decreases were observed in DO, pH, TSS, and turbidity (figs. 3.2, 3.3, and 3.5). These changes reflect the composition of the wastewater effluent, which adds to the dissolved load of Boulder Creek but has low TSS and turbidity. Effluent comprised a greater proportion of flow during low flow than during high flow, and therefore had a greater effect on water quality of Boulder Creek during low flow. Mass-balance calculations were used to estimate the contribution of effluent to the discharge at the 75th Street streamgaging station using SC, alkalinity, hardness, NO₂+NO₃, and total P values in the effluent and in samples taken

from above and below the Boulder 75th Street WWTP (BC-aWWTP and BC-75). These calculations suggest that effluent contributed about 49 percent of the discharge of Boulder Creek at the 75th Street streamgaging station in June, and 71 percent during low-flow conditions. Other mass-balance calculations performed for this sampling event by Barber and others (2003) and Verplanck and others (2003) suggest that the effluent contributed about 38 percent during high flow and about 76 to 78 percent during low flow. Discharge calculations indicate that the effluent contributed between 15 and 20 percent during high flow, and between 50 and 65 percent during low flow (range due to varying rates of effluent discharged; Murphy and others, 2003). Mass-balance discrepancies for the high-flow event may be due to different sampling times (and therefore different contributions of effluent) by the USGS and the city of Boulder. Additional discharge and mass-balance calculation discrepancies may be due to the collection of grab samples at BC-75, where baseflow and effluent had not completely mixed; the sample was collected from the same bank where effluent was discharged, so may contain a higher proportion of effluent than would a fully width-integrated sample.

Wastewater/Agricultural/Aggregate-Mining Region

Dissolved oxygen and pH increased substantially downstream of BC-75 (figs. 3.2 and 3.3). Supersaturated levels of oxygen and high pH values are similar to daytime measurements of lower Boulder Creek made by Aquatic and Wetland Consultants (1987). These workers evaluated Boulder Creek over 24-hour periods and observed diurnal fluctuations in DO and pH; maximum diel variations of 2.1 pH units and 12 mg/L DO concentrations were recorded at a site on Boulder Creek immediately upstream of Coal Creek. These fluctuations are driven by aquatic vegetation. Photosynthesis, which occurs during daylight hours, produces oxygen and

consumes carbon dioxide, causing pH to increase. Respiration and decomposition, which occur 24 hours a day, consume oxygen and produce carbon dioxide, causing pH to increase. Therefore, DO and pH levels are elevated during the day and low at night. While this is a naturally-occurring process, several factors exaggerate the fluctuations. Lower Boulder Creek has been channelized, loses much of its water to diversions, and has little riparian vegetation shading the creek. The shallow, slow-moving water receives direct sunlight and reaches very high temperatures (fig. 3.2a), accelerating vegetation growth. Wastewater effluent contributes nutrients to the creek, further increasing growth rates and thus exaggerating DO and pH fluctuations. This study found that oxygen saturation values were typically higher during low flow than during high flow, due to lower water temperatures and the subsequent ability of waters to hold more oxygen.

Specific conductance, TDS, alkalinity, and hardness decreased at the site downstream of BC-75, then increased downstream (figs. 3.3, and 3.4). These increases are partly due to inputs from Dry Creek and Coal Creek. Coal Creek receives effluent from Erie, Lafayette, Louisville, and Superior WWTPs, which are permitted to discharge a total of 0.36 m³/s (8.2 million gallons per day) of effluent to Coal Creek or its tributary Rock Creek (USEPA, 2003). Coal Creek may also be affected by agricultural return flows and a greater proportion of sedimentary rock along its channel. Incoming ground water that has interacted with sedimentary bedrock may also contribute solutes to Boulder Creek. Bruce and O'Riley (1997) found that ground water in wells near lower Boulder Creek had SC values between 380 and 1347 mg/L and alkalinity levels of 108 to 466 mg/L as CaCO₃, which are higher than those measured at the lower Boulder Creek sites. In addition, evaporation may concentrate constituents in the creek.

Concentrations of NO₂+NO₃, NO₂, NH₃, total P, and orthophosphate decreased downstream of site BC-75 (figs. 3.6 and 3.7).

These nutrients are used by vegetation and can also sorb to sediment and organic matter. Ammonia in surface waters is typically converted rapidly to NO₂ and then to NO₃ by bacteria. Nutrient concentrations may also be diluted by incoming ground water. An August 1996 study found that wells near lower Boulder Creek had NO₂+NO₃ concentrations between 1 and 5 mg/L as N, NO₂ concentrations ranging from less than 0.01 to 0.05 mg/L as N, NH₃ concentrations ranging from less than 0.01 to 0.06 mg/L as N, and dissolved P concentrations ranging from less than 0.01 to 0.09 mg/L as P (Bruce and O'Riley, 1997). Most NO₂, NH₃, and dissolved P concentrations were lower in ground water than in surface water, while NO₂+NO₃ concentrations were similar to or higher than surface water concentrations. However, studies in the South Platte River Basin found that microorganisms in streambed sediments remove a substantial portion of NO₃ as ground water moves into surface water (McMahon and Böhlke, 1996).

Comparison to Previous Studies

Boulder Creek

The city of Boulder has monitored Boulder Creek water quality since 1983. Water quality data is available for the years 1998 to the present (August 2003) on the BASIN website (www.BASIN.org; Murphy and Waterman, 2003). Water-quality during the June and October 2000 study was similar to 1998-2003 data, with dissolved constituents typically higher during low-flow conditions than during high-flow conditions. Additional studies of Boulder Creek chemistry were performed by Hall and others (1979), Patterson (1980), and Aquatic and Wetland Consultants (1987). Unfortunately, few water-quality measurements were common to all studies. Comparison of water quality is further complicated by the considerable annual, seasonal, and diel variability of discharge in the Boulder Creek Watershed. Historical data collected at similar times of the year as the 2000 study are

provided in table 3.3. Hall and others (1979) evaluated Boulder Creek, Dry Creek, and Fourmile Creek for temperature, SC, TDS, alkalinity, hardness, fecal coliform, NO_2+NO_3 , NO_2 , and orthophosphate during low-flow conditions in 1975 (table 3.3). Values were similar to the October 2000 data with the exception of higher fecal coliform at sampling sites on Middle Boulder Creek in Nederland, Boulder Creek at Orodell, Boulder Creek within the city of Boulder, and Fourmile Creek, but lower concentrations in Dry Creek, in 1975.

Patterson (1980) evaluated Boulder Creek chemistry during high-flow (June) and low-flow (September) conditions in 1977. Most of the 1977 measurements (temperature, pH, TDS, alkalinity, NO_2+NO_3 , and total P) were similar to those measured in 2000, with the exception of higher TDS, alkalinity, and total P, and lower NO_2+NO_3 in 1977 for some samples from lower Boulder Creek. Discharge was similar during low-flow conditions in 1977 and 2000. However, during high flow, discharge in the upper watershed was lower in 1977 than in 2000, but much higher in the lower watershed. The greater discharge in the lower watershed is largely explained by a much greater input from the Boulder Creek Supply Canal in June 1977, when Boulder Creek received an average daily input of $4.1 \text{ m}^3/\text{s}$ of water from the canal (Colorado Water Conservation Board and Colorado Division of Water Resources, 2002). The canal supplied Boulder Creek with only $0.63 \text{ m}^3/\text{s}$ of water during sampling in June 2000 (table 3.1). Because of the drastically different discharge, it is difficult to assess if water quality has changed substantially. Higher NO_2+NO_3 concentrations in 2000 may be due to the installation of a nitrifying trickling filter at the Boulder 75th Street WWTP in 1989, which decreased NH_3 concentrations in the effluent but increased NO_2+NO_3 (Floyd Bebler, city of Boulder, written commun., 2002). Ammonia was not included in the 1977 study, so this hypothesis cannot be verified. A solids contact system and deep secondary clarifiers were also installed in 1989.

Aquatic and Wetland Consultants (1987) measured temperature, DO, pH, SC, TDS, alkalinity, turbidity, and NH_3 in lower Boulder Creek at several times of the year during 1985; the October 1985 data is included in table 3.3. Discharge was similar in October 1985 and October 2000. Most of the water-quality constituents were similar in 1985 and 2000, with some exceptions. Dissolved-oxygen values immediately downstream of the Boulder 75th Street WWTP outfall were lower in 1985, while turbidity values were higher. Improvements in DO and turbidity values are likely due to the 1989 WWTP upgrades mentioned above. Ammonia concentrations were similar in 1985 and 2000; NO_2+NO_3 concentrations were not measured in 1985. Some sites had lower SC and TDS in 1985 than in 2000.

South Platte River

The South Platte River Basin, which includes the Boulder Creek Watershed, has been extensively studied as part of the USGS National Water-Quality Assessment (NAWQA) Program (Leahy and others, 1990; Dennehy, 1991). The NAWQA study evaluated data based on five land use categories: forest, agricultural, urban, mixed urban/agricultural, and rangeland (Litke and Kimbrough, 1998). Data from the present study were similar to data from the South Platte River Basin NAWQA study in the same land-use categories. The NAWQA study found that most surface-water sampling sites located in urban, agricultural, and mixed urban-agricultural land-use areas of the South Platte River Basin had nutrient concentrations that were among the highest 25 percent of all 20 NAWQA Study Units sampled during 1992-95 (that is, 75 percent or more of samples from each site had total nitrogen concentrations greater than 7.3 mg/L as N and total P concentrations greater than 0.87 mg/L as P; Dennehy and others, 1998). Nutrient levels in mountain and rangeland sampling sites in the South Platte River Basin, however, were among the lowest nationally. These findings are similar

Table 3.3. Water quality data from previous Boulder Creek studies

[Units are milligrams per liter unless otherwise indicated; alkalinity and hardness reported as CaCO₃; m³/s, cubic meters per second; T_{water}, water temperature; turbidity units (1 JTU is approximately equal to 1 nephelometric turbidity unit); cols/100 mL, number of colonies per 100 milliliters; NO₂+NO₃-N, nitrite+nitrate-nitrogen; E, estimated]

Site	Similar 2000 site	Date	Time	Discharge (m ³ /s)	T _{water} (°C)	DO	SC (µS/cm)	pH
HIGH FLOW- 1977 (Patterson, 1980)								
Nederland	MBC-W	6/1977	--	4.22	11	--	--	6.9
Castle Rock	MBC-aNBC	6/1977	--	2.61	14.5	--	--	7.2
Orodel	BC-ORO	6/1977	--	3.54	16.5	--	--	7.4
Eben Fine Park	BC-CAN	6/1977	--	1.56	16.5	--	--	7.1
55 th	BC-30 & BC-61	6/1977	--	0.48	23	--	--	8.8
75 th	BC-75	6/1977	--	9.06	20	--	--	7.5
County Line	BC-bCC	6/1977	--	>8	26	--	--	8.9
North Boulder Cr.- Caribou	NBC-LW	6/1977	--	0.85	16	--	--	7.3
Fourmile	FOURMILE	6/1977	--	5.95	19.5	--	--	7.7
LOW FLOW- 1975 (Hall and others, 1979)								
MBC1	MBC-ELD	10/02/1975	1000	--	4	--	<50	--
MBC2	MBC-W	09/30/1975	1800	0.40	6.5	--	60	--
BC1	BC-ORO	09/30/1975	1200	--	11	--	65	--
BC3	BC-30 & BC-61	09/30/1975	1100	--	12.5	--	160	--
BC4	BC-107 & BC-aCC	09/26/1975	1500	--	20.5	--	575	--
NBC1	NBC-LW	09/30/1975	1850	--	--	--	40	--
NBC2	NBC-FALLS	09/30/1975	1450	--	7	--	112	--
FC2	FOURMILE	09/30/1975	1130	--	9	--	391	--
DC1	DC	09/26/1975	1600	--	20	--	858	--
LOW FLOW- 1977 (Patterson, 1980)								
Nederland	MBC-W	9/1977	--	0.34	9	--	--	6.9
Castle Rock	MBC-aNBC	9/1977	--	0.00	8	--	--	7
Orodel	BC-ORO	9/1977	--	0.40	16.5	--	--	6.9
Eben Fine Park	BC-CAN	9/1977	--	0.48	14	--	--	7.3
55 th	BC-30 & BC-61	9/1977	--	0.45	20	--	--	8.7
75 th	BC-75	9/1977	--	1.98	20	--	--	7.4
County Line	BC-bCC	9/1977	--	0.89	20	--	--	8.9
North Boulder Cr.- Caribou	NBC-LW	9/1977	--	0.08	10	--	--	6.8
Fourmile	FOURMILE	9/1977	--	0.14	12	--	--	7.4
Arapahoe Pass	Williams and others (2003)	9/1977	--	0.04	8	--	--	6.7
LOW FLOW- 1985 (Aquatic and Wetland Consultants, 1987)								
BC-1	BC-aWWTP	10/7-14/1985	--	0.52	9.5	10.6	150	8.11
BC-3	BC-75	10/7-14/1985	--	1.33	16.0	5.4	398	2.29 ¹
BC-4b	BC-95	10/7-14/1985	--	1.46	14.0	5.8	285	7.60
BC-5	BC-107	10/7-14/1985	--	1.06	9.5	10.1	285	7.93
BC-6	--	10/7-14/1985	--	0.98	10.5	12.6	330	8.32
BC-7a	BC-aCC	10/7-14/1985	--	0.95	12.5	13.8	360	8.68
BC-7b	BC-bCC	10/7-14/1985	--	1.66	13.5	12.4	430	8.83
BC-8	--	10/7-14/1985	--	1.91	9.5	11.1	305	8.95
BC-9	--	10/7-14/1985	--	2.27	9.5	11.1	335	8.60
BC-10	BC-aSV	10/7-14/1985	--	2.14	12.0	10.2	340	8.60

¹ Alkaline pH values recorded at this site during other sampling events by these workers indicate this is probably an erroneous measurement.

temperature; °C, degrees Celsius; DO, dissolved oxygen; SC, specific conductance; µS/cm, microsiemens per centimeter; TDS, total dissolved solids; JTU, nitrite plus nitrate as N; NO₂, nitrite as N; NH₃-N, ammonia as N; PO₄, phosphate as P; --, not measured; >, greater than; <, less than; Cr., Creek; B, non

Site	TDS	Alka- linity	Hard- ness	Turbidity (JTU)	Fecal coliform (cols/100 mL)	NO ₂ + NO ₃ -N	NO ₂ -N	NH ₃ -N	PO ₄ -P	P, ortho
Nederland	25.2	11.7	--	--	--	0.07	--	--	0.01	--
Castle Rock	29.6	12.3	--	--	--	0.08	--	--	0.00	--
Orodell	34.4	14.9	--	--	--	0.15	--	--	0.01	--
Eben Fine Park	42.4	16.2	--	--	--	0.32	--	--	0.02	--
55 th	102.7	34.9	--	--	--	0.18	--	--	0.03	--
75 th	265.3	97.6	--	--	--	0.32	--	--	0.72	--
County Line	379.7	151.1	--	--	--	0.25	--	--	0.40	--
North Boulder Cr.- Caribou	36.7	16.9	--	--	--	0.08	--	--	0.02	--
Fourmile	112.5	43.8	--	--	--	0.04	--	--	0.02	--
MBC1	19	10	12	--	B1	0.07	0.00	--	--	0.00
MBC2	37	25	25	--	B120	0.03	0.01	--	--	0.00
BC1	39	22	25	--	>1000	0.03	0.00	--	--	0.00
BC3	111	58	73	--	B4700	0.47	0.03	--	--	0.00
BC4	364	194	240	--	B73	2.30	0.47	--	--	0.82
NBC1	31	18	17	--	<1	0.08	0.01	--	--	0.00
NBC2	70	40	47	--	B3	0.04	0.00	--	--	0.00
FC2	232	71	160	--	B250	0.01	0.00	--	--	0.01
DC1	620	235	440	--	B280	0.34	0.01	--	--	0.00
Nederland	45	20	--	--	--	0.13	--	--	0.10	--
Castle Rock	83	39	--	--	--	0.25	--	--	0.00	--
Orodell	47	19	--	--	--	0.16	--	--	0.00	--
Eben Fine Park	49	20	--	--	--	0.13	--	--	0.08	--
55 th	152	64	--	--	--	0.32	--	--	0.09	--
75 th	413	161	--	--	--	2.61	--	--	4.01	--
County Line	736	271	--	--	--	3.07	--	--	1.07	--
North Boulder Cr.- Caribou	77	35	--	--	--	0.13	--	--	0.07	--
Fourmile	257	102	--	--	--	0.30	--	--	0.07	--
Arapahoe Pass	45	19	--	--	--	0.30	--	--	0.00	--
BC-1	120	96	--	6	--	--	--	0	--	--
BC-3	348	132.5	--	16	--	--	--	5.7	--	--
BC-4b	324	1045	--	7.5	--	--	--	3.14	--	--
BC-5	180	95.5	--	10	--	--	--	1.80	--	--
BC-6	230	103.5	--	9	--	--	--	0.78	--	--
BC-7a	96	125.5	--	10.5	--	--	--	1.23	--	--
BC-7b	612	151	--	15	--	--	--	0	--	--
BC-8	388	159	--	16	--	--	--	0	--	--
BC-9	440	164.5	--	14	--	--	--	1.12	--	--
BC-10	452	164	--	16	--	--	--	0.84	--	--

to the 2000 study of Boulder Creek. Notably, however, nitrogen concentrations at sites within the city of Boulder were low (fig. 3.6).

Comparison to Water Quality Standards

The Colorado Department of Public Health and Environment (CDPHE) has established water-quality use classifications for the surface waters of Colorado (CDPHE, 2002a). Stream water-quality standards vary based on the use classification for each stream segment, and include recreational, aquatic-life, domestic water supply, and agricultural standards. The classifications and standards for segments of the Boulder Creek Watershed are provided in table 3.4 (CDPHE, 2002b). Effluent concentrations are not included in this comparison to stream water standards; nor is the Saint Vrain Creek sample, which is outside of the Boulder Creek Watershed.

Temperature

Temperature standards are provided for waters with Aquatic-life class 1 cold and warm classifications (CDPHE, 2002a). Aquatic-life class 1 cold waters should have temperatures less than 20°C; aquatic-life class 1 warm waters should have temperatures less than 30°C. The sampling sites on Middle Boulder Creek, North Boulder Creek, and Boulder Creek upstream of the confluence with South Boulder Creek are classified as suitable for cold-water aquatic-life class 1 (CDPHE, 2002b). All of these sites had temperatures below 20°C (tables 3.1 and 3.2). The remaining mainstem Boulder Creek sites are classified as suitable for warm-water aquatic-life class 1. All of these sites had temperatures below 30°C. Tributary sites DC, BCSC-aBC, and CC are classified as warm-water aquatic-life class 2 (no temperature requirement).

Dissolved Oxygen

Minimum DO stream standards for Boulder Creek and its tributaries range from 5.0 to 7.0 mg/L (table 3.4; CDPHE, 2002a). None of the stream water DO concentrations were below 5.0 mg/L (tables 3.1 and 3.2). However, as discussed earlier, DO in lower Boulder Creek varies diurnally, with lowest DO values occurring at night. This study did not include night-time measurements.

pH

Stream standards for Boulder Creek and its tributaries allow a pH in the range of 6.5 to 9.0 (table 3.4; CDPHE, 2002a). Four sites in June 2000 (BC-107, BC-aCC, BC-bCC, and CC) and one site in October 2000 (BC-aCC) had pH values greater than 9.0 (tables 3.1 and 3.2). These elevated pH values are due to high rates of photosynthetic activity in the lower watershed; because of diurnal variation, nighttime pH values would be substantially lower.

Fecal Coliform

All of the Boulder Creek and tributary sampling sites are classified as suitable for recreation class 1a, which require fecal coliform concentrations to be below 200 cols/100 mL (table 3.4; CDPHE, 2002a). One site (CC) exceeded 200 cols/100 mL in June 2000 (table 3.1), while six sites (BC-30, BC-75, BC-aDC, BC-aCC, DC, and CC) exceeded 200 cols/100 mL in October 2000 (table 3.2).

Nitrogen- Nitrite and Nitrate

All of the Boulder Creek and tributary sampling sites except the Coal Creek site are classified as suitable for domestic water supply, which has a NO₂+NO₃ stream standard of 10 mg/L as N at the point of intake (table 3.4; CDPHE, 2002b). None of the Boulder Creek or tributary sites had NO₂+NO₃ concentrations

Table 3.4. Selected standards for stream segments evaluated in this study

[from Colorado Department of Public Health and Environment (CDPHE), 2002b; mg/L, milligrams per liter; Cr., Creek; Aq., aquatic; DO, dissolved oxygen; NH₃, ammonia; ac, acute; TVS, table value standard (numerical criteria set forth in CDPHE, 2002a); sp, spawning; ch, chronic; NO₂, nitrite; F. Coli, fecal coliform; S., South]

Stream Segment Description	Sample sites		Segment classification *	Numeric standards	
	Mainstem	Tributaries		Physical and biological	Inorganic (mg/L)
Mainstem of Boulder Cr., including all tributaries, lakes, reservoirs, and wetlands, from the boundary of Indian Peaks Wilderness Area to a point immediately above the confluence with S. Boulder Cr. (excluding Middle Boulder Cr. from source to the outlet of Barker Reservoir)	MBC-aNBC	NBC-LW	Aq. life cold 1	DO=6.0 mg/L	NH ₃ (ac)=TVS
	BC-ORO	NBC-FALLS	Recreation 1a	DO(sp)=7.0 mg/L	NH ₃ (ch)=0.02
	BC-CAN	SLP	Water supply	pH=6.5-9.0	NO ₂ =0.05
	BC-30	COMO FOURMILE	Agriculture	F.Coli=200/100 mL	NO ₃ =10
Mainstem of Middle Boulder Cr., Including all tributaries, lakes, reservoirs, and wetlands, from source to the outlet of Barker Reservoir	MBC-ELD	BEAVER	Aq. life cold 1	DO=6.0 mg/L	NH ₃ (ac)=TVS
	MBC-WTP		Recreation 1a	DO(sp)=7.0 mg/L	NH ₃ (ch)=0.02
	MBC-W		Water supply	pH=6.5-9.0	NO ₂ =0.05
			Agriculture	F.Coli=200/100 mL	NO ₃ =10
Mainstem of S. Boulder Cr. from S. Boulder Road to the confluence with Boulder Cr.		SBC-aBC	Aq. life warm 1	DO=5.0 mg/L	NH ₃ (ac)=TVS
			Recreation 1a	pH=6.5-9.0	NH ₃ (ch)=0.06
			Water supply	F.Coli=200/100 mL	NO ₂ =0.5
			Agriculture		NO ₃ =10
Mainstem of Coal Cr. from Highway 36 to the confluence with Boulder Cr.		CC	Aq. life warm 2	DO=5.0 mg/L	NH ₃ (ac)=TVS
			Recreation 1a	pH=6.5-9.0	NH ₃ (ch)=0.06
			Agriculture	F.Coli=200/100 mL	NO ₂ =0.5
Mainstem of Boulder Cr. from a point immediately above the confluence with S. Boulder Cr. to the confluence with Coal Cr.	BC-61		Aq. life warm 1	DO=5.0 mg/L	NH ₃ (ac)=TVS
	BC-aWWTP		Recreation 1a	pH=6.5-9.0	NH ₃ (ch)=0.06
	BC-75		Water supply	F.Coli=200/100 mL	NO ₂ =0.5
	BC-aDC		Agriculture		NO ₃ =10
	BC-95 BC-107 BC-aCC				
Mainstem of Boulder Cr. from the confluence with Coal Cr. to the confluence with St. Vrain Cr.	BC-bCC		Aq. life warm 1	DO=5.0 mg/L	NH ₃ (ac)=TVS
	BC-aSV		Recreation 1a	pH=6.5-9.0	NH ₃ (ch)=0.06
			Water supply	F.Coli=200/100 mL	NO ₂ =0.5
			Agriculture		NO ₃ =10
All tributaries to Boulder Cr. from immediately above the S. Boulder Cr. confluence to Saint Vrain Cr. confluence (excluding S. Boulder Cr. and Coal Cr.)		BCSC-aBC	Aq. life warm 2	DO=5.0 mg/L	NH ₃ (ac)=TVS
		DC	Recreation 1a	pH=6.5-9.0	NH ₃ (ch)=0.10
			Agriculture	F.Coli=200/100 mL	NO ₂ =0.5
					NO ₃ =10

* Segment classifications are defined as follows: Aq. Life cold 1 (aquatic life cold water 1)- surface waters that presently sustain a wide variety of cold water biota, including sensitive species, or could sustain such biota but for correctable water quality conditions; Aq. Life warm 1 (aquatic life warm water 1)- surface waters that presently sustain a wide variety of warm water biota, including sensitive species, or could sustain such biota but for correctable water quality conditions; Aq. Life warm 2 (aquatic life warm water 2- surface waters that are not capable of sustaining a wide variety of warm water biota, including sensitive species, due to physical habitat, water flows or levels, or uncorrectable water quality conditions that result in substantial impairment of the abundance and diversity of species; Recreation 1a (recreation class 1a, existing primary contact)- surface waters in which primary contact uses (recreation in or on the water when the ingestion of small quantities of water is likely to occur) have been documented or are presumed to be present; Water supply-surface waters suitable or intended to become suitable for potable water supplies; Agriculture- surface waters suitable or intended to become suitable for irrigation of crops usually grown in Colorado and which are not hazardous as drinking water for livestock.

greater than 10 mg/L as N (tables 3.1 and 3.2). Maximum NO₂ standards for aquatic-life are determined on a case-by-case basis, according to species present and chloride concentration (CDPHE, 2002b). The sampling sites on Middle Boulder Creek, North Boulder Creek, and Boulder Creek upstream of the confluence with South Boulder Creek have a maximum NO₂ standard of 0.05 mg/L as N (table 3.4). All of these sites had NO₂ concentrations below the detection limit of 0.001 mg/L as N (tables 3.1 and 3.2). The remaining Boulder Creek and tributary sites have a maximum NO₂ standard of 0.5 mg/L as N. None of these sites exceeded 0.5 mg/L as N.

Nitrogen- Ammonia

Acute and chronic stream standards for ammonia in Boulder Creek and its tributaries are provided for un-ionized ammonia (table 3.4; CDPHE, 2002b). Un-ionized ammonia (dissolved ammonia gas) is much more toxic to aquatic life than the ammonium ion (USEPA, 1999). Un-ionized ammonia can be calculated from total ammonia concentrations, pH, and temperature with the equation $f = 1/(10^{pK_a - pH} + 1)$, where f is the fraction of ammonia in un-ionized form, $pK_a = 0.09018 + 2729.92/(273.2 + T)$, and T is water temperature in degrees Celsius (Emerson and others, 1975). Un-ionized ammonia concentrations in Boulder Creek in June and October 2000 ranged from below detection to 0.62 mg/L as N. Chronic stream standards for un-ionized ammonia in Boulder Creek are 0.02 mg/L in the upper watershed and 0.06 mg/L in the lower watershed (table 3.4). These standards were exceeded at lower Boulder Creek sites BC-aDC, BC-95, and BC-107 in June and October 2000, and BC-75, BC-aCC, and BC-bCC in October 2000. Acute un-ionized ammonia standards vary based on pH, temperature, and presence of cold-water species (CDPHE, 2002a) and are not discussed here. Elevated concentrations of un-ionized ammonia have been an issue in lower Boulder Creek for years due to high water temperatures and high daytime pH values

(TetraTech, Inc., 1993). The reach of Boulder Creek from South Boulder Creek to Saint Vrain Creek is included in the State of Colorado 303(d) list of impaired waters because of un-ionized ammonia (CDPHE, 2003). The city of Boulder has attempted to improve water quality in lower Boulder Creek by restoring streambank stability, planting willows, and deepening channels (TetraTech, Inc., 1993).

SUMMARY

Water quality of a 70-km reach of Boulder Creek was evaluated by the city of Boulder and the U.S. Geological Survey during high-flow and low-flow conditions of the year 2000. Dissolved constituents generally were present in lower concentrations during high-flow conditions, due to dilution by greater streamflow volumes from snowmelt runoff. Total suspended solids and turbidity were typically higher during high-flow conditions, likely due to greater water velocity. Constituent concentrations were relatively low in the upper Boulder Creek Watershed, due to minimal bedrock contribution and few anthropogenic sources. An increase in some variables was observed as Boulder Creek flowed through the city of Boulder, as geology changes to sedimentary rocks and anthropogenic sources increase. Downstream of the Boulder 75th Street Wastewater Treatment Plant (WWTP), water quality is effluent-dominated, with dissolved constituents showing a large increase immediately downstream of the plant. Total suspended solids and turbidity in Boulder Creek typically decreased after receiving the effluent. Impact of the WWTP was greater during low flow, when WWTP effluent comprises a greater proportion of stream discharge. Downstream of the WWTP, nutrients decreased along the profile due to chemical and biological processes and possibly ground water input, while alkalinity, hardness, SC, and TDS increased after the creek received tributary and ground water input. Dissolved oxygen, pH, and temperature reached

high levels in lower Boulder Creek during daylight hours. Diurnal fluctuations in DO and pH are controlled by the growth of aquatic vegetation; growth rates are accelerated due to shallow waters, direct sunlight, and elevated nutrient concentrations. Comparison of water-quality variables measured in this study to those measured in earlier studies showed that many were similar; however, it is difficult to assess whether substantial changes in water quality have occurred due to differing variables measured and variations in discharge. Samples collected from Boulder Creek and its tributaries met most Colorado water-quality standards; however, fecal coliform concentrations in some lower Boulder Creek samples exceeded state standards, primarily during low-flow conditions. Maximum pH standards were exceeded, again primarily during low-flow conditions, due to high rates of photosynthesis activity. High temperatures and pH values led to un-ionized ammonia concentrations higher than chronic stream standards.

REFERENCES CITED

- American Public Health Association, American Water Works Association, and Water Environment Federation, 1998, *Standard methods for the examination of water and wastewater* (20th ed.): Washington, D.C., American Public Health Association, 1220 p.
- Aquatic and Wetland Consultants, 1987, A one year, biweekly, 24-hour sampling study of Boulder Creek and Coal Creek water quality: Boulder, Colo., Aquatic and Wetland Consultants, Prepared for the City of Boulder Public Works Department, 117 p.
- Barber, L.B., Furlong, E.T., Keefe, S.H., Brown, G.K., and Cahill, J.D., 2003, Natural and contaminant organic compounds in the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000— Chapter 5 in Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 103-144.
- Bruce, B.W. and O'Riley, Christopher, 1997, Comparative study of ground-water quality, 1976 and 1996, and initial gain-and-loss assessment of Boulder Creek, Boulder County, Colorado: U.S. Geological Survey Water-Resources Investigations Report 97-4091, 49 p.
- City of Boulder, 2002, Middle Boulder Creek water source management plan, Boulder, Colo., version 1: Boulder, Colo., Boulder Public Works Department, accessed May 10, 2002, at <http://www.ci.boulder.co.us/publicworks/depts/utilities/projects/barker-res/pdf/draftreport.pdf>
- Colorado Department of Public Health and Environment Water Quality Control Division, 2002a, Surface water quality classifications and standards— Regulation 31— Basic standards and methodologies for surface water (5 CCR 1002-31): Denver, Colo., Colorado Department of Public Health and Environment, accessed August 23, 2002, at <http://www.cdphe.state.co.us/op/regs/waterqualityregs.asp>
- _____, 2002b, Surface water quality classifications and standards— Regulation 38— Classification and numeric standards for South Platte River Basin, Laramie River Basin, Republican River Basin, Smoky Hill River Basin: Denver, Colo., Colorado Department of Public Health and Environment, accessed August 23, 2002, at <http://www.cdphe.state.co.us/op/regs/waterqualityregs.asp>
- _____, 2003, Total maximum daily load process: Denver, Colo., Colorado Department of Public Health and Environment, accessed June 9, 2003, at http://www.cdphe.state.co.us/wq/Assessment/TMDL/tmdl_status.htm
- Colorado Water Conservation Board and Colorado Division of Water Resources, 2002, Colorado Decision Support Systems website, accessed August 30, 2002, at <http://cdss.state.co.us>
- Dennehy, K.F., Litke, D.W., Tate, C.M., Qi, S.L., McMahon, P.B., Bruce, B.W., Kimbrough, R.A., and Heiny, J.S., 1998, Water quality in the South Platte River Basin, Colorado, Nebraska, and Wyoming, 1992-95: U.S. Geological Survey Circular 1167, 38 p.
- Dennehy, K.F., 1991, National Water-Quality Assessment program— South Platte River Basin: U.S. Geological Survey Open-File Report 91-155, 2 p.
- Emerson, Kenneth, Russo, R.C., Lund, R.E., and Thurston, R.V., 1975, Aqueous ammonia equilibrium calculations— Effect of pH and temperature: *Journal of Fisheries Research Board of Canada*, vol. 32, p. 2379-2383.
- Hach Company, 2001, DR/4000 spectrophotometer procedures manual (10th ed.): Hach Company, Loveland, Colo., accessed May 15, 2002, at http://www.hach.com/dr4k_manual/index.htm
- Hall, D.C., Boyd, E.L., and Cain, D., 1979, Hydrologic data for wells, springs, and streams in Boulder County, Colorado: U.S. Geological Survey Open-File Report 79-979, 106 p.

- Leahy, P. P., Rosenshein, J.S., and Knopman, D.S., 1990, Implementation plan for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 90-174, 10 p.
- Litke, D.W. and Kimbrough, R.A., 1998, Water-quality assessment of the South Platte River Basin, Colorado, Nebraska, and Wyoming— Environmental setting and water quality of fixed sites, 1993-1995: U.S. Geological Survey Water-Resources Investigations Report 97-4220, 61 p.
- McMahon, P.B. and Böhlke, J.K., 1996, Denitrification and mixing in a stream-aquifer system— effects on nitrate loading to surface water: *Journal of Hydrology*, v. 186, p. 105-128.
- Murphy, S.F., Barber, L.B., Verplanck, P.L., and Kinner, D.A., 2003, Environmental setting and hydrology of the Boulder Creek Watershed, Colorado— Chapter 1 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 5-26.
- Murphy, S.F. and Waterman, J.R., 2003, Water quality: Boulder Area Sustainability Information Network (BASIN), accessed June 9, 2003, at www.basin.org/watershed/wqhome.html
- Patterson, C.G., 1980, Geochemistry of Boulder Creek, Boulder, Jefferson, and Gilpin counties, Colorado: Boulder, University of Colorado, Master's thesis, 105 p.
- Paulson, C.L., 1994, Partitioning and speciation of copper, lead and zinc in stormwater runoff: Boulder, University of Colorado, Ph.D. dissertation, 182 p.
- TetraTech, Inc., 1993, Boulder Creek, Colorado— TMDL case study: Denver, Colo., Office of Water, U.S. Environmental Protection Agency, EPA number EPA/841/F-93/006, 8 p., accessed May 10, 2002, at <http://www.epa.gov/OWOW/TMDL/cs8/cs8.htm>
- U.S. Environmental Protection Agency, 1983, Results of the nationwide urban runoff program— Executive summary: Washington, D.C., Water Planning Division, U.S. Environmental Protection Agency, National Technical Information Service accession number PB84-185545, 4 v.
- _____, 1999, 1999 update of ambient water quality criteria for ammonia: Washington, D.C., Office of Water, U.S. Environmental Protection Agency, EPA 822-R-99-014, 147 p.
- _____, 2000, Storm water phase II final rule— An overview: Washington, D.C., Office of Water, U.S. Environmental Protection Agency, EPA 833-F-00-001, 4 p.
- _____, 2001, Delivering timely environmental information to your community— The Boulder Area Sustainability Information Network (BASIN): Washington, D.C., Office of Research and Development, U.S. Environmental Protection Agency, EPA 625-R-01-010, 96 p.
- _____, 2003, Permit Compliance System database: accessed April 15, 2003, at <http://www.epa.gov/enviro/html/pcs/index.html>
- Verplanck, P.L., McCleskey, R.B., and Roth, D.A., 2003, Inorganic water chemistry of the Boulder Creek watershed, Colorado, during high-flow and low-flow conditions, 2000— Chapter 4 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 71-102.
- Williams, M.W., Hood, Eran, and Caine, Nel, 2003, Headwater catchments of North Boulder Creek— Chapter 8 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 185-198.

Chapter 4 - Inorganic Water Chemistry of the Boulder Creek Watershed, Colorado, During High-Flow and Low-Flow Conditions, 2000

By Philip L. Verplanck, R. Blaine McCleskey and David A. Roth

Abstract

Spatial and temporal variability of major and trace constituents in the Boulder Creek Watershed, Colorado were determined on a suite of water samples collected during high and low flow in the year 2000. Field parameters and inorganic water analyses are reported for twenty-nine sites including sixteen stream sites, twelve tributaries/inflows, and Saint Vrain Creek. The most upstream site was above the town of Eldora, and the most downstream site was at the confluence of Boulder Creek and Saint Vrain Creek. Most dissolved constituents display similar downstream variations with relatively low concentrations in the upper 30 kilometers section (above the mouth of Boulder Canyon), an increase in concentration in the reach between the mouth of Boulder Canyon and the Boulder 75th Street Wastewater Treatment Plant (WWTP), and a further increase in solute concentrations in the lower reach. Alkalinity, calcium, chloride, magnesium, silica, sodium, and sulfate are the dominant dissolved constituents in Boulder Creek, accounting for over 90 percent of the mass of dissolved inorganic constituents. The relative proportion of these constituents varied during high and low flow and from the upper sampling sites to the lower sites. Most constituents were higher in concentration during low flow than during high flow. The rare earth element patterns of the effluent from the Boulder 75th Street WWTP and the first Boulder Creek sampling site downstream of the inflow of the effluent contain a peak in gadolinium.

Using the low-flow results, preliminary interpretations of the sources of solutes and the processes controlling their downstream

variations are discussed. Interpretations are based on geochemical modeling results and identification of geochemical signatures. In the upper part of the watershed, above the range front, natural weathering of crystalline bedrock appears to be the primary source of solutes. Historical mining, the towns of Eldora and Nederland, and road runoff did not appear to have a major effect on Boulder Creek during the samplings. The chemistry of Boulder Creek in the reach between the range front and the Boulder 75th Street WWTP appears to be dominated by ground-water inflows that have interacted with sedimentary bedrock. Anthropogenic sources of some solutes cannot be ruled out. During the low-flow sampling, effluent from the WWTP accounted for 77 percent of the flow of Boulder Creek at the next downstream site. The large percentage of flow and the high concentrations of most constituents make the Boulder effluent the largest loading inflow to Boulder Creek. Because of numerous potential sources of solutes and various in-stream processes downstream of the WWTP, differentiating between anthropogenic and natural sources of solutes is difficult solely using the inorganic data set. Wastewater treatment plant effluent from Erie, Lafayette, Louisville, and Superior, agriculture diversion ditch return flow, and ground water also enter Boulder Creek.

INTRODUCTION

Spatial and temporal variability of major and trace constituents in the Boulder Creek Watershed were determined on a suite of water samples collected during high- and low-flow in the year 2000. Stream chemistry is controlled by

Water-quality samples were collected using a depth-integrated sampler following the equal-width-increments method (Edwards and Glysson, 1988), unless the discharge was too great to safely wade the width of the creek. In these situations a plastic bucket was pulled across the width of the creek to integrate the sample. Water quality samples for major, minor, and trace element determinations were filtered with a 142-mm diameter, 0.1- μm pore-size tortuous path, filter membrane. Anion samples were filtered and not acidified, cation samples were filtered and acidified with concentrated nitric acid, and samples for iron speciation were filtered and acidified with six-molar hydrochloric acid. Total-recoverable samples were unfiltered aliquots from the same sample-collection bottle as the filtered samples, which were acidified with concentrated nitric acid. All filtration was performed on site except for samples NED-EFF, SLP, MBC-WTP and BLD-EFF, which were filtered at the laboratory from a one-gallon grab sample. Samples from NED-EFF and BLD-EFF were filtered with cartridge-style, 0.45- μm pore-size filters. Possible contamination of samples was minimized by using new, acid- and deionized-water-washed bottles. Each container was rinsed on-site three times with sample water prior to filling.

Water-Quality Analyses

All reagents were of a purity at least equal to the reagent-grade standards of the American Chemical Society. Double-distilled de-ionized water and re-distilled acids using a sub-boiling purification technique (Kuehner and others, 1972) were used in all preparations. For inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES), external standards, blanks, sample dilutions, and spiking solutions were made with commercial trace analysis grade elemental standards. Mercury standards were prepared gravimetrically from semi-conductor grade 99.9995 percent purity HgCl_2 . For ion

chromatography (IC) determinations, standards were prepared from compounds of the highest commercially available purity. USGS standard reference water samples (SRWS) and National Institute of Standards and Technology (NIST), formerly National Bureau of Standards, standard reference materials were used as independent quality control standards. Samples were diluted as necessary to bring the analyte concentration within the optimal range of the method. For elemental analyses, several dilutions of each sample were analyzed to check for concentration effects on the analytical method.

Trace metal concentration determinations for dissolved samples were performed using a Perkin Elmer Sciex Elan 6000 ICP-MS using a method similar to that described in Garbarino and Taylor (1979). Elements analyzed by this method included aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, cerium, cesium, chromium, cobalt, copper, lead, lithium, manganese, molybdenum, nickel, the rare earth elements (cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, samarium, terbium, thulium, and ytterbium), rhenium, rubidium, selenium, strontium, tellurium, thallium, thorium, uranium, vanadium, yttrium, zinc, and zirconium. Mercury concentrations were determined by the method described in Roth (1994) using a PS Analytical Merlin Cold Vapor-Atomic Fluorescence Spectrometer System. Major cations (calcium, magnesium, potassium, and sodium) and silica for dissolved samples were determined using a Leeman Labs – Direct Reading Echelle (DRE) ICP-OES. Major cations, silica and trace elements (aluminum, arsenic, barium, boron, beryllium, cadmium, chromium, cobalt, copper, lead, lithium, manganese, nickel, selenium, strontium, vanadium, and zinc) for total recoverable samples were determined using a Leeman Labs - DRE ICP-OES. Major cations were analyzed using the radial view while the axial view was used for trace elements. Iron redox species were determined using a modification of the FerroZine colorimetric method (Stookey,

1970; To and others, 1999) with a Hewlett Packard 8453 diode array UV/VIS spectrophotometer. Concentrations of major anions were determined by ion chromatography (Brinton and others, 1995) using a Dionex 2010i ion chromatograph with 10- μ L and 50- μ L sample loops. Alkalinity (as HCO_3^-) was determined using an Orion 960 autotitrator and standardized H_2SO_4 (Barringer and Johnsson, 1989).

Calibration curves were constructed by using standards within each set of analyses. Standard reference water samples 67, 69, T115, T143, T153, and T159 were used to check the analytical methods for major and trace metals for those analytes determined by ICP-OES. Standard reference water samples T135, T147, T149, T157, NIST 1643b, NIST 1643d, and PPREE1 and SCREE1 (Verplanck and others, 2001) were used as quality control checks for ICP-MS analyses. Quality control for the determination of mercury concentrations was monitored using USGS SRWS Hg7, Hg14, Hg15, and Hg22, all at a dilution of 1/100. Standard reference water samples M136, M140, and M150 were used to check the analytical methods for major anions. The quality-control data are presented in tables 4.1 to 4.4. Mercury detection limits (table 4.4) were determined using the method described by Skogerboe and Grant (1970) at the 97.5 percent confidence level.

Data for all samples with complete analyses were checked using the computer program WATEQ4F (Ball and Nordstrom, 1991) for charge imbalance (C.I.) using the following calculation:

$$\text{C.I. (percent)} = \frac{100 * (\text{sum cations} - \text{sum anions})}{(\text{sum cations} + \text{sum anions}) \div 2}$$

The sum anions and sum cations are the summation of the anions and cations in milliequivalents per liter (meq/L). The percent charge imbalance was low (< 10 percent) for most samples (tables 4.5 and 4.6). Dilute headwaters samples collected during high-flow had charge imbalances that were greater because

of analytical imprecisions when determining concentrations at or near the detection limits.

RESULTS

Analytical results are tabulated in tables 4.5 and 4.6. Sample sites are listed in downstream order starting with the most upstream Middle Boulder Creek site (MBC-ELD). Sites not located on the mainstem of Middle Boulder Creek-Boulder Creek are listed below the mainstem sites in downstream order of where they flow into Boulder Creek. Sampling sites are shown in figure 4.1 and described in table 1.1 of Murphy and others (2003), and discharge measurements are tabulated in table 1.2.

Results less than the detection limit are identified in the tables using the less than symbol (<) preceding the detection limit. Parameters that were not determined for a particular sample are identified by dashes (--) within the table. If concentrations of trace elements were at least 3 times the detection limit by ICP-OES, good agreement between ICP-OES and ICP-MS results was observed (fig. 4.2). Field blanks are included in the bottom line of the high- and low-flow data tables.

For the upper portion of Boulder Creek (above the mouth of Boulder Canyon at 36.7 kilometers), bicarbonate, calcium, chloride, magnesium, silica, sodium, and sulfate are the dominant dissolved constituents, accounting for 97 and 94 percent of dissolved inorganic constituents at BC-CAN during high- and low-flow, respectively. The order of descending concentrations (in millimoles per liter) during high flow was bicarbonate, calcium, sodium, silica, chloride, magnesium, and sulfate, and during low flow was bicarbonate, calcium, sodium, chloride, silica, magnesium, and sulfate. For the lower portion of Boulder Creek (below BC-CAN), bicarbonate, calcium, chloride, magnesium, silica, sodium and sulfate were still the dominant dissolved constituents, accounting for 98 and 92 percent of dissolved inorganic constituents during high- and low-flow

Table 4.1. Results of standard reference water samples used in the ICP-OES analyses of Boulder Creek water samples

[mg/L, milligrams per liter; --, element not analyzed; MPV, most probable value; <, less than; ND, not determined in standard]

	HIGH-FLOW						LOW-FLOW						MPV					
	SRWS69 (mg/L)	T115 (mg/L)	T143 (mg/L)	T153 (mg/L)	T159 (mg/L)	T159 (mg/L)	SRWS67 (mg/L)	SRWS69 (mg/L)	T153 (mg/L)	T159 (mg/L)	SRWS67 (mg/L)	SRWS69 (mg/L)	T115 (mg/L)	T143 (mg/L)	T153 (mg/L)	T159 (mg/L)		
Al	0.52	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	0.67	<0.08	<0.08	0.018	0.62	0.014	0.015	0.001	0.028		
As	<0.02	<0.02	<0.02	<0.02	<0.02	<0.03	<0.03	<0.03	<0.03	0.018	0.012	0.040	0.022	0.035	0.032	0.032		
B	0.11	0.091	0.026	0.096	0.022	0.035	0.12	0.11	0.028	ND	ND	0.099	0.035	0.099	0.026	0.026		
Ba	0.038	--	0.089	0.2	0.04	--	0.037	--	0.039	0.219	0.043	0.250	0.082	0.184	0.038	0.038		
Be	0.035	0.059	0.007	<0.0001	0.011	0.051	0.034	<0.0001	0.011	0.044	0.032	0.054	0.009	ND	0.011	0.011		
Ca	50	55	57	28	26	44	50	29	26	ND	ND	51	54	28	26	26		
Cd	<0.001	0.013	0.02	0.016	0.026	0.01	<0.001	0.017	0.026	0.01	0.001	0.014	0.0191	0.016	0.024	0.024		
Co	0.01	0.014	0.015	<0.001	0.011	0.013	0.015	0.001	0.014	0.011	0.014	0.0154	0.017	ND	0.0133	0.0133		
Cr	0.001	0.036	0.036	0.014	0.028	0.03	0.003	0.015	0.028	0.028	0.028	0.005	0.037	0.015	0.027	0.027		
Cu	0.31	0.015	0.021	0.024	0.033	0.027	0.33	0.026	0.036	0.028	0.297	0.017	0.022	0.024	0.033	0.033		
Fe	0.11	1.2	0.12	0.074	<0.007	0.81	0.22	0.078	0.052	ND	ND	1.175	0.222	0.075	0.0489	0.0489		
K	3.3	--	2.5	1.6	1.8	3.2	3.9	1.8	1.9	ND	ND	5.41	2.5	1.6	1.52	1.52		
Li	0.44	0.19	0.026	0.06	0.013	--	0.47	0.064	0.011	0.627	0.397	0.132	0.018	0.053	0.009	0.009		
Mg	--	--	--	8.9	5.7	--	--	9.2	5.9	ND	ND	27.6	10.4	8.72	5.6	5.6		
Mn	0.23	0.47	0.005	0.07	0.015	0.61	0.23	0.078	0.023	ND	ND	0.455	0.018	0.075	0.022	0.022		
Na	49	--	37	29	--	27	51	31	--	ND	ND	140	34	28.7	100	100		
Ni	<0.02	<0.02	0.076	0.034	0.024	0.004	0.017	0.036	0.024	0.096	0.018	0.017	0.071	0.032	0.022	0.022		
Pb	0.02	0.011	0.089	0.05	0.017	<0.006	0.023	0.051	0.019	0.005	0.023	0.013	0.083	0.046	0.017	0.017		
SiO ₂	7.8	11	--	5.8	12	3.6	7.9	6.2	12	ND	ND	9.9	23.4	5.79	11.5	11.5		
Se	<0.02	<0.02	<0.02	<0.02	<0.02	<0.04	<0.04	<0.04	<0.04	0.012	ND	0.010	0.023	0.006	0.012	0.012		
Sr	--	--	0.32	0.32	0.2	0.39	--	0.33	0.19	0.375	0.612	0.67	0.31	0.31	0.19	0.19		
V	<0.001	0.014	0.027	0.016	0.012	<0.001	<0.001	0.017	0.013	ND	ND	0.018	0.030	0.019	0.014	0.014		
Zn	0.013	0.4	0.014	0.067	0.014	0.016	0.03	0.087	0.024	0.017	0.028	0.381	0.020	0.073	0.019	0.019		

Table 4.2. Results of standard reference water samples used in the IC analyses of Boulder Creek water samples

[mg/L, milligram per liter; --, not analyzed; MPV, most probable value]

	HIGH-FLOW		LOW-FLOW			MPV		
	M140 (mg/L)	M150 (mg/L)	M136 (mg/L)	M140 (mg/L)	M150 (mg/L)	M136 (mg/L)	M140 (mg/L)	M150 (mg/L)
Cl	26	18	94	27	20	92	25.8	17
F	--	1.0	1.07	--	1.00	1.04	0.53	1
SO ₄	149	5.23	157	153	5.2	150	150	5.5

respectively, but the relative proportion of these constituents changed. The order of descending concentrations (in millimoles per liter) during high and low flow was bicarbonate, sodium, sulfate, magnesium, calcium, chloride, and silica.

The downstream profiles and seasonal variations for Middle Boulder-Creek-Boulder Creek and the sampled inflows for specific conductance, boron, calcium, chloride, magnesium, silica, sodium, sulfate, and zinc are displayed in figures 4.3 to 4.5 Most dissolved constituents, with the exception of silica, display similar downstream variation with relatively low concentrations in the upper 30-kilometer section, above the mouth of Boulder Canyon (BC-CAN), an increase in concentration in the reach between BC-CAN and the Boulder 75th Street Wastewater Treatment Plant (BC-aWWTP), and a greater increase in solute concentrations in the lower reach (BC-75 to BC-aSV). Most dissolved constituents had higher concentrations during low flow than during high flow. The chemistry of the inflows was quite variable during both high- and low-flow sampling.

The rare earth elements (REEs) are a suite of fourteen trace metals from atomic number 57 (La) to 71 (Lu) that have similar chemical and physical properties because they generally form stable 3⁺ ions of similar size. The REEs have been utilized as geochemical tracers to constrain geologic and hydrologic processes. Rare earth element patterns, the plot of the concentration of each REE normalized to a standard reference, provide a graphical means to evaluate changes across the REEs for a given sample or suite of samples. The REE pattern for BLD-EFF has a distinctive enrichment in gadolinium compared to

its neighboring REEs europium and terbium (fig. 4.6) None of the upstream Boulder Creek samples have this gadolinium anomaly, but the REE pattern of the first Boulder Creek sampling site downstream of the effluent discharge channel (BC-75) does display a peak at gadolinium. In contrast, the REE pattern of the NED-EFF does not have a peak at gadolinium (fig. 4.6). Similar patterns were observed at high and low flow.

DISCUSSION

Two of the objectives of this study are to determine the natural and anthropogenic sources of dissolved constituents and to identify processes that control the downstream variations of dissolved constituents in Boulder Creek. This chapter focuses on the inorganic chemistry of Boulder Creek, and the following discussion describes the downstream evolution of Boulder Creek's inorganic chemistry. Low-flow data is discussed because similar trends were observed in both sampling events, but the high-flow data have lower concentrations as a result of dilution by snowmelt.

Boulder Creek Upstream of the Range Front

In the headwater portion of the Boulder Creek Watershed, surface and ground waters have short residence times and originate as precipitation from rain or snowmelt. The headwater sites (MBC-ELD, COMO, NBC-LW, and SLP) are fed by precipitation-derived water that has few potential anthropogenic sources

including atmospheric deposition, historical hardrock mining, and waste from mountain cabins. The University of Colorado Mountain Research Station monitors the chemistry of precipitation, and numerous research studies have investigated the sources of solutes in precipitation and nearby down-gradient surface waters (Williams and others, 2003). Monthly precipitation samples are collected and analyzed for a suite of constituents through the National Atmospheric Deposition Program. In addition, Mast and others (M.A. Mast, written commun., 2002) have analyzed snowpack samples for a suite of inorganic constituents, including trace metals. Research at University of Colorado's Mountain Research Station on Niwot Ridge has documented that, although the precipitation is quite dilute (specific conductance $\sim 5 \mu\text{S}/\text{cm}$), some anthropogenic input is observed. Williams and others (2003) document that anthropogenic nitrogen, derived primarily from the combustion of fossil fuels and agricultural practices, is present in Niwot Ridge precipitation.

Most major-constituent concentrations in headwater sites were enriched by factors of 10 to 20 compared to Niwot Ridge precipitation. To evaluate possible weathering reactions between meteoric water and bedrock geology, mass balances were constructed using the geochemical modeling program NETPATH (Plummer and others, 1994). In these simulations, meteoric water was reacted with known minerals in bedrock in the upper portion of the watershed to determine whether measured water chemistry was consistent with weathering of the local bedrock. The chemistry of meteoric water was estimated using annual, volume-weighted mean concentrations measured at the precipitation monitoring station at Niwot Ridge. Bedrock geology in the headwater parts of the Boulder Creek Watershed consists mostly of Precambrian-age igneous and metamorphic rocks including the Boulder Creek granodiorite, the Silver Plume monzonite, and an assortment of orthogneisses. The mineralogy is presented in Kile and Eberl (2003).

The measured water chemistry at the uppermost site (MBC-ELD) is consistent with minor weathering of the local bedrock. The modeling results are presented in table 4.7. The minor amount of weathering required to produce the measured chemistry is consistent with relatively short residence time of ground water in the upper part of the watershed and, in general, is similar to results of previous studies in the region (Patterson, 1980; Reddy and Caine, 1989; Clow and others, 1997). To account for the dissolved sulfate, minor dissolution of pyrite is called for, but since metal concentrations are quite low, historical hardrock mining does not appear to affect the metal chemistry at MBC-ELD.

Downstream from MBC-ELD, potential anthropogenic influences include homes in the town of Eldora, Eldora Mountain Ski Area, and the town of Nederland. Within Nederland most wastewater goes to the Nederland WWTP, but some of the surrounding homes have individual septic systems. Comparing the chemistry of MBC-ELD and MBC-W, little change is observed, and the overall water chemistry is consistent with weathering of local bedrock. Nitrate, generally associated with septic systems, had slightly lower concentration at MBC-W compared to MBC-ELD. The effluent from the Nederland WWTP (NED-EFF) enters Middle Boulder Creek just below MBC-W, immediately upstream of Barker Reservoir. Because of the low nitrate concentration at the time of sampling, private septic systems do not appear to affect Boulder Creek upstream of MBC-W. Under different hydrologic conditions, this may change.

For many constituents, NED-EFF has the highest concentrations of all the samples in this study. The next downstream site (MBC-aNBC) has slightly higher concentrations of many elements compared to MBC-W, but the overall water chemistry is still relatively dilute (specific conductance of $84 \mu\text{S}/\text{cm}$). At the time of sampling, NED-EFF did not appear to have a major effect on the downstream sites because of dilution by water in Barker Reservoir and Middle Boulder Creek. For example, the boron

Table 4.3. Results of standard reference water samples used in the ICP-MS analyses of Boulder Creek water samples

[µg/L, micrograms per liter; --, element not analyzed; MPV, most probable value; ND, not determined in standard]

	HIGH-FLOW						LOW-FLOW				
	NIST1643b (µg/L)	NIST1643d ¹ (µg/L)	T135 (µg/L)	T147 (µg/L)	T149 (µg/L)	T157 (µg/L)	PPREE1 ² (µg/L)	NIST1643b (µg/L)	NIST1643d ¹ (µg/L)	T135 (µg/L)	T147 (µg/L)
Al	--	12.7	8.87	12.6	35.3	54.9	--	--	12.8	9.09	12.5
As	--	5.33	10.4	2.31	0.81	25.3	--	56.7	5.59	10.0	2.36
B	--	17	12	50	124	71	--	118	17.9	9.10	50.2
Ba	42.2	51.6	65.9	74.8	42.5	118	--	42.2	51.6	65.9	74.8
Be	--	1.31	63.4	16.1	--	13.2	--	20.2	1.31	58.7	15.6
Cd	17.8	0.63	50.2	15.1	2.09	5.43	--	20.1	0.63	50.4	15.9
Co	26.7	2.48	40.1	--	--	3.92	--	28.6	2.57	39.8	--
Cr	19.0	1.96	81.9	12.4	48.9	32.4	--	19.9	1.84	79.4	12.1
Cu	21.1	2.10	62.4	10.4	5.50	24.1	--	22.4	2.21	61.9	11.8
Li	--	1.72	75.6	17.2	41.4	32.3	--	--	1.79	74.0	17.3
Mn	32.7	4.22	426	18.5	12.3	128	--	33.2	4.06	198	17.4
Mo	93.8	11.1	63.1	11.7	1.07	11.2	--	101	11.8	63.2	12.5
Ni	47.0	5.88	65.7	13.6	31.0	29.7	--	49.3	5.90	64.3	13.3
Pb	23.2	1.86	103	13.6	8.77	6.39	--	23.9	1.91	103	14.4
Sb	--	5.29	76.4	10.0	19.9	10.2	--	--	5.52	76.4	10.3
Se	6.8	1.0	10.0	9.9	1.7	4.0	--	9.89	1.09	9.98	10.6
Sr	227	30.30	49.1	318	332	59.7	--	233	30.6	46.6	318
Th	--	--	--	--	--	--	0.002	--	--	--	--
Tl	7.50	0.74	--	19.3	31.4	8.59	--	7.40	0.72	--	19.6
U	--	--	--	3.24	2.62	3.23	0.005	--	0.009	--	3.23
V	44.0	3.52	54.6	14.8	29.9	15.9	--	46.6	3.69	52.5	14.7
Zn	55.2	6.80	48.2	11.3	2.12	21.9	--	69.6	7.54	48.3	13.9
La	--	--	--	--	--	--	0.81	--	--	--	--
Ce	--	--	--	--	--	--	1.63	--	--	--	--
Pr	--	--	--	--	--	--	0.211	--	--	--	--
Nd	--	--	--	--	--	--	0.94	--	--	--	--
Sm	--	--	--	--	--	--	0.204	--	--	--	--
Eu	--	--	--	--	--	--	0.060	--	--	--	--
Gd	--	--	--	--	--	--	0.239	--	--	--	--
Tb	--	--	--	--	--	--	0.037	--	--	--	--
Dy	--	--	--	--	--	--	0.223	--	--	--	--
Ho	--	--	--	--	--	--	0.045	--	--	--	--
Er	--	--	--	--	--	--	0.120	--	--	--	--
Tm	--	--	--	--	--	--	0.015	--	--	--	--
Yb	--	--	--	--	--	--	0.081	--	--	--	--
Lu	--	--	--	--	--	--	0.011	--	--	--	--

¹analyzed at 1:10 dilution

²analyzed at 1:100 dilution

Table 4.3. Results of standard reference water samples used in the ICP-MS analyses of Boulder Creek water samples--continued

	LOW-FLOW				MPV							
	T149 (µg/L)	T157 (µg/L)	PPREE1 ² (µg/L)	SCREE1 ² (µg/L)	NIST1643b (µg/L)	NIST1643d ¹ (µg/L)	T135 (µg/L)	T147 (µg/L)	T149 (µg/L)	T157 (µg/L)	PPREE1 ² (µg/L)	SCREE1 ² (µg/L)
Al	35.5	55.1	--	--	ND	12.8	10.50	14.0	35.5	55.5	--	--
As	0.83	25.3	--	--	ND	5.60	10.0	2.39	0.98	25.4	--	--
B	130	72.2	--	--	ND	14.5	13.10	50.0	128	70.4	--	--
Ba	42.5	118	--	--	44	50.7	67.8	73.0	42.5	118	--	--
Be	--	12.9	--	--	ND	1.25	59.0	16.0	ND	13.0	--	--
Cd	2.17	5.76	--	--	18.6	0.65	50.5	41.0	2.18	5.80	--	--
Co	--	4.08	--	--	26	2.50	40.0	ND	ND	4.03	--	--
Cr	48.7	32.1	--	--	19.9	1.84	79.0	12.8	48.8	31.3	--	--
Cu	7.90	25.4	--	--	21.9	2.05	62.0	11.4	8.00	24.8	--	--
Li	43.4	33.2	--	--	ND	1.65	73.7	18.0	44.2	32.4	--	--
Mn	11.8	57.3	--	--	28	3.77	423	17.2	11.8	143.0	--	--
Mo	1.08	8.99	--	--	85	1.1	63.0	11.8	1.25	13.00	--	--
Ni	31.1	32.6	--	--	49	5.81	65.6	13.6	31.2	30.0	--	--
Pb	9.10	5.94	--	--	23.7	1.82	103	13.8	8.84	6.90	--	--
Sb	20.4	10.5	--	--	ND	5.41	76.3	10.5	21.1	10.8	--	--
Se	1.48	4.12	--	--	9.7	1.14	10.0	10.1	2.10	4.60	--	--
Sr	331	60.2	--	--	227	29.5	46.0	313	331	59.6	--	--
Th	--	--	0.001	0.001	ND	ND	ND	ND	ND	ND	0.001	--
Tl	31.3	8.65	--	--	8.0	0.728	ND	20.0	31.4	8.75	--	--
U	2.57	3.21	0.005	0.006	ND	ND	ND	3.21	2.71	3.19	0.001	0.003
V	29.8	15.6	--	--	45.2	3.51	52.8	15.2	31.0	15.7	--	--
Zn	4.80	23.4	--	--	66.00	7.25	48.2	14.0	5.80	23.5	--	--
La	--	--	0.80	0.099	ND	ND	ND	ND	ND	ND	0.80	0.099
Ce	--	--	1.63	0.246	ND	ND	ND	ND	ND	ND	1.61	0.246
Pr	--	--	0.214	0.044	ND	ND	ND	ND	ND	ND	0.212	0.043
Nd	--	--	0.93	0.228	ND	ND	ND	ND	ND	ND	0.92	0.221
Sm	--	--	0.207	0.069	ND	ND	ND	ND	ND	ND	0.203	0.067
Eu	--	--	0.059	0.015	ND	ND	ND	ND	ND	ND	0.060	0.015
Gd	--	--	0.237	0.085	ND	ND	ND	ND	ND	ND	0.238	0.082
Tb	--	--	0.037	0.014	ND	ND	ND	ND	ND	ND	0.037	0.013
Dy	--	--	0.221	0.084	ND	ND	ND	ND	ND	ND	0.220	0.081
Ho	--	--	0.044	0.016	ND	ND	ND	ND	ND	ND	0.044	0.016
Er	--	--	0.121	0.044	ND	ND	ND	ND	ND	ND	0.119	0.044
Tm	--	--	0.014	0.006	ND	ND	ND	ND	ND	ND	0.015	0.006
Yb	--	--	0.083	0.034	ND	ND	ND	ND	ND	ND	0.082	0.034
Lu	--	--	0.011	0.005	ND	ND	ND	ND	ND	ND	0.011	0.005

Table 4.4. Results of standard reference water samples and blanks used in mercury analysis of Boulder Creek water samples

[ng/L, nanograms per liter; stddev, standard deviation; --, element not analyzed; MPV, most probable value; DL, detection limit]

		Hg7 ¹ (ng/L)	stddev (ng/L)	Hg22 ¹ (ng/L)	stddev (ng/L)	Hg14 ¹ (ng/L)	stddev (ng/L)	Hg15 ¹ (ng/L)	stddev (ng/L)	blank (ng/L)	stddev (ng/L)	DL (ng/L)
Hg-SRWS	High flow	3.1	0.2	11.5	0.3	8.3	0.3	4.1	0.2	0.0	0.2	0.5
Hg-SRWS	Low flow	2.3	0.5	10.7	0.3	7.0	0.3	3.4	0.2	0.0	0.2	0.4
Hg-SRWS	MPV	2.2	0.8	12.4	1.3	7.0	2.9	4.1	2.0	--	--	--

¹all mercury concentrations for Hg-standards reported at 1/100 dilution, error terms are also at 1/100 assuming no change in relative standard deviation

concentration in NED-EFF is 320 g/L, but at MBC-aNBC, boron is below the detection limit of 3 g/L.

Overall, the major-element chemistry of MBC-aNBC, BC-ORO and BC-CAN is consistent with weathering of the surrounding bedrock. Mass-balance results for BC-CAN are tabulated in table 4.7. In general, mineral proportions are similar to results from MBC-ELD, but a greater amount of mineral dissolution is required and expected because of longer ground-water flow paths and greater residence time in the lower portion of the crystalline part of the watershed.

Overall, the chemistry of Boulder Creek above BC-CAN is consistent with progressive weathering of the crystalline rocks. Historical mining does not seem to have contributed to the metal loading because the metals concentrations (arsenic, cadmium, chromium, copper, lead, nickel, silver, and zinc) are all below 1 g/L. Minor amounts of pyrite dissolution is needed to account for the dissolved sulfate concentrations. Gypsum is another potential source of sulfate but has not been reported as a mineral phase within the upper part of the watershed, although calcic gneisses crop out in the area. Slightly greater concentrations of silica, sulfate, and zinc in Fourmile Creek (FOURMILE) may be a result of historical mining. During high- and low-flow sampling the discharge in Fourmile Creek (0.11 and 0.02 cubic meters per second, m³/s, respectively; Murphy and others, 2003) were much less than the discharge in the main stem of Boulder Creek (7.1 and 1.1 m³/s at site BC-ORO), thus these elevated concentrations do not

appear elevated in Boulder Creek. These results are similar to the conclusions of Patterson (1980).

Boulder Creek from the Range Front to Boulder 75th Street Wastewater Treatment Plant

As Boulder Creek crosses the range front, at site BC-CAN, the composition of the bedrock and the potential anthropogenic sources of solutes change. Murphy and others (2003) describe these changes. In summary, the bedrock geology changes from crystalline bedrock consisting of felsic igneous and metamorphic rocks, to sedimentary rocks consisting of shales, limestones, and sandstones. These sedimentary rocks are more easily eroded, thus producing the dramatic change in topography. Potential anthropogenic sources are numerous, including transportation, industrial, and urban sources. Figures 4.3 to 4.5 show the general trend of increasing major dissolved solutes from BC-CAN to BC-61 (calcium, chloride, magnesium, sodium, and sulfate). Specific conductance increases from 61 S/cm (BC-CAN) to 232 S/cm (BC-61). In contrast, the dissolved silica concentration decreases from 4.5 to 2.4 mg/L in this reach.

Differentiation between natural and anthropogenic sources of some solutes is difficult because both sources likely contribute to the stream chemistry and a unique, geochemical signature of one source is not always apparent. An example of this is sodium chloride. Anthropogenic sources include the application of sodium chloride to roads and residential uses of sodium and chloride (laundry detergents, for

example). The Pierre Shale, one of the primary geologic units in this reach, formed in a marine environment, and not only contains a sodium chloride mineral (halite) but also contains sodium-rich minerals and possibly trapped ocean water.

A water balance study by Bruce and O'Riley (1997) documented the input of ground water in this reach. Simulations with NETPATH, using known minerals from the Pierre Shale (illite, montmorillonite [smectite], chlorite, quartz, potassium feldspar, plagioclase, calcite, dolomite, and halite), were undertaken to evaluate if input of ground water that has reacted with sedimentary bedrock is consistent with the measured chemistry of Boulder Creek. The results are tabulated in table 4.7. Although weathering of known minerals within the shale can account for the measured chemistry of Boulder Creek at site BC-61, these results should not be interpreted as a unique solution. For example, dolomite is present in the Pierre Shale and is included in the model to account for the increase in magnesium, although magnesium also is likely to be on clay sites, and ion exchange with clay minerals could account for the magnesium.

The relative proportion of halite dissolution is high and is needed to account for the chloride in the water. These results are consistent with a previous study of ground-water modeling of the Pierre Shale (Von Damm, 1989), but another potential natural source of chloride in the shale could be trapped fluids, rather than chloride solely residing in a mineral phase. Conversely, a portion of the chloride in Boulder Creek could be derived from anthropogenic sources. Bruce and O'Riley (1997) compared ground-water chemistry of 30 domestic wells in Boulder County that were sampled in 1976 and 1996. The median chloride concentration increased from 10.3 to 15.5 mg/L. Three of the eight wells that had an increase in chloride by a factor of two or more had a similar increase in sodium, which is consistent with salt entering the ground-water system.

Although there are numerous potential anthropogenic sources, the trace metal concentrations of Boulder Creek remained low through the urban reach. This observation is consistent with a storm-water study by Paulson (1994), which documented that during non-storm-event sampling, baseline metal (copper, lead, and zinc) concentrations were low, but increased by an order of magnitude or greater during storm-generated runoff.

Boulder Creek Downstream of the Boulder 75th Street Wastewater Treatment Plant

Compared to Boulder Creek, effluent from the Boulder 75th Street WWTP (BLD-EFF) has elevated concentrations of most constituents. At low flow, mass-balance calculations document that the effluent accounted for 77 percent of the discharge of Boulder Creek at the 75th Street streamgaging station (and 37 percent during the high-flow sampling). The relative proportion of flow was calculated using eight parameters (alkalinity, boron, calcium, chloride, magnesium, silica, sodium, and sulfate) that had different concentrations, and were at least three times greater than the detection limit in BLD-EFF and sample BC-aWWTP. Knowing the dissolved concentrations in the effluent and in Boulder Creek above and below the input of the effluent, the load equation was solved for the relative proportion of flow. A step increase in concentration at BC-75 is displayed in figures 4.3 to 4.5. Although most major constituents in the WWTP effluent have natural and anthropogenic sources, many elevated concentrations of trace elements in BLD-EFF result from domestic and industrial practices.

The positive gadolinium anomaly in the REE pattern of BLD-EFF is a good example of a geochemical signature of the effluent (fig. 4.6). Gadolinium is not naturally enriched relative to other REEs, but has industrial uses. The positive gadolinium anomaly in REE patterns of rivers was first documented in large urban areas of

Table 4.5. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000

[Distance, distance upstream from Boulder Creek/Saint Vrain Creek confluence; SC, specific conductance; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; per liter; ng/L, nanograms per liter; --, sample not analyzed for this constituent; <, less than; meq/L, milliequivalents per liter; %, percent;

Site	Distance (meters)	Date collected	Time	pH	SC ($\mu\text{S}/\text{cm}$)	DO (mg/L)	T _{H2O} (°C)	T _{air} (°C)
Middle Boulder Creek/Boulder Creek								
MBC-ELD	69590	06/12/2000	820	7.47	25.0	9.5	4.0	15
MBC-WTP	62970	06/12/2000	1210	7.57	25.0	--	8.2	--
MBC-W	60920	06/12/2000	1250	7.43	27.5	8.8	9.5	29
BC-aNBC	49440	06/13/2000	845	7.67	36.4	9.1	11.2	18
BC-ORO	41520	06/13/2000	1000	7.54	36.3	8.6	11.6	22
BC-CAN	36710	06/13/2000	1315	7.46	38.7	8.4	13.8	30
BC-30	32990	06/12/2000	1430	7.47	46.3	8.6	14.6	23
BC-61	27320	06/14/2000	900	7.67	96.6	8.4	12.9	17
BC-aWWTP	24440	06/13/2000	1910	8.20	104	7.7	17.8	22
BC-75	23850	06/13/2000	2000	7.19	326	7.2	18.0	18
BC-aDC	20180	06/14/2000	1040	8.48	264	10.7	16.7	26
BC-95	18790	06/14/2000	1300	8.87	310	11.2	19.3	29
BC-107	16320	06/14/2000	1415	8.56	383	10.8	21.9	30
BC-aCC	10970	06/13/2000	1645	9.80	292	12.3	23.2	28
BC-bCC	10540	06/13/2000	1745	9.03	501	11.0	23.1	28
BC-aSV	110	06/12/2000	1700	9.53	651	12.0	32.5	33
Inflows/other flows								
COMO	59340	06/12/2000	1000	7.56	35.8	8.0	9.8	28
NBC-LW	59370	06/12/2000	1100	7.56	25.1	8.7	10.5	30
SLP	59340	06/12/2000	1100	7.57	20.0	--	10.9	--
BEAVER	60910	06/12/2000	1210	8.13	104	8.5	10.3	28
NED-EFF	60880	06/12/2000	1330	7.10	578	--	15.2	--
NBC-FALLS	49420	06/13/2000	800	7.29	29.3	9.5	9.8	18
FOURMILE	40120	06/13/2000	1115	7.79	93.4	8.1	13.1	28
SBC-aBC	29070	06/14/2000	800	8.25	362	6.3	22.1	17
BCSC-aBC	24680	06/14/2000	1515	8.40	182	7.2	21.6	32
BLD-EFF	24380	06/13/2000	2000	7.07	595	--	19.9	--
DC	20040	06/14/2000	1120	8.51	383	11.0	16.1	28
CC	10970	06/13/2000	1615	8.30	810	9.3	24.3	30
SV-aBC	90	06/12/2000	1745	8.73	811	9.3	23.7	33
Field blank		06/13/2000	1600	--	--	--	--	--

DO, dissolved oxygen; T_{H2O}, water temperature; T_{air}, air temperature; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms
Dissolved, filtered aliquot; Total, unfiltered aliquot; T, total; II, ferrous]

Site		Alkalinity, HCO ₃ ⁻ (mg/L)	Br (mg/L)	Ca (mg/L)	Cl (mg/L)	F (mg/L)	Fe(T) (mg/L)	Fe(II) (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	NO ₃ (mg/L)	SiO ₂ (mg/L)	SO ₄ (mg/L)
MBC-ELD	Dissolved	5.0	<0.05	3.0	0.8	<0.1	<0.007	--	0.26	0.70	0.61	0.63	3.8	1.8
	Total	--	--	3.0	--	--	0.013	--	0.22	0.66	0.60	--	3.7	--
MBC-WTP	Dissolved	9.5	<0.05	3.1	0.2	<0.1	0.022	--	0.27	0.71	0.72	0.64	4.1	1.9
	Total	--	--	3.2	--	--	0.047	--	0.26	0.71	0.71	--	4.0	--
MBC-W	Dissolved	10.1	<0.05	3.2	0.3	<0.1	<0.007	--	0.29	0.72	0.76	0.59	4.1	2.0
	Total	--	--	3.2	--	--	0.06	--	0.30	0.71	0.72	--	4.1	--
BC-aNBC	Dissolved	12.1	<0.05	4.0	1.4	0.1	<0.007	--	0.37	0.99	1.2	<0.3	2.7	2.5
	Total	--	--	4.1	--	--	0.072	--	0.40	0.99	1.2	--	2.7	--
BC-ORO	Dissolved	11.8	<0.05	3.9	1.1	<0.1	<0.007	--	0.39	0.90	1.5	<0.3	3.7	2.6
	Total	--	--	4.0	--	--	0.17	--	0.44	0.92	1.5	--	3.9	--
BC-CAN	Dissolved	11.0	<0.05	4.0	2.2	<0.1	<0.007	--	0.43	0.98	1.6	<0.3	4.0	2.8
	Total	--	--	4.2	--	--	0.17	--	0.50	1.0	1.5	--	4.2	--
BC-30	Dissolved	15.5	<0.05	4.7	1.9	<0.1	<0.007	--	0.47	1.2	1.7	<0.3	4.2	3.2
	Total	--	--	4.9	--	--	0.18	--	0.46	1.2	2.0	--	4.3	--
BC-61	Dissolved	35.2	<0.05	9.3	5.6	0.1	0.066	0.053	0.65	3.0	4.6	0.6	4.7	6.0
	Total	--	--	9.5	--	--	0.24	--	0.70	3.1	4.0	--	5.0	--
BC-aWWTP	Dissolved	34.9	<0.05	11	3.8	0.1	0.032	0.029	0.66	3.3	4.3	0.31	4.5	11
	Total	--	--	11	--	--	0.33	--	0.81	3.4	4.7	--	5.4	--
BC-75	Dissolved	64.0	<0.05	21	22	0.5	0.020	0.007	3.8	7.2	23	20	5.9	35
	Total	--	--	21	--	--	0.29	--	4.2	7.5	23	--	6.7	--
BC-aDC	Dissolved	60.9	<0.05	19	14	0.3	0.219	0.065	2.8	7.2	16	15	6.8	32
	Total	--	--	20	--	--	0.35	--	2.8	7.1	16	--	6.9	--
BC-95	Dissolved	77.9	<0.05	24	13	0.4	0.017	--	3.3	10	19	16	6.3	41
	Total	--	--	25	--	--	0.34	--	3.4	10	19	--	7.2	--
BC-107	Dissolved	110	0.35	28	16	0.4	0.044	0.027	2.8	12	21	8.0	5.9	44
	Total	--	--	28	--	--	0.17	--	2.4	13	21	--	6.3	--
BC-aCC	Dissolved	88.0	<0.05	22	11	0.5	<0.007	--	2.3	12	18	6.1	5.4	44
	Total	--	--	22	--	--	0.27	--	2.2	12	18	--	6.0	--
BC-bCC	Dissolved	145	<0.05	29	18	0.6	0.187	0.075	3.1	15	39	7.3	7.4	69
	Total	--	--	29	--	--	0.25	--	3.2	16	41	--	7.2	--
BC-aSV	Dissolved	187	0.69	41	21	0.8	0.074	0.066	2.6	34	51	3.7	6.2	170
	Total	--	--	40	--	--	0.099	--	2.5	35	52	--	6.2	--
COMO	Dissolved	15.6	<0.05	3.5	0.5	<0.1	<0.007	--	0.40	1.1	2.0	<0.3	11	1.7
	Total	--	--	3.7	--	--	0.40	--	0.36	1.1	2.0	--	10	--
NBC-LW	Dissolved	8.4	<0.05	2.8	0.1	<0.1	0.04	--	0.32	0.47	0.97	<0.3	5.4	2.1
	Total	--	--	2.9	--	--	0.16	--	0.31	0.47	0.97	--	5.1	--
SLP	Dissolved	5.3	<0.05	2.9	0.3	<0.1	0.011	--	0.31	0.33	0.65	<0.3	3.1	2.5
	Total	--	--	3.0	--	--	0.1	--	0.29	0.34	0.66	--	3.1	--
BEAVER	Dissolved	49.5	<0.05	12	1.2	<0.1	0.02	--	0.69	4.1	2.4	<0.3	13	7.4
	Total	--	--	12	--	--	0.21	--	0.75	4.2	2.3	--	13	--
NED-EFF	Dissolved	200	0.21	19	63	<0.1	0.08	--	12.1	7.5	42	<0.3	11	20
	Total	--	--	19	--	--	0.42	--	12.0	7.9	42	--	11	--
NBC-FALLS	Dissolved	10.6	<0.05	3.3	0.3	<0.1	0.13	--	0.34	0.65	1.1	<0.3	5.5	2.4
	Total	--	--	3.4	--	--	0.25	--	0.36	0.66	1.1	--	5.4	--
FOURMILE	Dissolved	34.2	<0.05	8.5	1.9	<0.1	<0.007	--	0.88	3.5	2.9	<0.3	11	9.9
	Total	--	--	8.6	--	--	0.05	--	0.86	3.6	2.8	--	10	--
SBC-aBC	Dissolved	136	<0.05	32	21	0.6	<0.007	--	2.8	11	23	<0.3	2.9	35
	Total	--	--	33	--	--	0.11	--	2.8	12	24	--	3.0	--
BCSC-aBC	Dissolved	58.7	<0.05	21	1.6	0.1	0.031	0.22	0.86	5.9	5.9	<0.3	4.6	34
	Total	--	--	21	--	--	0.43	--	0.92	6.1	5.8	--	5.4	--
BLD-EFF	Dissolved	118	0.37	37	57	1.1	0.12	--	9.3	13	52	49	8.5	69
	Total	--	--	38	--	--	0.2	--	10.3	14	53	--	8.7	--
DC	Dissolved	136	<0.05	33	6.5	0.4	0.016	--	1.8	18	18	0.5	8.1	67
	Total	--	--	34	--	--	0.24	--	1.7	19	18	--	8.9	--
CC	Dissolved	298	0.41	49	41	0.9	<0.007	--	5.8	26	110	12	10	150
	Total	--	--	50	--	--	0.64	--	6.0	29	110	--	12	--
SV-aBC	Dissolved	165	<0.05	58	19	0.7	0.13	--	3.4	38	56	11	7.3	260
	Total	--	--	61	--	--	0.51	--	3.2	40	58	--	8.0	--
Field blank	Dissolved	<1	<0.05	0.068	0.1	<0.1	<0.007	--	0.01	0.057	0.043	<0.3	<0.01	<0.1
	Total	--	--	<0.05	--	--	0.073	--	0.01	0.009	0.007	--	0.017	--

Table 4.5. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000--continued

Site	Al (µg/L)	As (µg/L)	B (µg/L)	Ba (µg/L)	Be (µg/L)	Bi (µg/L)	Cd (µg/L)	Ce (µg/L)	Co (µg/L)	Cr (µg/L)	Cs (µg/L)	Cu (µg/L)	Dy (µg/L)
Middle Boulder Creek/Boulder Creek													
MBC-ELD	26	0.12	< 2	10.0	< 0.004	0.0091	0.004	0.13	0.012	< 0.2	< 0.02	0.34	0.027
	<80	<20	4	11	<0.1	--	<1	--	<1	<1	--	4	--
MBC-WTP	32	0.07	< 2	9.9	0.004	0.0014	0.022	0.16	0.021	< 0.2	< 0.02	0.52	0.025
	<80	<20	<3	11	<0.1	--	<1	--	<1	<1	--	3	--
MBC-W	20	0.14	< 2	10	< 0.004	0.0019	0.007	0.091	0.019	< 0.2	< 0.02	0.54	0.019
	<80	<20	5	11	<0.1	--	<1	--	<1	<1	--	5	--
BC-aNBC	21	0.09	5	12	0.005	0.0008	0.007	0.12	0.018	< 0.2	< 0.02	0.70	0.021
	<80	<20	4	14	<0.1	--	<1	--	<1	<1	--	6	--
BC-ORO	13	0.11	3	10.0	< 0.004	0.0009	0.002	0.078	0.018	< 0.2	0.26	0.63	0.014
	84	<20	5	13	<0.1	--	<1	--	<1	<1	--	2	--
BC-CAN	12	0.11	5	10.0	0.005	0.0008	0.011	0.073	0.013	< 0.2	< 0.02	0.67	0.012
	<80	<20	5	13	<0.1	--	<1	--	<1	<1	--	<1	--
BC-30	10	0.14	7	12	0.004	0.0005	0.007	0.074	0.015	< 0.2	0.02	0.65	0.012
	<80	<20	7	14	<0.1	--	<1	--	<1	<1	--	5	--
BC-61	29	0.32	13	19	0.006	0.0026	0.007	0.15	0.031	< 0.2	< 0.02	0.75	0.015
	110	<20	25	24	<0.1	--	<1	--	<1	<1	--	<1	--
BC-aWWTP	29	0.33	13	19	< 0.004	0.0014	0.004	0.085	0.021	< 0.2	< 0.02	0.76	0.0088
	220	<20	24	25	<0.1	--	<1	--	<1	<1	--	4	--
BC-75	11	0.39	79	19	< 0.004	0.012	0.021	0.031	0.089	< 0.2	0.05	1.7	0.0054
	270	<20	86	23	<0.1	--	<1	--	<1	<1	--	<1	--
BC-aDC	380	0.62	59	27	0.018	0.028	0.044	0.53	0.18	0.6	0.13	2.1	0.037
	390	<20	63	29	0.2	--	<1	--	<1	<1	--	<1	--
BC-95	15	0.63	72	26	< 0.004	0.0029	0.020	0.029	0.098	< 0.2	3.1	1.00	0.0034
	320	<20	76	33	<0.1	--	<1	--	<1	<1	--	<1	--
BC-107	23	0.82	76	36	< 0.004	0.0053	0.013	0.058	0.17	< 0.2	< 0.02	0.61	0.0087
	100	<20	77	39	<0.1	--	<1	--	<1	<1	--	<1	--
BC-aCC	7.1	0.91	68	22	< 0.004	0.0017	0.015	0.0091	0.13	< 0.2	< 0.02	0.55	0.0023
	280	<20	74	26	<0.1	--	<1	--	<1	<1	--	<1	--
BC-bCC	340	1.1	136	30	0.018	0.023	0.035	0.75	0.48	0.5	0.05	0.70	0.052
	260	<20	140	32	<0.1	--	<1	--	<1	<1	--	<1	--
BC-aSV	133	1.4	172	41	0.006	0.0074	0.023	0.25	0.35	< 0.2	< 0.02	< 0.04	0.017
	<80	<20	180	44	<0.1	--	<1	--	<1	<1	--	4	--
Inflows/other flows													
COMO	18	0.17	< 2	5.4	0.004	0.0011	0.067	0.12	0.054	< 0.2	< 0.02	0.48	0.014
	<80	<20	<3	7	<0.1	--	<1	--	<1	<1	--	4	--
NBC-LW	22	0.19	< 2	4.8	0.006	0.0022	0.065	0.11	0.026	< 0.2	< 0.02	0.73	0.011
	<80	<20	4	6	<0.1	--	<1	--	<1	<1	--	7	--
SLP	9.1	0.08	3	4.3	0.004	0.0018	0.028	0.040	0.008	< 0.2	< 0.02	0.81	0.0068
	<80	<20	3	6	0.2	--	<1	--	<1	<1	--	<1	--
BEAVER	10	0.13	2	30	< 0.004	0.0030	0.026	0.036	0.029	< 0.2	0.03	0.79	0.0042
	<80	<20	5	33	<0.1	--	<1	--	<1	<1	--	5	--
NED-EFF	8.3	0.24	294	7.0	< 0.004	0.040	0.012	0.0076	0.37	< 0.2	0.08	2.1	0.0010
	170	<20	300	24	<0.1	--	<1	--	<1	<1	--	16	--
NBC-FALLS	64	0.11	3	7.0	0.008	0.0022	0.018	0.24	0.056	< 0.2	< 0.02	0.92	0.016
	<80	<20	<3	8	<0.1	--	<1	--	<1	<1	--	<1	--
FOURMILE	3.3	0.84	9	19	< 0.004	0.0013	0.013	0.013	0.007	< 0.2	< 0.02	0.67	0.0025
	<80	<20	10	22	<0.1	--	<1	--	<1	<1	--	3	--
SBC-aBC	3.2	1.0	465	99	0.005	0.0019	0.002	0.0074	< 0.001	< 0.2	< 0.02	0.81	0.0010
	89	<20	470	100	<0.1	--	<1	--	<1	<1	--	<1	--
BCSC-aBC	105	0.46	13	30	0.010	0.0022	0.008	0.081	< 0.001	< 0.2	< 0.02	1.0	0.0076
	380	<20	12	41	<0.1	--	<1	--	<1	<1	--	<1	--
BLD-EFF	18	0.46	197	14	< 0.004	0.080	0.058	0.0094	0.22	0.3	0.12	8.5	0.0027
	110	<20	210	18	<0.1	--	<1	--	<1	<1	--	4	--
DC	5.2	0.49	38	34	< 0.004	0.0033	0.003	0.041	< 0.001	< 0.2	< 0.02	< 0.04	0.0055
	240	<20	41	38	0.2	--	<1	--	<1	<1	--	<1	--
CC	4.7	1.5	340	43	< 0.004	0.0092	0.071	0.034	1.0	< 0.2	< 0.02	0.37	0.014
	470	<20	360	--	57	--	<1	--	<1	<1	--	2	--
SV-aBC	250	1.2	163	36	0.014	0.024	0.036	0.43	0.15	0.6	0.07	< 0.04	0.028
	450	<20	170	--	43	--	<1	--	<1	<1	--	3	--
Field blank	0.6	< 0.01	< 2	0.031	< 0.004	< 0.0005	0.011	0.0019	0.006	< 0.2	0.05	0.12	< 0.0002
	<80	<20	4	--	<0.5	--	<1	--	<1	<1	--	<1	--

Site	Er (µg/L)	Eu (µg/L)	Gd (µg/L)	Ho (µg/L)	La (µg/L)	Li (µg/L)	Lu (µg/L)	Mn (µg/L)	Mo (µg/L)	Nd (µg/L)	Ni (µg/L)	Pb (µg/L)	Pr (µg/L)	Rb (µg/L)
MBC-ELD	0.013	0.0084	0.040	0.0047	0.24	0.14	0.0016	1.9	0.35	0.31	0.08	0.086	0.076	0.36
	--	--	--	--	--	<8	--	<1	--	--	<20	<1	--	--
MBC-WTP	0.012	0.0086	0.040	0.0048	0.24	0.14	0.0015	3.5	0.35	0.30	0.19	0.042	0.074	0.42
	--	--	--	--	--	<8	--	<1	--	--	<20	<1	--	--
MBC-W	0.0087	0.0053	0.028	0.0036	0.16	0.17	0.0010	3.1	0.49	0.20	0.22	0.027	0.048	0.41
	--	--	--	--	--	<8	--	<1	--	--	<20	<1	--	--
BC-aNBC	0.012	0.0084	0.030	0.0041	0.18	0.43	0.0013	1.7	0.52	0.22	0.24	0.083	0.052	0.52
	--	--	--	--	--	<8	--	<1	--	--	<20	<1	--	--
BC-ORO	0.0078	0.0046	0.020	0.0027	0.097	0.36	0.0011	2.2	0.54	0.13	0.19	0.058	0.029	0.50
	--	--	--	--	--	<8	--	5	--	--	<20	<1	--	--
BC-CAN	0.0057	0.0041	0.015	0.0026	0.085	0.43	0.0010	2.4	0.50	0.12	0.20	0.034	0.025	0.54
	--	--	--	--	--	<8	--	6	--	--	<20	<1	--	--
BC-30	0.0062	0.0040	0.016	0.0023	0.084	0.54	0.0009	3.3	0.52	0.11	0.22	0.027	0.025	0.56
	--	--	--	--	--	<8	--	7	--	--	<20	<1	--	--
BC-61	0.0080	0.0042	0.016	0.0033	0.12	1.9	0.0013	9.9	0.68	0.14	0.38	0.18	0.035	0.70
	--	--	--	--	--	<8	--	19	--	--	<20	<1	--	--
BC-aWWTP	0.0052	0.0036	0.011	0.0017	0.055	2.0	0.0007	7.7	0.67	0.069	0.44	0.079	0.016	0.61
	--	--	--	--	--	9	--	15	--	--	<20	<1	--	--
BC-75	0.0035	0.0020	0.021	0.0013	0.023	11	0.0009	18	6.3	0.031	1.3	0.22	0.0070	3.0
	--	--	--	--	--	13	--	27	--	--	<20	<1	--	--
BC-aDC	0.021	0.012	0.060	0.0074	0.30	6.9	0.0025	22	2.9	0.30	1.4	0.72	0.074	2.8
	--	--	--	--	--	<8	--	23	--	--	<20	<1	--	--
BC-95	0.0027	<0.0001	0.014	0.0009	0.018	8.4	0.0006	9.7	3.2	0.021	1.1	0.16	0.0048	2.4
	--	--	--	--	--	9	--	25	--	--	<20	4	--	--
BC-107	0.0077	0.0017	0.016	0.0022	0.034	12	0.0017	39	3.6	0.043	1.2	0.19	0.0092	1.5
	--	--	--	--	--	13	--	42	--	--	<20	<1	--	--
BC-aCC	0.0021	0.0009	0.0049	0.0007	0.0055	8.8	0.0005	2.9	3.3	0.0089	1.1	0.072	0.0017	1.1
	--	--	--	--	--	10	--	18	--	--	<20	7	--	--
BC-bCC	0.026	0.014	0.073	0.0091	0.37	15	0.0035	26	3.3	0.40	2.0	0.71	0.093	2.3
	--	--	--	--	--	18	--	25	--	--	<20	<1	--	--
BC-aSV	0.014	0.0040	0.027	0.0042	0.13	23	0.0027	29	3.6	0.13	2.0	0.31	0.031	1.5
	--	--	--	--	--	34	--	28	--	--	<20	<1	--	--
COMO	0.0081	0.0047	0.017	0.0033	0.078	0.33	0.0016	7.7	0.67	0.087	0.26	0.044	0.021	0.23
	--	--	--	--	--	<8	--	8	--	--	<20	<1	--	--
NBC-LW	0.0061	0.0037	0.013	0.0023	0.076	0.14	0.0009	4.1	0.69	0.096	0.15	0.13	0.024	0.41
	--	--	--	--	--	<8	--	2	--	--	<20	<1	--	--
SLP	0.0038	0.0020	0.0076	0.0015	0.035	0.14	0.0007	1.5	0.51	0.052	0.20	0.030	0.012	0.42
	--	--	--	--	--	<8	--	7	--	--	<20	<1	--	--
BEAVER	0.0027	0.0009	0.0050	0.0009	0.022	0.52	0.0006	14	4.6	0.023	0.41	0.36	0.0052	0.52
	--	--	--	--	--	<8	--	10	--	--	<20	<1	--	--
NED-EFF	0.0010	0.0005	0.0018	0.0004	0.0042	53	0.0004	38	1.0	0.0066	1.8	0.19	0.0013	9.3
	--	--	--	--	--	65	--	38	--	--	<20	<1	--	--
NBC-FALLS	0.0099	0.0064	0.023	0.0033	0.15	0.23	0.0012	7.4	0.47	0.17	0.27	0.30	0.044	0.54
	--	--	--	--	--	<8	--	7	--	--	<20	<1	--	--
FOURMILE	0.0016	0.0010	0.0020	0.0005	0.0087	1.2	0.0003	4.2	0.40	0.011	0.57	0.017	0.0024	0.75
	--	--	--	--	--	<8	--	3	--	--	<20	<1	--	--
SBC-aBC	0.0018	<0.0001	0.0019	0.0004	0.0052	12	0.0006	5.7	6.7	0.0062	0.81	0.026	0.0010	1.3
	--	--	--	--	--	14	--	16	--	--	<20	<1	--	--
BCSC-aBC	0.0047	0.0019	0.0088	0.0016	0.045	4.1	0.0006	2.5	0.67	0.045	0.64	0.069	0.011	0.51
	--	--	--	--	--	<8	--	21	--	--	<20	<1	--	--
BLD-EFF	0.0030	0.0011	0.040	0.0008	0.0056	23	0.0009	35	17	0.0065	3.3	0.81	0.0013	7.2
	--	--	--	--	--	31	--	38	--	--	<20	2	--	--
DC	0.0033	0.0012	0.0072	0.0014	0.027	6.9	0.0006	20	1.8	0.034	0.73	0.027	0.0076	0.72
	--	--	--	--	--	<8	--	31	--	--	<20	3	--	--
CC	0.013	0.0019	0.021	0.0042	0.016	32	0.0031	43	4.0	0.028	3.2	0.44	0.0051	2.9
	--	--	--	--	--	45	--	90	--	--	<20	3	--	--
SV-aBC	0.014	0.0065	0.040	0.0053	0.20	24	0.0016	14	3.4	0.22	0.71	0.39	0.052	2.0
	--	--	--	--	--	30	--	29	--	--	<20	<1	--	--
Field blank	0.0002	<0.0001	<0.0003	<0.0001	0.0010	0.03	0.0001	0.20	0.06	0.0010	0.03	0.024	<0.0001	0.021
	--	--	--	--	--	<8	--	<1	--	--	<20	4	--	--

Table 4.5. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000--continued

Site	Re (µg/L)	Sb (µg/L)	Se (µg/L)	Sm (µg/L)	Sr (µg/L)	Tb (µg/L)	Te (µg/L)	Th (µg/L)	Tl (µg/L)	Tm (µg/L)	U (µg/L)	V (µg/L)	Y (µg/L)
Middle Boulder Creek/Boulder Creek													
MBC-ELD	0.0008	0.020	< 0.1	0.054	22	0.0049	< 0.005	0.025	0.003	0.0016	0.14	0.06	0.14
	--	--	<20	--	21	--	--	--	--	--	--	<1	--
MBC-WTP	0.0011	0.019	< 0.1	0.053	23	0.0051	< 0.005	0.022	0.003	0.0016	0.15	0.09	0.13
	--	--	<20	--	24	--	--	--	--	--	--	<1	--
MBC-W	0.0012	0.036	< 0.1	0.035	24	0.0037	< 0.005	0.020	0.003	0.0012	0.11	0.11	0.10
	--	--	<20	--	24	--	--	--	--	--	--	<1	--
BC-aNBC	0.0014	0.045	< 0.1	0.039	31	0.0040	< 0.005	0.019	0.003	0.0012	0.14	0.11	0.12
	--	--	<20	--	32	--	--	--	--	--	--	<1	--
BC-ORO	0.0014	0.046	< 0.1	0.024	32	0.0024	< 0.005	0.017	0.004	0.0010	0.099	0.12	0.081
	--	--	<20	--	34	--	--	--	--	--	--	<1	--
BC-CAN	0.0014	0.043	< 0.1	0.022	34	0.0023	< 0.005	0.013	0.004	0.0010	0.098	0.14	0.072
	--	--	<20	--	36	--	--	--	--	--	--	<1	--
BC-30	0.0015	0.050	< 0.1	0.019	40	0.0021	< 0.005	0.015	0.003	0.0009	0.11	0.14	0.070
	--	--	<20	--	41	--	--	--	--	--	--	<1	--
BC-61	0.0033	0.083	< 0.1	0.026	89	0.0027	0.006	0.013	0.006	0.0010	0.26	0.26	0.079
	--	--	<20	--	91	--	--	--	--	--	--	<1	--
BC-aWWTP	0.0042	0.071	< 0.1	0.014	92	0.0017	< 0.005	0.0097	0.004	0.0006	0.34	0.35	0.051
	--	--	<20	--	98	--	--	--	--	--	--	<1	--
BC-75	0.016	0.16	0.3	0.0075	176	0.0010	< 0.005	0.015	0.006	0.0006	0.37	0.42	0.032
	--	--	<20	--	180	--	--	--	--	--	--	<1	--
BC-aDC	0.014	0.14	0.3	0.058	182	0.0070	0.009	0.079	0.013	0.0031	0.95	1.6	0.19
	--	--	<20	--	180	--	--	--	--	--	--	<1	--
BC-95	0.017	0.23	0.4	0.0038	229	0.0005	0.009	0.0060	0.004	0.0004	1.4	0.66	0.022
	--	--	<20	--	240	--	--	--	--	--	--	<1	--
BC-107	0.018	0.15	< 0.1	0.011	317	0.0015	0.007	0.0096	0.006	0.0013	2.6	0.97	0.051
	--	--	<20	--	320	--	--	--	--	--	--	<1	--
BC-aCC	0.016	0.50	0.4	0.0022	305	0.0003	0.009	0.0048	0.004	0.0003	2.8	1.3	0.016
	--	--	<20	--	320	--	--	--	--	--	--	2	--
BC-bCC	0.026	0.19	0.8	0.076	385	0.0086	0.013	0.055	0.011	0.0034	5.1	2.7	0.25
	--	--	<20	--	420	--	--	--	--	--	--	2	--
BC-aSV	0.049	0.17	0.8	0.024	686	0.0029	0.030	0.050	0.008	0.0020	8.0	2.6	0.11
	--	--	<20	--	720	--	--	--	--	--	--	2	--
Inflows/other flows													
COMO	0.0016	0.087	< 0.1	0.019	34	0.0023	< 0.005	0.017	0.003	0.0011	0.020	0.27	0.080
	--	--	<20	--	35	--	--	--	--	--	--	<1	--
NBC-LW	0.0013	0.054	< 0.1	0.016	26	0.0020	< 0.005	0.012	0.006	0.0008	0.034	0.16	0.064
	--	--	<20	--	25	--	--	--	--	--	--	<1	--
SLP	0.0015	0.031	< 0.1	0.011	26	0.0011	< 0.005	0.014	0.003	0.0005	0.048	< 0.06	0.038
	--	--	<20	--	27	--	--	--	--	--	--	<1	--
BEAVER	0.0081	0.18	< 0.1	0.0050	95	0.0007	< 0.005	0.0064	0.003	0.0005	0.54	0.24	0.026
	--	--	<20	--	100	--	--	--	--	--	--	<1	--
NED-EFF	0.0071	0.46	< 0.1	0.0013	99	0.0002	0.009	0.0045	0.005	0.0002	0.011	0.41	0.0074
	--	--	<20	--	110	--	--	--	--	--	--	<1	--
NBC-FALLS	0.0017	0.036	< 0.1	0.029	30	0.0032	< 0.005	0.013	0.004	0.0013	0.051	0.31	0.092
	--	--	<20	--	31	--	--	--	--	--	--	<1	--
FOURMILE	0.0023	0.12	< 0.1	0.0030	106	0.0003	0.006	0.0034	0.005	0.0003	0.16	0.17	0.013
	--	--	<20	--	110	--	--	--	--	--	--	<1	--
SBC-aBC	0.019	0.39	1.0	0.0020	374	0.0002	< 0.005	0.0033	0.004	0.0003	2.3	1.0	0.012
	--	--	<20	--	410	--	--	--	--	--	--	<1	--
BCSC-aBC	0.0097	0.090	0.3	0.0090	162	0.0014	< 0.005	0.016	0.005	0.0006	0.72	0.75	0.046
	--	--	<20	--	170	--	--	--	--	--	--	<1	--
BLD-EFF	0.031	0.78	0.3	0.0082	300	0.0004	0.009	0.0056	0.008	0.0005	0.67	0.55	0.022
	--	--	<20	--	320	--	--	--	--	--	--	<1	--
DC	0.014	0.084	0.4	0.0078	366	0.0010	0.011	0.010	0.009	0.0005	3.1	0.74	0.041
	--	--	<20	--	380	--	--	--	--	--	--	<1	--
CC	0.052	0.34	1.8	0.0069	632	0.0021	0.023	0.024	0.008	0.0018	11	3.1	0.10
	--	--	<20	--	670	--	--	--	--	--	--	3	--
SV-aBC	0.058	0.42	1.9	0.042	976	0.0061	0.036	0.054	0.009	0.0020	9.7	2.7	0.16
	--	--	<20	--	100	--	--	--	--	--	--	3	--
Field blank	0.0002	0.009	< 0.1	0.0005	0.07	0.0001	< 0.005	< 0.0007	0.002	< 0.0001	< 0.002	< 0.06	0.0008
	--	--	<20	--	<1	--	--	--	--	--	--	<1	--

Site	Yb (µg/L)	Zn (µg/L)	Zr (µg/L)	Hg (ng/L)	Sum Cations (meq/L)	Sum Anions (meq/L)	Charge Imbalance (%)
MBC-ELD	0.0097	1.5	0.023	0.9	0.24	0.15	46
	--	<1	--	--			
MBC-WTP	0.010	0.92	0.018	--	0.25	0.21	17
	--	<1	--	--			
MBC-W	0.0089	1.0	0.021	1.4	0.26	0.22	15
	--	<1	--	--			
BC-aNBC	0.0094	0.83	0.024	3.0	0.34	0.29	15
	--	<1	--	--			
BC-ORO	0.0059	0.93	0.019	3.5	0.34	0.28	21
	--	<1	--	--			
BC-CAN	0.0057	0.49	0.017	1.7	0.36	0.3	19
	--	<1	--	--			
BC-30	0.0057	1.0	0.021	2.7	0.41	0.37	11
	--	<1	--	--			
BC-61	0.0066	0.84	0.020	--	0.92	0.87	6.0
	--	4	--	--			
BC-aWWTP	0.0047	0.26	0.021	1.6	1.0	0.9	11
	--	<1	--	--			
BC-75	0.0046	8.2	0.035	2.5	2.7	2.7	0.1
	--	13	--	--			
BC-aDC	0.016	7.0	0.39	--	2.2	2.2	0.1
	--	10	--	--			
BC-95	0.0032	5.5	0.032	--	2.8	2.6	5.7
	--	10	--	--			
BC-107	0.0096	2.4	0.038	--	3.2	3.1	2.0
	--	5	--	--			
BC-aCC	0.0027	0.98	0.021	1.7	2.5	2.4	2.8
	--	5	--	--			
BC-bCC	0.023	5.2	0.28	--	4.1	4.1	0.1
	--	9	--	--			
BC-aSV	0.014	0.17	0.14	5.1	5.7	5.9	-3.8
	--	<1	--	--			
COMO	0.0088	14	0.045	2.3	0.36	0.3	17
	--	<1	--	--			
NBC-LW	0.0056	3.0	0.017	<0.5	0.22	0.18	22
	--	<1	--	--			
SLP	0.0041	3.0	0.017	--	0.21	0.15	33
	--	3	--	--			
BEAVER	0.0032	7.8	0.014	3.0	1.0	0.99	6.0
	--	9	--	--			
NED-EFF	0.0015	9.9	0.093	2.0	5.2	5.4	-3.8
	--	24	--	--			
NBC-FALLS	0.0082	2.2	0.020	0.6	0.28	0.23	19
	--	<1	--	--			
FOURMILE	0.0020	3.1	0.0079	2.0	0.85	0.81	5.1
	--	<1	--	--			
SBC-aBC	0.0025	0.82	0.019	--	3.4	3.4	-0.7
	--	2	--	--			
BCSC-aBC	0.0044	0.06	0.070	--	1.7	1.6	4.2
	--	3	--	--			
BLD-EFF	0.0042	23	0.20	6.4	5.6	5.6	-1.2
	--	30	--	--			
DC	0.0036	<0.05	0.043	--	3.6	3.6	1.3
	--	3	--	--			
CC	0.014	13	0.12	1.1	8.6	8.7	-1.3
	--	26	--	--			
SV-aBC	0.015	0.61	0.18	1.1	7.3	7.7	-4.5
	--	8	--	--			
Field blank	<0.0003	0.66	<0.0006	<0.5	--	--	--
	--	<1	--	--			

Table 4.6. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000

[Distance, distance upstream from Boulder Creek/Saint Vrain Creek confluence; SC, specific conductance; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; per liter; ng/L, nanograms per liter; --, sample not analyzed for this constituent; <, less than; meq/L, milliequivalents per liter; %, percent;

Site	Distance (meters)	Date collected	Time	pH	SC ($\mu\text{S}/\text{cm}$)	DO (mg/L)	DO (%)	T _{H₂O} (°C)	T _{air} (°C)
Middle Boulder Creek/Boulder Creek									
MBC-ELD	69590	10/09/2000	830	7.72	38	10.2	96.5	0.3	0.5
MBC-WTP	62970	10/09/2000	1204	7.52	48	--	--	--	--
MBC-W	60920	10/09/2000	1300	7.74	48	9.40	101	5.8	19
MBC-aNBC	49440	10/10/2000	815	7.93	84	9.70	95.3	4.1	2.5
BC-ORO	41520	10/10/2000	1000	7.85	54	9.46	99.3	7.9	9.5
BC-CAN	36710	10/10/2000	1230	7.82	61	9.37	100	9.3	9.7
BC-30	32990	10/10/2000	1345	7.61	118	10.1	109	9.6	14.5
BC-61	27320	10/11/2000	1415	9.25	232	12.5	145	13.8	26
BC-aWWTP	24440	10/11/2000	815	7.97	240	8.78	91.5	8.7	7
BC-75	23850	10/11/2000	900	7.28	569	7.20	92.0	17.6	9.8
BC-aDC	20180	10/11/2000	1015	7.60	449	7.26	85.0	13.7	14.4
BC-95	18790	10/11/2000	1215	8.02	472	9.05	109	15.2	18
BC-107	16320	10/11/2000	1315	8.34	510	10.3	124	15.5	24
BC-aCC	10970	10/10/2000	1640	9.17	510	10.8	133	16.6	20.5
BC-bCC	10540	10/10/2000	1745	8.62	771	9.31	111	14.9	16.5
BC-aSV	110	10/09/2000	1545	9.58	695	17.1	199	14.5	17.5
Inflows/other flows									
COMO	59340	10/09/2000	1015	7.59	70	10.0	101	3.4	18
NBC-LW	59370	10/09/2000	1050	7.68	33	9.58	96.1	3.0	20
SLP	59340	10/09/2000	1058	7.04	25	--	--	--	--
BEAVER	60910	10/09/2000	1210	8.33	183	8.95	95.1	5.3	19.5
NED-EFF	60880	10/09/2000	1317	7.24	601	--	--	--	--
NBC-FALLS	49420	10/10/2000	900	7.92	72	10.0	96.0	3.0	12
FOURMILE	40120	10/10/2000	1050	8.02	286	9.73	97.0	5.8	10.5
SBC-aBC	29070	10/10/2000	1445	8.08	325	7.47	90.3	14.9	20.2
BCSC-aBC	24680	10/09/2000	1745	8.80	131	8.61	102	15.0	17
BLD-EFF	24380	10/11/2000	830	7.28	624	--	--	--	--
DC	20040	10/11/2000	1100	8.51	1023	10.4	111	9.9	22
CC	10970	10/10/2000	1600	8.35	923	8.6	103	14.8	19
SV-aBC	90	10/09/2000	1630	9.09	1238	14.9	174	14.4	18
Field blank		10/11/2000	830	--	--	--	--	--	--

DO, dissolved oxygen; T_{H2O}, water temperature; T_{air}, air temperature; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms
 Dissolved, filtered aliquot; Total, unfiltered aliquot; T, total; II, ferrous]

Site		Alkalinity, HCO ₃ (mg/L)	Br (mg/L)	Ca (mg/L)	Cl (mg/L)	F (mg/L)	Fe(T) (mg/L)	Fe(II) (mg/L)	K (mg/L)	Mg (mg/L)
MBC-ELD	Dissolved	10.3	<0.1	4.4	3.3	0.04	0.025	0.020	0.25	1.0
	Total	--	--	4.4	--	--	<0.008	--	0.27	1.0
MBC-WTP	Dissolved	19.2	<0.1	5.7	0.8	0.04	0.095	0.072	0.38	1.3
	Total	--	--	5.7	--	--	0.21	--	0.39	1.3
MBC-W	Dissolved	19.7	<0.1	5.9	1.2	0.04	0.081	0.061	0.40	1.4
	Total	--	--	6.0	--	--	0.19	--	0.41	1.4
MBC-aNBC	Dissolved	27.7	<0.1	8.6	7.2	0.06	0.026	0.023	0.68	2.2
	Total	--	--	8.8	--	--	0.050	--	0.72	2.2
BC-ORO	Dissolved	20.2	<0.1	5.7	2.4	0.04	0.102	0.099	0.47	1.4
	Total	--	--	5.8	--	--	0.29	--	0.47	1.5
BC-CAN	Dissolved	21.7	<0.1	6.3	3.1	0.04	0.089	0.089	0.52	1.7
	Total	--	--	6.2	--	--	0.27	--	0.53	1.7
BC-30	Dissolved	39.5	<0.1	12	7.9	0.07	0.083	0.074	0.77	3.2
	Total	--	--	12	--	--	0.30	--	0.79	3.4
BC-61	Dissolved	87.7	<0.1	25	18	0.2	0.020	0.020	1.5	8.2
	Total	--	--	24	--	--	0.25	--	1.4	8.6
BC-aWWTP	Dissolved	89.4	<0.1	24	14	0.2	0.041	0.039	1.2	8.5
	Total	--	--	24	--	--	0.35	--	1.3	8.5
BC-75	Dissolved	116	<0.1	35	35	0.9	0.044	0.014	8.0	12
	Total	--	--	35	--	--	0.22	--	8.1	12
BC-aDC	Dissolved	108	<0.1	34	31	0.7	0.039	0.020	5.1	13
	Total	--	--	32	--	--	0.35	--	5.0	14
BC-95	Dissolved	105	<0.1	33	29	0.7	0.048	0.031	5.2	14
	Total	--	--	33	--	--	0.27	--	5.5	14
BC-107	Dissolved	126	<0.1	37	28	0.8	0.043	0.029	5.5	17
	Total	--	--	37	--	--	0.19	--	5.5	18
BC-aCC	Dissolved	158	<0.1	35	32	0.9	0.011	0.008	5.2	19
	Total	--	--	37	--	--	0.14	--	5.2	19
BC-bCC	Dissolved	205	<0.1	41	36	0.9	0.015	0.009	5.2	21
	Total	--	--	41	--	--	0.37	--	5.2	22
BC-aSV	Dissolved	215	<0.1	43	33	1.1	0.010	0.007	4.4	30
	Total	--	--	47	--	--	0.11	--	4.5	32
COMO	Dissolved	37.9	<0.1	6.8	0.8	0.05	0.161	0.160	0.64	2.1
	Total	--	--	7.2	--	--	0.67	--	0.68	2.2
NBC-LW	Dissolved	15.8	<0.1	3.9	0.3	<0.03	0.135	0.130	0.30	0.76
	Total	--	--	4.0	--	--	0.28	--	0.33	0.76
SLP	Dissolved	8.6	<0.1	3.3	0.7	<0.03	0.012	0.011	0.21	0.35
	Total	--	--	3.2	--	--	0.22	--	0.22	0.34
BEAVER	Dissolved	84.9	<0.1	21	3.2	0.04	0.189	0.157	1.3	7.6
	Total	--	--	20	--	--	0.47	--	1.3	7.6
NED-EFF	Dissolved	154	<0.1	19	73	0.1	0.102	0.099	11	10
NBC-FALLS	Dissolved	32.3	<0.1	7.7	1.6	0.04	0.045	0.045	0.68	2.1
	Total	--	--	7.7	--	--	0.19	--	0.70	2.1
FOURMILE	Dissolved	92.3	<0.1	28	9.0	0.09	0.037	0.037	2.1	12
	Total	--	--	31	--	--	0.063	--	2.3	12
SBC-aBC	Dissolved	118	<0.1	29	22	0.5	0.071	0.070	2.6	11
	Total	--	--	29	--	--	0.11	--	2.7	10
BCSC-aBC	Dissolved	48.0	<0.1	16	1.5	0.1	0.013	0.009	0.63	4.4
	Total	--	--	16	--	--	1.0	--	0.85	4.5
BLD-EFF	Dissolved	119	<0.1	39	41	1.0	0.092	0.028	11	14
DC	Dissolved	373	<0.1	83	17	1.1	0.017	0.016	2.5	70
	Total	--	--	84	--	--	0.083	--	2.5	70
CC	Dissolved	313	<0.1	53	45	1.0	0.022	0.008	5	28
	Total	--	--	53	--	--	0.63	--	5.6	32
SV-aBC	Dissolved	260	<0.1	90	48	1.0	0.042	0.032	3.3	63
	Total	--	--	89	--	--	0.12	--	3.7	63
Field blank	Dissolved	<1	<0.1	<0.05	0.3	<0.03	0.004	---	0.039	<0.0001

Table 4.6. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000--continued

Site	Na (mg/L)	NH ₄ (mg/L)	NO ₃ (mg/L)	NO ₂ (mg/L)	SiO ₂ (mg/L)	SO ₄ (mg/L)	Al (µg/L)	As (µg/L)	B (µg/L)	Ba (µg/L)	Be (µg/L)	Bi (µg/L)
Middle Boulder Creek/Boulder Creek												
MBC-ELD	0.72	<0.01	0.79	<0.1	3.9	3.7	6.4	0.08	< 3	12	0.010	< 0.001
	0.73	--	--	--	3.8	--	< 80	< 30	< 3	12	<0.1	--
MBC-WTP	1.2	<0.01	0.58	<0.1	5.4	4.2	3.5	0.07	< 3	15	< 0.008	0.002
	1.2	--	--	--	5.4	--	120	< 30	< 3	16	0.6	--
MBC-W	1.3	<0.01	0.57	<0.1	5.7	4.3	4.6	0.07	< 3	14	<0.01	0.0032
	1.3	--	--	--	5.7	--	< 80	< 30	< 3	17	<0.1	--
MBC-aNBC	4.1	<0.01	0.29	<0.1	4.3	5.6	4.4	0.07	< 3	24	< 0.008	< 0.001
	4.1	--	--	--	4.2	--	< 80	< 30	< 3	27	0.9	--
BC-ORO	2.1	<0.01	0.53	<0.1	4.4	4.1	5.5	0.12	4	17	< 0.008	0.006
	2.1	--	--	--	4.6	--	140	< 30	5	19	0.5	--
BC-CAN	2.4	<0.01	0.43	<0.1	4.5	5.0	5.4	0.16	5	17	< 0.008	0.003
	2.5	--	--	--	4.7	--	130	< 30	4	19	0.4	--
BC-30	5.5	<0.01	1.4	<0.1	5.1	10.3	5.3	0.20	22	27	< 0.008	0.002
	5.6	--	--	--	5.4	--	150	< 30	24	31	0.6	--
BC-61	14	<0.01	<0.1	<0.1	2.4	18	3.1	0.31	53	40	< 0.008	< 0.001
	13	--	--	--	2.4	--	120	< 30	50	43	0.2	--
BC-aWWTP	12	<0.01	<0.1	<0.1	2.6	24	26	0.30	46	46	< 0.008	0.002
	12	--	--	--	3.8	--	260	< 30	47	53	0.2	--
BC-75	42	7.2	53	14	8.3	62	8.4	0.39	200	17	< 0.008	0.027
	42	--	--	--	8.5	--	100	< 30	200	20	0.2	--
BC-aDC	34	2.5	29	1.7	5.8	51	4.1	0.44	150	25	< 0.008	0.008
	31	--	--	--	6.1	--	110	< 30	140	30	<0.1	--
BC-95	32	2.1	46	<0.1	5.5	59	21	0.47	140	26	< 0.008	0.012
	32	--	--	--	6.0	--	130	< 30	140	30	0.5	--
BC-107	37	2.0	29	<0.1	4.9	64	4.8	0.57	150	27	< 0.008	0.005
	38	--	--	--	5.3	--	120	< 30	140	29	0.4	--
BC-aCC	41	1.5	17	<0.1	4.9	69	6.7	0.61	160	29	< 0.008	0.005
	41	--	--	--	5.5	--	<80	< 30	180	31	0.2	--
BC-bCC	62	1.0	18	<0.1	6.8	98	6.8	0.59	240	32	< 0.008	0.009
	63	--	--	--	8.3	--	290	< 30	240	38	<0.1	--
BC-aSV	64	<0.01	24.	<0.1	5.3	128	8.1	0.85	240	35	< 0.008	0.005
	70	--	--	--	6.6	--	110	< 30	280	38	0.2	--
Inflows/other flows												
COMO	3.4	<0.01	<0.1	<0.1	18	2.9	7.7	0.11	< 3	8.2	< 0.008	0.006
	3.7	--	--	--	19	--	< 80	< 30	< 3	9.0	<0.1	--
NBC-LW	1.2	<0.01	<0.1	<0.1	6.6	2.3	9.2	0.08	< 3	5.2	< 0.008	0.002
	1.2	--	--	--	6.7	--	< 80	< 30	< 3	7.0	<0.1	--
SLP	0.64	<0.01	<0.1	<0.1	2.9	2.1	2.6	0.08	< 3	3.9	< 0.008	< 0.001
	0.60	--	--	--	3.0	--	< 80	< 30	< 3	5.0	<0.1	--
BEAVER	4.8	<0.01	<0.1	<0.1	14	19.3	2.7	0.13	< 3	51	< 0.008	0.002
	4.7	--	--	--	12	--	< 80	< 30	< 3	53	<0.1	--
NED-EFF	46	16.9	14	<0.1	8.8	26.0	10	0.40	360	4.1	< 0.008	0.067
NBC-FALLS	3.4	<0.01	<0.1	<0.1	10	6.0	3.2	0.11	< 3	15	< 0.008	< 0.001
	3.4	--	--	--	10	--	< 80	< 30	< 3	15	0.6	--
FOURMILE	11	<0.01	<0.1	<0.1	12	50	1.3	1.5	21	54	< 0.008	< 0.001
	12	--	--	--	13	--	< 80	< 30	23	58	0.4	--
SBC-aBC	22	<0.01	<0.1	<0.1	2.9	33	29	0.68	280	67	< 0.008	0.002
	22	--	--	--	3.0	--	< 80	< 30	290	74	<0.1	--
BCSC-aBC	4.8	<0.01	<0.1	<0.1	5.3	21	8.9	0.52	8	27	< 0.008	0.003
	4.5	--	--	--	10	--	1200	< 30	9	42	0.9	--
BLD-EFF	51	7.8	62	2.0	11	70	8.5	0.50	260	9.9	-0.01	0.056
DC	57	<0.01	1.5	<0.1	6	263	3.6	0.32	140	60	0.027	0.017
	56	--	--	--	6.2	--	< 80	< 30	140	63	<0.1	--
CC	110	<0.01	19	<0.1	11	160	27	0.66	390	41	0.013	0.020
	120	--	--	--	14	--	570	< 30	400	50	<0.1	--
SV-aBC	110	<0.01	23.	<0.1	7.6	398	19	0.61	310	31	< 0.008	0.008
	110	--	--	--	7.9	--	< 80	< 30	320	33	<0.1	--
Field blank	0.021	<0.01	<0.1	<0.1	<0.01	<0.3	0.8	< 0.02	< 3	0.03	0.018	< 0.001

Site	Cd (µg/L)	Ce (µg/L)	Co (µg/L)	Cr (µg/L)	Cs (µg/L)	Cu (µg/L)	Dy (µg/L)	Er (µg/L)	Eu (µg/L)	Gd (µg/L)	Ho (µg/L)
MBC-ELD	0.008 <1	0.065 --	0.030 <1	0.5 <1	0.02 --	0.32 <1	0.0088 --	0.0047 --	0.0020 --	0.0098 --	0.0017 --
MBC-WTP	0.031 <1	0.080 --	0.029 <1	< 0.3 <1	< 0.01 --	0.36 <1	0.0061 --	0.0042 --	0.0017 --	0.0091 --	0.0014 --
MBC-W	0.061 <1	0.070 --	0.019 <1	0.4 <1	--	1.2 3	0.0059 --	0.0030 --	0.0025 --	0.0093 --	0.0012 --
MBC-aNBC	0.006 <1	0.037 --	< 0.002 <1	0.4 <1	0.02 --	0.60 <1	0.0063 --	0.0033 --	0.0026 --	0.0084 --	0.0012 --
BC-ORO	< 0.002 <1	0.10 --	0.023 <1	0.5 <1	0.01 --	0.63 <1	0.0080 --	0.0052 --	0.0024 --	0.013 --	0.0016 --
BC-CAN	< 0.002 <1	0.085 --	0.015 <1	< 0.3 <1	< 0.01 --	0.65 <1	0.0073 --	0.0041 --	0.0025 --	0.011 --	0.0015 --
BC-30	0.004 <1	0.077 --	0.013 <1	< 0.3 2	< 0.01 --	0.80 <1	0.0071 --	0.0051 --	0.0021 --	0.0078 --	0.0014 --
BC-61	0.052 <1	0.023 --	< 0.002 <1	< 0.3 <1	< 0.01 --	0.86 <1	0.0033 --	0.0031 --	0.0004 --	0.0034 --	0.0008 --
BC-aWWTP	< 0.002 <1	0.047 --	< 0.002 <1	0.4 <1	< 0.01 --	0.87 2	0.0040 --	0.0029 --	0.0012 --	0.0059 --	0.0008 --
BC-75	0.009 <1	0.012 --	1.2 <1	0.5 2	0.08 --	3.7 7	0.0033 --	0.0035 --	0.0003 --	0.057 --	0.0010 --
BC-aDC	0.033 <1	0.016 --	0.76 <1	0.4 <1	0.04 --	2.9 9	0.0037 --	0.0038 --	0.0005 --	0.041 --	0.0011 --
BC-95	0.010 <1	0.047 --	0.69 <1	0.4 2	0.04 --	3.2 4	0.0051 --	0.0043 --	0.0019 --	0.041 --	0.0014 --
BC-107	0.014 <1	0.016 --	0.93 <1	0.4 <1	0.04 --	2.8 3	0.0056 --	0.0057 --	0.0006 --	0.026 --	0.0016 --
BC-aCC	0.010 <1	0.019 --	0.10 <1	< 0.3 <1	0.06 --	2.4 4	0.0052 --	0.0049 --	< 0.0003 --	0.014 --	0.0014 --
BC-bCC	0.027 <1	0.027 --	0.36 <1	0.3 2	0.04 --	2.3 3	0.0083 --	0.0071 --	0.0009 --	0.026 --	0.0022 --
BC-aSV	0.014 <1	0.025 --	0.28 <1	0.7 <1	0.01 --	1.6 3	0.0072 --	0.0077 --	0.0015 --	0.039 --	0.0020 --
COMO	0.011 <1	0.076 --	0.041 <1	0.3 <1	0.01 --	0.29 1	0.0055 --	0.0035 --	0.0017 --	0.0076 --	0.0012 --
NBC-LW	0.015 <1	0.056 --	0.024 <1	0.5 <1	0.03 --	0.50 3	0.0044 --	0.0022 --	0.0010 --	0.0055 --	0.0008 --
SLP	0.012 <1	0.013 --	0.021 <1	< 0.3 <1	< 0.01 --	0.60 2	0.0011 --	0.0014 --	0.0004 --	0.0014 --	0.0003 --
BEAVER	0.004 <1	0.028 --	< 0.002 <1	< 0.3 <1	0.02 --	0.60 2	0.0034 --	0.0018 --	0.0006 --	0.0036 --	0.0007 --
NED-EFF	0.039	0.019	0.63	< 0.3	0.06	9.0	0.0012	0.0014	0.0005	0.0023	0.0005
NBC-FALLS	0.005 <1	0.032 --	< 0.002 <1	< 0.3 <1	0.03 --	0.42 <1	0.0029 --	0.0016 --	0.0010 --	0.0038 --	0.0006 --
FOURMILE	0.029 <1	0.017 --	< 0.002 <1	< 0.3 <1	< 0.01 --	0.67 3	0.0031 --	0.0024 --	0.0010 --	0.0025 --	0.0007 --
SBC-aBC	< 0.002 <1	0.093 --	< 0.002 <1	< 0.3 <1	< 0.01 --	0.90 5	0.0054 --	0.0037 --	0.0014 --	0.0061 --	0.0011 --
BCSC-aBC	< 0.002 <1	0.0091 --	< 0.002 <1	0.4 <1	< 0.01 --	2.0 <1	0.0017 --	0.0023 --	< 0.0003 --	0.0016 --	0.0006 --
BLD-EFF	0.073	0.010	1.4	0.5	--	6.0	0.0028	0.0038	0.0004	0.068	0.0008
DC	0.019 <1	0.026 --	< 0.002 <1	< 0.3 2	< 0.01 --	0.30 2	0.0034 --	0.0028 --	0.0003 --	0.0040 --	0.0009 --
CC	0.061 <1	0.080 --	0.82 <1	< 0.3 2	< 0.01 --	2.1 5	0.017 --	0.014 --	0.0025 --	0.045 --	0.0042 --
SV-aBC	0.007 <1	0.037 --	< 0.002 <1	0.4 <1	0.01 --	2.0 4	0.0058 --	0.0044 --	0.0016 --	0.0075 --	0.0016 --
Field blank	0.009	0.0013	0.004	< 0.3	< 0.01	0.05	< 0.0005	< 0.0004	< 0.0003	< 0.0004	0.0001

Table 4.6. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000--continued

Site	La (µg/L)	Li (µg/L)	Lu (µg/L)	Mn (µg/L)	Mo (µg/L)	Nd (µg/L)	Ni (µg/L)	Pb (µg/L)	Pr (µg/L)	Rb (µg/L)	Re (µg/L)
Middle Boulder Creek/Boulder Creek											
MBC-ELD	0.052	0.13	0.0006	9.2	0.46	0.071	0.14	0.24	0.017	0.46	0.0013
	--	<8	--	<1	--	--	<2	<6	--	--	--
MBC-WTP	0.057	0.22	0.0005	10	0.67	0.070	0.13	0.033	0.018	0.59	0.0017
	--	<8	--	14	--	--	<2	<6	--	--	--
MBC-W	0.056	0.20	0.0005	7.6	0.53	0.067	0.14	0.027	0.016	0.57	0.0017
	--	<8	--	11	--	--	<2	<6	--	--	--
MBC-aNBC	0.050	0.91	0.0004	0.60	0.55	0.064	0.16	0.065	0.014	1.1	0.0021
	--	<8	--	1	--	--	<2	<6	--	--	--
BC-ORO	0.086	0.76	0.0008	8.8	0.79	0.098	0.19	0.17	0.024	0.72	0.0020
	--	<8	--	18	--	--	<2	<6	--	--	--
BC-CAN	0.071	0.90	0.0006	5.2	0.74	0.085	0.19	0.16	0.020	0.82	0.0019
	--	<8	--	13	--	--	<2	<6	--	--	--
BC-30	0.059	1.9	0.0010	7.8	0.70	0.065	0.19	0.15	0.016	0.88	0.0033
	--	<8	--	13	--	--	<2	<6	--	--	--
BC-61	0.016	6.2	0.0010	7.5	1.1	0.019	0.27	0.060	0.0042	1.1	0.0069
	--	<8	--	17	--	--	<2	<6	--	--	--
BC-aWWTP	0.029	6.0	0.0010	16	1.1	0.032	0.34	0.077	0.0075	0.91	0.011
	--	<8	--	22	--	--	<2	<6	--	--	--
BC-75	0.0081	19	0.0010	21	3.7	0.0083	3.0	0.58	0.0019	6.4	0.028
	--	21	--	26	--	--	3	<6	--	--	--
BC-aDC	0.0091	14	0.0010	29	3.1	0.014	2.1	0.46	0.0026	4.1	0.029
	--	16	--	39	--	--	<2	<6	--	--	--
BC-95	0.025	15	0.0013	18	3.0	0.027	2.1	0.46	0.0065	4.0	0.028
	--	17	--	28	--	--	3	<6	--	--	--
BC-107	0.0077	17	0.0013	7.3	3.6	0.015	2.4	0.35	0.0027	4.0	0.029
	--	19	--	12	--	--	<2	<6	--	--	--
BC-aCC	0.0095	19	0.0015	2.6	4.0	0.016	1.5	0.20	0.0033	4.5	0.029
	--	23	--	7	--	--	3	<6	--	--	--
BC-bCC	0.013	24	0.0016	6.2	4.2	0.023	1.7	0.26	0.0046	3.9	0.038
	--	28	--	16	--	--	<2	<6	--	--	--
BC-aSV	0.014	25	0.0022	2.3	4.4	0.021	1.6	0.17	0.0045	2.6	0.047
	--	34	--	6	--	--	3	<6	--	--	--
Inflows/other flows											
COMO	0.042	0.53	0.0006	12	0.89	0.043	0.28	0.042	0.010	0.41	0.0026
	--	<8	--	10	--	--	<2	<6	--	--	--
NBC-LW	0.035	0.17	0.0005	5.2	0.56	0.039	0.44	0.15	0.0098	0.39	0.0016
	--	<8	--	8	--	--	<2	<6	--	--	--
SLP	0.0071	0.15	0.0002	8.3	0.89	0.0084	0.14	0.058	0.0017	0.43	0.0010
	--	<8	--	17	--	--	<2	<6	--	--	--
BEAVER	0.021	1.5	0.0005	16	8.7	0.020	0.23	0.27	0.0048	0.96	0.019
	--	<8	--	21	--	--	<2	<6	--	--	--
NED-EFF	0.0095	129	0.0003	30	1.8	0.012	2.2	0.41	0.0028	10	0.0009
NBC-FALLS	0.022	0.73	0.0003	1.2	0.69	0.024	0.13	0.047	0.0055	0.74	0.0024
	--	<8	--	3	--	--	<2	<6	--	--	--
FOURMILE	0.012	4.4	0.0008	8.0	0.55	0.015	0.90	0.023	0.0030	2.0	0.0053
	--	<8	--	10	--	--	4	<6	--	--	--
SBC-aBC	0.050	11	0.0012	42	4.1	0.048	0.53	0.17	0.012	1.5	0.015
	--	11	--	90	--	--	<2	<6	--	--	--
BCSC-aBC	0.0057	2.9	0.0002	0.93	0.66	0.0073	0.27	0.010	0.0015	0.27	0.0077
	--	<8	--	220	--	--	<2	<6	--	--	--
BLD-EFF	0.0057	20	0.0009	20	4.1	0.0058	3.5	0.70	0.0014	7.1	0.029
DC	0.013	29	0.0005	5.0	3.7	0.016	< 0.007	0.095	0.0035	0.68	0.041
	--	27	--	7	--	--	<2	<6	--	--	--
CC	0.038	35	0.0031	17	4.8	0.052	2.1	0.40	0.011	3.1	0.063
	--	44	--	36	--	--	3	<6	--	--	--
SV-aBC	0.018	37	0.0009	6.8	4.0	0.022	0.65	0.14	0.0064	1.6	0.10
	--	50	--	11	--	--	<2	<6	--	--	--
Field blank	0.0004	< 0.04	< 0.0001	0.09	0.05	0.0009	0.091	0.023	0.0002	0.009	< 0.0002

Site	Sb (µg/L)	Se (µg/L)	Sm (µg/L)	Sr (µg/L)	Tb (µg/L)	Te (µg/L)	Th (µg/L)	Tl (µg/L)	Tm (µg/L)	U (µg/L)	V (µg/L)
MBC-ELD	0.022	<0.1	0.014	34.1	0.0013	<0.009	0.0086	0.007	0.0006	0.053	0.13
	--	<40	--	--	--	--	--	--	--	--	<1
MBC-WTP	0.022	<0.1	0.010	43.7	0.0012	<0.009	0.0075	0.004	0.0004	0.044	0.10
	--	<40	--	--	--	--	--	--	--	--	<1
MBC-W	0.020	-0.09	0.011	40.9	0.0011	<0.009	0.0069	<0.01	0.0006	0.055	-0.2
	--	<40	--	--	--	--	--	--	--	--	<1
MBC-aNBC	0.044	<0.1	0.012	78.5	0.0013	<0.009	0.0048	0.007	0.0004	0.097	<0.06
	--	<40	--	--	--	--	--	--	--	--	<1
BC-ORO	0.041	<0.1	0.017	48.9	0.0017	<0.009	0.0096	0.006	0.0006	0.13	0.12
	--	<40	--	--	--	--	--	--	--	--	<1
BC-CAN	0.049	<0.1	0.015	55.3	0.0012	<0.009	0.0085	0.004	0.0006	0.15	0.12
	--	<40	--	--	--	--	--	--	--	--	<1
BC-30	0.059	<0.1	0.012	98	0.0009	<0.009	0.0067	0.007	0.0006	0.45	0.12
	--	<40	--	--	--	--	--	--	--	--	<1
BC-61	0.12	<0.1	0.0047	221	0.0005	<0.009	0.0036	0.006	0.0005	1.3	<0.06
	--	<40	--	--	--	--	--	--	--	--	<1
BC-aWWTP	0.11	<0.1	0.0063	230	0.0007	<0.009	0.0060	0.007	0.0006	1.1	0.07
	--	<40	--	--	--	--	--	--	--	--	<1
BC-75	0.25	<0.1	0.0019	278	0.0005	<0.009	0.0065	0.007	0.0005	0.76	0.52
	--	<40	--	--	--	--	--	--	--	--	<1
BC-aDC	0.20	0.20	0.0036	301	0.0006	<0.009	0.0049	0.006	0.0007	1.2	0.40
	--	<40	--	--	--	--	--	--	--	--	<1
BC-95	0.20	0.15	0.0060	330	0.0010	<0.009	0.0081	0.007	0.0007	1.6	0.51
	--	<40	--	--	--	--	--	--	--	--	<1
BC-107	0.22	<0.1	0.0035	341	0.0008	<0.009	0.0034	0.008	0.0008	2.5	0.59
	--	<40	--	--	--	--	--	--	--	--	<1
BC-aCC	0.20	<0.1	0.0040	485	0.0007	<0.009	0.0059	0.009	0.0007	5.1	0.92
	--	<40	--	--	--	--	--	--	--	--	<1
BC-bCC	0.23	0.53	0.0046	516	0.0011	<0.009	0.0038	0.008	0.0011	7.1	1.0
	--	<40	--	--	--	--	--	--	--	--	3
BC-aSV	0.21	<0.1	0.0050	675	0.0013	0.014	0.016	0.008	0.0012	8.3	1.6
	--	<40	--	--	--	--	--	--	--	--	2
COMO	0.017	<0.1	0.0087	61.8	0.0010	<0.009	0.0081	<0.003	0.0005	0.024	0.36
	--	<40	--	--	--	--	--	--	--	--	<1
NBC-LW	0.029	<0.1	0.0064	33.3	0.0007	<0.009	0.0031	<0.003	0.0002	0.019	0.13
	--	<40	--	--	--	--	--	--	--	--	<1
SLP	0.038	<0.1	0.0012	23.9	0.0004	<0.009	0.0038	0.007	<0.0001	0.026	0.12
	--	<40	--	--	--	--	--	--	--	--	<1
BEAVER	0.16	<0.1	0.0050	174	0.0006	<0.009	0.0039	0.003	0.0003	1.0	0.16
	--	<40	--	--	--	--	--	--	--	--	<1
NED-EFF	0.40	<0.1	0.0029	74.0	0.0002	<0.009	0.0035	0.005	0.0001	0.019	0.19
NBC-FALLS	0.046	<0.1	0.0040	70.7	0.0005	<0.009	0.0033	0.003	0.0002	0.26	0.12
	--	<40	--	--	--	--	--	--	--	--	<1
FOURMILE	0.22	<0.1	0.0030	314	0.0005	<0.009	0.0017	0.007	0.0005	1.6	0.09
	--	<40	--	--	--	--	--	--	--	--	<1
SBC-aBC	0.24	0.16	0.0089	308	0.0009	<0.009	0.016	0.004	0.0006	2.1	0.44
	--	<40	--	--	--	--	--	--	--	--	<1
BCSC-aBC	0.086	0.25	0.0016	115	0.0003	<0.009	0.0029	0.003	0.0001	0.42	0.64
	--	<40	--	--	--	--	--	--	--	--	3
BLD-EFF	0.26	0.42	0.0010	300	0.0002	<0.009	0.0037	-0.010	0.0005	0.62	0.9
DC	0.087	0.46	0.0029	166	0.0007	0.020	0.0093	0.016	0.0004	11	0.33
	--	<40	--	--	--	--	--	--	--	--	<1
CC	0.29	2.0	0.013	664	0.0023	<0.009	0.011	0.010	0.0018	12	1.4
	--	<40	--	--	--	--	--	--	--	--	2
SV-aBC	0.18	2.3	0.0050	1640	0.0013	0.023	0.013	0.005	0.0005	16	0.84
	--	<40	--	--	--	--	--	--	--	--	<1
Field blank	0.017	<0.1	<0.0008	<0.1	<0.0002	<0.009	0.0008	0.004	<0.0001	<0.002	0.06

Table 4.6. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000--continued

Site	Y (µg/L)	Yb (µg/L)	Zn (µg/L)	Zr (µg/L)	Hg (ng/L)	Sum Cations (meq/L)	Sum Anions (meq/L)	Charge Imbalance (%)
Middle Boulder Creek/Boulder Creek								
MBC-ELD	0.046	0.0040	2.4	--	0.5	0.34	0.35	-3.4
	--	--	<1	--	--			
MBC-WTP	0.038	0.0032	0.98	--	--	0.46	0.43	4.8
	--	--	3	--	--			
MBC-W	0.036	0.0032	0.82	0.005	1.1	0.48	0.45	5.1
	--	--	2	--	--			
MBC-aNBC	0.037	0.0028	1.3	--	4.6	0.80	0.78	3.4
	--	--	3	--	--			
BC-ORO	0.054	0.0042	1.0	--	0.9	0.51	0.49	2.5
	--	--	3	--	--			
BC-CAN	0.047	0.0041	1.0	--	0.6	0.57	0.55	3.9
	--	--	3	--	--			
BC-30	0.040	0.0049	1.9	--	0.7	1.1	1.1	1.5
	--	--	6	--	--			
BC-61	0.023	0.0040	1.8	--	--	2.4	2.2	10.4
	--	--	5	--	--			
BC-aWWTP	0.029	0.0044	1.9	--	0.5	2.4	2.3	3.5
	--	--	4	--	--			
BC-75	0.020	0.0048	18	--	3.3	5.0	5.2	-4.1
	--	--	25	--	--			
BC-aDC	0.025	0.0066	13	--	--	4.4	4.1	7.1
	--	--	20	--	--			
BC-95	0.032	0.0060	12	--	--	4.3	4.4	-2.4
	--	--	16	--	--			
BC-107	0.030	0.0070	12	--	--	4.9	4.5	8.8
	--	--	15	--	--			
BC-aCC	0.031	0.0072	9.1	--	1.9	4.9	4.8	1.2
	--	--	11	--	--			
BC-bCC	0.055	0.0096	14	--	--	6.3	6.3	-1.3
	--	--	18	--	--			
BC-aSV	0.054	0.011	8.0	--	1.1	6.5	6.5	-0.5
	--	--	12	--	--			
Inflows/Other flows								
COMO	0.036	0.0043	4.7	--	0.4	0.68	0.70	-3.4
	--	--	1	--	--			
NBC-LW	0.025	0.0028	4.4	--	<0.4	0.32	0.31	2.4
	--	--	1	--	--			
SLP	0.0085	0.0011	1.4	--	--	0.23	0.20	11.3
	--	--	4	--	--			
BEAVER	0.023	0.0020	7.4	--	0.6	1.9	1.8	2.3
	--	--	11	--	--			
NED-EFF	0.0097	0.0017	20	--	7.5	5.0	5.3	-6.5
NBC-FALLS	0.019	0.0019	1.1	--	1.0	0.7	0.7	3.3
	--	--	5	--	--			
FOURMILE	0.020	0.0037	5.9	--	0.9	2.8	2.7	4.4
	--	--	9	--	--			
SBC-aBC	0.031	0.0055	1.5	--	--	3.3	3.2	4.0
	--	--	1	--	--			
BCSC-aBC	0.014	0.0016	0.23	--	--	1.3	1.2	9.9
	--	--	13	--	--			
BLD-EFF	0.017	0.0040	21	0.13	2.9	5.9	5.3	6.5
DC	0.037	0.0031	2.8	--	--	11.0	10.6	3.2
	--	--	7	--	--			
CC	0.12	0.017	21	--	<0.4	9.2	9.5	-2.5
	--	--	220	--	--			
SV-aBC	0.042	0.0045	5.5	--	--	12.3	12.1	2.0
	--	--	7	--	2.0			
Field blank	0.0005	0.0003	1.8	--	--			

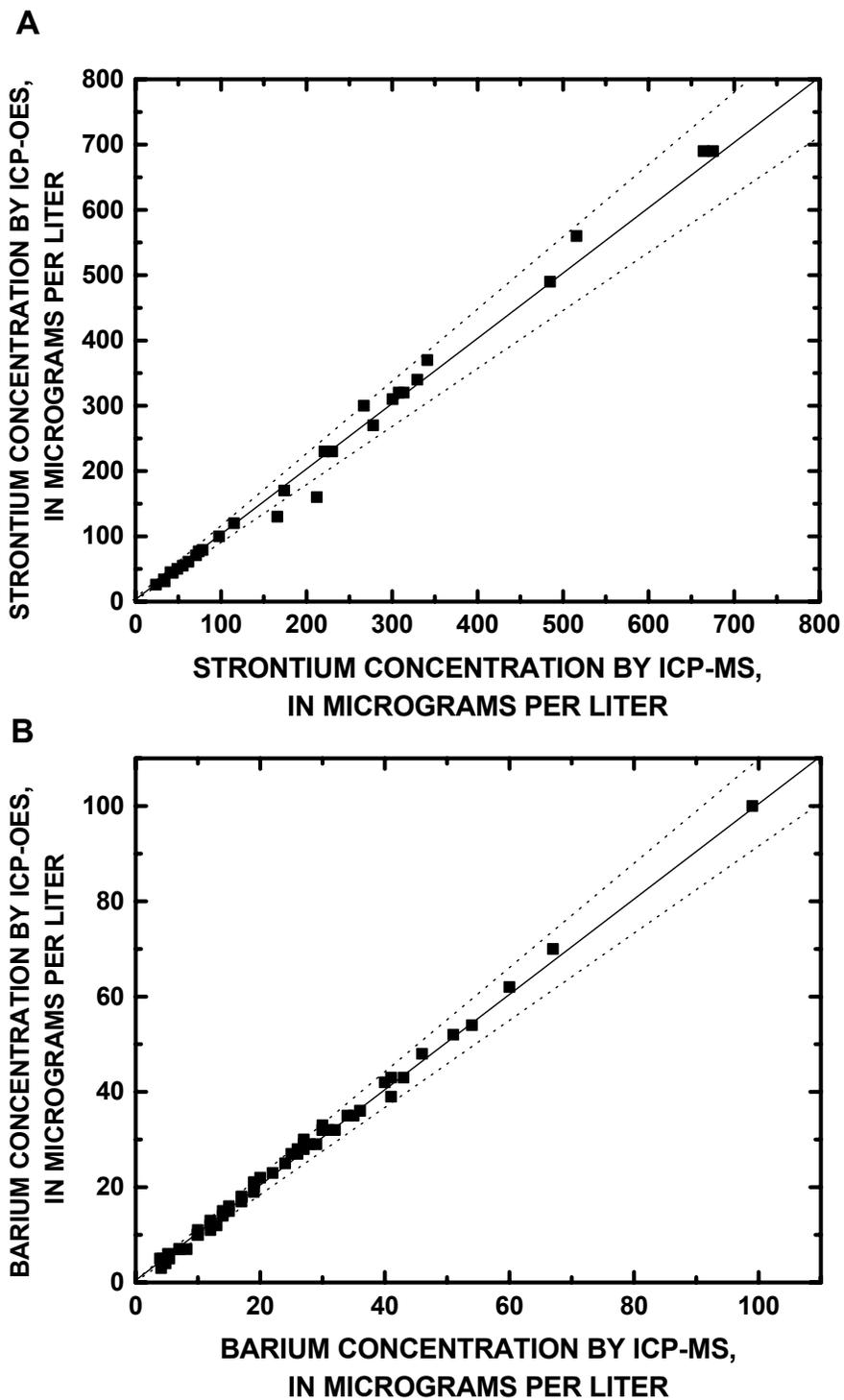


Figure 4.2. Graphs showing (A) dissolved strontium concentrations and (B) dissolved barium concentrations analyzed by ICP-OES and ICP-MS. (Diagonal line is 1:1 correspondence, dashed lines are ± 10 percent.)

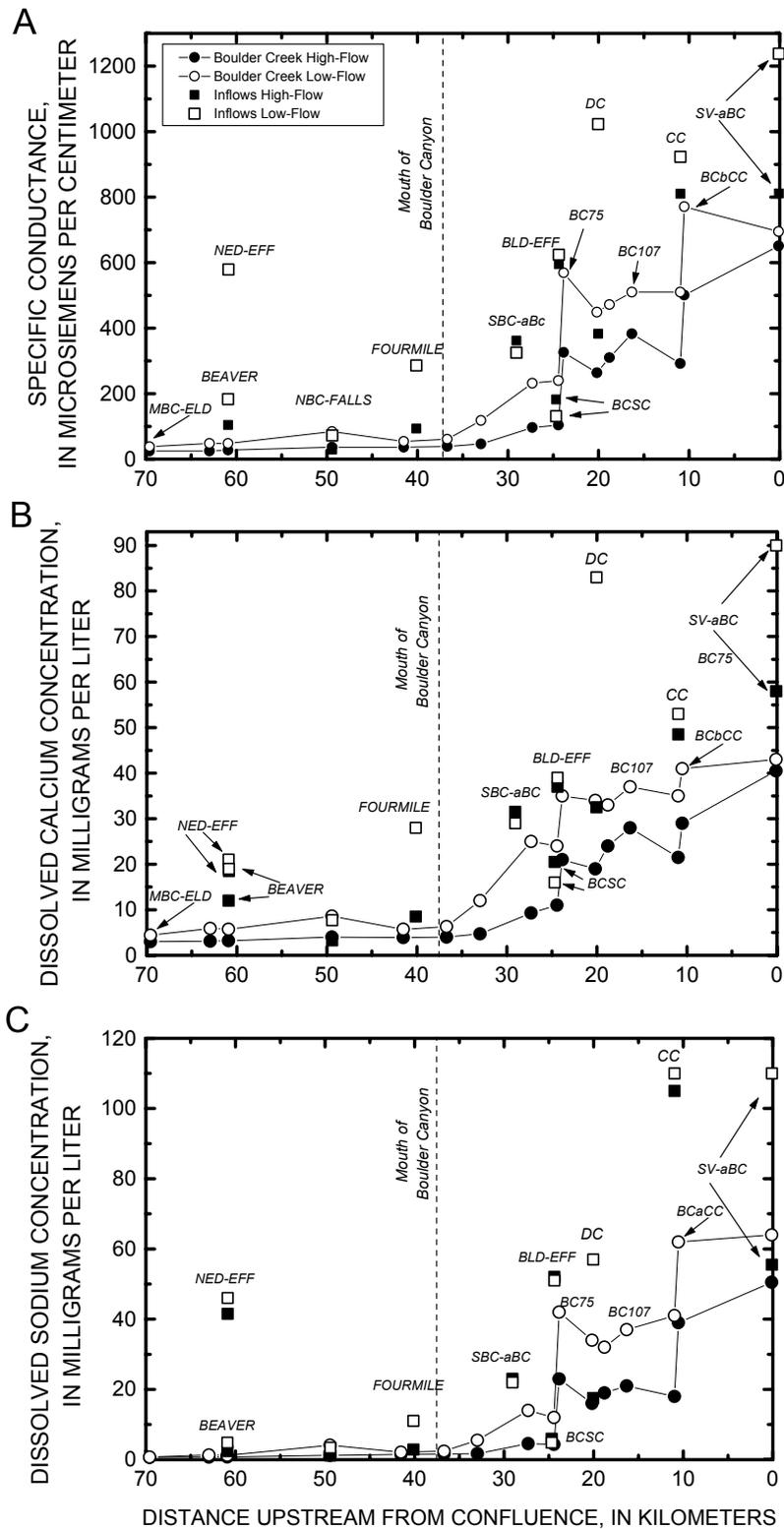


Figure 4.3. Graphs showing downstream variation in (A) specific conductance, (B) dissolved calcium concentrations, and (C) dissolved sodium concentrations for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence)

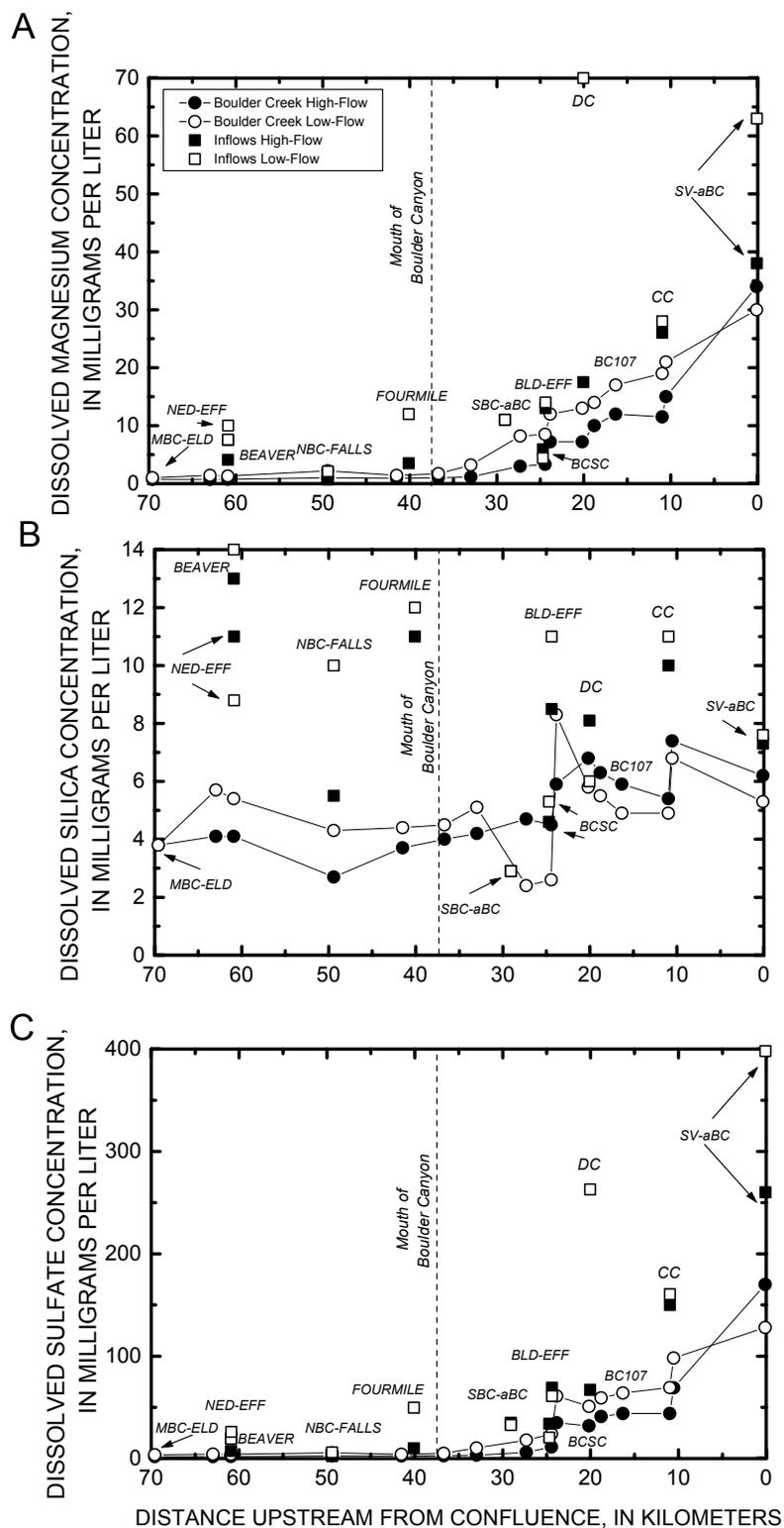


Figure 4.4. Graphs showing downstream variation in (A) dissolved magnesium concentrations, (B) dissolved silica concentrations, and (C) dissolved sulfate concentrations for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence)

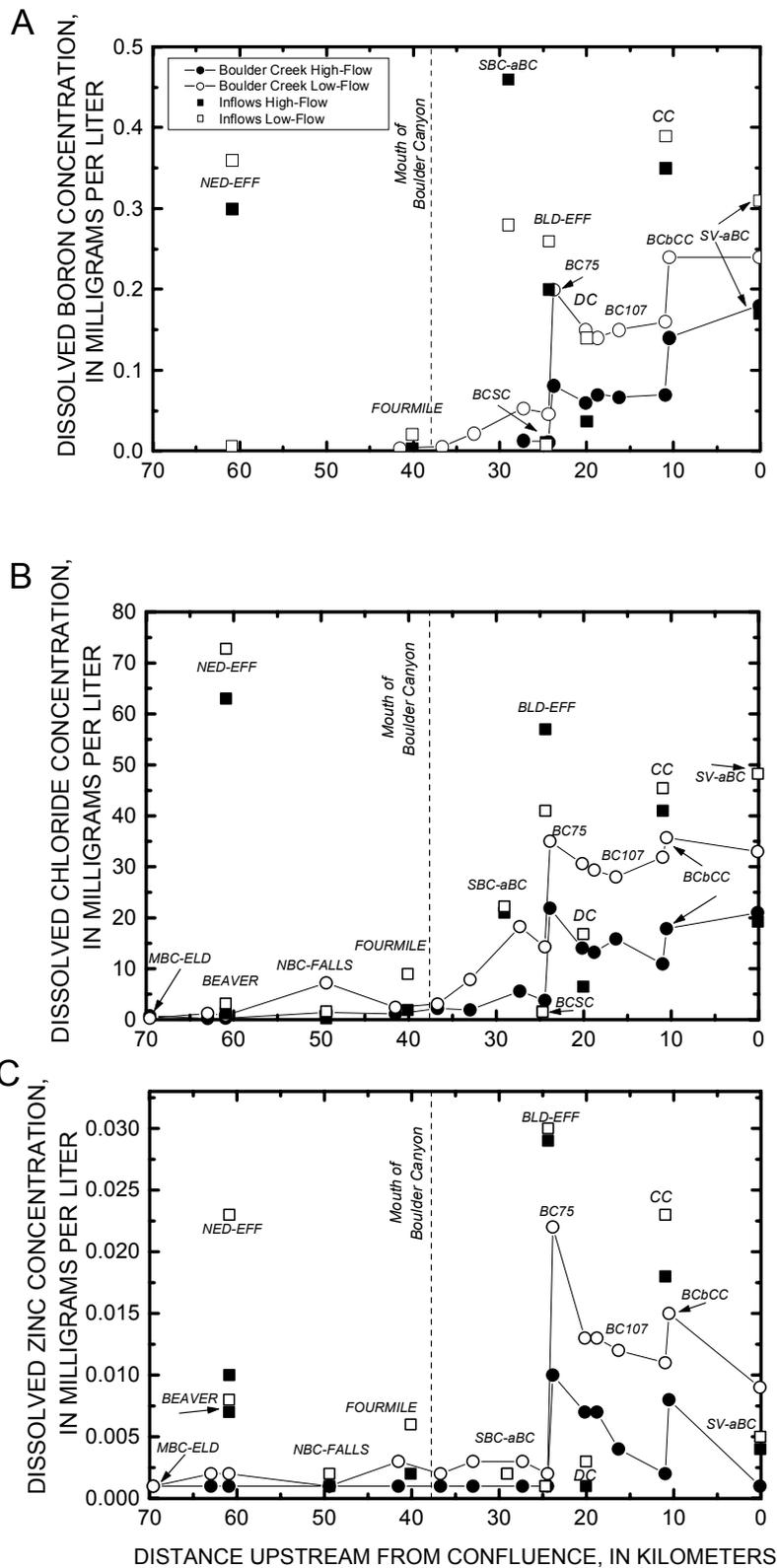


Figure 4.5. Graphs showing downstream variation in (A) dissolved boron concentrations, (B) dissolved chloride concentrations, and (C) dissolved zinc concentrations for Middle Boulder Creek/Boulder Creek and major inflows, June and October 2000. (Distance from Boulder Creek and Saint Vrain Creek confluence)

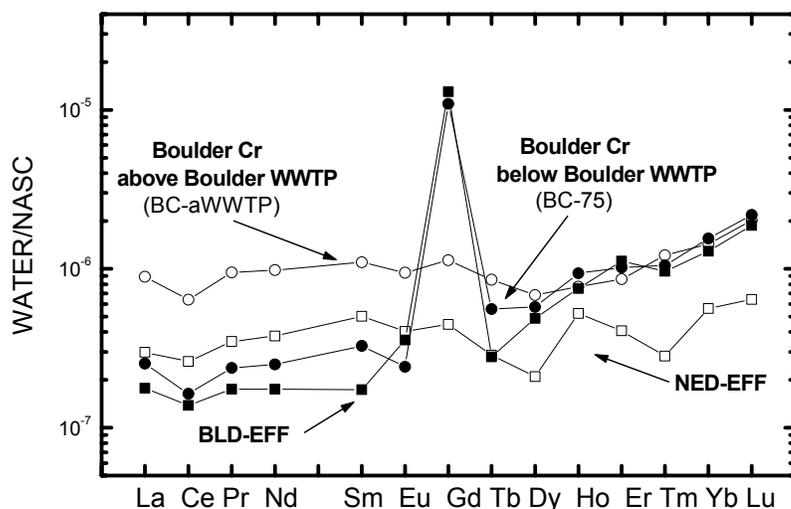


Figure 4.6. Graph showing the rare earth element patterns of select low-flow water samples. (Dissolved rare earth elements concentrations normalized to North American Shale Composite [NASC] with values from Haskin and others, 1968, and Gromet and others, 1984)

Germany and is believed to have originated from the use of gadopentetic acid in magnetic resonance imaging (Bau and Dulski, 1996). This acid is ingested as a contrasting agent and then quickly excreted, entering the urban wastewater system. Boulder has one magnetic resonance imaging facility. In contrast, Nederland does not have any, and the REE pattern of NED-EFF does not have a positive gadolinium anomaly.

Downstream of BC-75, identifying sources of solutes and geochemical processes that may control stream chemistry and quantifying their relative contribution is difficult because multiple sources and processes are likely at work. Sources of solutes include surface- and ground-water inflows, chemical reactions with bed sediments and particulates in the water column, and biological reactions. Processes that potentially control the dissolved concentrations of inorganic constituents in Boulder Creek include evaporation, dilution, sorption, precipitation, photoreduction, gas transfer, and biogeochemical reactions. In addition, the relative proportion of effluent to stream water varies throughout the day, primarily because of variation in effluent discharge (Murphy and others, 2003). The daily effluent maximum

moves downstream as a pulse. At low-flow, the wastewater dominated reach was sampled in one day (October 11) by sampling at the Boulder 75th Street WWTP, and then sampling sites downstream in order from BC-aWWTP to BC-107. An accurate estimate of stream water travel time was not available for this flow regime, so it is likely that the same package of water was not sampled at all the downstream sites.

Concentrations of most dissolved constituents decrease in the reach of Boulder Creek downstream of BC-75. Between sites BC-75 and BC-aDC discharge in Boulder Creek decreased from 1.5 to 1.1 m³/s during low flow, in part due to removal of water by the Leggett Ditch (Murphy and others, 2003). Removal of water does not lower concentration, but if water were replaced by more dilute water, perhaps from ground-water inflows, concentrations would decrease. In-stream chemical and biogeochemical reactions likely also are partially responsible for the change in solute concentrations.

In the reach between BC-aDC and BC-aCC, some constituents continue to decrease (silica and zinc), while others increase (calcium, magnesium, sodium, and sulfate; figs. 4.3 to

Table 4.7. Results of mass-balance modeling of Boulder Creek water. (Positive values indicate mineral dissolution and negative values indicate mineral precipitation in units of millimoles of mineral per liter of water)

PHASE	MBC-ELD	BC-CAN	BC-61
Hornblende	+0.032	+0.050	--
Plagioclase (An ₂₅)	+0.039	+0.136	--
Calcite	+0.063	+0.067	+0.117
Biotite	+0.006	+0.013	--
Pyrite	+0.016	+0.023	--
SiO ₂	-0.171	-0.514	-1.449
Goethite	-0.056	-0.091	--
Dolomite	--	--	+0.320
Gypsum	--	--	+0.182
Illite	--	--	+0.062
Montmorillonite	--	--	+0.346
Halite	--	--	+0.494

4.5) in concentration. No surface-water inflows were observed in this reach, but between BC-107 and BC-aCC discharge increased from 0.68 to 0.88 m³/s. Input of ground water that has reacted with sedimentary bedrock is consistent with the observed variation in stream chemistry. As discussed above, ground water that has interacted with sedimentary bedrock is enriched in calcium, chloride, magnesium, sodium, and sulfate and has low concentrations of silica and metals.

Concentrations of most dissolved constituents in Coal Creek (CC) are high, and, since the discharge is approximately one third of Boulder Creek, a step increase in figures 4.3 to 4.5 is displayed. Water in Coal Creek has a complex history including receiving WWTP from Erie, Lafayette, Louisville, and Superior, as well as receiving agriculture diversion ditch return flow. Coal Creek was the only other inflow that contained a positive gadolinium anomaly in the REE pattern (fig. 4.7), consistent with the presence of medical facilities in upstream communities.

Land use along the lowest reach of Boulder Creek, BC-bCC to BC-aSV, is dominated by agricultural and aggregate mining. The chemical change in dissolved constituents is quite variable, but, in general, displays similar variations to the reach between BC-aDC and BC-aCC (fig. 4.3 to

4.5). Differentiating between natural and anthropogenic sources and identifying geochemical processes is difficult in this reach. Some of the chemical variation is likely due to the input of ground water that has interacted with sedimentary bedrock.

SUMMARY

During high and low flow of 2000, field parameters and water samples were collected and analyzed for twenty-nine sites along Boulder Creek, Colorado, including sixteen mainstem and twelve tributary/inflow sites from upstream of the town of Eldora to the confluence of Boulder Creek and Saint Vrain Creek. In general, most dissolved constituents in Boulder Creek increased in concentration downstream, with a slight increase between the most upstream site and the mouth of Boulder Canyon, a greater increase between the mouth of Boulder Canyon and the Boulder 75th Street Wastewater Treatment Plant (WWTP), and the greatest increase downstream of the WWTP. These trends were observed in both the high- and low-flow samples, but the low-flow samples tended to have higher concentrations of dissolved constituents. Dilution of Boulder Creek by snowmelt leads to lower

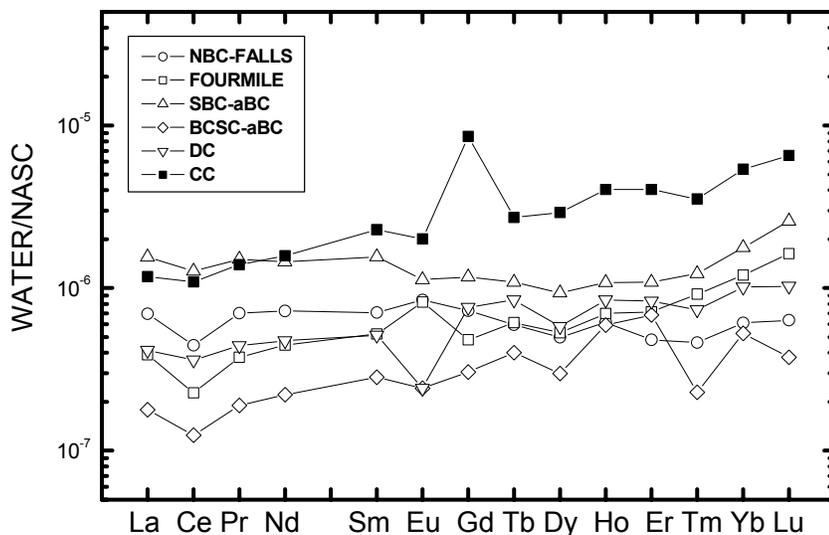


Figure 4.7. Graph showing the rare earth element patterns of select low-flow, inflow water samples. (Dissolved rare earth elements concentrations normalized to North American Shale Composite [NASC] with values from Haskin and others, 1968, and Gromet and others, 1984).

dissolved inorganic concentrations during high-flow conditions.

The inorganic water chemistry of the upper reach, above BC-CAN, is consistent with weathering of the local bedrock, which is composed primarily of Precambrian-age igneous and high-grade metamorphic rocks. The inorganic chemistry of the reach between BC-CAN and the Boulder 75th Street WWTP is more complex because of numerous potential natural and anthropogenic sources of solutes, but in general is consistent with the weathering of the local bedrock, composed of Mesozoic-age sedimentary units. Effluent from the WWTP is the greatest loading inflow to Boulder Creek, and dominates the chemistry of the Creek downstream from BC-75. In the lowest reach, differentiating between sources of solutes and processes that affect the stream chemistry is difficult, but by integrating information from the entire data set (inorganic and organic constituents, pesticides, and bed sediment composition) it may be possible.

REFERENCES CITED

- Ball, J.W. and Nordstrom, D.K., 1991, User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geological Survey Open-File Report 91-183, 189 p.
- Barringer, J.L. and Johnsson, P.A., 1989, Theoretical considerations and a simple method for measuring alkalinity and acidity in low-pH waters by gran titration: U.S. Geological Survey Water-Resources Investigations Report 89-4029, 35 p.
- Bau, Michael and Dulski, Peter, 1996, Anthropogenic origin of positive gadolinium anomalies in river waters: *Applied Geochemistry*, v. 143, 245-255.
- Brinton, T.I., Antweiler, R.C., and Taylor, H.E., 1995, Method for the determination of dissolved chloride, nitrate and sulfate in natural water using ion chromatography: U.S. Geological Survey Open-File Report 95-426, 16 p.
- Bruce, B.W. and O'Riley, Christopher, 1997, Comparative study of ground-water quality, 1976 and 1996, and initial gain-and-loss assessment of Boulder Creek, Boulder Creek, Boulder County, Colorado: U.S. Geological Survey Water-Resources Investigations Report 97-4091, 49 p.
- Clow, D.W., Mast, M.A., Bullen, T.D., and Turk, J.T., 1997, Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine watershed, Loch Vale, Colorado: *Water Resources Research*, v. 33, p.1335-1351.

- Edwards, T.K. and Glysson, D.G., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.
- Garbarino, J.R. and Taylor, H.E., 1979, Inductively coupled plasma-emission spectrometric method for routine water quality testing: *Applied Spectroscopy*, v. 33, p. 220-226.
- Gromet, L.P., Dymek, R.F., Haskin, L.A., and Korotev, R.L., 1984, The "North American shale composite"; its compilation, major and trace element characteristics: *Geochimica et Cosmochimica Acta*, v. 48, p. 2469-2482.
- Haskin, L.A., Haskin, M.A., Frey, F.A., and Wildman, T.R., 1968, Relative and absolute terrestrial abundances of the rare earths, *in* Ahrens, L.H., ed., *Origin and Distribution of the Elements*: New York, Pergamon, pp. 889-912.
- Kile, D.E. and Eberl, D.D., 2003, Quantitative mineralogy and particle size distribution of bed sediments in the Boulder Creek Watershed stream sediment— Chapter 7 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 173-184.
- Kuehner, E.C., Alvarez, Robert, Paulsen, P.J., and Murphy, T.J., 1972, Production and analysis of special high-purity acids purified by sub-boiling distillation: *Analytical Chemistry*, v. 44, p. 2050-2056.
- Murphy, S.F., Barber, L.B., Verplanck, P.L., and Kinner, D.A., 2003, Environmental setting and hydrology of the Boulder Creek Watershed— Chapter 1 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 5-26.
- Patterson, C.G., 1980, *Geochemistry of Boulder Creek, Boulder, Jefferson, and Gilpin counties, Colorado*: Boulder, University of Colorado, Master's thesis, 105 p.
- Paulson, C.L., 1994, Partitioning and speciation of copper, lead, zinc in stormwater runoff: Boulder, University of Colorado, Ph.D. dissertation, 182 p.
- Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L., 1994, An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, version 2.0: U.S. Geological Survey Water-Resources Investigations Report 94-4169, 130 p.
- Reddy, M.M. and Caine, Nel, 1989, Dissolved solutes budget of a small alpine basin, Colorado. *in* Poppoff, I.G., Goldman, C.R., Loeb, S.L., and Leopold, L.B., eds., *Proceedings, International Mountain Watershed Symposium— Subalpine Processes and Water Quality: South Lake Tahoe, Calif.*, Tahoe Resource Conservation District, p. 370-380.
- Roth, D.A., 1994, *Ultratrace analysis of mercury and its distribution in some natural waters in the United States*: Fort Collins, Colorado State University, Ph.D. dissertation, 309 p.
- Skogerboe, R.K. and Grant, C.L., 1970, Comments on the definition of the terms sensitivity and detection limit: *Spectroscopy Letters*, v. 3, p. 215-220.
- Stookey, L. L., 1970, FerroZine— a new spectrophotometric reagent for iron: *Analytical Chemistry*, v. 42, p. 779-781.
- To, T. B., Nordstrom, D. K., Cunningham, K. M., Ball, J. W., and McCleskey, R. B., 1999, New method for direct determination of dissolved Fe (III) concentrations in acid mine waters: *Environmental Science and Technology*, v. 33, p. 807-813.
- Verplanck, P.L., Antweiler, R.C., Nordstrom, D.K., and Taylor, H.E., 2001, Standard reference water samples for rare earth element determinations: *Applied Geochemistry*, v. 16, p. 231-244.
- Von Damm, K.L., 1989, Geochemical controls on groundwater chemistry in shales: *Proceedings of the 6th International Symposium on Water-Rock Interactions*, Balkema, Rotterdam, p. 727-730.
- Williams, M.W., Hood, E.W., and Caine, Nel, 2003, Headwater catchments of North Boulder Creek— Chapter 8 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 185-198.

Chapter 5 – Natural and Contaminant Organic Compounds in the Boulder Creek Watershed, Colorado During High-Flow and Low-Flow Conditions, 2000

By Larry B. Barber, Edward T. Furlong, Steffanie H. Keefe, Gregory K. Brown, and Jeffery D. Cahill

Abstract

Total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet light absorbance at 254 nanometers (UV₂₅₄) were determined in water samples collected under high-flow (June 2000) and low-flow (October 2000) conditions at 29 sites located along Boulder Creek and its major inflows. At 10 selected sites, samples were analyzed for 47 wastewater-derived organic compounds and 22 prescription and nonprescription pharmaceutical compounds. Concentrations of TOC in the mainstem sites ranged from 2.1 to 5.4 milligram per liter (mg/L) during high flow and from 1.1 mg/L to 8.3 mg/L during low flow. Concentrations of DOC ranged from 2.0 to 5.4 mg/L during high flow and from 1.1 to 7.8 mg/L during low flow. During high flow, 31 of the 47 specific wastewater compounds were detected in the mainstem samples at concentrations ranging from less than 1 nanogram per liter (ng/L) to 100,000 ng/L. During low flow, 31 of the 47 wastewater compounds were detected at concentrations ranging from less than 1 ng/L to 210,000 ng/L. A variety of pharmaceutical compounds were detected, at much lower concentrations than other wastewater compounds, in samples from both high and low flow. During high flow, individual pharmaceutical compound concentrations in mainstem samples ranged from 0.4 to 66 ng/L. During low flow, concentrations were higher, ranging from 5.2 to 510 ng/L. The concentrations and complexity of anthropogenic trace organic chemicals in Boulder Creek increased from the upper to the lower watershed with the greatest increase in chemical loading occurring

downstream of the Boulder 75th Street Wastewater Treatment Plant.

INTRODUCTION

The presence of organic compounds in Boulder Creek and its major inflows is influenced by a variety of natural (plants, animals, and microorganisms) and anthropogenic (wastewater and industrial discharges, agricultural and urban runoff) factors. Total organic carbon (TOC) is a measurement of aquatic organic carbon in a raw water sample, and dissolved organic carbon (DOC) is operationally defined as organic carbon that passes through a 0.7-micrometer (µm) pore size glass fiber filter. Both TOC and DOC are bulk chemical measurements that do not distinguish the individual compounds that make up the aquatic organic matter continuum (Thurman, 1985), which ranges from macroscopic particles to dissolved compounds. However, TOC and DOC are important parameters for understanding biogeochemical cycles, and concentrations are typically controlled by natural organic matter (NOM) sources such as plant-derived humic and fulvic acids. DOC can be further characterized by its spectroscopic properties to provide insight into molecular characteristics.

In addition to carbon loading from natural sources, Boulder Creek is influenced by organic compounds (both natural and synthetic) introduced from highway runoff, industrial discharges, spills, and municipal wastewater discharge. Because of their presence in treated municipal wastewater and potential adverse human health and ecological impacts (Barber and others, 2000; Kolpin and others, 2002), a variety

METHODS

Sampling

Sampling sites are shown in figure 5.1 and described in table 1.1 of Murphy and others (2003). Samples were collected for analysis of TOC, DOC, and ultraviolet light absorption at 254 nm (UV_{254}) from all 29 sites. Samples for additional wastewater and pharmaceutical analysis were collected at 10 sites.

Samples for analysis of DOC and UV_{254} were filtered through 0.7- μm glass fiber filters (GFF) and collected in pre-cleaned amber glass bottles. Samples for EDTA, nitrilotriacetic acid (NTA), and nonylphenolpolyethoxycarboxylate (NPEC) analyses were filtered through 0.7- μm GFF, collected in amber glass bottles, and preserved with 2 percent by volume (v/v) formalin. Raw samples for TOC and wastewater compound analyses were collected in 1-L amber glass bottles. Raw samples for steroid and hormone analysis were collected in 1-L Teflon bottles. Samples for pharmaceutical analysis were filtered through GFF and collected in 1-L pre-cleaned amber glass bottles. All samples were stored at 4°C prior to analysis.

Analysis

Details of the organic carbon analytical methods are reported elsewhere (Barber and others, 2001). Briefly, TOC and DOC were measured by UV/ammonium persulfate oxidation, with conductivity detection using a Sievers Model 800 carbon analyzer. Ultraviolet light absorbance of the filtered samples was measured at 254 nm in a 1-cm light path quartz cell using a Spectronics/Unicam Genesys model 10UV spectrometer.

EDTA, NTA, and nonylphenol monoethoxycarboxylate to nonylphenol pentaethoxycarboxylate (NP1EC-NP5EC) were measured using a modification (Barber and others, 2000) of the method of Schaffner and Giger (1984). Samples (100 mL) were evaporated

to dryness, acidified with 5 mL 50 percent (v/v) formic acid/distilled water, and evaporated to dryness. Acetyl chloride/propanol (10 percent v/v) was added, the sample heated at 90°C for 1 hour to form the propyl-esters, and the propyl-esters were extracted into chloroform. The chloroform extracts were evaporated to dryness and re-dissolved in toluene for analysis by gas chromatography/mass spectrometry (GC/MS) as described below.

Alkylphenol and other wastewater compounds were measured as described in Barber and others (2000). This method uses continuous liquid-liquid extraction (CLLE) with methylene chloride at pH 2. The CLLE exposes the sample to methylene chloride by refluxing and dispersing the solvent through a coarse glass frit, resulting in formation of micro-droplets that travel an extended path through the sample matrix allowing effective partitioning of the wastewater compounds into the solvent. After extraction, the solvent was dried over sodium sulfate and the volume reduced to 500 μL under a stream of nitrogen for GC/MS analysis.

Hormones were extracted by solid-phase extraction (SPE) using octadecyl surface-modified-silica (C_{18}) ENVI-Disk™ (47 mm, 5 μm mean flow through porosity) using a stainless steel pressurized filtration apparatus (Barber and others, 2000). All glassware used in the hormone isolation procedure was deactivated with Sylon-CT (Supelco). The SPE disks were placed in the filtration apparatus and conditioned by double rinsing with methanol followed by distilled water. A 1-L raw sample was passed through the disk at a flow rate of 4 mL/min, the disk was dried for 5 minutes with nitrogen gas at ambient temperature, and the disk was eluted with 25 mL of methanol followed by two rinses with 10 mL of methanol. The methanol was reduced in volume to 2 mL by nitrogen evaporation, quantitatively transferred to a 5 mL reaction vial, and evaporated to dryness. The residue was reacted with 2 percent *o*-methoxyamine hydrochloride (MOX) in pyridine followed by reaction with bis(trimethylsilyl)trifluoroacetamide (BSTFA)

Table 5.1. List of organic compounds analyzed in this study

[Surrogate standards are italicized; Abbr., abbreviation used in this report; CAS#, chemical abstracts registry number; MCL, maximum contaminant level (U.S. Environmental Protection Agency, 2002); LC50, lowest lethal concentration for 50% of the population of the most sensitive indicator species; studies, number of studies; --, not available; nm, nanometers; *n*, normal; *t*, tert]

Method/compound	Abbr.	CAS#	Source/use	MCL, LC50/studies
Organic carbon				
Dissolved organic carbon	DOC	--	natural organic matter	--, --/0
Total organic carbon	TOC	--	natural organic matter	--, --/0
Ultraviolet light absorption, 254 nm	UV ₂₅₄	--	natural organic matter	--, --/0
Specific ultraviolet light absorption	SA	--	natural organic matter	--, --/0
EDTA/NTA/NPEC				
Ethylenediaminetetraacetic acid	EDTA	60-00-4	metal complexing agent	--, --/0
Nitritotriacetic acid	NTA	139-13-9	metal complexing agent	--, --/0
4-Nonylphenolmonoethoxycarboxylate	NP1EC	3115-49-9	surfactant metabolite	--, --/0
4-Nonylphenoldiethoxycarboxylate	NP2EC	106807-78-7	surfactant metabolite	--, --/0
4-Nonylphenoltriethoxycarboxylate	NP3EC	--	surfactant metabolite	--, --/0
4-Nonylphenoltetraethoxycarboxylate	NP4EC	--	surfactant metabolite	--, --/0
<i>4-Bromophenyl acetic acid</i>	<i>BPAA</i>	<i>1878-68-8</i>	<i>surrogate standard</i>	--, --/0
<i>D12-ethylenediaminetetraacetic acid</i>	<i>D12 EDTA</i>	<i>203806-08-0</i>	<i>surrogate standard</i>	--, --/0
<i>4-n-Nonylphenolmonoethoxycarboxylate</i>	<i>nNP1EC</i>	--	<i>surrogate standard</i>	--, --/0
<i>4-n-Nonylphenoldiethoxycarboxylate</i>	<i>nNP2EC</i>	--	<i>surrogate standard</i>	--, --/0
Wastewater compounds				
Bisphenol A	BPA	80-05-7	plasticizer	--, 3600 ¹ /26
4- <i>t</i> -Butylphenol	TBP	98-54-4	antioxidant	--, --/0
2[3]- <i>t</i> -Butyl-4-methoxyphenol	BHA	25013-16-5	antioxidant	--, 870 ² /14
Caffeine	CAFF	58-08-2	stimulant	--, 40000 ¹ /77
2,6-Di- <i>t</i> -butyl-1,4-benzoquinone	DTBB	719-22-2	antioxidant byproduct	--, --/0
2,6-Di- <i>t</i> -butyl-4-methylphenol	BHT	128-37-0	antioxidant	--, 1140 ³ /15
2,6-Di- <i>t</i> -butylphenol	DTBP	128-39-2	antioxidant	--, --/2
1,2-Dichlorobenzene	1,2DCB	95-50-1	fumigant	--, --/0
1,3-Dichlorobenzene	1,3DCB	541-73-1	fumigant	--, --/0
1,4-Dichlorobenzene	1,4DCB	106-46-7	deodorizer	75, 1100 ² /190
4-Ethylphenol	EP	123-07-9	plasticizer	--, --/0
4-Methylphenol	MP	106-44-5	disinfectant	--, 1400 ³ /74
4-Nonylphenol	NP	25154-52-3	surfactant metabolite	--, 130 ¹ /135
4-Nonylphenolmonoethoxylate	NP1EO	9016-45-9	surfactant metabolite	--, 14450 ³ /4
4-Nonylphenoldiethoxylate	NP2EO	--	surfactant metabolite	--, 5500 ³ /6
4-Nonylphenoltriethoxylate	NP3EO	--	surfactant metabolite	--, --/0
4-Nonylphenoltetraethoxylate	NP4EO	--	surfactant metabolite	--, --/0
4- <i>n</i> -Octylphenol	NOP	1806-26-4	plasticizer	--, --/0
4- <i>t</i> -Octylphenol	TOP	140-66-9	surfactant metabolite	--, --/0
4- <i>t</i> -Octylphenolmonoethoxylate	OP1EO	9036-19-5	surfactant metabolite	--, --/0
4- <i>t</i> -Octylphenoldiethoxylate	OP2EO	--	surfactant metabolite	--, --/0
4- <i>t</i> -Octylphenoltriethoxylate	OP3EO	--	surfactant metabolite	--, --/0
4- <i>t</i> -Octylphenoltetraethoxylate	OP4EO	--	surfactant metabolite	--, --/0
4- <i>t</i> -Octylphenolpentaethoxylate	OP5EO	--	Surfactant metabolite	--/--/0
4- <i>t</i> -Pentylphenol	TPP	80-46-6	plasticizer	--, --/0
4-Propylphenol	PP	645-56-7	plasticizer	--, --/0
Triclosan	TRI	3380-34-5	antimicrobial	--, 180 ¹ /3
<i>D6-Bisphenol A</i>	<i>D6 BPA</i>	<i>86588-58-1</i>	<i>surrogate standard</i>	--, --/0
<i>D21-2,6-Di-t-butyl-4-methylphenol</i>	<i>D21 BHT</i>	<i>64502-99-4</i>	<i>surrogate standard</i>	--, --/0
<i>4-n-Nonylphenol</i>	<i>nNP</i>	<i>104-40-5</i>	<i>surrogate standard</i>	--, --/0
<i>4-n-Nonylphenolmonoethoxylate</i>	<i>nNP1EO</i>	--	<i>surrogate standard</i>	--, --/0
<i>4-n-Nonylphenoldiethoxylate</i>	<i>nNP2EO</i>	--	<i>surrogate standard</i>	--, --/0

Table 5.1. List of organic compounds analyzed in this study--continued

Method/Compound	Abbr.	CAS#	Source/use	MCL, LC50/studies
Hormones and steroids				
<i>cis</i> -Androsterone	AND	53-41-8	urinary steroid	--, --/0
Cholesterol	CHO	57-88-5	animal steroid	--, --/0
3- β -Coprostanol	COP	360-68-9	animal fecal steroid	--, --/0
Equilenin	EQUI	517-09-9	hormone replacement therapy	--, --/0
Equilin	EQUIN	474-86-2	hormone replacement therapy	--, --/0
17- α -Estradiol	AE2	57-91-0	reproductive hormone	--, --/0
17- β -Estradiol	BE2	50-28-2	reproductive hormone	--, --/0
Estriol	E3	50-27-1	reproductive hormone	--, --/0
Estrone	E1	53-16-7	reproductive hormone	--, --/11
17- α -Ethinylestradiol	EE2	57-63-6	ovulation inhibitor	--, --/22
Mestranol	MES	72-33-3	ovulation inhibitor	--, --/0
19-Norethisterone	NOR	68-22-4	ovulation inhibitor	--, --/0
Progesterone	PRO	57-83-0	reproductive hormone	--, --/0
Testosterone	TES	58-22-0	reproductive hormone	--, --/4
<i>D₄</i> -17- β -Estradiol	<i>D4 E2</i>	66789-03-5	<i>surrogate standard</i>	--, --/0
<i>D7</i> -Cholesterol	<i>D7 CHO</i>	--	<i>surrogate standard</i>	--, --/0
Human health pharmaceuticals				
Acetaminophen	ACET	103-90-2	Antipyretic	--, 6000 ³ /14
Albuterol	ALB	18559-94-9	Antiasthmatic	--, --/0
Caffeine	CAFF	58-08-2	Stimulant	--, 40000 ¹ /77
Cimetidine	CIM	51481-61-9	Antacid	--, --/0
Codeine	COD	76-57-3	Analgesic	--, --/0
Cotinine	COT	486-56-6	nicotine metabolite	--, --/0
Dehydronifedipine	DHNF	67035-22-7	Antianginal	--, --/0
Digoxigenin	DIGN	1672-46-4	digoxin metabolite	--, --/0
Digoxin	DIG	20830-75-5	cardiac stimulant	--, 1000000 ¹ /24
Diltiazem	DILT	42399-41-7	Antihypertensive	--, --/0
1,7-Dimethylxanthine	DMX	611-59-6	caffeine metabolite	--, --/0
Diphenhydramine	DPHA	58-73-1	Antihistamine	--, --/0
Enalaprilat	ENL	76420-72-9	antihypertensive metabolite	--, --/0
Fluoxetine	FLUO	54910-89-3	Antidepressant	--, --/0
Gemfibrozil	GEM	25812-30-0	Antihyperlipidemic	--, --/0
Ibuprofen	IBU	15687-27-1	Antiinflammatory	--, --/0
Metformin	MET	657-24-9	Antidiabetic	--, --/0
Paroxetine metabolite	PRXM	--	antidepressant metabolite	--, --/0
Ranitidine	RANI	66357-35-5	Antacid	--, --/0
Sulfamethoxazole	SULF	723-46-6	Antibiotic	--, --/0
Trimethoprim	TMP	738-70-5	Antibiotic	--, 3000 ² /4
Warfarin	WRF	81-81-2	Anticoagulant	--, 166000 ² /33
¹³ C3 Caffeine	<i>13C CAFF</i>	--	<i>surrogate standard</i>	--, --/0
¹³ C Phenacetin	<i>13C PHEN</i>	--	<i>surrogate standard</i>	--, --/0

¹ *Pimephales promelas* (fathead minnow), 96-hour exposure (U.S. Environmental Protection Agency [USEPA], 2001)

² *Oncorhynchus mykiss* (rainbow trout), 96-hour exposure (USEPA, 2001)

³ *Daphnia magna* (water flea), 48-hour exposure (USEPA, 2001)

containing 10 percent trimethylchlorosilane (TMCS). This reaction forms the MOX ethers of the keto groups and the trimethylsilyl (TMS) ethers of the hydroxy groups, and makes the compounds more amenable to GC/MS analysis.

The propyl-ester, wastewater-compound, and steroid/hormone compound extracts were analyzed by electron impact GC/MS in both the full-scan and selected ion monitoring (SIM) modes. The general gas chromatography conditions were: Hewlett Packard (HP) 6890 GC; column - HP Ultra II (5 percent phenylmethyl silicone), 25 m x 0.2 mm, 33 μ m film thickness; carrier gas, ultra high purity helium with a linear-flow velocity of 27 cm/sec; injection port temperature, 300°C; initial oven temperature, 50°C; split vent open, 0.75 minutes; ramp rate, 6°C/minute to 300°C; hold time, 15 minutes at 300°C. The mass spectrometer conditions are as follows: HP 5973 Mass Selective Detector; tune with perfluorotributylamine; ionization energy, 70 eV; source pressure, 1×10^{-5} torr; source temperature, 250°C; interface temperature, 280°C; full scan, 40 to 550 atomic mass units (amu) at 1 scan/sec. Concentrations were calculated based on SIM data using diagnostic ions for each compound (table 5.2). Each compound was identified based on matching of retention times (± 0.02 min) and ion ratios (± 20 percent) determined from analysis of authentic standards. An 8-point calibration curve (typically ranging from 0.01 to 50 ng/ μ L) and internal standard (deuterated polycyclic aromatic hydrocarbons, table 5.2) procedures were used for calculating concentrations. Surrogate standards (table 5.1) were added to the samples prior to extraction and derivatization to evaluate compound recovery and whole method performance.

Pharmaceutical compounds (table 5.1) were measured by liquid chromatography/mass spectrometry (LC/MS) as described in Kolpin and others (2002) and J.D. Cahill (written commun., 2003). Compounds were extracted from filtered 1-L water samples using 0.5 g Waters Oasis HLB (hydrophilic-lipophilic balance) SPE cartridges,

processed at a flow rate of 15 mL/minute. After extraction, the adsorbed compounds were eluted with 6 mL of pesticide-grade methanol followed by 4 mL of pesticide-grade methanol acidified to pH 3.7 with reagent-grade trifluoroacetic acid. The two fractions were reduced under nitrogen gas to near dryness, combined, and brought to a final volume of 1 mL in 10 percent acetonitrile/water (v/v) buffered with pH 3.7 ammonium formate/formic acid (prepared from 1M solutions of ammonium formate and formic acid, 40 mL and 48 mL respectively, diluted to 4 L in high purity reagent-grade water). Compounds were separated using an HP 1100 series high-performance liquid chromatograph (HPLC) and a C₁₈ reverse-phase HPLC column (Metasil Basic, 3 μ m, 150 x 2.0 mm; Metachem Technologies). Compounds were separated using a programmed gradient of buffered ammonium formate/formic acid aqueous phase and acetonitrile, starting at six percent acetonitrile in aqueous buffer and increasing in seven steps to 100 percent acetonitrile in 27 minutes. The HPLC was coupled to an HP 1100 Series LC/MSD with an electrospray ionization interface (ESI) and quadrupole mass spectrometer for compound identification and quantitation. Extracts were analyzed under positive electrospray ionization conditions. The ESI source conditions were as follows: source temperature, 150°C; nebulizer gas pressure, 100 kPa; drying gas (nitrogen) flow rate, 9 L/minute; drying gas temperature, 350°C. The potential difference between the source and the capillary was held at 3500 volts and the detector gain was held at a value of 2. Programmed fragmentor and/or capillary exit voltage changes (table 5.2) were used to produce sufficient fragmentation of each compound so a quantitation ion, typically the protonated molecular ion, and at least one characteristic fragment ion were produced for each pharmaceutical compound. Selected-ion monitoring (table 5.2) was used to improve sensitivity and decrease chemical noise. For each sample, compounds were identified by comparison of the presence and abundance of

SIM ions to authentic standards. Concentrations were calculated by the injection internal standard method using ^{13}C caffeine. Two surrogates were used to estimate method performance. ^{13}C Phenacetin was used for samples collected in the June 2000 high-flow sampling. An improved surrogate, D_4 ethyl nicotinoate, was used for the October 2000 low-flow sampling.

RESULTS

Total Organic Carbon, Dissolved Organic Carbon, and Ultraviolet Light Absorption

Results for TOC, DOC, and UV_{254} during the high-flow sampling (June 2000) of the mainstem and inflow sites are presented in table 5.3, and results for the low-flow sampling (October 2000) are presented in table 5.4. The UV_{254} data were converted to specific UV absorbance (SA; Chin and others, 1994) by normalizing to DOC concentration ($\text{SA}=\text{UV}_{254}/\text{DOC}$). The TOC, DOC, and SA results for high- and low-flow sampling are summarized in figure 5.2. The profiles show an increase in TOC and DOC from the upper to lower watershed indicating contributions from both natural and anthropogenic sources. At the headwater MBC-ELD site, concentrations of TOC and DOC were relatively low, and due to the absence of urban influences in the area, most likely represents carbon contributions from natural sources, primarily degradation of plant-derived material (Thurman, 1985). Concentrations were higher during the spring flush (June) than under base-flow (October) conditions. During low flow, as Boulder Creek passed through the Highway 119 corridor in Boulder Canyon, TOC and DOC concentrations increased, presumably due to runoff from automobile and other transportation sources as well as increased residential development. As Boulder Creek passed through the city of Boulder, TOC and DOC continued to increase due to domestic, commercial, transportation, and recreational sources. Finally,

Boulder Creek east of the city of Boulder had a large increase in TOC and DOC below the Boulder 75th Street Wastewater Treatment Plant (WWTP), indicating significant organic carbon loading from the effluent discharged from the plant. Based on DOC results from the BC-aWWTP, BC-75, and BLD-EFF sites, the WWTP effluent comprised about 39 percent of the flow at BC-75 under high-flow conditions and approximately 69 percent under low-flow conditions. Downstream from BC-75, TOC and DOC concentrations decreased due to in-stream removal processes (biodegradation, photolysis, sorption) and dilution by waters of lower organic-carbon concentrations. Under low-flow conditions, Coal Creek had similar TOC and DOC concentrations as mainstem Boulder Creek above the confluence, indicating that the waters from the two creeks were of similar composition. However, under high-flow conditions TOC and DOC concentrations in Coal Creek were higher than in mainstem Boulder Creek, indicating Coal Creek had less dilution with runoff from the upper watershed.

There were distinct seasonal differences, with concentrations of TOC and DOC upstream of the WWTP being larger during high flow because of flushing of NOM from the upper watershed by spring runoff. Because of greater in-stream dilution resulting from higher stream flow, the impact of the WWTP was not as great at high flow as it was at low flow.

There was a distinct difference in the characteristics of the DOC between the natural organic matter in the upper watershed and the wastewater-dominated portion of Boulder Creek below the Boulder 75th Street WWTP as shown by the decrease in SA values at BC-75 (fig. 5.2c). This decrease in SA reflects the more aliphatic character of the wastewater-derived DOC relative to the aromatic character of natural DOC (Barber and others, 2001).

Table 5.2. List of ions used in selected ion monitoring (SIM) gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) methods

[See table 5.1 for compound abbreviations; compounds are presented in order of relative chromatographic elution; internal standards are shown in italics; surrogate standards are shown in bold italics; [M]⁺, molecular ion; Tgt, target ion used for quantitation; Q1, first qualifier ion; Q2, second qualifier ion; Q3, third qualifier ion; C1, first confirmation ion; C2, second confirmation ion; C3, third confirmation ion; --, not applicable; MOX/TMS, methoxyamine/trimethylsilyl; [M+H]⁺, nominal protonated molecular ion; FV, fragmentor voltage; Na⁺, sodium adduct]

Compound	[M] ⁺	Tgt	Q1	Q2	Q3
Wastewater compounds					
1,3DCB	146	146	111	75	--
<i>D4-1,4-Dichlorobenzene</i>	<i>151</i>	<i>115</i>	<i>151</i>	<i>78</i>	--
1,4DCB	146	146	111	75	--
1,2DCB	146	146	111	75	--
MP	108	108	107	77	--
EP	122	107	122	77	--
<i>D8-Napthalene</i>	<i>136</i>	<i>136</i>	<i>108</i>	<i>68</i>	--
PP	136	107	136	77	--
TBP	150	135	150	107	--
TPP	164	135	164	107	--
DTBP	206	191	206	57	--
DTBB	220	177	220	135	--
<i>D10-Acenaphthene</i>	<i>164</i>	<i>164</i>	<i>162</i>	<i>80</i>	--
BHA	180	165	180	137	--
<i>D21 BHT</i>	<i>240</i>	<i>222</i>	<i>240</i>	<i>66</i>	--
BHT	220	205	220	57	--
TOP	206	135	206	107	--
NP	220	135	220	107	--
NOP	206	107	206	77	--
<i>D10-Phenanthrene</i>	<i>188</i>	<i>188</i>	<i>160</i>	<i>80</i>	--
CAFF	194	194	109	82	--
OP1EO	250	179	250	135	--
<i>nNP</i>	<i>220</i>	<i>107</i>	<i>220</i>	<i>77</i>	--
NP1EO	264	179	264	193	--
TRI	289	218	289	145	--
<i>nNP1EO</i>	<i>264</i>	<i>107</i>	<i>264</i>	<i>151</i>	--
OP2EO	294	135	294	223	--
<i>D6 BPA</i>	<i>234</i>	<i>216</i>	<i>234</i>	<i>121</i>	--
BPA	228	213	228	119	--
NP2EO	308	135	308	223	--
<i>nNP2EO</i>	<i>308</i>	<i>107</i>	<i>308</i>	<i>195</i>	--
OP3EO	338	267	338	135	--
<i>D12-Chrysene</i>	<i>240</i>	<i>240</i>	<i>236</i>	<i>120</i>	--
NP3EO	352	281	352	267	--
OP4EO	382	135	382	311	--
NP4EO	396	325	396	311	--
OP5EC	426	355	426	135	--
Hormones and steroid compound (MOX/TMS) derivatives					
<i>D12-Chrysene</i>	<i>240</i>	<i>240</i>	<i>236</i>	<i>120</i>	--
<i>Triphenylene</i>	<i>228</i>	<i>228</i>	<i>113</i>	<i>226</i>	--
AND	392	270	391	360	300
AE2	416	285	416	326	401
<i>D4 E2</i>	<i>420</i>	<i>420</i>	<i>330</i>	<i>329</i>	<i>273</i>
BE2	416	416	285	326	401
E1	371	371	323	312	340
TES	389	389	358	268	281

Table 5.2. List of ions used in selected ion monitoring (SIM) gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) methods--continued

Compound	[M] ⁺	Tgt	Q1	Q2	Q3	
MES	382	367	382	227	242	
NOR	399	384	399	259	209	
EQUI	367	367	279	352	337	
EQUN	369	369	354	338	229	
EE2	440	425	440	285	300	
E3	504	311	504	345	386	
<i>D12-Perylene</i>	264	264	260	132	--	
PRO	372	372	341	286	100	
COP	460	370	460	355	257	
D7 CHO	465	336	465	375	360	
CHO	458	329	458	368	353	
EDTA, NTA, and NPEC (propyl esters)						
<i>C9 Benzene</i>	204	92	204	133	--	
4-Bromophenyl acetic acid	257	171	257	90	--	
NTA	317	317	230	144	--	
NP1EC	320	249	320	235	--	
NP2EC	364	103	364	293	--	
nNP2EC	364	103	364	145	--	
D12 EDTA	472	236	472	150	--	
EDTA	460	460	230	144	--	
NP3EC	408	323	408	103	--	
NP4EC	452	367	452	103	--	
Pharmaceutical compounds	[M+H]⁺	Q1	C1	C2	C3	FV
ACET	152	110	152	--	--	88
ALB	240	166	222	240	--	70
CAFF	195	195	138	--	--	110
¹³ C3 Caffeine	198	198	139	--	--	110
CIM	253	159	253	--	--	88
COD	300	300	241	--	--	120
COT	177	177	80	98	--	80
DHNF	345	345	268	284	--	120
DIGN	391	391	355	373	--	70
DIG	781	521	651	--	--	90
DILT	415	415	178	--	--	110
DPHA	256	167	256	--	--	70
DMX	181	181	124	--	--	88
ENL	385	349	230	303	--	100
FLUO	310	310	148	--	--	70
GEM	273 (Na ⁺)	273	205	233	--	50
IBU	207	207	161	--	--	60
MET	130	130	113	--	--	80
PRXM	332	332	192	--	--	100
¹³ C Phenacetin	181	181	139	--	--	100
RANI	315	176	315	--	--	88
SULF	254	254	156	--	--	100
TMP	291	291	206	--	--	100
WRF	309	309	163	251	--	70

Table 5.3. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000

[See table 5.1 for compound abbreviations; specific compounds listed in order of chromatographic retention time; distance, distance upstream from --, sample not analyzed for this constituent; <, less than; E, estimated concentration; <LRL below laboratory reporting level; LRL*, present above LRL but

Site	Distance (meters)	Date	Time	Sample Type	DOC/TOC (mg/L)	UV254 (cm)	SA (L/mg/m)	NTA (ng/L)	EDTA (ng/L)	NP1EC (ng/L)	NP2EC (ng/L)	NP3EC (ng/L)
Middle Boulder Creek/Boulder Creek												
MBC-ELD	69590	6/12/00	820	Dissolved	2.2	0.086	3.9	<500	<500	<500	<500	<500
				Total	2.2	0.084	--	--	--	--	--	--
MBC-WTP	62970	6/12/00	1210	Dissolved	2.2	0.081	3.8	--	--	--	--	--
				Total	2.2	0.082	--	--	--	--	--	--
MBC-W	60920	6/12/00	1250	Dissolved	2.0	0.077	3.8	--	--	--	--	--
				Total	2.1	0.081	--	--	--	--	--	--
MBC-aNBC	49440	6/13/00	845	Dissolved	3.1	0.109	3.5	--	--	--	--	--
				Total	3.2	0.107	--	--	--	--	--	--
BC-ORO	41520	6/13/00	1000	Dissolved	2.9	0.106	3.6	--	--	--	--	--
				Total	2.8	0.098	--	--	--	--	--	--
BC-CAN	36710	6/13/00	1315	Dissolved	2.9	0.097	3.4	<500	<500	800	600	<500
				Total	2.6	0.087	--	--	--	--	--	--
BC-30	32990	6/12/00	1430	Dissolved	2.7	0.099	3.7	<500	<500	<500	<500	<500
				Total	2.7	0.096	--	--	--	--	--	--
BC-61	27320	6/14/00	900	Dissolved	2.9	0.104	3.5	--	--	--	--	--
				Total	2.9	0.096	--	--	--	--	--	--
BC-aWWTP	24440	6/13/00	1910	Dissolved	3.2	0.108	3.3	<500	<500	800	1100	<500
				Total	3.1	0.108	--	--	--	--	--	--
BC-75	23850	6/13/00	2000	Dissolved	5.4	0.110	2.1	3300	100000	24000	48000	1100
				Total	5.4	0.110	--	--	--	--	--	--
BC-aDC	20180	6/14/00	1040	Dissolved	4.4	0.107	2.5	--	--	--	--	--
				Total	4.5	0.109	--	--	--	--	--	--
BC-95	18790	6/14/00	1300	Dissolved	4.7	0.115	2.5	--	--	--	--	--
				Total	4.7	0.113	--	--	--	--	--	--
BC-107	16320	6/14/00	1415	Dissolved	5.1	0.123	2.4	--	--	--	--	--
				Total	5.1	0.120	--	--	--	--	--	--
BC-aCC	10970	6/13/00	1645	Dissolved	4.6	0.122	2.7	1200	8200	12000	17000	<500
				Total	4.6	0.123	--	--	--	--	--	--
BC-bCC	10540	6/13/00	1745	Dissolved	4.8	0.124	2.6	--	--	--	--	--
				Total	4.8	0.123	--	--	--	--	--	--
BC-aSV	110	6/12/00	1700	Dissolved	5.3	0.127	2.4	700	17000	13000	20000	<500
				Total	5.3	0.130	--	--	--	--	--	--
Inflows/other flows												
COMO	59340	6/12/00	1000	Dissolved	3.6	0.170	4.7	--	--	--	--	--
				Total	3.8	0.176	4.6	--	--	--	--	--
NBC-LW	59370	6/12/00	1100	Dissolved	2.3	0.080	3.5	--	--	--	--	--
				Total	2.3	0.082	3.5	--	--	--	--	--
SLP	59340	6/12/00	1100	Dissolved	--	--	--	--	--	--	--	--
				Total	2.9	0.074	2.6	--	--	--	--	--
BEAVER	60910	6/12/00	1210	Dissolved	2.1	0.074	3.6	--	--	--	--	--
				Total	2.1	0.074	3.6	--	--	--	--	--
NED-EFF	60880	6/12/00	1330	Dissolved	26	0.550	2.1	51000	17000	360000	830000	9000
				Total	24	0.550	2.3	--	--	--	--	--
NBC-FALLS	49420	6/13/00	800	Dissolved	2.6	0.094	3.6	--	--	--	--	--
				Total	2.6	0.085	3.3	--	--	--	--	--
FOURMILE	40120	6/13/00	1115	Dissolved	1.4	0.042	3.0	--	--	--	--	--
				Total	1.3	0.034	2.7	--	--	--	--	--
SBC-aBC	29070	6/14/00	800	Dissolved	5.4	0.112	2.1	--	--	--	--	--
				Total	5.4	0.105	1.9	--	--	--	--	--
BCSC-aBC	24680	6/14/00	1515	Dissolved	3.6	0.137	3.8	--	--	--	--	--
				Total	3.6	0.152	4.2	--	--	--	--	--
BLD-EFF	24380	6/13/00	2000	Dissolved	8.9	0.134	1.5	8400	370000	62000	140000	3200
				Total	9.4	0.142	1.5	--	--	--	--	--
DC	20040	6/14/00	1120	Dissolved	4.7	0.149	3.2	--	--	--	--	--
				Total	4.7	0.145	3.1	--	--	--	--	--
CC	10970	6/13/00	1615	Dissolved	7.0	0.161	2.3	1700	120000	26000	110000	1100
				Total	7.0	0.166	2.4	--	--	--	--	--
SV-aBC	90	6/12/00	1745	Dissolved	5.1	0.130	2.5	--	--	--	--	--
				Total	4.9	0.125	2.6	--	--	--	--	--
Quality assurance/quality control												
Field Blank	--	6/13/00	1700	Total	<0.1	0.001	--	<500	<500	<500	<500	<500
Lab Blank	--	2/15/00	--	Total	<0.1	0.001	--	<500	<500	<500	<500	<500
DW Spike (% Rec)	--	6/13/00	--	Total	98	--	--	108	70	94	120	110
BC-aCC Rep1	10970	6/13/00	1725	Dissolved	--	--	--	--	--	--	--	--
BC-aCC Rep2	10970	6/13/00	1725	Dissolved	--	--	--	--	--	--	--	--

Boulder Creek/SaintVrain Creek confluence; mg/L, milligrams per liter; cm, centimeter; L/mg/m, liter per milligram per meter; ng/L; nanograms per liter; at same level as measured in the laboratory reagent blank; Rep, replicate; DW, distilled water; DW spike values given in percent recovery, % Rec]

Site	NP4EC (ng/L)	Total NPEC (ng/L)	1,3DCB (ng/L)	1,4DCB (ng/L)	1,2DCB (ng/L)	MP (ng/L)	EP (ng/L)	PP (ng/L)	TBP (ng/L)	TPP (ng/L)	DTBP (ng/L)
MBC-ELD	<500	<500	--	--	--	--	--	--	--	--	--
MBC-WTP	--	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MBC-W	--	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--	--
BC-CAN	<500	1400	--	--	--	--	--	--	--	--	--
BC-30	<500	<500	<0.5	<0.5	<0.5	<0.5	<0.5	2.2	1.1	<0.5	<0.5
BC-61	--	--	0.6	<0.5	<0.5	1.1	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aWWTP	<500	1900	--	--	--	--	--	--	--	--	--
BC-75	<500	73000	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aDC	--	--	1.1	17	<0.5	2.8	0.6	<0.5	5.6	28	<0.5
BC-95	--	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--	--
BC-aCC	<500	30000	--	--	--	--	--	--	--	--	--
BC-bCC	--	--	1.7	<0.5	1.7	1.7	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aSV	<500	33000	--	--	--	--	--	--	--	--	--
	--	--	<0.5	<0.5	<0.5	1.1	1.1	<0.5	0.6	0.6	<0.5
COMO	--	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--	--
NED-EFF	4900	1200000	--	--	--	--	--	--	--	--	--
NBC-FALLS	--	--	<0.5	5.6	<0.5	10	3.4	<0.5	150	35	2.2
FOURMILE	--	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--	--
BLD-EFF	1600	200000	--	--	--	--	--	--	--	--	--
DC	--	--	<0.5	35	<0.5	<0.5	<0.5	<0.5	7.0	39	<0.5
CC	<500	140000	--	--	--	--	--	--	--	--	--
SV-aBC	--	--	<0.5	<0.5	<0.5	1.1	<0.5	<0.5	3.4	0.6	<0.5
	--	--	--	--	--	--	--	--	--	--	--
Field Blank	<500	<500	0.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Lab Blank	<500	<500	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
DW Spike (% Rec)	100	--	26	27	29	26	44	48	50	51	43
BC-aCC Rep1	--	--	--	--	--	--	--	--	--	--	--
BC-aCC Rep2	--	--	--	--	--	--	--	--	--	--	--

Table 5.3. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000--continued

Site	DTBB (ng/L)	BHA (ng/L)	BHT (ng/L)	TOP (ng/L)	NP (ng/L)	NOP (ng/L)	CAFF (ng/L)	OP1EO (ng/L)	NP1EO (ng/L)	TRI (ng/L)	OP2EO (ng/L)
Middle Boulder Creek/Boulder Creek											
MBC-ELD	--	--	--	--	--	--	--	--	--	--	--
	63	<0.5	<0.5	2.3	14	<0.5	11	<0.5	0.6	2.9	<0.5
MBC-WTP	--	--	--	--	--	--	--	--	--	--	--
MBC-W	--	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--	--
BC-CAN	--	--	--	--	--	--	--	--	--	--	--
	61	<0.5	<0.5	6.1	15	<0.5	12	<0.5	0.6	<0.5	<0.5
BC-30	--	--	--	--	--	--	--	--	--	--	--
	41	<0.5	<0.5	1.1	15	<0.5	25	<0.5	0.6	<0.5	<0.5
BC-61	--	--	--	--	--	--	--	--	--	--	--
BC-aWWTP	--	--	--	--	--	--	--	--	--	--	--
	43	<0.5	<0.5	1.1	12	<0.5	18	<0.5	<0.5	<0.5	<0.5
BC-75	--	--	--	--	--	--	--	--	--	--	--
	110	<0.5	3.4	50	340	9.0	42	110	160	170	1600
BC-aDC	--	--	--	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--	--
BC-aCC	--	--	--	--	--	--	--	--	--	--	--
	59	<0.5	0.6	7.3	80	3.9	38	1.1	10	23	<0.5
BC-bCC	--	--	--	--	--	--	--	--	--	--	--
BC-aSV	--	--	--	--	--	--	--	--	--	--	--
	52	<0.5	<0.5	3.9	71	<0.5	45	0.6	2.8	24	<0.5
Inflows/other flows											
COMO	--	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--	--	--	--
	130	<0.5	2.2	500	12200	<0.5	<0.5	5.6	86	530	<0.5
NBC-FALLS	--	--	--	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--	--	--	--
	84	2.3	7.6	46	360	11	22	430	620	120	6000
DC	--	--	--	--	--	--	--	--	--	--	--
CC	--	--	--	--	--	--	--	--	--	--	--
	140	<0.5	1.1	3.9	88	<0.5	170	1.1	7.3	18	<0.5
SV-aBC	--	--	--	--	--	--	--	--	--	--	--
Quality assurance/quality control											
Field Blank	63	<0.5	1.7	2.8	25	<0.5	<0.5	0.6	1.1	<0.5	<0.5
Lab Blank	27	<0.5	0.6	1.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
DW Spike (% Rec)	97	52	18	79	64	67	154	67	78	71	69
BC-aCC Rep1	--	--	--	--	--	--	--	--	--	--	--
BC-aCC Rep2	--	--	--	--	--	--	--	--	--	--	--

Site	BPA (ng/L)	NP2EO (ng/L)	OP3EO (ng/L)	NP3EO (ng/L)	OP4EO (ng/L)	NP4EO (ng/L)	OP5EO (ng/L)	AND (ng/L)	AE2 (ng/L)	BE2 (ng/L)	E1 (ng/L)
MBC-ELD	--	--	--	--	--	--	--	--	--	--	--
MBC-WTP	150	27	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MBC-W	--	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--	--
BC-CAN	--	--	--	--	--	--	--	--	--	--	--
BC-30	<0.5	14	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-61	5.7	45	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aWWTP	--	--	--	--	--	--	--	--	--	--	--
BC-75	0.6	25	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aDC	15	800	90	560	<0.5	170	<0.5	<0.5	<0.5	<0.5	<0.5
BC-95	--	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--	--
BC-aCC	--	--	--	--	--	--	--	--	--	--	--
BC-bCC	6.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aSV	--	--	--	--	--	--	--	--	--	--	--
	42	16	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
COMO	--	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--	--	--	--
NBC-FALLS	130	200	11	360	<0.5	320	<0.5	39	<0.5	<0.5	<0.5
FOURMILE	--	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--	--	--	--
DC	30	2800	180	900	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
CC	--	--	--	--	--	--	--	--	--	--	--
SV-aBC	20	120	<0.5	79	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Field Blank	51	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	--	--	--	--
Lab Blank	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
DW Spike (% Rec)	95	76	58	69	56	59	38	16	38	37	7.5
BC-aCC Rep1	--	--	--	--	--	--	--	--	--	--	--
BC-aCC Rep2	--	--	--	--	--	--	--	--	--	--	--

Table 5.3. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000--continued

Site	EQUIN (ng/L)	TES (ng/L)	MES (ng/L)	NOR (ng/L)	EQUI (ng/L)	EE2 (ng/L)	E3 (ng/L)	PRO (ng/L)	COP (ng/L)	CHO (ng/L)	MET (ng/L)
Middle Boulder Creek/Boulder Creek											
MBC-ELD	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	270	--
MBC-WTP	--	--	--	--	--	--	--	--	--	--	--
MBC-W	--	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--	--
BC-CAN	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	5.0	840	--
BC-30	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	7.5	800	--
BC-61	--	--	--	--	--	--	--	--	--	--	--
BC-aWWTP	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	22	1200	--
BC-75	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3.1	<0.5	2300	3300	--
BC-aDC	--	--	--	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--	--
BC-aCC	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1200	3700	--
BC-bCC	--	--	--	--	--	--	--	--	--	--	--
BC-aSV	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	290	2600	--
Inflows/other flows											
COMO	--	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	9200	18000	--
NBC-FALLS	--	--	--	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	25000	24000	--
DC	--	--	--	--	--	--	--	--	--	--	--
CC	--	--	--	--	--	--	--	--	--	--	<LRL
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	480	1800	--
SV-aBC	--	--	--	--	--	--	--	--	--	--	--
Quality assurance/quality control											
Field Blank	--	--	--	--	--	--	--	--	--	--	--
Lab Blank	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	7.8	98	<LRL
DW Spike (% Rec)	<1	20	23	5.6	1.9	15	19	5.6	28	35	0
BC-aCC Rep1	--	--	--	--	--	--	--	--	--	--	<LRL
BC-aCC Rep2	--	--	--	--	--	--	--	--	--	--	<LRL

Site	COT (ng/L)	ALB (ng/L)	CIM (ng/L)	ACET (ng/L)	RANI (ng/L)	DMX (ng/L)	COD (ng/L)	CAFF (ng/L)	ENL (ng/L)	TMP (ng/L)	DIGN (ng/L)
MBC-ELD	<LRL	<LRL	<LRL	<LRL*	9.6	<LRL	E11	<LRL	<LRL	<LRL	<LRL
MBC-WTP	--	--	--	--	--	--	--	--	--	--	--
MBC-W	--	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--	--
BC-CAN	<LRL	<LRL	<LRL	<LRL*	<LRL	<LRL	<LRL	E8.8	<LRL	<LRL	<LRL
BC-30	<LRL	<LRL	<LRL	<LRL*	<LRL	56	<LRL	18	<LRL	<LRL	<LRL
BC-61	--	--	--	--	--	--	--	--	--	--	--
BC-aWWTP	<LRL	<LRL	<LRL	<LRL*	<LRL	<LRL	<LRL	15	<LRL	<LRL	<LRL
BC-75	E16	<LRL	<LRL	<LRL*	<LRL	<LRL	E29	26	<LRL	66	<LRL
BC-aDC	--	--	--	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--	--
BC-aCC	<LRL	<LRL	<LRL	<LRL*	<LRL	<LRL	E14	18	<LRL	E12.9	<LRL
BC-bCC	--	--	--	--	--	--	--	--	--	--	--
BC-aSV	E0.4	<LRL	8.6	<LRL*	<LRL	55	E10	23	<LRL	E4.2	<LRL
COMO	--	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--	--
NED-EFF	<LRL	<LRL	270	<LRL*	17	<LRL	E16	<LRL	<LRL	57	<LRL
NBC-FALLS	--	--	--	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--	--
BLD-EFF	71	<LRL	36	<LRL*	<LRL	80	<LRL	57	<LRL	170	<LRL
DC	--	--	--	--	--	--	--	--	--	--	--
CC	<LRL	<LRL	0.4	<LRL*	<LRL	59	<LRL	15	<LRL	<LRL	<LRL
SV-aBC	--	--	--	--	--	--	--	--	--	--	--
Field Blank	--	--	--	--	--	--	--	--	--	--	--
Lab Blank	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
DW Spike (% Rec)	61	65	20	105	28	20	58	84	60	66	120
BC-aCC Rep1	<LRL	<LRL	7.7	<LRL*	<LRL	43	E15	18	<LRL	12	<LRL
BC-aCC Rep2	E3.1	<LRL	40	<LRL*	<LRL	110	<LRL	120	<LRL	39	<LRL

Table 5.3. Results of water analyses for Boulder Creek, inflows, and other flows, June 2000--continued

Site	SULF (ng/L)	DIG (ng/L)	DILT (ng/L)	FLUO (ng/L)	DHNF (ng/L)	WRF (ng/L)	IBU (ng/L)	GEM (ng/L)
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<LRL	<LRL	25	<LRL	<LRL	<LRL	<LRL	<LRL
MBC-WTP	--	--	--	--	--	--	--	--
MBC-W	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--
BC-CAN	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-30	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-61	--	--	--	--	--	--	--	--
BC-aWWTP	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-75	52	<LRL	19	<LRL	<LRL	<LRL	<LRL	<LRL
BC-aDC	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--
BC-aCC	E14	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-bCC	--	--	--	--	--	--	--	--
BC-aSV	E8.8	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
Inflows/other flows								
COMO	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--
NED-EFF	40	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
NBC-FALLS	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--
BLD-EFF	150	<LRL	E3.4	<LRL	<LRL	<LRL	<LRL	<LRL
DC	--	--	--	--	--	--	--	--
CC	<LRL	<LRL	<LRL	<LRL	25	<LRL	<LRL	<LRL
SV-aBC	--	--	--	--	--	--	--	--
Quality assurance/quality control								
Field Blank	--	--	--	--	--	--	--	--
Lab Blank	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
DW Spike (% Rec)	70	40	63	38	89	79	68	40
BC-aCC Rep1	E15	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-aCC Rep2	32	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL

Wastewater Compounds

Tables 5.5 and 5.6 summarize results for surrogate standard recoveries for samples collected under high- and low-flow conditions. During high flow, average recoveries for the mainstem samples ranged from <10 percent for D_{21} BHT to 116 percent for n -NP2EC. Under low-flow conditions, average recoveries ranged from <10 percent for D_{21} BHT to 82 percent for n -NP2EC. The low recoveries for D_{21} BHT were likely due to oxidation during the CLLE extraction process. Recoveries for the other surrogate standards were variable, due in part to the low initial spiking concentrations that were near the method detection limits. The field data were not corrected for surrogate recoveries, but the results suggest that reported concentrations for the target compounds potentially have a low bias. Recoveries from distilled water for samples spiked with the 27 target compounds averaged 55 percent (tables 5.3 and 5.4).

During high flow, 66 percent (31 of 47) of the total wastewater-derived compounds (wastewater compounds, NTA/EDTA/NPEC, hormones, and steroids) were detected in one or more mainstem sample (fig. 5.3a, table 5.3), and 5 compounds were detected in all of the mainstem samples. Concentrations of individual compounds ranged from 1.1 to 100,000 ng/L (fig. 5.4), and 22 compounds had maximum concentrations greater than 10 ng/L. When the inflow samples are included, the maximum single compound concentration was 830,000 ng/L (NP2EC in NED-EFF), and 6 additional compounds were detected in the 2 WWTP effluents. The maximum concentration of total wastewater-derived compounds at a given site in the high-flow mainstem samples was 187,000 ng/L (BC-75), which accounts for 1.8 percent of the TOC (5.4 mg/L) after correcting for the carbon content of the individual compounds (about 50 percent).

During low flow, 66 percent (31 of 47) of the wastewater compounds were detected in at least one mainstem sample (fig. 5.3b, table 5.4),

and 3 compounds were detected in all of the mainstem samples. Although the frequency of detection and concentrations differed, 87 percent of the compounds detected at high flow also were detected at low flow. At low flow, concentrations ranged from 3.8 ng/L to 210,000 ng/L (fig. 5.4b), and 23 compounds had maximum concentrations greater than 10 ng/L. When the inflow samples are included, the maximum single compound concentration was 530,000 ng/L (NP2EC in NED-EFF) and 3 additional compounds were detected. The maximum concentration for total wastewater-derived compounds at a given site in the low-flow mainstem samples was 535,000 ng/L (BC-75), which accounts for 3.3 percent of the TOC (8.3 mg/L) after correcting for carbon content. The maximum mainstem concentrations for both sampling events occurred directly downstream from the Boulder 75th Street WWTP discharge.

The most abundant compounds detected during high- and low-flow conditions were NPEC, EDTA, and NTA (fig. 5.5). Note that total NPEC is shown (NP1EC comprised 7 to 59 percent, NP2EC comprised 41 to 92 percent, NP3EC comprised 1 to 2 percent, and NP4EC comprised 1 percent). Concentrations of NPEC, EDTA, and NTA were generally low in the upper watershed (although NPEC were detected as far upstream as BC-CAN), with a large increase downstream of the Boulder 75th Street WWTP discharge. Although the ratios between the compounds were similar in the BC-75 and BLD-EFF samples, under high-flow conditions concentrations were greater in the effluent than the downstream site, indicating the diluting effect of in-stream flow. At low flow, concentrations of NPEC, EDTA, and NTA in the BC-75 and BLD-EFF samples were similar, indicating little in-stream dilution (also noted for TOC and DOC).

Figures 5.6 and 5.7 show distributions of select wastewater compounds as a function of maximum concentrations grouped by high concentrations, generally greater than 200 ng/L,

Table 5.4. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000

[See table 5.1 for compound abbreviations; specific compounds are listed in order of chromatographic retention time; distance, distance upstream from Boulder Creek/Saint Vrain constituent; <, less than; E, estimated concentration; <LRL, below laboratory reporting level; DW, distilled water; DW spike values given in percent recovery, % Rec; NED-EFF

Site	Distance (meters)	Date	Time	Sample Type	DOC/TOC (mg/L)	UV254 (cm)	SA (L/mg/m)	NTA (ng/L)	EDTA (ng/L)
Middle Boulder Creek/Boulder Creek									
MBC-ELD	69590	10/09/2000	830	Dissolved	1.3	0.042	3.4	<500	<500
				Total	1.1	0.035	--	--	--
MBC-WTP	62970	10/09/2000	1204	Dissolved	1.1	0.039	3.5	--	--
				Total	1.2	0.042	--	--	--
MBC-W	60920	10/09/2000	1257	Dissolved	1.4	0.061	4.3	--	--
				Total	1.3	0.050	--	--	--
MBC-aNBC	49440	10/10/2000	900	Dissolved	1.7	0.053	3.1	--	--
				Total	1.8	0.054	--	--	--
BC-ORO	41520	10/10/2000	1000	Dissolved	2.3	0.087	3.8	--	--
				Total	2.3	0.086	--	--	--
BC-CAN	36710	10/10/2000	1045	Dissolved	2.7	0.105	3.9	<500	<500
				Total	2.5	0.081	--	--	--
BC-30	32990	10/10/2000	1345	Dissolved	2.3	0.078	3.5	<500	<500
				Total	2.2	0.073	--	--	--
BC-61	27320	10/10/2000	1120	Dissolved	3.0	0.106	3.6	--	--
				Total	2.6	0.075	--	--	--
BC-aWWTP	24440	10/10/2000	1255	Dissolved	2.8	0.080	2.9	<500	<500
				Total	2.9	0.092	--	--	--
BC-75	23850	10/10/2000	1325	Dissolved	7.8	0.116	1.5	2100	210000
				Total	8.3	0.120	--	--	--
BC-aDC	20180	10/10/2000	1355	Dissolved	7.3	0.115	1.6	--	--
				Total	7.8	0.124	--	--	--
BC-95	18790	10/10/2000	1435	Dissolved	7.3	0.133	1.8	--	--
				Total	7.8	0.139	--	--	--
BC-107	16320	10/10/2000	1510	Dissolved	5.9	0.107	1.8	--	--
				Total	6.3	0.108	--	--	--
BC-aCC	10970	10/10/2000	1545	Dissolved	5.7	0.107	1.9	2400	12000
				Total	5.9	0.114	--	--	--
BC-bCC	10540	10/10/2000	1610	Dissolved	5.9	0.119	2.0	--	--
				Total	6.4	0.142	--	--	--
BC-aSV	110	10/09/2000	1545	Dissolved	5.9	0.133	2.3	800	12000
				Total	6.2	0.143	--	--	--
Inflows/other flows									
COMO	59340	10/09/2000	1023	Dissolved	2.4	0.113	4.8	--	--
				Total	2.5	0.118	--	--	--
NBC-LW	59370	10/09/2000	1040	Dissolved	1.7	0.062	3.7	--	--
				Total	1.8	0.064	--	--	--
SLP	59340	10/09/2000	1058	Dissolved	1.9	0.056	2.9	--	--
				Total	2.0	0.064	--	--	--
BEAVER	60910	10/09/2000	1230	Dissolved	2.0	0.075	3.8	--	--
				Total	2.1	0.081	--	--	--
NED-EFF	60880	10/17/2000	1310	Dissolved	24	0.345	1.5	<500	4400
				Total	29	0.465	--	--	--
NBC-FALLS	49420	10/10/2000	920	Dissolved	1.9	0.066	3.5	--	--
				Total	1.9	0.064	--	--	--
FOURMILE	40120	10/10/2000	1050	Dissolved	1.9	0.055	2.9	--	--
				Total	2.0	0.066	--	--	--
SBC-aBC	29070	10/10/2000	1445	Dissolved	5.5	0.117	2.1	--	--
				Total	5.9	0.129	--	--	--
BCSC-aBC	24680	10/09/2000	1745	Dissolved	3.6	0.198	5.6	--	--
				Total	3.7	0.230	--	--	--
BLD-EFF	24380	10/17/2000	--	Dissolved	10	0.125	1.3	2800	240000
				Total	11	0.135	--	--	--
DC	20040	10/11/2000	1030	Dissolved	2.9	0.062	2.1	--	--
				Total	3.0	0.064	--	--	--
CC	10970	10/10/2000	1555	Dissolved	6.3	0.126	2.0	4500	46000
				Total	6.6	0.146	--	--	--
SV-aBC	90	10/09/2000	1630	Dissolved	5.6	0.119	2.1	--	--
				Total	5.6	0.110	--	--	--
Quality assurance/quality control									
Field Blank (ELD)	--	10/09/00	0815	Dissolved	--	--	--	<500	<500
Field Blank (CC)	--	10/10/00	1545	Dissolved	--	--	--	--	--
Lab Blank	--	10/12/2000	--	Total	0.2	--	--	<500	<500
DW Spike (% Rec)	--	10/12/2000	--	Total	97	--	--	94	38
BLD-EFF Rep	24380	10/17/2000	--	Total	--	--	--	--	--
BC-aCC Rep	10970	10/10/00	1635	Dissolved	--	--	--	--	--

Creek confluence; mg/L, milligrams per liter; cm, centimeters; L/mg/m, Liter per milligram per meter; ng/L; nanograms per liter; Rep, replicate; --, sample not analyzed for this and BLD-EFF samples for NTA/EDTA/NPEC, wastewater, and pharmaceutical analyses were collected at a later date (10/17/2000) than the other samples]

Site	NP1EC (ng/L)	NP2EC (ng/L)	NP3EC (ng/L)	NP4EC (ng/L)	Total NPEC (ng/L)	1,3DCB (ng/L)	1,4DCB (ng/L)	1,2DCB (ng/L)	MP (ng/L)	EP (ng/L)
MBC-ELD	<500	<500	<500	<500	<500	--	--	--	--	--
MBC-WTP	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5
MBC-W	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--
BC-CAN	1300	900	<500	<500	2100	--	--	--	--	--
BC-30	1400	1000	<500	<500	2300	<0.5	<0.5	<0.5	<0.5	<0.5
BC-61	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aWWTP	700	<500	<500	<500	700	--	--	--	--	--
BC-75	89000	210000	4100	1300	300000	<0.5	17	5.5	5.5	<0.5
BC-aDC	--	--	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--
BC-aCC	49000	80000	2400	800	130000	--	--	--	--	--
BC-bCC	--	--	--	--	--	<0.5	<0.5	<0.5	5.6	<0.5
BC-aSV	48000	75000	1000	<500	120000	--	--	--	--	--
COMO	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5
NBC-LW	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--
NED-EFF	43000	530000	3100	<500	570000	--	--	--	--	--
NBC-FALLS	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5
FOURMILE	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--
BLD-EFF	97000	220000	5000	1500	320000	--	--	--	--	--
DC	--	--	--	--	--	5.6	28	11	<0.5	<0.5
CC	69000	150000	1400	<500	220000	--	--	--	--	--
SV-aBC	--	--	--	--	--	<0.5	<0.5	<0.5	5.5	<0.5
Field Blank (ELD)	<500	<500	<500	<500	<500	<0.5	<0.5	<0.5	<0.5	<0.5
Field Blank (CC)	--	--	--	--	--	--	--	--	--	--
Lab Blank	<500	<500	<500	<500	<500	<0.5	<0.5	<0.5	<0.5	<0.5
DW Spike (% Rec)	160	150	120	83	--	5	5	6	20	32
BLD-EFF Rep	--	--	--	--	--	<0.5	28	5.5	11	<0.5
BC-aCC Rep	--	--	--	--	--	--	--	--	--	--

Table 5.4. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000--continued

Site	PP (ng/L)	TBP (ng/L)	TPP (ng/L)	DTBP (ng/L)	DTBB (ng/L)	BHA (ng/L)	BHT (ng/L)	TOP (ng/L)	NP (ng/L)	NOP (ng/L)
Middle Boulder Creek/Boulder Creek										
MBC-ELD	--	--	--	--	--	--	--	--	--	--
MBC-WTP	<0.5	<0.5	<0.5	<0.5	28	<0.5	<0.5	<0.5	11	<0.5
MBC-W	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--
BC-CAN	--	--	--	--	--	--	--	--	--	--
BC-30	<0.5	<0.5	<0.5	<0.5	39	<0.5	<0.5	<0.5	22	<0.5
BC-61	<0.5	<0.5	<0.5	<0.5	33	<0.5	<0.5	<0.5	11	<0.5
BC-aWWTP	--	--	--	--	--	--	--	--	--	--
BC-75	<0.5	<0.5	<0.5	<0.5	49	<0.5	<0.5	<0.5	22	<0.5
BC-aDC	<0.5	5.5	5.5	<0.5	60	<0.5	5.5	11	180	<0.5
BC-95	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--
BC-aCC	--	--	--	--	--	--	--	--	--	--
BC-bCC	<0.5	5.6	<0.5	<0.5	67	<0.5	<0.5	11	110	<0.5
BC-aSV	--	--	--	--	--	--	--	--	--	--
	<0.5	3.3	<0.5	<0.5	<0.5	<0.5	<0.5	7.1	85	<0.5
Inflows/other flows										
COMO	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--	--	--
NBC-FALLS	<0.5	<0.5	<0.5	<0.5	51	<0.5	<0.5	<0.5	240	<0.5
FOURMILE	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--	--	--
DC	<0.5	5.6	5.6	<0.5	94	<0.5	5.6	17	280	5.6
CC	--	--	--	--	--	--	--	--	--	--
SV-aBC	<0.5	11	<0.5	<0.5	72	<0.5	<0.5	5.5	83	<0.5
	--	--	--	--	--	--	--	--	--	--
Quality assurance/quality control										
Field Blank (ELD)	<0.5	<0.5	<0.5	<0.5	11	<0.5	<0.5	<0.5	<0.5	<0.5
Field Blank (CC)	--	--	--	--	--	--	--	--	--	--
Lab Blank	<0.5	<0.5	<0.5	<0.5	12.4	<0.5	<0.5	<0.5	12.4	<0.5
DW Spike (% Rec)	37	38	39	2	92	1	4	68	58	67
BLD-EFF Rep	<0.5	11	17	<0.5	82	<0.5	5.5	17	340	<0.5
BC-aCC Rep	--	--	--	--	--	--	--	--	--	--

Site	CAFF (ng/L)	OP1EO (ng/L)	NP1EO (ng/L)	TRI (ng/L)	OP2EO (ng/L)	BPA (ng/L)	NP2EO (ng/L)	OP3EO (ng/L)	NP3EO (ng/L)	OP4EO (ng/L)
MBC-ELD	--	--	--	--	--	--	--	--	--	--
MBC-WTP	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MBC-W	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--
BC-CAN	--	--	--	--	--	--	--	--	--	--
BC-30	17	<0.5	<0.5	<0.5	<0.5	72	<0.5	<0.5	<0.5	<0.5
BC-61	22	<0.5	<0.5	<0.5	<0.5	22	<0.5	<0.5	<0.5	<0.5
BC-aWWTP	27	<0.5	<0.5	<0.5	<0.5	5.5	<0.5	<0.5	<0.5	<0.5
BC-75	28	22	250	<0.5	250	11	1900	17	1000	<0.5
BC-aDC	--	--	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--
BC-aCC	67	<0.5	17	45	<0.5	5.6	160	17	420	5.6
BC-bCC	--	--	--	--	--	--	--	--	--	--
BC-aSV	280	<0.5	1.6	21	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
COMO	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--
NED-EFF	<0.5	<0.5	9.7	110	<0.5	66	<0.5	<0.5	<0.5	<0.5
NBC-FALLS	--	--	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--
BLD-EFF	100	45	510	130	610	5.6	4900	50	3300	<0.5
DC	--	--	--	--	--	--	--	--	--	--
CC	350	<0.5	11	17	<0.5	5.5	110	<0.5	170	<0.5
SV-aBC	--	--	--	--	--	--	--	--	--	--
Field Blank (CC)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Field Blank (ELD)	--	--	--	--	--	--	--	--	--	--
Lab Blank	<0.5	<0.5	<0.5	<0.5	12.4	<0.5	<0.5	<0.5	<0.5	<0.5
DW Spike (% Rec)	147	64	78	54	78	68	89	67	82	53
BLD-EFF Rep	66	33	370	99	480	11	3500	38	2100	<0.5
BC-aCC Rep	--	--	--	--	--	--	--	--	--	--

Table 5.4. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000--continued

Site	NP4EO (ng/L)	OP5EO (ng/L)	AND (ng/L)	AE2 (ng/L)	BE2 (ng/L)	E1 (ng/L)	EQUIN (ng/L)	TES (ng/L)	MES (ng/L)	NOR (ng/L)
Middle Boulder Creek/Boulder Creek										
MBC-ELD	--	--	--	--	--	--	--	--	--	--
MBC-WTP	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MBC-W	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--
BC-CAN	--	--	--	--	--	--	--	--	--	--
BC-30	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-61	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aWWTP	--	--	--	--	--	--	--	--	--	--
BC-75	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aDC	270	<0.5	<0.5	8.4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-95	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--
BC-aCC	--	--	--	--	--	--	--	--	--	--
BC-bCC	230	<0.5	27	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
BC-aSV	--	--	--	--	--	--	--	--	--	--
	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Inflows/other flows										
COMO	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--	--	--
NBC-FALLS	<0.5	<0.5	24	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
FOURMILE	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--	--	--
DC	1100	<0.5	<0.5	24	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
CC	--	--	--	--	--	--	--	--	--	--
SV-aBC	50	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	--	--	--	--	--	--	--	--	--	--
Quality assurance/quality control										
Field Blank (ELD)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Field Blank (CC)	--	--	--	--	--	--	--	--	--	--
Lab Blank	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
DW Spike (% Rec)	67	36	45	35	36	52	8.1	46	39	43
BLD-EFF Rep	600	<0.5	--	--	--	--	--	--	--	--
BC-aCC Rep	--	--	--	--	--	--	--	--	--	--

Site	EQUI (ng/L)	EE2 (ng/L)	E3 (ng/L)	PRO (ng/L)	COP (ng/L)	CHO (ng/L)	MET (ng/L)	COT (ng/L)	ALB (ng/L)	CIM (ng/L)
MBC-ELD	--	--	--	--	--	--	<LRL	<LRL	<LRL	<LRL
MBC-WTP	<0.5	<0.5	<0.5	<0.5	6.4	210	--	--	--	--
MBC-W	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--
BC-CAN	--	--	--	--	--	--	<LRL	<LRL	<LRL	<LRL
BC-30	<0.5	<0.5	<0.5	<0.5	7.8	490	--	--	--	--
BC-61	--	--	--	--	--	--	<LRL	<LRL	<LRL	<LRL
BC-aWWTP	<0.5	<0.5	<0.5	<0.5	30	810	--	--	--	--
BC-75	<0.5	<0.5	<0.5	<0.5	6700	6500	<LRL	200	<LRL	<LRL
BC-aDC	--	--	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--
BC-aCC	<0.5	<0.5	<0.5	<0.5	4900	5800	<LRL	98	<LRL	11
BC-bCC	--	--	--	--	--	--	--	--	--	--
BC-aSV	3.8	<0.5	<0.5	<0.5	680	2000	<LRL	E20	<LRL	14
COMO	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--
NED-EFF	<0.5	<0.5	<0.5	<0.5	4400	11000	--	--	--	--
NBC-FALLS	--	--	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--
BLD-EFF	<0.5	<0.5	<0.5	<0.5	12000	9000	--	--	--	--
DC	--	--	--	--	--	--	--	--	--	--
CC	<0.5	<0.5	<0.5	<0.5	460	1400	<LRL	30	<LRL	74
SV-aBC	--	--	--	--	--	--	--	--	--	--
Field Blank (ELD)	<0.5	<0.5	<0.5	<0.5	<0.5	12.5	<LRL	<LRL	<LRL	<LRL
Field Blank (CC)	--	--	--	--	--	--	<LRL	<LRL	<LRL	<LRL
Lab Blank	<0.5	<0.5	<0.5	<0.5	<0.5	4.2	<LRL	<LRL	<LRL	<LRL
DW Spike (% Rec)	8	37	45	50	34	33	0	62	91	37
BLD-EFF Rep	--	--	--	--	--	--	--	--	--	--
BC-aCC Rep	--	--	--	--	--	--	<LRL	92	<LRL	8.7

Table 5.4. Results of water analyses for Boulder Creek, inflows, and other flows, October 2000--continued

Site	ACET (ng/L)	RANI (ng/L)	DMX (ng/L)	COD (ng/L)	CAFF (ng/L)	ENL (ng/L)	TMP (ng/L)	DIGN (ng/L)	SULF (ng/L)	DIG (ng/L)
Middle Boulder Creek/Boulder Creek										
MBC-ELD	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
MBC-WTP	--	--	--	--	--	--	--	--	--	--
MBC-W	--	--	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--	--	--
BC-CAN	<LRL	<LRL	E16	<LRL	E9.1	<LRL	<LRL	<LRL	<LRL	<LRL
BC-30	5.2	<LRL	E16	<LRL	42	<LRL	<LRL	<LRL	<LRL	<LRL
BC-61	--	--	--	--	--	--	--	--	--	--
BC-aWWTP	<LRL	<LRL	<LRL	<LRL	15	<LRL	<LRL	<LRL	<LRL	<LRL
BC-75	<LRL	<LRL	120	<LRL	<LRL	<LRL	160	<LRL	220	<LRL
BC-aDC	--	--	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--
BC-aCC	<LRL	<LRL	190	<LRL	16	<LRL	68	<LRL	160	<LRL
BC-bCC	--	--	--	--	--	--	--	--	--	--
BC-aSV	<LRL	<LRL	330	<LRL	160	<LRL	31	<LRL	100	<LRL
Inflows/other flows										
COMO	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--	--	--
NBC-FALLS	--	--	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--	--	--
DC	--	--	--	--	--	--	--	--	--	--
CC	17	<LRL	310	<LRL	510	<LRL	31	<LRL	110	<LRL
SV-aBC	--	--	--	--	--	--	--	--	--	--
Quality assurance/quality control										
Field Blank (ELD)	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
Field Blank (CC)	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
Lab Blank	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
DW Spike (% Rec)	105	48	169	76	90	81	74	117	70	117
BLD-EFF Rep	--	--	--	--	--	--	--	--	--	--
BC-aCC Rep	<LRL	<LRL	140	28	26	<LRL	64	<LRL	100	<LRL

Site	DILT (ng/L)	FLUO (ng/L)	DHNF (ng/L)	WRF (ng/L)	IBU (ng/L)	GEM (ng/L)	PRXM (ng/L)	DPHA (ng/L)
MBC-ELD	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
MBC-WTP	--	--	--	--	--	--	--	--
MBC-W	--	--	--	--	--	--	--	--
MBC-aNBC	--	--	--	--	--	--	--	--
BC-ORO	--	--	--	--	--	--	--	--
BC-CAN	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-30	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-61	--	--	--	--	--	--	--	--
BC-aWWTP	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-75	14	<LRL	<LRL	<LRL	108	<LRL	<LRL	82.5
BC-aDC	--	--	--	--	--	--	--	--
BC-95	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--
BC-aCC	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
BC-bCC	--	--	--	--	--	--	--	--
BC-aSV	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
COMO	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--
NBC-FALLS	--	--	--	--	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--
DC	--	--	--	--	--	--	--	--
CC	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
SV-aBC	--	--	--	--	--	--	--	--
Field Blank (ELD)	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
Field Blank (CC)	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
Lab Blank	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL	<LRL
DW Spike (% Rec)	63	57	93	86	98	71	0	59
BLD-EFF Rep	--	--	--	--	--	--	--	--
BC-aCC Rep	<LRL	<LRL	<LRL	<LRL	290	<LRL	<LRL	<LRL

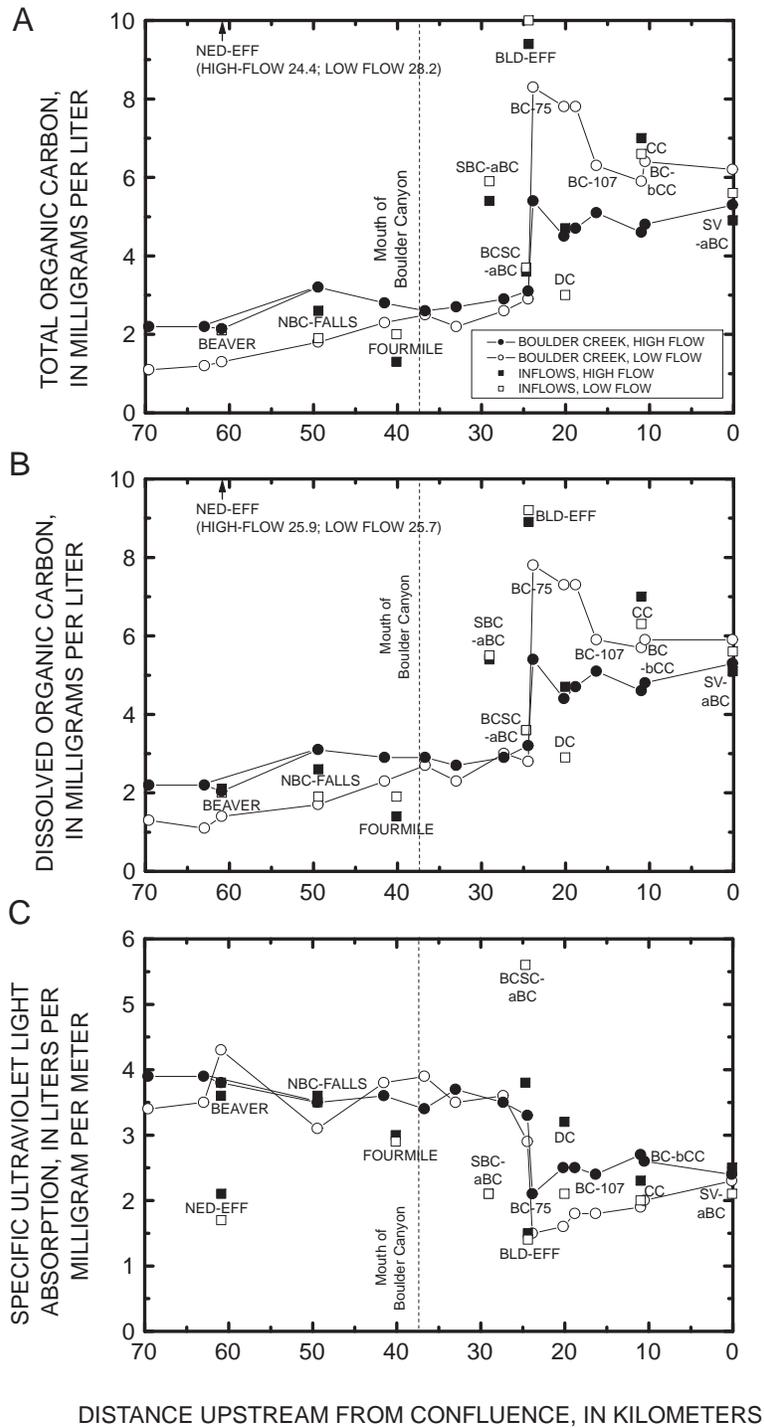


Figure 5.2. Concentrations of (A) total organic carbon, (B) dissolved organic carbon, and (C) specific absorbance for Middle Boulder Creek/Boulder Creek, inflows, and other flows, June and October 2000.

Table 5.5. Results for surrogate standard recoveries, Middle Boulder Creek/Boulder Creek, inflows, and other flows, June 2000

[See Table 5.1 for compound abbreviations; %, percent; <, less than; --, not applicable]

Site	Distance (meters)	Date	n-NP2EC (%)	D21-BHT (%)	nNP (%)	n-NP1EO (%)	D6-BPA (%)	n-NP2EO (%)	D4-E2 (%)	D7-CHO (%)
Middle Boulder Creek/Boulder Creek										
MBC-ELD	69590	6/12/00	84	13	29	15	54	13	71	70
BC-CAN	36710	6/13/00	116	15	17	20	31	16	68	80
BC-30	32990	6/12/00	98	<10	41	23	72	19	67	85
BC-aWWTP	24440	6/13/00	115	10	<10	25	12	12	65	105
BC-75	23850	6/13/00	116	<10	24	36	44	22	26	88
BC-aCC	10970	6/13/00	128	<10	12	37	16	21	33	108
BC-aSV	110	6/12/00	155	<10	33	36	68	15	<10	91
Inflow/other flows										
NED-EFF	60880	6/12/00	150	<10	<10	263	46	<10	<10	115
BLD-EFF	24380	6/13/00	78	<10	<10	18	15	<10	19	43
CC	10970	6/13/00	181	12	<10	21	23	<10	<10	77
Quality assurance/quality control										
Blank	--	--	110	<10	58	29	56	45	--	--
Spike	--	--	<10	17	64	51	95	48	--	--

Table 5.6. Results for surrogate standard recoveries, Middle Boulder Creek/Boulder Creek, inflows, and other flows, October 2000

[See Table 5.1 for compound abbreviations; % percent; <, less than; --, not applicable; Rep, replicate]

Site	Distance (meters)	Date	n-NP2EC (%)	D21-BHT (%)	nNP (%)	n-NP1EO (%)	D6-BPA (%)	n-NP2EO (%)	D4-E2 (%)	D7-CHO (%)
Middle Boulder Creek/Boulder Creek										
MBC-ELD	69590	10/9/00	89	<10	17	10	23	11	45	51
BC-CAN	36710	10/10/00	78	<10	27	22	42	20	43	49
BC-30	32990	10/10/00	77	<10	13	10	19	<10	29	48
BC-aWWTP	24440	10/10/00	65	<10	19	17	34	13	<10	40
BC-75	23850	10/10/00	76	<10	<10	16	10	<10	<10	30
BC-aCC	10970	10/10/00	88	<10	14	19	30	<10	10	43
BC-aSV	110	10/9/00	100	<10	31	29	56	19	10	44
Inflow/other flows										
NED-EFF	60880	10/9/00	71	<10	<10	<10	38	<10	10	58
BLD-EFF	24380	10/10/00	75	<10	<10	37	<10	15	13	21
CC	10970	10/10/00	110	<10	13	21	21	13	<10	33
Quality assurance/quality control										
Field blank	--	--	--	<10	<10	12	<10	<10	<10	<10
Lab Blank	--	--	94	<10	<10	<10	<10	<10	<10	<10
BLD-EFF Rep	24380	10/10/00	<10	<10	<10	26	25	11	<10	<10
DW Spike	--	--	--	<10	22	30	39	20	12	<10

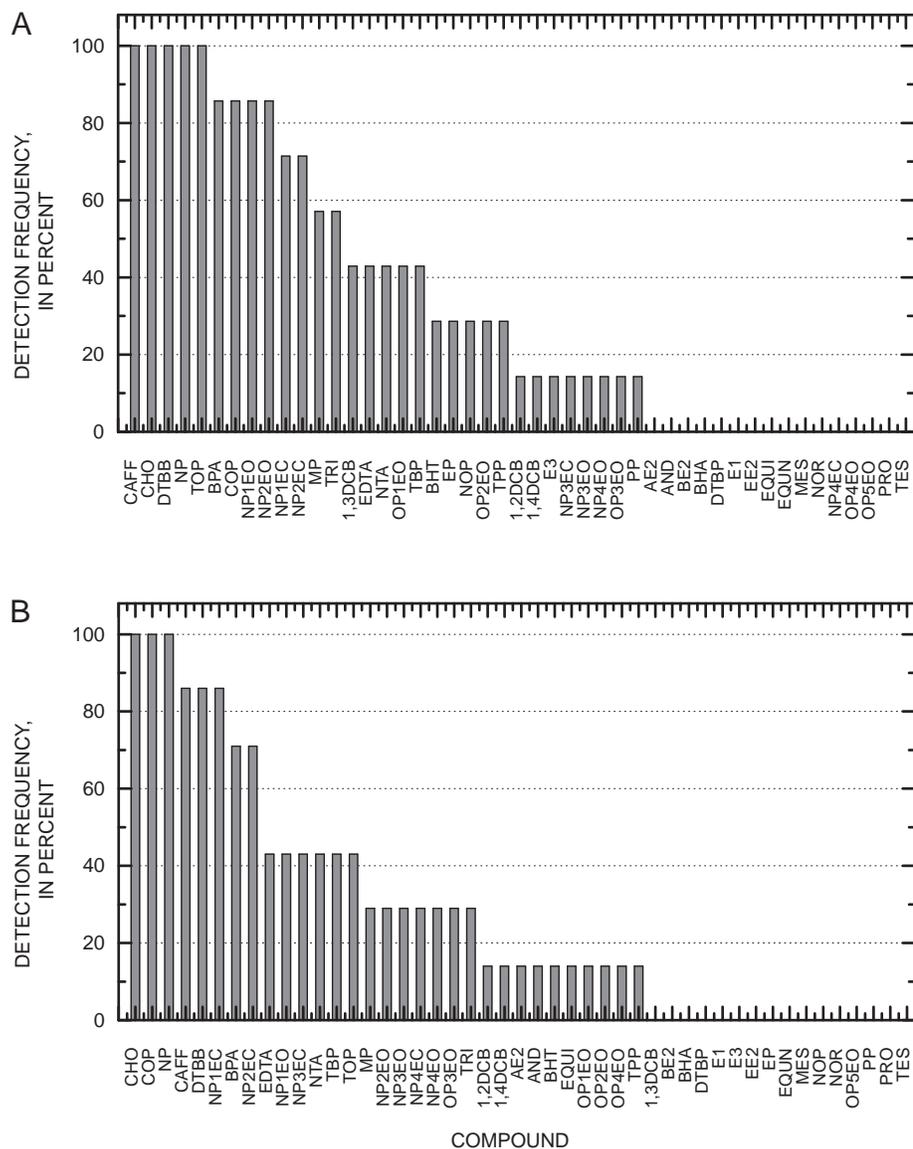


Figure 5.3. Wastewater compound detection frequency, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

and low concentrations, generally less than 200 ng/L. During high flow, 6 compounds had maximum concentrations greater than 200 ng/L in the mainstem samples in comparison to 8 compounds during low flow (fig. 5.6, tables 5.3 and 5.4). Although compound distributions and concentrations were similar between both sampling events, under low-flow conditions concentrations in the mainstem samples were typically greater. Cholesterol (CHO) and coprostanol (COP) were the next most abundant

compounds after NPEC, EDTA, and NTA, with concentrations similar to NTA. These two compounds were detected in all samples and showed a trend of increasing concentration downstream from MBC-ELD. As was observed for NPEC, EDTA, and NTA, BC-75 had similar compound distributions as BLD-EFF, but at lower concentrations. Concentrations of wastewater compounds decreased downstream of BC-75, with CHO and COP being the most persistent. There were differences in composition

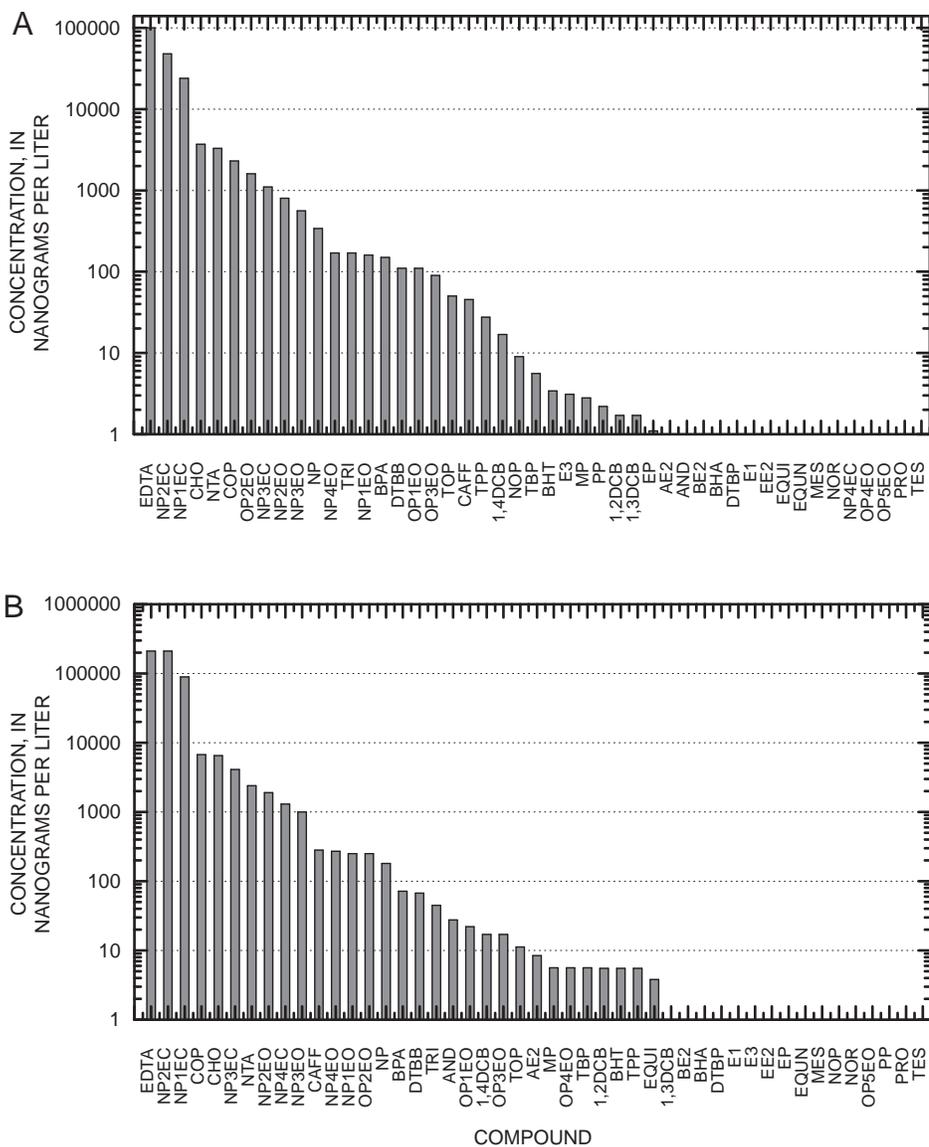


Figure 5.4. Wastewater compound maximum concentrations, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

between BLD-EFF and NED-EFF during the June sampling, including fewer compounds detected at lower concentrations in NED-EFF, but notably, there were greater concentrations of nonylphenol (NP). During October, NED-EFF was dominated by CHO and COP with low concentrations of the other wastewater compounds relative to BLD-EFF.

During high flow, 20 compounds were detected in the mainstem samples at concentrations less than 200 ng/L (table 5.3, fig.

5.4a). The spatial distribution of select compounds in this concentration group is shown in figure 5.7a. Several compounds were detected in the upper watershed as well as below the WWTP discharge. During low flow, 17 compounds were detected at concentrations less than 200 ng/L (table 5.4, fig. 5.4b); the distribution of select compounds is shown in figure 5.7b.

During high flow, DTBB, BHT, TOP, NP, OP1EO, NP1EO, and BPA were detected in

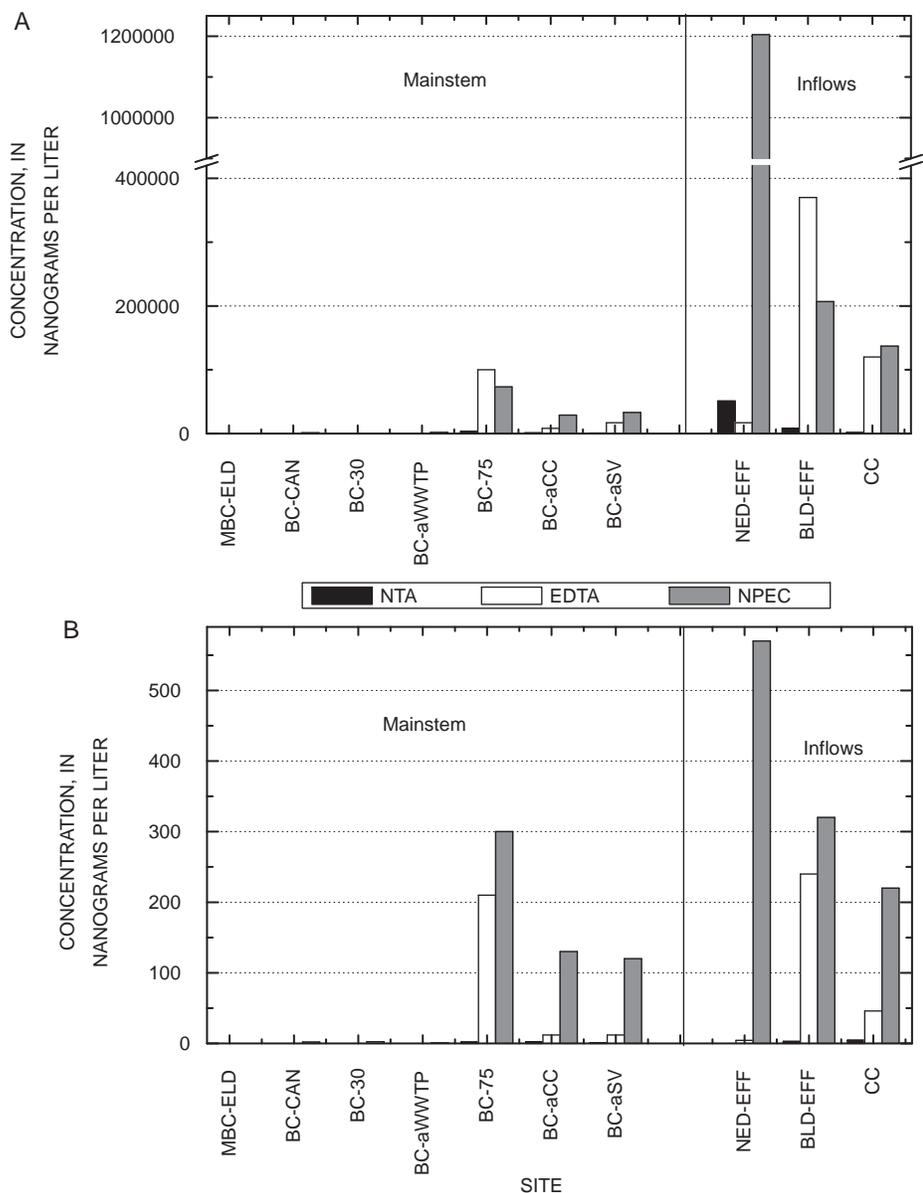


Figure 5.5. Concentrations of nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and total nonylphenolethoxycarboxylates (NPEC), Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000.

either the field or laboratory blanks. During low flow, DTBB was the only compound detected in the blanks.

Pharmaceutical Compounds

Results for pharmaceutical compounds from high and low flow are presented in tables 5.3 and 5.4. Individual compound laboratory reporting limits and a summary of laboratory reagent spike

and recovery data are summarized in table 5.7. The recovery results reflect performance variations occurring over time, differing instrumental conditions and operators, and thus are representative of overall method performance. Recoveries ranged between 12 percent for diltiazem (DILT) and 95 percent for digoxin (DIG). This wide range of recoveries is not surprising as the list of pharmaceutical compounds determined was developed from the

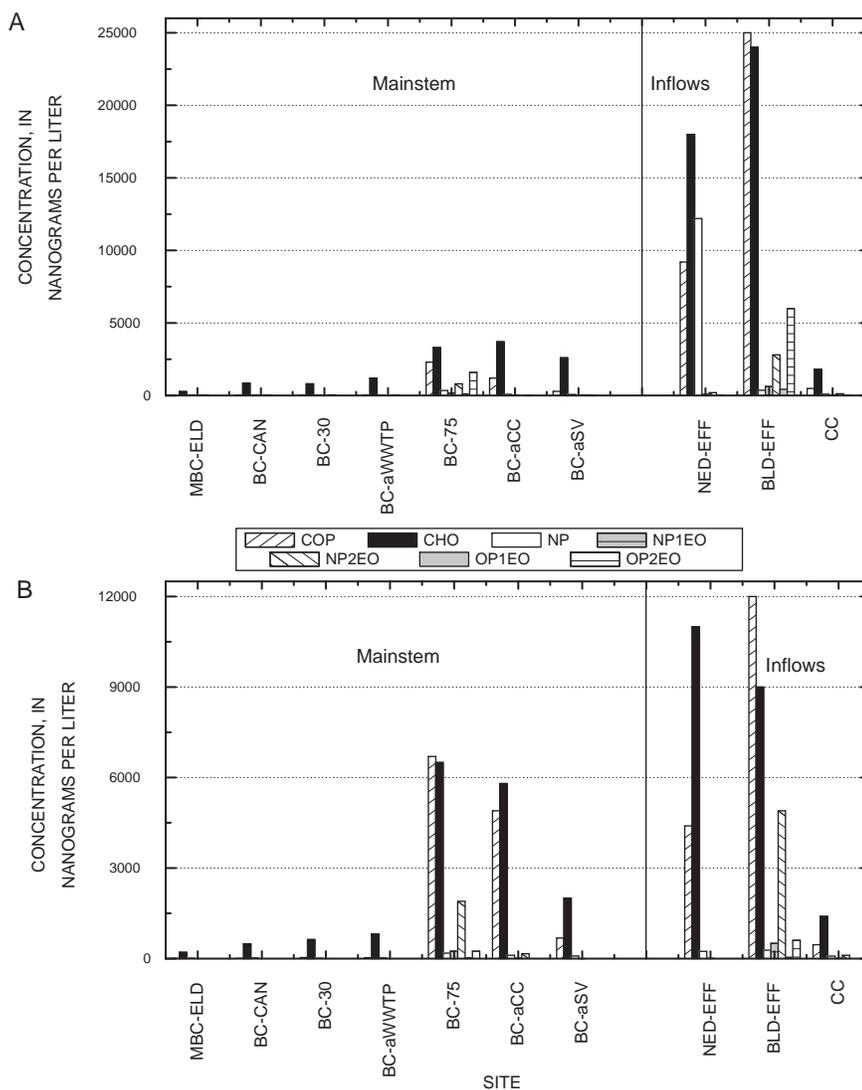


Figure 5.6. Concentrations of wastewater compounds with maximum concentrations greater than 200 nanograms per liter, Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

most commonly used, and thus representative, pharmaceuticals, and not focused specifically on a few compounds that are well recovered. Tables 5.3 and 5.4 also contain data for spikes, field replicates, and field blanks.

During high flow, 9 of the 20 pharmaceutical compounds measured were detected at one or more mainstem sites (table 5.3, fig. 5.8a). The results are qualitatively similar to those observed by Kolpin and others (2002), with caffeine

(CAFF), trimethoprim (TMP), sulfamethoxazole (SULF), and codeine (COD) being present in 40 percent or more of the samples. The distribution of maximum mainstem concentrations (fig. 5.9a) was similar to the most frequently detected compounds, with the 5 most frequently detected compounds having 5 of the 7 maximum concentrations. Concentrations of pharmaceutical compounds in mainstem Boulder Creek ranged from 0.4 ng/L for cotinine (COT) at BC-aSV to

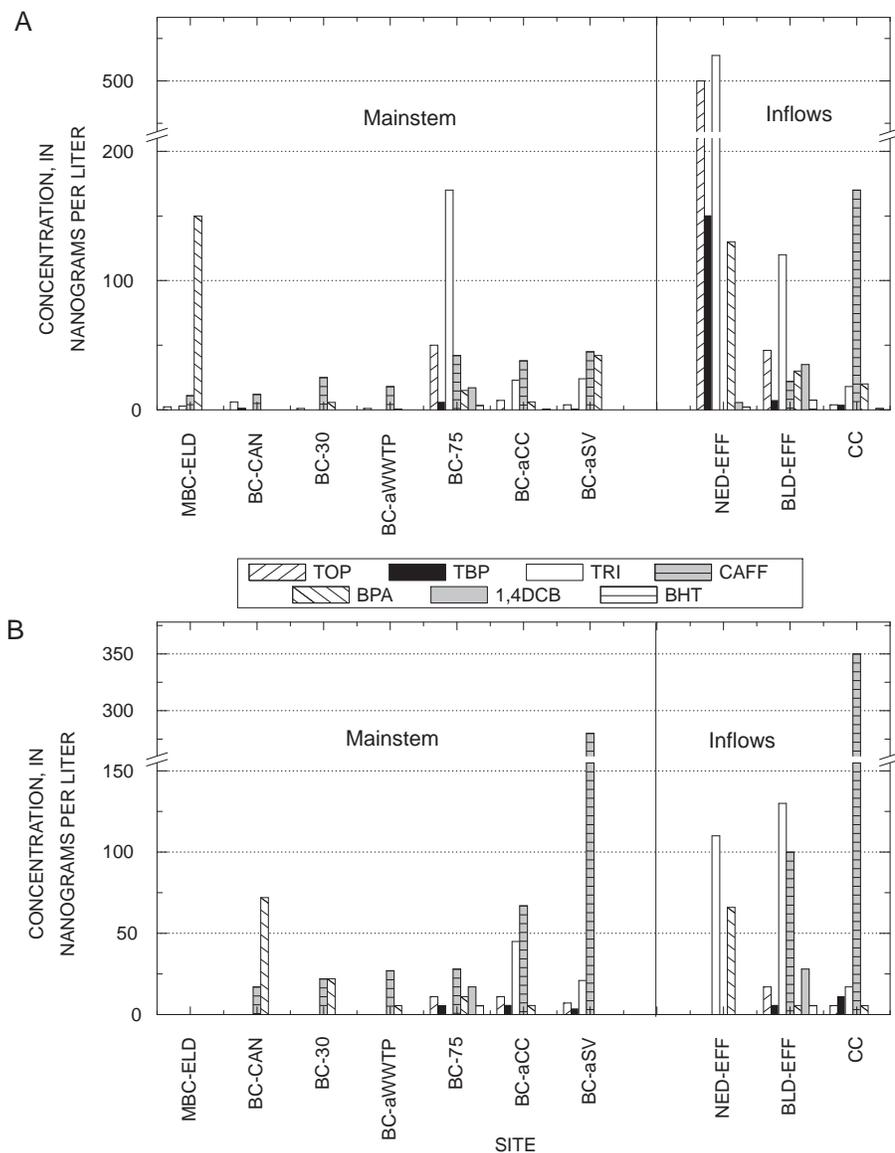


Figure 5.7. Concentrations of wastewater compounds with maximum concentrations less than 200 nanograms per liter, Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

66 ng/L for TMP (table 5.3). At least one pharmaceutical compound was detected in every mainstem sample, with up to 7 compounds detected at some sites.

Although acetaminophen (ACET) was detected in all but one sample in June, laboratory reagent blanks contained comparable concentrations (table 5.3); thus, the field sample detections could not be considered positive hits and are reported as less than laboratory reporting limits (LRL). It was later determined that these

low detections of ACET resulted from degradation of the ^{13}C phenacetin surrogate. The replacement of ^{13}C phenacetin with D_4 ethyl nicotinoate eliminated this ACET artifact in analyses of low-flow samples.

During high flow, the distribution of pharmaceutical compounds and their concentrations changed from upstream to downstream (fig. 5.10a). Fewer compounds and lower concentrations were detected at MBC-ELD, BC-CAN, BC-30, and BC-aWWTP than at

BC-75, where the number of compounds detected increased to 6, with concentrations ranging from 16 ng/L (DILT) to 66 ng/L (TMP). The compounds detected at BC-75 were similar to those observed in BLD-EFF, although at substantially lower concentrations. Only 3 pharmaceutical compounds (CAFF, DMX, and dehydronifedipine, DHNF) were detected at Coal Creek. At the most upstream site, MBC-ELD, ranitidine (RANI), COD, and DILT were detected, at concentrations ranging from 9.6 to 25 ng/L. Both RANI and DILT were only detected at MBC-ELD and BLD-EFF. The NED-EFF and BLD-EFF samples contained more compounds at higher concentrations than the mainstem Boulder Creek samples. Seven compounds were detected in BLD-EFF, at concentrations ranging from 3.4 ng/L (DILT) to 170 ng/L (TMP). Five compounds ranging in concentration from 16 ng/L (COD) to 270 ng/L (CIM), which was the highest single pharmaceutical compound concentration, were measured in NED-EFF.

Triplicate samples were collected at BC-aCC (table 5.3). Individual compound concentrations were in fair agreement between 2 of the 3 replicates. Three of seven compounds (CAFF, TMP, and SULF) were detected in all 3 replicates, 3 compounds (COD, CIM and DMX) were detected in 2 of the 3 samples, and COT was only detected in 1 sample, indicating considerable variation. This variability reflects the difficulty of accurately identifying ambient concentrations of pharmaceutical compounds in the presence of quantitatively much larger DOC concentrations. The effect of DOC on the determination of trace organic compound concentrations by LC/MS has been previously observed for polar pesticides (Furlong and others, 2000).

Low-flow sampling data are presented in table 5.4 and figures 5.8b, 5.9b, and 5.10b. Between the high- and low-flow sampling events, additional compounds were added to the pharmaceutical method and are included in the low-flow results: (1) a metabolite of paroxetine (PRXM), (2) diphenhydramine (DPHA), and (3) ibuprofen (IBU). During low flow, 10 of the 22

pharmaceutical compounds measured were detected at one or more mainstem sites (table 5.4, fig. 5.8b). Compounds most frequently detected at high flow also were detected at low flow, with DMX being detected most frequently. The same compounds detected in 40 percent or more of the samples at high flow also were detected in 40 percent or more of the samples at low flow, with the exception of COD, which was not detected at low flow. ACET, a contaminant in laboratory reagent blanks in the high-flow analyses, was not detected in any blanks in the low-flow analyses, but was detected in samples from BC-30 and CC at concentrations of 5.2 and 17 ng/L. DPHA was detected at 82 ng/L in the BC-75 sample. Ibuprofen, another compound not measured in the high-flow samples, had a maximum mainstem concentration of 108 ng/L. The maximum mainstem concentrations observed during low flow (fig. 5.9b) were 50 to 100 percent higher than values observed during high flow, suggesting a greater relative component of WWTP effluent. The compounds that were most frequently detected also had the greatest maximum concentrations. Note that effluent samples were not analyzed at low flow.

Concentrations along the Middle Boulder Creek/Boulder Creek profile during low flow (fig. 5.10b) follow a similar pattern to high flow, but the downstream increase in the number of observed compounds and concentrations was more pronounced. In contrast to high flow, no pharmaceutical compounds were detected at the farthest upstream site (MBC-ELD). Between 1 and 3 compounds (primarily CAFF and DMX) were detected at concentrations ranging from 5.2 ng/L (ACET) to 42 ng/L (CAFF) at BC-CAN, BC-30, and BC-aWWTP. At BC-75, the number of compounds detected increased to 7 (DMX, COT, TMP, SULF, DILT, IBU, and DPHA) with concentrations ranging from 14 ng/L (DILT) to 220 ng/L (SULF). The compounds detected and concentrations at BC-aCC and BC-aSV were similar to those observed at BC-75, with 6 to 8 compounds present in each sample at concentrations ranging from 11 ng/L (CIM) to

Table 5.7. Laboratory performance characteristics for pharmaceutical compounds for the period of this study

[The mean and standard deviations of recovery are for all laboratory reagent spike samples analyzed in 2000, a total of 28; provisional laboratory reporting limits calculated using the procedures outlined in Childress and others (1999); %, percent; ng/L, nanograms per liter; PR, poorly recovered, included in method because of high use; *, estimated; ND, not determined]

<i>Compound</i>	Mean recovery (%)	Standard deviation of recovery (%)	Laboratory reporting limit (ng/L)
Acetaminophen	21	8.4	17
Albuterol	68	8.4	58
Caffeine	60	30	28
Cimetidine	78	13	13
Codeine	21	12	50*
Cotinine	78	9.6	46
Dehydronifedipine	69	12	19
Digoxigenin	72	7.8	15
Digoxin	95	17	50*
Diltiazem	12	15	24
1,7-Dimethylxanthine	27	8.4	36
Diphenhydramine	ND	ND	30*
Enalaprilat	13	13	300
Fluoxetine	69	11	36
Gemfibrozil	72	13	28
Ibuprofen	85	9.8	36
Metformin	PR	PR	6.8
Paroxetine metabolite	94	20	50*
Ranitidine	85	19	20
Sulfamethoxazole	93	11	46
Trimethoprim	25	16	28
Warfarin	47	18	12

330 ng/L (DMX). Note that the composition varies slightly, although some compounds, such as COT, are present at all of these sites. The Coal Creek sample collected at low flow contained more compounds at higher concentrations (table 5.4) than the sample collected during high flow (table 5.3). Seven compounds, many common to the other sites, were detected at concentrations between 17 ng/L (ACET) and 510 ng/L (CAFF). The high-flow CC sample contained 4 compounds at concentrations between 0.4 ng/L (CIM) and 59 ng/L (DMX). The disparity between the pharmaceutical composition and concentrations between the two sampling events suggests a pharmaceutical source makes a greater relative contribution to Coal Creek during low-flow conditions because of less dilution from spring runoff.

Duplicate samples were collected and analyzed at BC-aCC during the low-flow

sampling. Eight compounds were detected in both samples; six (COT, CIM, DMX, CAFF, TMP, and SULF) were present in both samples at similar concentrations (table 5.4). Two compounds, COD and IBU, were detected in only one sample. These results suggest reasonable reproducibility of the analysis at the low ambient concentrations. Field blanks processed during the entire sample collection procedure at the beginning and end of the day were analyzed to determine if sampling introduced pharmaceutical compounds. No pharmaceutical compounds were detected in either field blank, indicating that the concentrations measured in Boulder Creek are unlikely the result of contamination. Laboratory blanks were similarly free of pharmaceutical compounds.

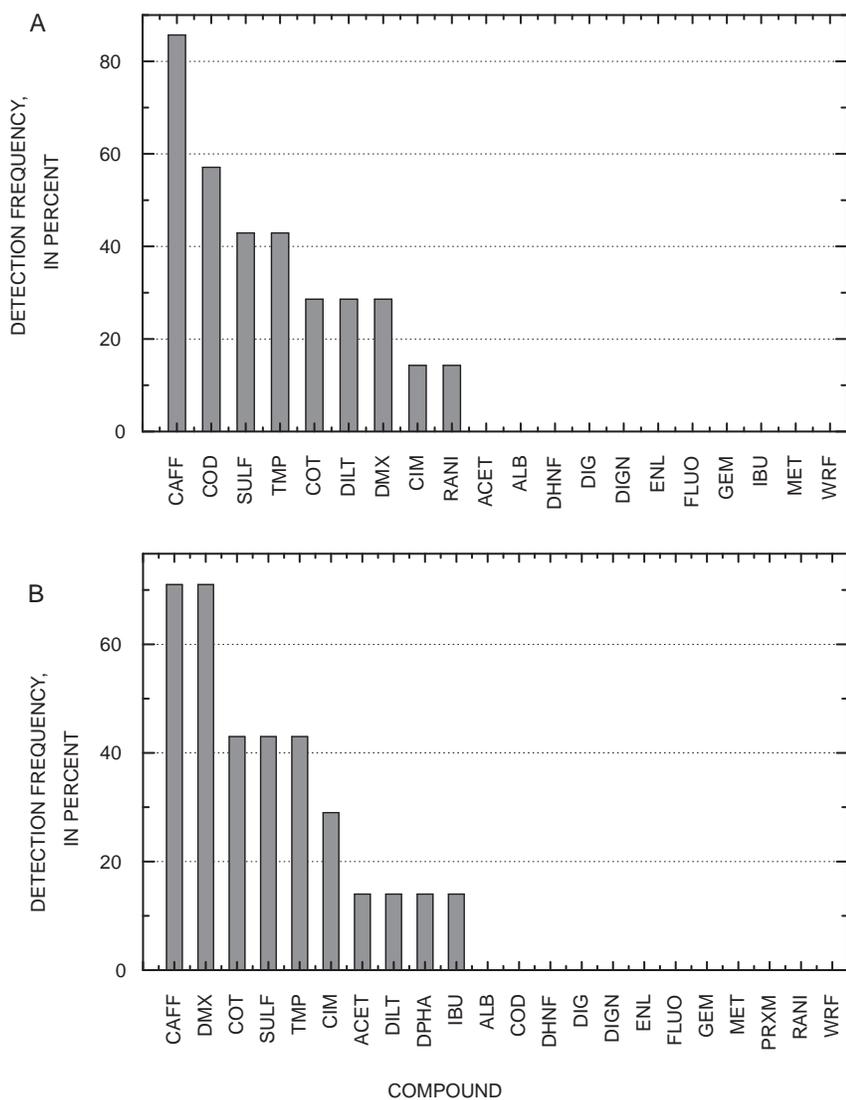


Figure 5.8. Pharmaceutical compound detection frequency, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

DISCUSSION

The data presented in this report show distinct spatial and temporal trends in the Boulder Creek watershed related to natural and anthropogenic factors. These trends have implications for both aquatic ecology and human health, as demands on the watershed increase with the growing population of the Colorado Front Range. Many of the effects and associated management issues that are most easily identified

in a detailed urban-gradient study, such as reported here, have larger applications and can be extrapolated to other urban systems of comparable hydrogeology and demographics.

The NOM cycle in the upper Boulder Creek Watershed reflects the biogeochemical interactions of the native flora and fauna with the hydrosphere, and has significant water resource management implications. In particular, the relationship between NOM and the formation of disinfection byproducts (DBP), such as the

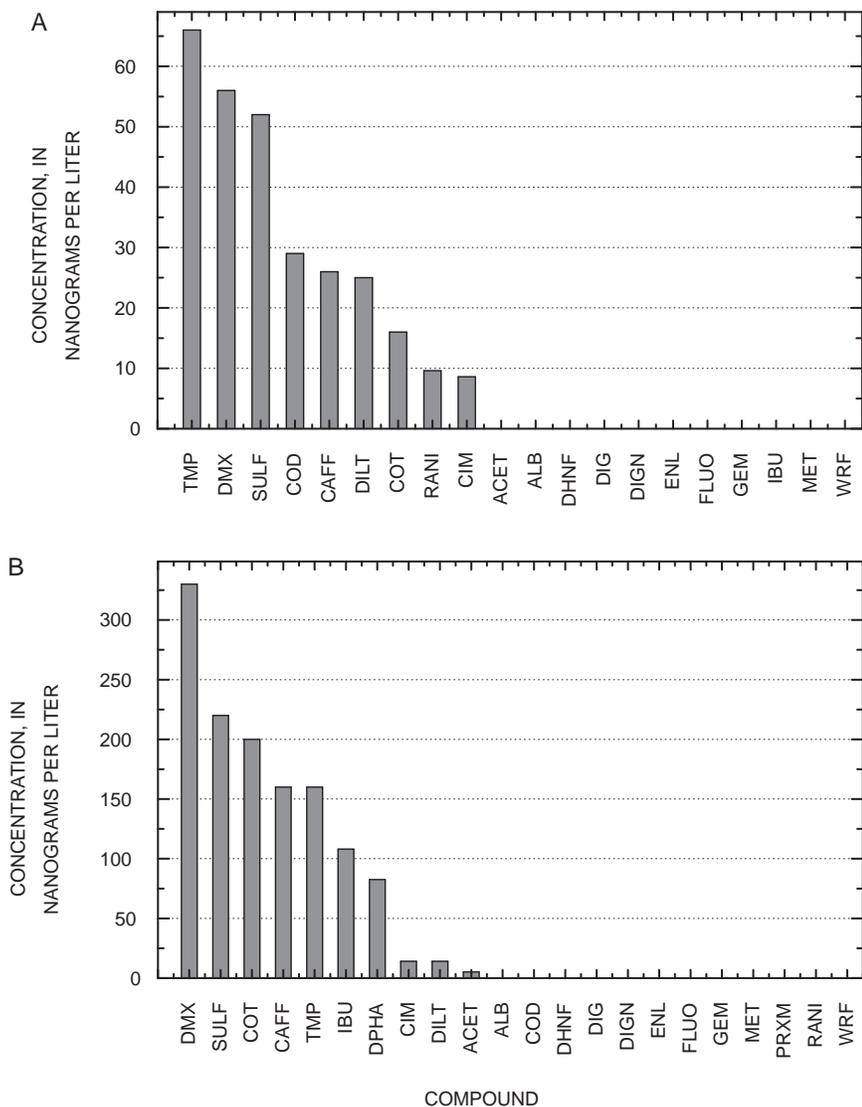


Figure 5.9. Pharmaceutical compound maximum concentrations, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

trihalomethane (THM) chloroform and total organic halogens (TOX), when the water is treated with chlorine for potable use and consumption is of importance. Typically, DBP concentrations increase with increasing TOC concentrations (Milner and Amy, 1996; Singer, 1999). The range of TOC concentrations measured in the upper watershed (1.1 to 3.8 mg/L) were below limits recommended by the U.S. Environmental Protection Agency (USEPA, 1998) to maintain acceptable DBP levels.

Although there was a significant increase in TOC downstream of the Boulder 75th Street WWTP (up to 8.3 mg/L), the relative reactivity of WWTP effluent organic matter for the formation of DBP is less than NOM coming from plant-derived sources in the upper watershed (Debroux, 1998; Rostad and others, 2000). One of the reasons that WWTP effluent organic matter has lower chlorine reactivity than NOM is that it has already undergone chlorination (to reduce pathogens) as part of the wastewater treatment

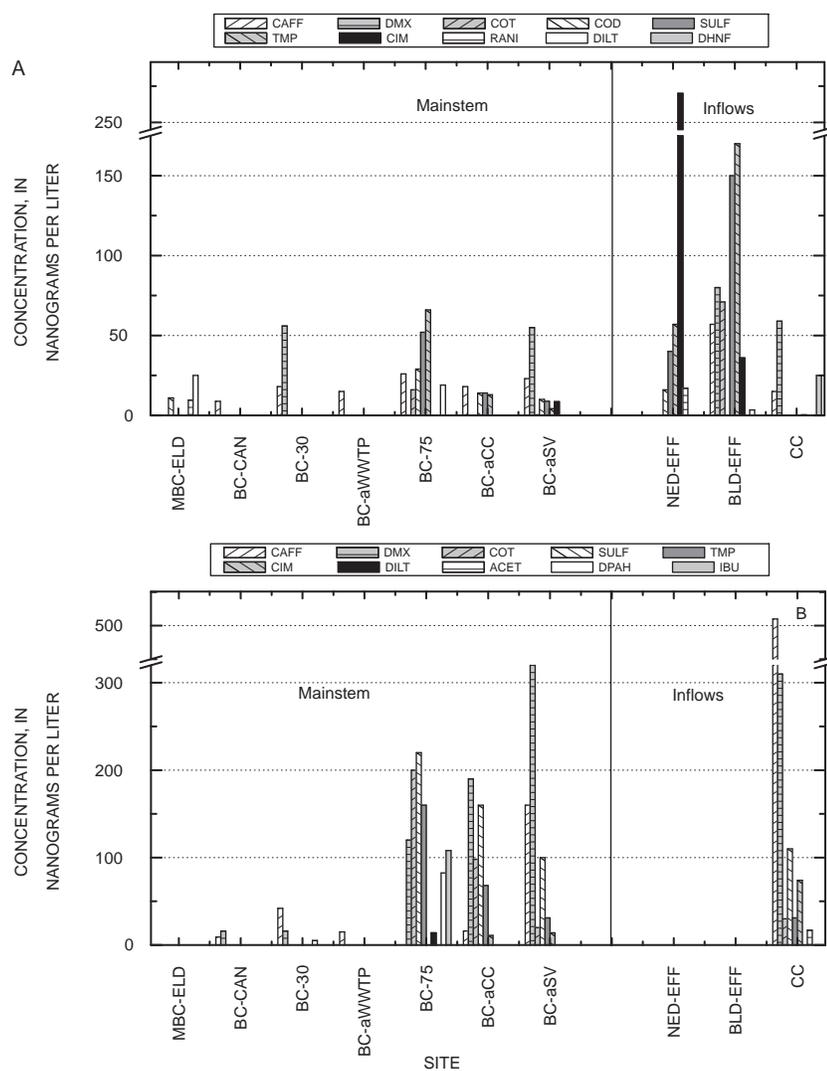


Figure 5.10. Concentrations of individual pharmaceutical compounds, Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

process. Chlorination results in the formation of DPB; thus, although they were not measured in this study, THM and TOX are potential organic contaminants in WWTP effluent impacted streams.

Although the upper watershed has a relatively pristine character, a variety of wastewater-derived compounds were detected, even at the farthest upstream site. The presence of these compounds in this environment indicates that anthropogenic chemicals find their way into Boulder Creek, even reaches with low population

densities and no WWTP point discharges. The consumer product and pharmaceutical compounds detected in the upper watershed appeared to be transient (in contrast to a WWTP point discharge) which is consistent with the type of impacts that might occur with individual household on-site wastewater disposal practices and other non-point sources. A short distance downstream from the headwaters of Middle Boulder Creek the first major point source, the Nederland WWTP, discharges into the Boulder Creek system. The Nederland WWTP provides

primary (facultative lagoon) treatment to domestic wastewater produced by the town of Nederland (population 1394 in 2000; Murphy and others, 2003), and discharges into Middle Boulder Creek just downstream from MBC-W. The Nederland WWTP discharged 0.006 and 0.003 m³/sec (0.2 and 0.1 ft³/sec) during the June and October samplings respectively, which accounts for less than 1 percent of the discharge at MBC-W, even at low flow.

As Boulder Creek passes through the urban corridor of the city of Boulder, concentrations of several compounds begin to increase, in particular, CHO and CAFF. Both compounds are indicators of direct human impact on the creek (Writer and others, 1995; Barber and others, 1996; Barber and Writer, 1998; Buerge and others, 2003). Likewise, TOC increases slightly through the urban corridor, likely the result of non-specific sources such as lawn and street runoff. Downstream from the Boulder 75th Street WWTP, Boulder Creek becomes a wastewater-impacted or even a wastewater-dominated stream. The WWTP point source results in a significant increase in the load of NOM from the biogeochemistry of the human fauna, as well as a range of synthetic organic chemicals used in domestic and commercial applications. The presence of wastewater derived organic contaminants in Boulder Creek reflects the source characteristics as well as the environmental fate characteristics of the particular compound. For example, concentrations of NPEC and EDTA were more abundant than NTA, likely due to the greater biodegradability of NTA relative to the other two compounds (Barber and others, 2000). In the high-flow BLD-EFF sample, EDTA was more abundant than NPEC, but the ratio shifts in the downstream samples with NPEC having higher concentrations than EDTA. Although NPEC concentrations exceeded EDTA concentrations in the low-flow BLD-EFF sample, a similar preferential removal of EDTA relative to NPEC was observed during in-stream transport. These results indicate greater in-stream removal of EDTA than NPEC, probably due to

photolytic degradation (Kari and Giger, 1995). Concentrations of NPEC, EDTA, and NTA in samples collected from the CC site were similar to BC-75, indicating Coal Creek also was impacted by WWTP effluent discharges from the communities of Erie, Lafayette, Louisville, and Superior.

There were major differences in organic and inorganic chemical composition between the Boulder and Nederland WWTP. The Nederland WWTP provides primary treatment of domestic sewage, whereas the Boulder 75th Street WWTP provides secondary treatment (trickling filter with solids contact and nitrification processes) of a mixed (domestic/commercial/industrial) wastewater and serves a much larger population (94,670 in 2000; Murphy and others, 2003). There also were significant differences in flow, with the Nederland WWTP discharge being a fraction (<1 percent) of the 0.88 and 0.91 m³/sec (31 and 32 ft³/sec) discharged from the Boulder 75th Street WWTP during the June and October samplings (Murphy and others, 2003). The difference in the level of treatment (primary versus secondary) is illustrated by the DOC data, which indicate that the NED-EFF has nearly 3 times higher DOC concentrations than BLD-EFF. There also are major differences in the specific compounds detected in the two effluent samples, reflecting both treatment level and differences in the composition of the wastewater input to the two WWTP. For example, the distribution of EDTA and NPEC in the NED-EFF sample was shifted from the BLD-EFF sample, with higher concentrations and a predominance of NPEC over EDTA in NED-EFF during both sampling events.

Generally speaking, most of the compounds that were evaluated in this study do not have established water quality criteria. The exception is 1,4-dichlorobenzene, which has a drinking water maximum contaminant level (MCL) of 75 g/L (USEPA, 1998). This compound had a maximum measured concentration of 35 ng/L in the high-flow BLD-EFF sample. Although no water quality regulations exist for most of the compounds, many do have measured aquatic

toxicity values (table 5.1). Of particular concern are NP, NPEO, and NPEC, which in addition to having acute and chronic toxicity (McLeese and others, 1981) are potential endocrine-disrupting compounds (White and others, 1994; Jobling and others, 1996) that may impact stream ecology. The concentrations for NP and related compounds are similar to those reported elsewhere (Ahel, Giger, and Koch, 1994; Ahel, Giger, and Schaffner, 1994; Bennie and others, 1997; Barber and others, 2000), and at BC-75, although well below toxic values (McLeese and others, 1981), concentrations approached those shown to cause feminization of fish populations (Jobling and others, 1996; Jobling and others, 1998). Although currently not regulated in the United States, proposed guidelines on allowable NP concentrations in European and Canadian waters are being developed (U.K. Environment Agency, 1998, 1999; Environment Canada and Health Canada, 2001).

Pharmaceutical composition and concentrations in Boulder Creek qualitatively reflect the compositions and concentrations observed on a national scale by Kolpin and others (2002). This comparability also is reflected in the typically lower pharmaceutical concentrations observed in Boulder Creek compared to wastewater compounds. The presence and concentrations of pharmaceuticals in Boulder Creek reflects the combined impacts of contemporary human health practices and the incomplete removal of pharmaceuticals in current wastewater treatment plant designs. Given that in the year 2001 more than a billion prescriptions were written (NDC Health, 2003), it is highly likely that many of these compounds are excreted and present in raw wastewater. As has been demonstrated (Ternes, 1998; Ternes and others, 2002), many pharmaceuticals are incompletely removed by standard wastewater treatment processes and will be discharged in treated effluent unless additional treatment, such as granular-activated carbon and ozonation are used. As a result, wastewater treatment plants of various configurations are important sources of

pharmaceuticals to surface water. Since wastewater discharges are relatively constant, the loading of pharmaceuticals present in wastewater discharge to surface water is likely to be relatively constant (Daughton and Ternes, 1999).

The concentrations of pharmaceutical compounds detected in Boulder Creek were typically low, with the highest concentrations (270 ng/L) occurring in a WWTP effluent sample. The environmental effects of these compounds, either singly or in combination, at ambient concentrations is not well defined, although sublethal effects for other wastewater indicator compounds have been determined in the laboratory (Metcalf and others, 2001). The presence of pharmaceuticals in surface water is not currently subject to regulatory oversight. Nevertheless, pharmaceuticals such as CAFF provide useful indicators of wastewater impacts in surface water systems (Barber and others 1996; Buerge and others, 2003). As the persistence and reactivity of pharmaceutical compounds in aquatic environments becomes better defined, the suite of pharmaceuticals measured in this study will provide additional insight into the dynamics of transport, degradation and sequestration of organic compounds in Boulder Creek and other watersheds where urbanization plays an increasingly important role in the hydrologic cycle. The fact that the watershed was sampled under both high- and low-flow conditions provides an estimate of the dynamics of these compounds during the hydrologic cycle. Future evaluations of water quality in Boulder Creek will be able to use the results from this study as a benchmark to evaluate changes in water quality as the watershed landscape changes in response to human activity.

Many of the trace organic contaminants introduced into Boulder Creek by the Boulder 75th Street WWTP are attenuated during transport downstream. Although dilution plays a significant role in decreasing concentrations, in-stream removal processes, including biodegradation, photolysis, volatilization, and sorption, also act to remove compounds. However, as shown by

concentrations in Coal Creek, relative wastewater loading to Boulder Creek increases as a larger portion of the watershed containing high population densities (Kinner, 2003) contributes to the stream flow. This continued input prevents the concentrations of wastewater compounds from decreasing to levels observed upstream of the Boulder 75th Street WWTP.

SUMMARY

This chapter presents the results of chemical analyses for a variety of organic wastewater indicator compounds. Measurement of total and dissolved organic carbon allows evaluation of both natural biogeochemical processes and anthropogenic impacts. Measurements of specific synthetic organic chemicals provide insight into the sources and levels of impacts, and also can be used as intrinsic tracers of in-stream removal processes. Nearly 50 wastewater contaminant and pharmaceutical compounds were identified in one or more samples collected from mainstem Boulder Creek at concentrations ranging over five orders of magnitude. Samples collected under high- and low-flow conditions contained similar wastewater and pharmaceutical compounds and had similar spatial distributions, but maximum and median concentrations were generally 1.5 to 2 times higher at low flow. The influence of the Boulder 75th Street Wastewater Treatment Plant (WWTP) discharge on water quality of Boulder Creek was significant in both samplings, but was particularly marked during low flow. Likewise, Coal Creek contributes a substantial quantity of wastewater-derived compounds to Boulder Creek. The wastewater and pharmaceutical compound data illustrate the relatively stable input of contaminants from WWTP effluents, and also the effect of flow regimes on in-stream concentrations.

Although this chapter reports on an extensive list of organic compounds of diverse use and characteristics, it is by no means exhaustive, and only hints at the complexity of the chemical matrix of Boulder Creek. Results from the urban

gradient transect sampled under high- and low-flow conditions during 2000 do not necessarily reflect long-term trends. Many of the compounds occurred at concentrations near their present detection limits, and replicate analyses were variable. Several compounds detected in the upper watershed samples were transient and likely reflect sporadic inputs. However, for other compounds, such as EDTA, CAFF, and COP, the data represented by these synoptic sampling events likely reflect long-term concentration trends and spatial distributions because of their continuous input and relation to population density (Barber and Writer, 1998).

The data set presented here is unique in the compounds evaluated and in the spatial and temporal detail, and provide a preliminary insight into emerging organic contaminants in the Boulder Creek Watershed. Compounds such as NP may be subject to future regulations, and should be considered as part of the important but unregulated water chemistry associated with streams that receive wastewater residuals. The specific results from this chapter, combined with the other inorganic and organic water quality data presented elsewhere in this report, show the importance of collecting complex data sets, and hopefully will lead to future monitoring of the comprehensive water quality in the Boulder Creek Watershed.

REFERENCES CITED

- Arcand-Hoy, L.D., Nimrod, A.C., and Benson, W.H., 1998, Endocrine modulating substances in the environment— Estrogenic effects of pharmaceutical products: *International Journal of Toxicology*, v. 17, p. 139-158.
- Ahel, Marijan, Giger, Walter, and Koch, Markus, 1994, Behavior of alkylphenol polyethoxylate surfactants in the aquatic environment - I - Occurrence and transformation in sewage treatment: *Water Research*, v. 28, p. 1131-1142.
- Ahel, Marijan, Giger, Walter, and Schaffner, Christian, 1994, Behavior of alkylphenol polyethoxylate surfactants in the aquatic environment- II- Occurrence and transformation in rivers: *Water Research*, v. 28, p. 1143-1152.
- Barber, L.B., II, 1992, Hierarchical analytical approach to evaluating the transport and biogeochemical fate of

- organic compounds in sewage-contaminated groundwater, Cape Cod, Massachusetts— Chapter 4 in Lesage, Susan and Jackson, R. E., eds., Groundwater contamination and analysis at hazardous waste sites: New York, Mercel Dekker, Inc., p. 73-120.
- Barber, L.B., Brown, G.K., and Zaugg, S.D., 2000, Potential endocrine disrupting organic chemicals in treated municipal wastewater and river water— Chapter 7 in Keith, L.H., Jones-Lepp, T.L., and Needham, L.L., eds., Analysis of environmental endocrine disruptors: Washington, D.C., American Chemical Society, American Chemical Society Symposium Series 747, p. 97-123.
- Barber, L.B., Leenheer, J.A., Noyes, T.I., and Stiles, E.A., 2001, Nature and transformation of dissolved organic matter in treatment wetlands: Environmental Science and Technology, v. 35, p. 4805-4816.
- Barber, L.B., II, Leenheer, J.A., Pereira, W.E., Noyes, T.I., Brown, G.K., Tabor, C.F., and Writer, J.H., 1996, Organic contamination of the Mississippi River from municipal and industrial wastewater: U.S. Geological Survey Circular 1133, p. 114-135.
- Barber, L.B. and Writer, J. H., 1998, Impact of the 1993 flood on the distribution of organic contaminants in bed sediments of the Upper Mississippi River: Environmental Science and Technology, v. 32, p. 2077-2083.
- Bennie, D.T., Sullivan, C.A., Lee, H.B., Peart, T.E., and Maguire, R.J., 1997, Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River: Science of the Total Environment, v. 193, p. 263-275.
- Buerge, I.J., Poiger, Thomas, Muller, M.D., and Buser, H.R., 2003, Caffeine, an anthropogenic marker for wastewater contamination of surface waters: Environmental Science and Technology, v. 37, p. 691-700.
- Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99-193, 19 p.
- Chin, Yu-Ping, Aiken, George, and O'Loughlin, Edward, 1994, Molecular weight, polydispersitivity, and spectroscopic properties of aquatic humic substances: Environmental Science and Technology, v. 28, p. 1853-1858.
- Daughton, C.G. and Ternes, T.A., 1999, Pharmaceutical and personal care products in the environment— Agents of subtle change?: Environmental Health Perspectives, v. 107 (Supplement 6), p. 907-938.
- Debroux, J.F., 1998, The physical-chemical and oxidant-reactive properties of effluent organic matter (EfOM) intended for potable reuse: Boulder, University of Colorado, Ph.D. dissertation, 227 p.
- Desbrow, C., Routledge, E.J., Brighty, G.C., Sumpter, J.P., and Waldock, M., 1998, Identification of estrogenic chemicals in STW effluent - 1. Chemical fractionation and in vitro biological screening: Environmental Science and Technology, v. 32, p. 1549-1558.
- Environment Canada and Health Canada, 2001, Canadian Environmental Protection Act, 1999— Priority substances list assessment report— Nonylphenol and its ethoxylates: Minister of Public Works and Government Services, 97 p.
- Furlong, E.T., Burkhardt, M.R., Gates, P.M., Werner, S.L., and Battaglin, W.A., 2000, Routine determination of sulfonylurea, imidazolinone, and sulfonamide herbicides at nanogram-per-liter concentrations by solid-phase extraction and liquid chromatography/mass spectrometry: Science of the Total Environment, v. 248, p. 135-146.
- Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Lutzhoft, H.C.H., and Jorgensen, S.E., 1998, Occurrence, fate and effects of pharmaceutical substances in the environment— A review: Chemosphere, v. 36, p. 357-393.
- Huang, C.-H. and Sedlak, D.L., 2001, Analysis of estrogenic hormones in municipal wastewater effluent and surface water using enzyme-linked immunosorbent assay and gas chromatography/tandem mass spectrometry: Environmental Toxicology and Chemistry, v. 20, p. 133-139.
- Jobling, Susan, Nolan, Monique, Tyler, C.R., Brighty, Geoff, and Sumpter, J.P., 1998, Widespread sexual disruption in wild fish: Environmental Science and Technology, v. 32, p. 2498-2506.
- Jobling, Susan, Sheahan, David, Osbourne, J.A., Mattheissen, Peter, and Sumpter, J.P., 1996, Inhibition of testicular growth in Rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals: Environmental Toxicology and Chemistry, v. 15, p. 194-202.
- Johnson, A.C. and Sumpter, J.P., 2001, Removal of endocrine-disrupting chemicals in activated sludge treatment works: Environmental Science and Technology, v. 35, p. 4697-4703.
- Kari, F.G. and Giger, Walter, 1995, Modeling the photochemical degradation of ethylenediaminetetraacetate in the River Glatt: Environmental Science and Technology, v. 29, p. 2814-2827.
- Kinner, D.A., 2003, Delineation and characterization of the Boulder Creek Watershed and its sub-watersheds— Chapter 2 in Murphy, S.F, Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological

- Survey Water-Resources Investigations Report 03-4045, p. 27-40.
- Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000—A national reconnaissance: *Environmental Science and Technology*, v. 36, p. 1202-1211.
- Leenheer, J.A., Rostad, C.E., Barber, L.B., Schroeder, R.A., Anders, Robert, and Davisson, M.L., 2001, Nature and chlorine reactivity of organic constituents from reclaimed water in groundwater, Los Angeles County, California: *Environmental Science and Technology*, v. 35, p. 3869-3876.
- McLeese, D.W., Zitko, V., Sargent, D.B., Burrige, L., and Metcalfe, C.D., 1981, Lethality and accumulation of alkylphenols in aquatic fauna: *Chemosphere*, v. 10, no. 7, p. 723-730.
- Metcalfe, C.D., Metcalfe, T.L., Kiparissis, Yiannis, Koenig, B.G., Khan, Colin, Hughes, R.J., Croley, T.R., March, R.E., and Potter, Thomas, 2001, Estrogenic potency of chemicals detected in sewage treatment plant effluents as determined by in vivo assays with Japanese medaka (*Oryzias latipes*): *Environmental Toxicology and Chemistry*, v. 20, p. 297-308.
- Milner, R.A. and Amy, G.L., Editors, 1996, *Disinfection by-products in water treatment - the chemistry of their formation and control*: Lewis Publishers, Boca Raton, Fla., 502 p.
- Murphy, S.F., Barber, L.B., Verplanck, P.L., and Kinner, D.A., 2003, Environmental setting and hydrology of the Boulder Creek Watershed— Chapter 1 in Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 5-26.
- NDC Health, 2003, Rx List - The internet drug index: RxList LLC., accessed May 1, 2003, at <http://www.rxlist.com>
- Rostad, C.E., Martin, B.S., Barber, L.B., Leenheer, J.A., and Daniel, S.R., 2000, Effect of a constructed wetland on disinfection byproducts: Removal processes and production of precursors: *Environmental Science and Technology*, v. 34, p. 2703-2710.
- Schaffner, C. and Giger, W., 1984, Determination of nitrilotriacetic acid in water by high-resolution gas chromatography: *Journal of Chromatography*, v. 312, p. 413-421.
- Singer, P.C., 1999, Humic substances as precursors for potentially harmful disinfection by-products: *Water Science and Technology*, v. 40, p. 25-30.
- Ternes, T.A., 1998, Occurrence of drugs in German sewage treatment plants and rivers: *Water Research*, v. 32, no. 11, p. 3245-3260.
- Ternes, T.A., Meisenheimer, Martin, McDowell, Derek, Sacher, Frank, Brauch, H.J., Haist-Gulde, Brigitte, Preuss, Gudrun, Wilme, Uwe, and Zulei-Seibert, Ninette, 2002, Removal of pharmaceuticals during drinking water treatment: *Environmental Science and Technology*, v. 36, p. 3855-3863.
- Thurman, E.M., 1985, *Organic geochemistry of natural waters*: Boston, Mass., Martinus Nijhoff/Dr W. Junk Publishers, 497 p.
- U.K. Environment Agency, 1998, Risk assessment of 4-nonylphenol (branched) and nonylphenol: London, U.K., Draft, September.
- _____, 1999, Risk assessment of 4-nonylphenol (branched) and nonylphenol— Human health effects: London, U.K., Draft, August.
- U.S. Environmental Protection Agency, 1998, National primary drinking water regulations— Disinfectants and disinfection byproducts— Final Rule: Washington, D.C., U.S. Government Printing Office, Federal Register, v. 63, no. 241, p.69389-69476.
- _____, 2002, National primary drinking water standards, accessed July 9, 2002 at <http://www.epa.gov/safewater>
- _____, 2001, Ecotoxicology data base: accessed June 24, 2003 at <http://www.epa.gov/medecotx>
- White, R.S., Jobling, S., Hoare, S.A., Sumpter, J.P., and Parker, M.G., 1994, Environmentally persistent alkylphenolic compounds are estrogenic: *Endocrinology*, v. 135, p. 175-182.
- Writer, J.H., Leenheer, J.A., Barber, L.B., Amy, G.L., and Chapra, S.C., 1995, Sewage contamination in the Upper Mississippi River as measured by the fecal sterol coprostanol: *Water Research*, v. 29, p. 1427-1436.

Chapter 6 - Pesticides in the Boulder Creek Watershed, Colorado, During High-Flow and Low-Flow Conditions, 2000

By Mark W. Sandstrom

Abstract

Pesticide analyses are reported for surface-water sites in the Boulder Creek Watershed from the headwaters to the confluence with Saint Vrain Creek during high-flow and low-flow conditions. Samples were collected from seven mainstem sites, a major tributary, and effluent from two wastewater treatment plants in June and October, 2000. This study used analytical methods that provided a broader range of pesticides and lower detection levels than any previous study in the watershed. Eleven of the 84 pesticides determined in the study were detected at one or more sites in Boulder Creek or the inflows. These pesticides were mainly found in the eastern downstream portion of the watershed, which is dominated by agricultural and wastewater input. The most frequently detected pesticides were diazinon, prometon and dichlobenil. Dichlobenil was the pesticide found at highest concentration, up to 9 µg/L. Atrazine, metolachlor, and methyl parathion, which are used mainly in corn production, were detected in Boulder Creek, but none of the other pesticides commonly used in agriculture were determined.

INTRODUCTION

This report describes the presence and distribution of selected dissolved pesticides in the Boulder Creek Watershed during June and October, 2000. The study of pesticides was part of a collaborative effort of the U.S. Geological Survey (USGS) and the city of Boulder (Murphy and others, 2003). The study was designed to provide a comprehensive analysis of Boulder Creek water quality. High-flow (June) and low-flow (October) water-quality sampling of Boulder Creek from upstream of the town of Eldora to the

confluence with Saint Vrain Creek, along with several inflows, was carried out to determine natural and human influences on water chemistry. Samples from ten sites were analyzed for pesticides using gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC).

Purpose and Scope

The main objective of this chapter is to document the results for pesticides in surface water in the study area during 2000. One of the unique aspects of this study was the use of analytical methods that provide a broader range of pesticides and lower detection levels than any previous study in the watershed. The pesticides determined include many not normally regulated nor considered to be problematic in Boulder Creek. The chapter describes the presence and distribution of pesticides in surface water, and contributions of pesticides to Boulder Creek from some major inflows, for two 3-day periods in year 2000. The data represent a baseline for comparing future measurements of pesticides.

Previous Studies

Little information on the presence of pesticides in Boulder Creek and its inflows is available. In 1991, a water-quality investigation of the South Platte River Basin was started as part of the USGS National Water-Quality Assessment (NAWQA) program. The Boulder Creek Watershed is a subbasin of the South Platte River. One of the first tasks of the assessment was a compilation, screening, and interpretation of available nutrient, suspended-sediment, and pesticide data collected from surface- and ground-water sites in the basin. A total of 3484

samples from 54 surface-water sites and 107 wells were used in the analysis from water years 1980 to 1992. Most pesticide concentrations were less than laboratory-reporting levels. The pesticides with the highest percentage detections in surface water among the six land uses studied were atrazine in agricultural areas and picloram in mixed agricultural and urban land use. Only one surface-water site, in the mixed agricultural and urban land-use area, had a pesticide (parathion) concentration that exceeded water-quality criteria (Dennehy and others, 1995).

As part of the South Platte NAWQA study, more recent samples were collected and analyzed using techniques similar to those used in this report. Pesticides were frequently detected in urban and agricultural land-use settings (Kimbrough and Litke, 1998). Thirty-nine pesticides were detected at least once at surface-water sites in agricultural areas along the South Platte River from Henderson, Colorado, to North Platte, Nebraska, during the 1994 growing season. The most commonly detected pesticides were herbicides generally associated with irrigated agriculture in the basin (atrazine, metolachlor, dacthal [DCPA], cyanazine, s-ethyl dipropylthiocarbamate [EPTC], and carbofuran), long-term weed control (prometon, simazine), and insecticide use (diazinon). Twenty-eight pesticides were detected at two sampling sites in the Denver metropolitan area. The most commonly detected pesticides were typically used by homeowners or commercial applicators in urban areas (carbaryl, chlorpyrifos, DCPA, diazinon, and malathion), or were used for nonselective weed control (prometon, simazine, and tebuthiuron). Pesticide concentrations measured in urban samples were small.

Approach

This study was developed from an existing network used by the city of Boulder in its routine water-quality monitoring. Individual sites were selected based on city of Boulder sampling sites (Murphy and others, 2003) and at locations

downstream of major tributary inputs. The spatial distribution of the sites across the watershed reflects the different land-use characteristics across the basin, namely forested and semirural in the mountains in the west, urban and suburban along the Front Range, and more rural and agricultural in the eastern part of the basin. Water samples were collected over a 3-day period in June and October, which represent high-flow and low-flow conditions in the streams. In addition, these different periods reflect different applications and uses of pesticides in the basin.

DESCRIPTION OF STUDY AREA

Location

The Boulder Creek Watershed covers about 1160 km², primarily in Boulder County, Colorado. The Boulder Creek Watershed consists of two physiographic provinces: the upper basin, defined on the west by the Continental Divide, and the lower basin, defined on the west by the foothills of the Rocky Mountains (fig. 6.1; table 1.1, Murphy and others, 2003). The watershed begins at the Continental Divide, and extends east from the headwaters in the mountains to the plains and finally to its confluence with Saint Vrain Creek. The watershed is nested between the Clear Creek Watershed to the south, the Saint Vrain Creek Watershed to the north, and the South Platte River Watershed to the east.

Land use

Land use in the basin is highly mixed, with mountainous forests dominating the western headwater region, a sparsely populated mountain corridor, a moderately populated urban corridor in the central region, and more agricultural and suburban areas in the eastern region. The headwater region lies within Roosevelt National Forest, and much of the area is wilderness where vehicles are prohibited. Small areas of low-density population, campgrounds, and the Eldora Mountain Ski Area are located within the

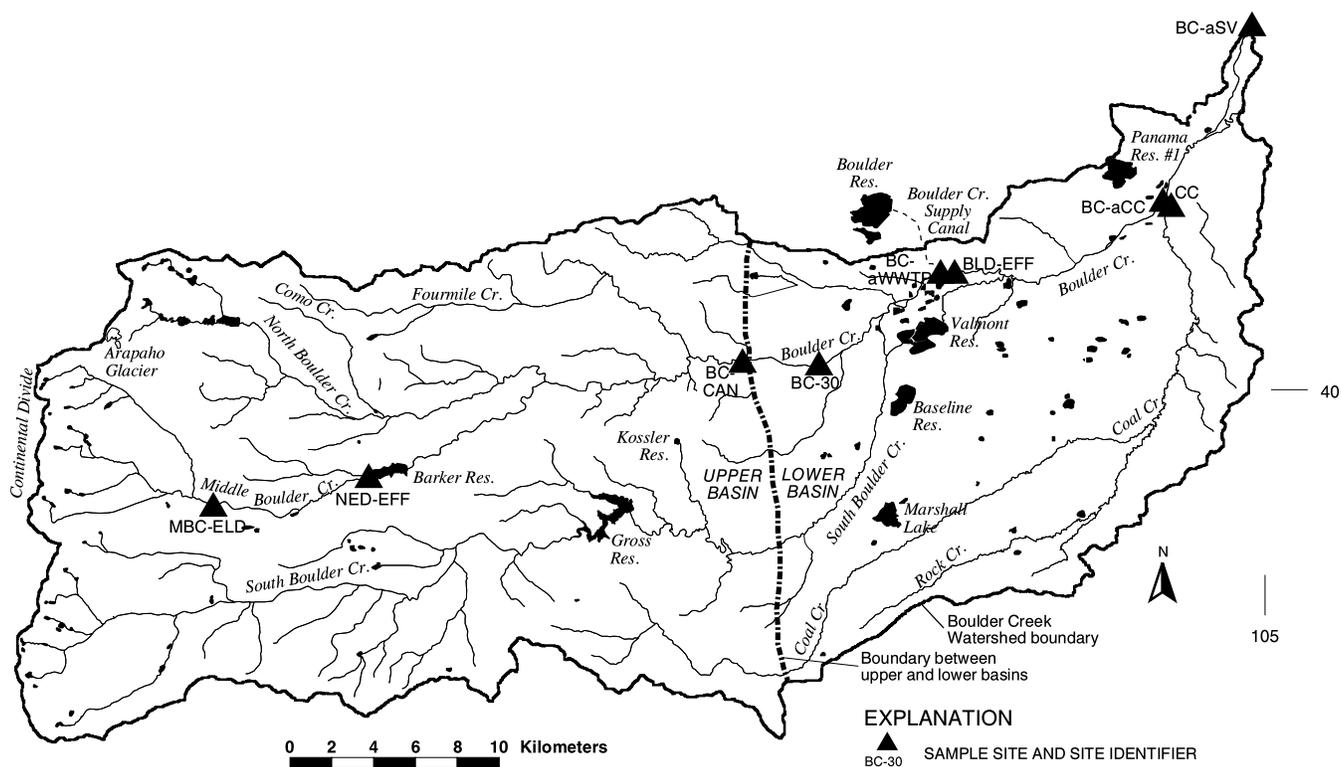


Figure 6.1. Map of Boulder Creek Watershed and sampling sites.

headwater region. The mountain corridor is characterized by a low density of homes, the town of Nederland, and two highways, one of which (Highway 119) runs alongside Middle Boulder Creek. The Nederland Wastewater Treatment Plant (WWTP) discharges effluent into Middle Boulder Creek upstream of Barker Reservoir. East of the mouth of Boulder Canyon, Boulder Creek enters the main urban corridor of the city of Boulder, which had a population of 94,673 in the year 2000 (Murphy and others, 2003). The Boulder 75th Street WWTP discharges effluent into Boulder Creek east of the corridor, and during low-flow conditions it can contribute a substantial portion of the total streamflow in lower Boulder Creek. The eastern region consists of less populated suburban areas and agricultural fields, pasture and open space. Coal Creek, a tributary that flows through the urban regions of Erie, Lafayette, Louisville, and Superior, enters

Boulder Creek about 11 km upstream of the confluence with Saint Vrain Creek.

Pesticide Use

Pesticides used within the watershed are associated with agricultural and urban applications. In the agricultural areas, herbicides are applied to fields to prevent weed growth mainly during pre-plant times. Insecticides are used to control insects during the growing season. In urban areas, herbicides are used to control weeds along roads, drainage ditches and railroads, in parks and golf courses, and in gardens. Insecticides are mainly applied during the growing season to control pests in lawns and gardens.

STUDY METHODS

Sampling-Site Selection

Pesticide sample-collection sites are shown in figure 6.1. The sites include seven mainstem locations stretching from the headwaters to the most downstream site, just above Saint Vrain Creek. The sites are mainly in the eastern part of the basin, where pesticide use is expected to be greatest. In addition, three inflows were sampled: Coal Creek, effluent from the Nederland WWTP, and effluent from the Boulder WWTP. Site descriptions are provided in table 1.1 of Murphy and others (2003).

Estimation of Pesticide Use in Boulder County

Pesticide use in Boulder County was estimated by combining state-level information on 1997 pesticide-use rates available from the National Center for Food and Agricultural Policy (2001) and county-level information on harvested crop acreage from the Census of Agriculture (Thelin and Gianessi, 2000). The harvested crop acreage for Boulder County in 1997 consisted mainly of corn, wheat, alfalfa, and barley (U.S. Department of Agriculture, 2000). Pesticide use was estimated by multiplying crop area acres for Boulder County by the Colorado estimated percentage of acres treated and application rate, in kilograms active ingredient applied, for each pesticide (table 6.1).

Sample Collection

The distribution of pesticides in Boulder Creek and inflows was studied during June and October, 2000. The June sampling was designed to coincide with high-flow conditions caused by snowmelt runoff, as well as early application of pesticides during the growing season. Agricultural pre-plant herbicides and insecticides generally are applied during March and April. The October sampling was designed to sample

when discharge was characteristically lower, and different types of pesticides are expected to be applied. Throughout spring and summer, insecticides are applied to agricultural crops, and on lawns and gardens in urban areas.

Sampling Protocols

Water-quality samples were collected using protocols designed to minimize contamination and to obtain a representative sample (Wilde and others, 1999). All samples were collected by wading into the shallow stream to obtain a grab sample from the centroid of flow using a 2-L stainless-steel bucket. Three or four grab samples were composited into a 20-L stainless-steel milk can.

For analysis of pesticides by GC/MS and by HPLC, composite samples were filtered at the sampling site through 0.7- μ m glass-fiber filters (Sandstrom, 1995). Filtered samples were collected in 1-L glass bottles and stored on ice until analyzed in the laboratory. For glyphosate determination, an unfiltered composite sample was placed into a glass 40-mL vial and stored on ice.

All sampling equipment, including filtration and compositing equipment, was cleaned at the collection site at the end of sampling by washing in dilute detergent (0.1 percent Liquinox), rinsing in tap water, followed by rinsing in methanol. Open surfaces of cleaned equipment were wrapped in aluminum foil, and the equipment was stored in plastic bags.

Quality Assurance and Quality Control

Quality-control samples used to estimate bias and variability in sampling and laboratory procedures included field blanks (bias) and replicate samples (variability). In addition, the laboratory analyses included laboratory blanks (bias) and reagent water fortified samples (bias and variability), and surrogates added to every sample (bias) as part of the routine quality-

assurance (QA) program. Field equipment blanks were prepared by processing pesticide-grade water through all sample collection and filtration equipment at the collection site, and then analyzing the sample in the laboratory along with environmental samples. Replicate samples consisted of two samples taken from the stream composite sample.

Field Blanks - Contamination of samples, either in the field or laboratory processing, was not found to be a problem for this study. No pesticides were detected in either of the blanks.

Field Replicates – Split filtered environmental water samples were collected from the Boulder Creek site upstream from the confluence with Coal Creek (BC-aCC). This site was chosen for evaluation of reproducibility during both sampling events because it was anticipated that pesticide detections would increase downstream. Although few pesticides were found, concentrations generally were within a factor of 2 (relative percent difference from 0 to 122 percent, table 6.2).

Surrogate compounds - Surrogate compounds, which are chemically similar to the pesticides determined and are expected to behave similarly in the analytical process, are added to the environmental samples and used to monitor gross sample processing bias. Surrogates are not expected to be found in environmental samples prior to processing. Surrogate recoveries indicated no substantial problems or bias for GC/MS, and ranged from 80 to 137 percent (table 6.3). Surrogate recoveries for HPLC ranged from 25 to 93 percent (table 6.4).

Sample Analysis

Pesticide samples were analyzed by two different analytical methods: GC/MS and HPLC. Details of the analytical methods are described by Zaugg and others (1995) for GC/MS, and by Werner and others (1996) for HPLC. The 83 pesticides determined by the two methods are listed in tables 6.3 and 6.4. For four samples collected in June, glyphosate was determined by

an HPLC method (Winfield and others, 1990; table 6.5).

With the GC/MS and HPLC analytical methods, different pesticides can be detected at varying low concentrations, as reflected by varying laboratory-reporting levels (LRLs; tables 6.3 and 6.4). Laboratory reporting levels for the GC/MS method are 10 to 50 times lower than reporting levels for the HPLC method. However, LRL concentrations are not absolute lower limits for detection, and any compounds that meet defined detection criteria in a sample (Zaugg and others, 1995; Werner and others, 1996) are reported as estimated values for the observed concentration.

The pesticide data that are reported by the USGS include less-than (“<”) remark codes with all nondetections, and estimated (“E”) remark codes to signify estimated concentrations for all detections that are less than the LRL, greater than the highest calibration standard, or otherwise less reliable than average because of sample-specific or compound-specific considerations. All “E”-coded data are believed to be reliable detections but with greater than average uncertainty in quantification. Most nondetections are shown in the data as “<” the LRL concentration. Nondetections with a “<” remark, but a concentration greater than the method detection limit (MDL), indicate that factors specific to that sample prevented reliable compound identification at less than the given concentration.

PESTICIDES IN SURFACE WATER

During sampling in 2000, only 11 of the 84 pesticides that were determined by the three methods were detected at one or more sites in Boulder Creek (tables 6.3, 6.4, and 6.5), despite the use of analytical methods that provided low detection levels (low nanogram per liter). The pesticides that were detected are listed in table 6.6. The values for “all” concentrations provide the total number of detections for a given compound, but are not comparable among compounds because detection capabilities vary.

Table 6.1. Target compounds and analytical method, crop use, and estimated application on agricultural crops in Boulder County, 1997

[Pesticides listed in decreasing order of use; a.i., active ingredient; values estimated using data from National Center for Food and Agricultural Policy, 2001 and U.S. Department of Agriculture, 2000; GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; Gly, glyphosate method; --, not analyzed; pesticides in **bold** detected in Boulder Creek samples]

Pesticide	Use	Method	Crop	Kilograms a.i. applied
Atrazine	Herbicide	GC/MS	Corn	1172
2,4-D (2,4-dichlorophenoxyacetic acid)	Herbicide	HPLC	Wheat, corn, barley	761
Terbufos	Insecticide	GC/MS	Corn	618
Dicamba	Herbicide	HPLC	Corn, wheat, barley	589
Glyphosate	Herbicide	Gly	Corn, wheat, barley	501
Metolachlor	Herbicide	GC/MS	Corn	384
Carbofuran	Insecticide	HPLC	Alfalfa, corn	352
Chlorpyrifos	Insecticide	GC/MS	Alfalfa, wheat, corn	282
Alachlor	Herbicide	GC/MS	Corn	277
Parathion-methyl	Insecticide	GC/MS	Corn, alfalfa, barley	208
Trifluralin	Herbicide	GC/MS	Alfalfa	176
2,4-DB (4-[2,4-dichlorophenoxy]butyric acid)	Herbicide	HPLC	Alfalfa	165
Hexazinone	Herbicide	--	Alfalfa	165
Propargite	Acaricide	GC/MS	Corn	159
Benefin	Herbicide	--	Alfalfa	149
Acetochlor	Herbicide	GC/MS	Corn	138
Carbaryl	Insecticide	HPLC	Alfalfa	132
Diuron	Herbicide	HPLC	Alfalfa	132
EPTC (s-ethyl dipropylthiocarbamate)	Herbicide	GC/MS	Corn	121
Dimethoate	Insecticide	--	Corn, alfalfa, wheat	119
Paraquat	Herbicide	--	Alfalfa, wheat, corn	115
Parathion	Insecticide	GC/MS	Alfalfa, corn, barley	113
Malathion	Insecticide	GC/MS	Alfalfa	110
Cyanazine	Herbicide	GC/MS	Corn	104
Pendimethalin	Herbicide	GC/MS	Corn	104
Pyridate	Herbicide	--	Corn	104
Bromoxynil	Herbicide	HPLC	Wheat, barley, corn	102
Butylate	Herbicide	GC/MS	Corn	98
Permethrin	Insecticide	GC/MS	Corn, alfalfa	76
Sethoxydim	Herbicide	--	Alfalfa, corn	61
Phorate	Insecticide	GC/MS	Corn, wheat	57
Disulfoton	Insecticide	GC/MS	Barley, wheat	44
Bentazon	Herbicide	HPLC	Corn	29
Dimethenamid	Herbicide	--	Corn	24
Imazethapyr	Herbicide	--	Alfalfa, corn	17
MCPA (2-methyl-4-chlorophenoxyacetic acid)	Herbicide	HPLC	Barley	16
Chlorethoxyfos	Insecticide	--	Corn	15
Clopyralid	Herbicide	HPLC	Wheat, corn, barley	14
Imazamethabenz	Herbicide	--	Barley	12
Triallate	Herbicide	GC/MS	Barley	10
Cyfluthrin	Insecticide	--	Alfalfa	9
Esfenvalerate	Insecticide	--	Corn	9
Diclofop	Herbicide	--	Barley	8

Table 6.1. Target compounds and analytical method, crop use, and estimated application on agricultural crops in Boulder County, 1997--continued

Pesticide	Use	Method	Crop	Kilograms a.i. Applied
Lambdacyhalothrin	Insecticide	--	Corn	8
Chlorsulfuron	Herbicide	--	Wheat, barley	5
Nicosulfuron	Herbicide	--	Corn	5
Metribuzin	Herbicide	GC/MS	Corn	3
Thifensulfuron	Herbicide	--	Barley, corn, wheat	3
Triasulfuron	Herbicide	--	Wheat	3
Bifenthrin	Insecticide	--	Corn	3
Total				7890

Most of the pesticides were detected by the GC/MS method, in part because of the greater sensitivity compared to the HPLC method. Because the analytical detection limits varied among the different pesticide compounds, three common detection thresholds were used in table 6.6 (0.01, 0.05, and 0.1 µg/L). The use of these detection thresholds facilitates cross-comparisons among compounds by bringing most of the data to a common reference point (Larson and others, 1999).

The pesticides detected most frequently at concentrations greater than 0.01 µg/L (table 6.6) were prometon (6 samples, or 30 percent), dichlobenil (25 percent), and diazinon (20 percent). Diazinon is an organophosphate insecticide commonly used in urban areas for control of insects in commercial and home gardens. Prometon and dichlobenil are primarily used for nonselective weed control in

nonagricultural areas. Atrazine, desethylatrazine, and metolachlor also were detected frequently, but at much lower concentrations. Atrazine and metolachlor are herbicides commonly used in agricultural practices in the study area (table 6.1). Desethylatrazine (2-chloro-4-amino-6-isopropylamino-5-triazine) is a degradate of atrazine.

Many of the pesticides frequently detected in Boulder Creek also were found in comparable studies. In the small urban watersheds in the South Platte Basin study, atrazine, carbaryl, diazinon, prometon, and simazine were detected in more than 50 percent of samples analyzed (Kimbrough and Litke, 1998). Similarly, in a national study (Larson and others, 1999), frequently-detected pesticides in small urban watersheds included prometon (87 percent), atrazine (85 percent), simazine (70 percent),

Table 6.2. Concentrations of pesticides in split filtered environmental water samples, June and October 2000

[Sample site Boulder Creek above Coal Creek (BC-aCC); values reported in micrograms per liter; <, less than; nc, not calculated; E, estimated concentration; relative percent difference for two samples = $[R1 - R2]/[(R1+R2)/2] \times 100$, where R1= sample 1 result and R2 = sample 2 result]

Pesticide	JUNE 2000			OCTOBER 2000		
	Sample 1	Sample 2	Relative percent difference	Sample 1	Sample 2	Relative percent difference
Atrazine	<0.001	<0.001	nc	E 0.004	E 0.005	22
Deethylatrazine	< .002	< .002	nc	E .004	E .006	40
Diazinon	< .002	< .002	nc	.094	.107	13
Dichlobenil	E .102	E .104	2	2.161	E 8.969	120
Lindane	< .004	< .004	nc	.027	.031	14
Metolachlor	< .002	< .002	nc	E .005	E .005	0
Parathion-methyl	.126	.126	0	< .006	< .006	nc
Prometon	< .018	.005	nc	E .01	E .013	26

Table 6.3. Concentrations of pesticides from the gas chromatography/mass spectrometry method, June and October 2000

[Chemical Abstracts Service registry numbers and National Water Information System parameter codes are given beneath the name of each pesticide; concentrations in micrograms per liter except for compounds marked with *, for which percent recovery is given; medium, sample medium code; 9, regular sample; R, replicate sample; <, actual value less than the method reporting level; E, estimated value; detections shown in **bold**]

Site	Date	Time	Medium	2,6-Diethylaniline		Alachlor	alpha-HCH	Atrazine	Azinphos-methyl	Benfluralin	Butylate
				579-66-8	82660E						
Middle Boulder Creek/Boulder Creek											
MBC-ELD	6/12/00	0820	9	<0.003	<0.002	<0.002	<0.002	<0.001	<0.001	<0.002	<0.002
MBC-ELD	10/9/00	0830	9	<0.002	<0.004	<0.002	<0.005	<0.007	<0.05	<0.01	<0.002
BC-CAN	6/13/00	1330	9	<0.003	<0.002	<0.002	<0.002	<0.001	<0.001	<0.002	<0.002
BC-CAN	10/10/00	1236	9	<0.002	<0.004	<0.002	<0.005	<0.007	<0.05	<0.01	<0.002
BC-30	6/12/00	1430	9	<0.003	<0.002	<0.002	<0.002	<0.001	<0.001	<0.002	<0.002
BC-30	10/ 10/00	1345	9	<0.002	<0.004	<0.002	<0.005	<0.007	<0.05	<0.01	<0.002
BC-aWWTP	6/13/00	1910	9	<0.003	<0.002	<0.002	<0.002	<0.001	<0.001	<0.002	<0.002
BC-aWWTP	10/11/00	0815	9	<0.002	<0.004	<0.002	<0.005	<0.007	<0.05	<0.01	<0.002
BC-75	6/13/00	2000	9	<0.003	<0.002	<0.002	<0.002	<0.001	<0.001	<0.002	<0.002
BC-75	10/ 11/00	0900	9	<0.002	<0.004	<0.002	<0.005	<0.007	<0.05	<0.01	<0.002
BC-aCC	6/13/00	1720	9	<0.003	<0.002	<0.002	<0.002	<0.001	<0.001	<0.002	<0.002
BC-aCC	6/13/00	1725	R	<0.003	<0.002	<0.002	<0.002	0.008	<0.001	<0.002	<0.002
BC-aCC	10/10/00	1630	9	<0.002	<0.004	<0.002	<0.005	E.004	<0.05	<0.01	<0.002
BC-aCC	10/10/00	1635	R	<0.002	<0.004	<0.002	<0.005	E.005	<0.05	<0.01	<0.002
BC-aSV	6/12/00	1700	9	<0.003	<0.002	<0.002	<0.002	0.017	<0.001	<0.002	<0.002
BC-aSV	10/9/00	1545	9	<0.002	<0.004	<0.002	<0.005	0.009	<0.05	<0.01	<0.002
Inflows											
CC 6/	13/00	1615	9	<0.003	<0.002	<0.002	<0.002	0.01	<0.001	<0.002	<0.002
CC 10/	10/00	1600	9	<0.002	<0.004	<0.002	<0.005	E.006	<0.05	<0.01	<0.002
NED-EFF	6/12/00	1330	9	<0.003	<0.002	<0.018	<0.002	<0.001	<0.001	<0.002	<0.002
NED-EFF	10/17/00	1345	9	<0.002	<0.004	<0.002	<0.005	<0.007	<0.05	<0.01	<0.002
BLD-EFF	6/13/00	2030	9	<0.003	<0.002	<0.002	<0.002	<0.005	<0.02	<0.002	<0.002
BLD-EFF	10/17/00	1600	9	<0.002	<0.004	<0.01	<0.005	<0.007	<0.05	<0.01	<0.002

Table 6.3. Concentrations of pesticides from the gas chromatography/mass spectrometry method, June and October 2000--continued

Site	Carbaryl 63-25-2 82680E	Carbofuran 1563-66-2 82674E	Chlorpyrifos 2921-88-2 38933E	cis- Permethrin 54774-45-7 82687E	Cyanazine 21725-46-2 04041E	Dacthal 1861-32-1 82682E	Desethyl- atrazine 6190-65-4 04040E	Diazinon 333-41-5 39572E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
MBC-ELD	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-CAN	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-CAN	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-30	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-30	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-aWWTP	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-aWWTP	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-75	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-75	<.041	<.02	<.005	<.006	<.018	<.003	<.006	0.022
BC-aCC	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-aCC	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-aCC	<.041	<.02	<.005	<.006	<.018	<.003	E.004	0.094
BC-aCC	<.041	<.02	<.005	<.006	<.018	<.003	E.006	0.107
BC-aSV	<.003	<.003	<.004	<.005	<.004	<.002	E.011	0.01
BC-aSV	<.041	<.02	<.005	<.006	<.018	<.003	E.009	<.005
Inflows								
CC	E.092	<.003	<.004	<.005	<.004	<.002	E.005	0.054
CC	E.018	<.02	<.005	<.006	<.018	<.003	E.006	E.004
NED-EFF	E.009	--	<.004	<.005	<.004	<.002	<.002	<.002
NED-EFF	<.041	<.075	<.005	<.006	<.018	<.003	<.006	<.005
BLD-EFF	<.02	<.003	<.004	<.005	<.004	<.002	<.002	0.008
BLD-EFF	<.041	<.075	<.005	<.006	<.018	<.003	<.006	0.01

Table 6.3. Concentrations of pesticides from the gas chromatography/mass spectrometry method, June and October 2000--continued

Site	Dieldrin 60-57-1 39381E	Disulfoton 298-04-4 82677E	EPTC 759-94-4 82668E	Ethalfuralin 55283-68-6 82663E	Ethoprophos 13194-48-4 82672E	Fonofos 944-22-9 04095E	Lindane 58-89-9 39341E	Linuron 330-55-2 82666E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
MBC-ELD	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-CAN	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-CAN	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-30	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-30	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-aWWTP	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aWWTP	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-75	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-75	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-aCC	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aCC	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aCC	<.005	<.021	<.002	<.009	<.005	<.003	0.027	<.035
BC-aCC	<.005	<.021	<.002	<.009	<.005	<.003	0.031	<.035
BC-aSV	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aSV	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
Inflows								
CC	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
CC	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
NED-EFF	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
NED-EFF	<.005	<.021	<.002	<.009	<.005	<.003	<.02	<.035
BLD-EFF	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BLD-EFF	<.005	<.021	<.006	<.009	<.005	<.003	<.004	<.035

Table 6.3. Concentrations of pesticides from the gas chromatography/mass spectrometry method, June and October 2000--continued

Site	Malathion 121-75-5 39532E	Metolachlor 51218-45-2 39415E	Metribuzin 21087-64-9 82630E	Molinate 2212-67-1 82671E	Napropamide 15299-99-7 82684E	p,p'-DDE 72-55-9 34653E	Parathion 56-38-2 39542E	Methyl parathion 298-00-0 82667E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
MBC-ELD	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BC-CAN	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
BC-CAN	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BC-30	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
BC-30	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BC-aWWTP	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
BC-aWWTP	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BC-75	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
BC-75	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BC-aCC	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	0.126
BC-aCC	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	0.126
BC-aCC	<0.027	E.005	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BC-aCC	<0.027	E.005	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BC-aSV	<0.005	0.008	<0.004	<0.004	<0.003	<0.006	<0.004	0.05
BC-aSV	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
Inflows								
CC	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	0.055
CC	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
NED-EFF	0.02	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
NED-EFF	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006
BLD-EFF	<0.005	<.01	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
BLD-EFF	<0.027	<0.013	<0.006	<0.002	<0.007	<0.003	<0.007	<0.006

Table 6.3. Concentrations of pesticides from the gas chromatography/mass spectrometry method, June and October 2000--continued

Site	Pebulate	Pendi-methalin	Phorate	Prometon	Propachlor	Propanil	Propargite	Propyzamide	Simazine
	1114-71-2 82669E	40487-42-1 82683E	298-02-2 82664E	1610-18-0 04037E	1918-16-7 04024E	709-98-8 82679E	2312-35-8 82685E	23950-58-5 82676E	122-34-9 04035E
Middle Boulder Creek/Boulder Creek									
MBC-ELD	<0.004	<0.004	<0.002	<0.018	<0.007	<0.004	<0.013	<0.003	<0.005
MBC-ELD	<0.002	<.01	<.011	<.015	<.01	<.011	<.023	<.004	<.011
BC-CAN	<.004	<.004	<.002	<.018	<.007	<.004	<.013	<.003	<.005
BC-CAN	<.002	<.01	<.011	<.015	<.01	<.011	<.023	<.004	<.011
BC-30	<.004	<.004	<.002	<.018	<.007	<.004	<.013	<.003	<.005
BC-30	<.002	<.01	<.011	<.015	<.01	<.011	<.023	<.004	<.011
BC-aWWTP	<.004	<.004	<.002	<.018	<.007	<.004	<.013	<.003	<.005
BC-aWWTP	<.002	<.01	<.011	<.015	<.01	<.011	<.023	<.004	<.011
BC-75	<.004	<.004	<.002	<.018	<.007	<.004	<.013	<.003	<.005
BC-75	<.002	<.01	<.011	<.015	<.01	<.011	<.023	<.004	<.011
BC-aCC	<.004	<.004	<.002	<.018	<.007	<.004	<.013	<.003	<.005
BC-aCC	<.004	<.004	<.002	E.005	<.007	<.004	<.013	<.003	<.005
BC-aCC	<.002	<.01	<.011	E.01	<.01	<.011	<.023	<.004	<.011
BC-aCC	<.002	<.01	<.011	E.013	<.01	<.011	<.023	<.004	<.011
BC-aSV	<.004	<.004	<.002	<.018	<.007	<.004	<.013	<.003	<.005
BC-aSV	<.002	<.01	<.011	E.014	<.01	<.011	<.023	<.004	<.011
Inflows									
CC	<.004	<.004	<.002	E.013	<.007	<.004	<.013	<.003	<.005
CC	<.002	<.01	<.011	0.017	<.01	<.011	<.023	<.004	<.011
NED-EFF	<.004	<.004	<.002	<.018	<.007	<.004	<.013	<.003	<.005
NED-EFF	<.002	<.01	<.011	<.015	<.01	<.011	<.023	<.004	<.011
BLD-EFF	<.004	<.004	<.002	E.014	<.007	<.025	<.013	<.003	<.005
BLD-EFF	<.002	<.01	<.011	0.016	<.01	<.011	<.023	<.005	<.011

Table 6.3. Concentrations of pesticides from the gas chromatography/mass spectrometry method, June and October 2000-continued

Site	Tebuthiuron 34014-18-1 82670E	Terbacil 5902-51-2 82665E	Terbufos 13071-79-9 82675E	Thio- bencarb 28249-77-6 82681E	Tri- allate 2303-17-5 82678E	Trifluralin 1582-09-8 82661E	Diazinon-D10, surrogate* 100155-47-3 91063E	alpha-HCH- D6, surrogate* 319-84-6-d6 91065E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<.01	<.007	<.013	<.002	<.001	<.002	102	85
MBC-ELD	<.016	<.034	<.017	<.005	<.002	<.009	104	103
BC-CAN	<.01	<.007	<.013	<.002	<.001	<.002	114	96
BC-CAN	<.016	<.034	<.017	<.005	<.002	<.009	101	94
BC-30	<.01	<.007	<.013	<.002	<.001	<.002	111	81
BC-30	<.016	<.034	<.017	<.005	<.002	<.009	109	106
BC-aWWTP	<.01	<.007	<.013	<.002	<.001	<.002	111	87
BC-aWWTP	<.016	<.034	<.017	<.005	<.002	<.009	104	100
BC-75	<.01	<.007	<.013	<.002	<.001	<.002	107	88
BC-75	<.016	<.034	<.017	<.005	<.002	<.009	80	88
BC-aCC	<.01	<.007	<.013	<.002	<.001	<.002	116	87
BC-aCC	<.01	<.007	<.013	<.002	<.001	<.002	104	94
BC-aCC	<.016	<.034	<.017	<.005	<.002	<.009	113	86
BC-aCC	<.016	<.034	<.017	<.005	<.002	<.009	137	106
BC-aSV	<.01	<.007	<.013	<.002	<.001	<.002	105	84
BC-aSV	<.016	<.034	<.017	<.005	<.002	<.009	101	99
Inflows								
CC	<.01	<.007	<.013	<.002	<.001	<.002	94	90
CC	<.016	<.034	<.017	<.005	<.002	<.009	106	103
NED-EFF	<.01	<.1	<.013	<.002	<.001	<.002	97	83
NED-EFF	<.016	<.075	<.017	<.005	<.002	<.009	99	80
BLD-EFF	<.01	<.007	<.013	<.002	<.001	<.002	89	80
BLD-EFF	<.016	<.034	<.017	<.005	<.002	<.009	95	85

Table 6.4. Concentrations of pesticides from the high-performance liquid chromatography method, June and October 2000

[Chemical Abstracts Service registry numbers and National Water Information System parameter codes are given beneath the name of each pesticide; concentrations in micrograms per liter except for compounds marked with *, for which percent recovery is given; medium, sample medium code; 9, regular sample; R, replicate sample; <, actual value less than the method reporting level; E, estimated value; detections shown in **bold**]

Site	Date	Time	Medium	2,4,5-T		2,4-D		2,4-DB		2-(2,4,5-Trichloro-phenoxy) propionic acid		3-Hydroxy-carbofuran		4,6-Dinitro-2-methylphenol		Acifluorfen		Aldicarb	
				93-76-5 39742B	94-75-7 39732B	94-82-6 38746A	93-72-1 39762B	16655-82-6 49308A	534-52-1 49299A	62476-59-9 49315A	116-06-3 49312A								
Middle Boulder Creek/Boulder Creek																			
MBC-ELD	6/12/00	0820	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
MBC-ELD	10/9/00	0830	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-30	6/12/00	1430	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-30	10/10/00	1345	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-CAN	6/13/00	1330	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-CAN	10/10/00	1236	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aWWTP	6/13/00	1910	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aWWTP	10/11/00	0815	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-75	6/13/00	2000	9	<0.15	<0.82	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-75	10/11/00	0900	9	<0.29	<0.23	<0.7	<0.39	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aCC	6/13/00	1720	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aCC	6/13/00	1725	R	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aCC	10/10/00	1630	9	<0.04	<0.14	<0.7	<0.25	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aCC	10/10/00	1635	R	<0.19	<0.56	<0.3	<0.26	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aSV	6/12/00	1700	9	<0.04	<0.31	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BC-aSV	10/9/00	1545	9	<0.38	<0.66	<0.8	<0.19	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
Inflows																			
CC	6/13/00	1615	9	<0.04	<0.29	<0.5	<0.06	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
CC	10/10/00	1600	9	<0.55	<0.51	<0.7	<0.38	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
NED-EFF	6/12/00	1330	9	<0.75	<0.11	<0.3	<1.11	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
NED-EFF	10/17/00	1345	9	<0.04	<0.259	<0.4	<0.135	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BLD-EFF	6/13/00	2030	9	<0.23	<0.11	<1.8	<0.5	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21
BLD-EFF	10/17/00	1600	9	<0.13	<0.75	<0.7	<0.25	<0.11	<0.42	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21	<0.09	<0.21

Table 6.4. Concentrations of pesticides from the high-performance liquid chromatography method, June and October 2000--continued

Site	Aldicarb sulfone 1646-88-4 49313A	Aldicarb sulfoxide 1646-87-3 49314A	Bentazon 25057-89-0 38711A	Bromacil 314-40-9 04029A	Bromoxynil 1689-84-5 49311A	Carbaryl 63-25-2 49310A	Carbofuran 1563-66-2 49309A	Chloramben methyl ester 7286-84-2 61188A
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.1	<0.021	<0.035	<0.06	<0.04	<0.07	<0.29	<0.14
MBC-ELD	<.26	<.188	<.035	<.09	<.07	<.024	<.29	<.14
BC-30	<.1	<.021	<.035	<.06	<.04	<.07	<.29	<.14
BC-30	<.26	<.021	<.035	<.09	<.07	<.024	<.29	<.14
BC-CAN	<.1	<.021	<.035	<.06	<.04	<.07	<.29	<.14
BC-CAN	<.26	<.105	<.035	<.09	<.07	<.024	<.29	<.14
BC-aWWTP	<.1	<.021	<.035	<.06	<.04	<.07	<.29	<.14
BC-aWWTP	<.26	<.172	<.035	<.09	<.07	<.024	<.29	<.14
BC-75	<.25	<.61	<.29	<.10	<.04	<.07	<.73	<.14
BC-75	<.5.3	<.673	<.035	<.2.1	<.07	<.156	<.2.3	<.14
BC-aCC	<.1	<.021	<.035	<.06	<.04	<.07	<.29	<.14
BC-aCC	<.3	<.13	<.035	<.11	<.04	<.07	<.23	<.14
BC-aCC	<.26	<.33	<.15	<.31	<.1	<.024	<.58	<.14
BC-aCC	<.2	<.64	<.26	<.2.41	<.07	<.024	<.29	<.14
BC-aSV	<.1	<.021	<.035	<.2	<.04	<.07	<.29	<.14
BC-aSV	<.26	<.021	<.302	<.36	<.07	<.024	<.44	<.14
Inflows								
CC	<0.1	<0.28	<0.14	<0.48	<0.04	<0.07	<1.3	<0.17
CC	<.69	<.2	<.32	<.77	<.07	<.024	<.29	<.31
NED-EFF	<.2.4	<.54	<.37	<.2.8	<.32	<.07	<.29	<.2
NED-EFF	<.1.7	<.1.2	<.185	<.1.0	<.07	<.024	<.2.1	<.14
BLD-EFF	<.1.2	<.36	<.21	<.4.9	<.04	<.12	<.2.0	<.14
BLD-EFF	<.7.1	<.3.5	<.035	<.51	<.18	<.024	<.2.3	<.14

Table 6.4. Concentrations of pesticides from the high-performance liquid chromatography method, June and October 2000--continued

Site	Chloro-thalonil	Clopyralid	Dacthal monoacid	Dicamba	Dichlobenil	Dichlorprop	Dinoseb	Diuron
	1897-45-6	1702-17-6	887-54-7	1918-00-9	1194-65-6	120-36-5	88-85-7	330-54-1
	49306A	49305A	49304A	38442A	49303A	49302A	49301A	49300A
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.48	<0.23	<0.039	<0.043	<0.07	<0.032	<0.06	<0.06
MBC-ELD	<.28	<.42	<.07	<.043	E.015	<.05	<.09	<.049
BC-30	<.48	<.23	<.039	<.043	<.07	<.032	<.06	<.06
BC-30	<.28	<.42	<.07	<.043	<.049	<.05	<.09	<.049
BC-CAN	<.48	<.23	<.039	<.043	<.07	<.032	<.06	<.06
BC-CAN	<.28	<.42	<.07	<.043	<.049	<.05	<.09	<.049
BC-aWWTP	<.48	<.23	<.039	<.043	<.07	<.032	<.12	<.06
BC-aWWTP	<.28	<.42	<.07	<.043	E.039	<.05	<.09	<.049
BC-75	<.48	<.40	<.039	<.17	<.27	<.032	<.06	<.88
BC-75	<.13	<.54	<.28	<.54	E2.49	<.57	<.23	<.29
BC-aCC	<.48	<.23	<.039	<.043	E.102	<.032	<.06	<.06
BC-aCC	<.48	<.23	<.12	<.043	E.104	<.032	<.06	<.06
BC-aCC	<.28	<.66	<.18	<.24	2.16	<.05	<.09	<.26
BC-aCC	<.13	<.57	<.12	<.15	E8.97	<.29	<.09	<.34
BC-aSV	<.48	<.23	<.039	<.043	<.07	<.032	<.06	<.06
BC-aSV	<.28	<.42	<.165	<.102	<.049	<.158	<.09	<.232
Inflows								
CC	<.48	<.23	<.14	<.11	<.1	<.032	<.06	<.99
CC	<.28	<.42	<.27	<.043	<.049	<.05	<.09	<.22
NED-EFF	<.48	<.44	<.178	<.59	<.44	<.032	<.54	<.77
NED-EFF	<.28	<.623	<.202	<.043	<.15	<.129	<.213	<.418
BLD-EFF	<.48	<.82	<.13	<.27	<.12	<.18	<.12	<.54
BLD-EFF	<.28	<.728	<.09	<.24	<.42	<.413	<.117	<.247

Table 6.4. Concentrations of pesticides from the high-performance liquid chromatography method, June and October 2000--continued

Site	Fenuron 101-42-8 49297A	Fluometuron 2164-17-2 38811A	Linuron 330-55-2 38478A	MCPA 94-74-6 38482A	MCPB 94-81-5 38487A	Methiocarb 2032-65-7 38501A	Methomyl 16752-77-5 49296A	Neburon 555-37-3 49294A
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.07	<0.06	<0.09	<0.17	<0.13	<0.026	<0.017	<0.07
MBC-ELD	<0.07	<0.06	<0.21	<0.08	<.13	<.07	<.017	<.017
BC-30	<0.07	<0.06	<0.09	<.17	<.13	<.026	<.017	<.07
BC-30	<0.07	<0.06	<0.21	<.08	<.13	<.07	<.017	<.017
BC-CAN	<0.07	<0.06	<0.09	<.17	<.13	<.026	<.017	<.07
BC-CAN	<0.07	<0.06	<0.21	<.08	<.13	<.07	<.017	<.017
BC-aWWTP	<0.07	<0.06	<0.09	<.17	<.13	<.026	<.017	<.07
BC-aWWTP	<0.07	<0.06	<0.21	<.08	<.13	<.07	<.017	<.017
BC-75	<.17	<.23	<.49	<.17	<.96	<.58	<.74	<.07
BC-75	<.18	<1.2	<.29	<.7	<1.7	<.22	<4.044	<.017
BC-aCC	<0.07	<0.06	<0.09	<.17	<.13	<.026	<.017	<.07
BC-aCC	<0.07	<0.06	<0.09	<.17	<.13	<.15	<.15	<.07
BC-aCC	<.34	<.2	<1.4	<.23	<.13	<.13	<1.04	<.28
BC-aCC	<.56	<0.06	<.24	<.15	<.92	<.19	<2.43	<.13
BC-aSV	<.18	<0.06	<0.09	<.17	<.23	<.22	<.85	<.07
BC-aSV	<.22	<0.06	<0.02	<.13	<.85	<.346	<.114	<.017
Inflows								
CC	<0.12	<0.06	<0.09	<0.17	<1.3	<1.4	<0.97	<0.19
CC	<.29	<.21	<.43	<.13	<1.5	<.78	<.47	<.017
NED-EFF	<.15	<.68	<.09	<.71	<.72	<.22	<.75	<.65
NED-EFF	<.77	<.66	<.36	<.08	<1.4	<.47	<1.0	<.14
BLD-EFF	<.4	<1.36	<1.4	<.17	<.13	<3.02	<.82	<.07
BLD-EFF	<.85	<.83	<1.0	<.92	<1.7	<1.2	<2.5	<.017

Table 6.4. Concentrations of pesticides from the high-performance liquid chromatography method, June and October 2000--continued

Site	Norflurazon	Oryzalin	Oxamyl	Picloram	Propham	Propoxur	Triclopyr	BMDC, surrogate*
	27314-13-2 49293A	19044-88-3 49292A	23135-22-0 38866A	21/18 49291A	122-42-9 49236A	114-26-1 38538A	55335-06-3 49235A	99835A
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.042	<0.31	<0.018	<0.05	<0.035	<0.08	<0.25	93
MBC-ELD	<0.42	<.28	<.018	<.09	<.09	<.12	<.07	81
BC-30	<.042	<.34	<.018	<.05	<.035	<.08	<.25	93
BC-30	<.042	<.28	<.17	<.09	<.09	<.12	<.104	80
BC-CAN	<.042	<.36	<.018	<.05	<.035	<.08	<.25	93
BC-CAN	<.042	<.28	<.527	<.09	<.09	<.12	<.07	82
BC-aWWTP	<.042	<.31	<.018	<.05	<.035	<.08	<.25	86
BC-aWWTP	<.042	<.28	<.202	<.09	<.09	<.12	<.07	81
BC-75	<.042	<.43	<.018	<.05	<.101	<.85	<.25	81
BC-75	<.042	<.59	<.018	<.12	<.09	<.44	<.6.0	52
BC-aCC	<.042	<.31	<.018	E.042	<.035	<.08	<.25	90
BC-aCC	<.042	<.36	<.21	<.05	<.19	<.25	<.25	62
BC-aCC	<.042	<.28	<.65	<.17	<.52	<.88	<.4.22	25
BC-aCC	<.042	<.296	<.1.34	<.09	<.09	<.12	<.6.2	74
BC-aSV	<.042	<.44	<.22	<.05	<.2	<.4	<.34	90
BC-aSV	<.042	<.28	<.966	<.106	<.137	<.752	<.1.7	73
Inflows								
CC	<.042	<.31	<.018	<.05	<.035	<.65	<.91	53
CC	<.042	<.28	<.14	<.29	<.12	<.67	<.98	24
NED-EFF	<.13	<.6.1	<.1.92	<.2	<.8	<.5.9	<.77	62
NED-EFF	<.191	<.28	<.018	<.22	<.39	<.35	<.1.4	41
BLD-EFF	<.042	<.31	<.74	<.35	<.2.24	<.1.8	<.7.4	51
BLD-EFF	<.042	<.41	<.159	<.19	<.09	<.96	<.32	45

Table 6.5. Concentrations of glyphosate, June 2000

[Chemical Abstracts Service registry numbers and National Water Information System parameter codes are given beneath the name of the pesticide; concentrations in micrograms per liter; medium, sample medium code; 9, regular sample; --, not analyzed; R, replicate sample; <, actual value less than the method reporting level]

Site	Date	Time	Medium	Glyphosate 1071-83-6 39941A
MBC-ELD	6/12/00	0820	9	--
BC-CAN	6/13/00	1330	9	--
BC-30	6/12/00	1430	9	--
BC-aWWTP	6/13/00	1910	9	<10
BC-75	6/13/00	2000	9	<10
BC-aCC	6/13/00	1720	9	<10
BC-aCC	6/13/00	1725	R	<10
BC-aSV	6/12/00	1700	9	<10

diazinon (69 percent), metolachlor (65 percent), and desethylatrazine (60 percent). Both of these studies found a greater variety and higher concentrations of pesticides compared to the Boulder Creek samples. Eighteen pesticides (11 herbicides and 7 insecticides) were determined in the South Platte River Basin study of sites in the Denver region. These other studies included more samples collected throughout the year, and were in smaller, predominantly urban land-use basins, which might explain the larger number of pesticides determined. In addition, local practices and laws restricting pesticide use and application in urban areas also might explain lower detection frequencies in Boulder Creek compared to other areas.

Spatial Variations

During sampling in 2000, eleven pesticides were detected at concentrations greater than 0.01 µg/L at one or more sites in Boulder Creek, mainly in the eastern downstream part of the watershed (table 6.7). One pesticide (dichlobenil) was detected at the site in the headwaters region, and at one of the two urban corridor sites. Two pesticides were detected in the wastewater-dominated reach, and five to six pesticides were detected in the agricultural region. Four pesticides were detected at the Coal Creek site. One

pesticide was detected in the Nederland WWTP effluent, and one pesticide was detected in the Boulder WWTP effluent.

Some of the pesticides were detected at more than one site. Dichlobenil, a herbicide used to control weeds and grasses in agricultural, residential, and industrial areas and to control tree-root growth in sewers, was detected at four of the seven Boulder Creek sites (table 6.7). It was the only pesticide detected at the Middle Boulder Creek site above Eldora (MBC-ELD). It also was detected in samples from the site just upstream of the Boulder 75th Street WWTP (BC-aWWTP), and the next two downstream sites (BC-75 and BC-aCC). The detection of dichlobenil in the headwaters region might be explained by its use to control tree-root growth near cabins and homes.

Diazinon, an insecticide used in residential areas and gardens to control insects, was detected at four sites in the wastewater-dominated reach and agricultural regions of Boulder Creek. In contrast to other urban watersheds (Hoffman and others, 2000), diazinon was not found in the urban corridor of Boulder Creek. Parathion-methyl, another organophosphate insecticide, also was detected at three of the same sites in the wastewater and agricultural reach of Boulder Creek. However, this insecticide is only registered for agricultural use in the basin (table 6.1).

Some of the pesticides were found at only one site (table 6.7), mainly in the agricultural reach of Boulder Creek. These include the herbicide picloram and the insecticide lindane (also known as *gamma*-HCH), which were found at the Boulder Creek site upstream of Coal Creek (BC-aCC). Picloram is not used in agriculture in the region, but is sold in garden-supply stores in the region for home use. It was not found in the South Platte urban pesticide samples (Kimbrough and Litke, 1998), although it was one of the pesticides with highest percentage detections in surface water in mixed agriculture and urban land use (Dennehy and others, 1995). Lindane is not used in agriculture in the region, but might be

Table 6.6. Detection frequency and maximum concentration of pesticides detected in June and October 2000 and comparison to human-health and aquatic-life criteria

[Samples from seven mainstem sites and three inflow sites; four threshold concentrations are summarized: all detections, greater than (>) 0.01 micrograms per liter (µg/L), >0.05 µg/L, and >0.1 µg/L; MCL, maximum contaminant level for drinking water; -, no criterion established; HAL, human health advisory level for drinking water; CAN, Canadian aquatic life criterion; IJC, International Joint Commission; USEPA, U.S. Environmental Protection Agency; source of criteria, Larson and others, 1999; concentrations in **bold** are greater than human-health or aquatic-life criteria]

Pesticide	Number of samples	Percent of samples				Maximum concentration (µg/L)	Human-health criteria (source) (µg/L)	Aquatic-life criteria (source) (µg/L)
		All	>0.01 µg/L	>0.05 µg/L	>0.1 µg/L			
Herbicides								
Atrazine	20	30	5	0	0	0.017	3 (MCL)	2 (CAN)
Desethylatrazine	20	25	5	0	0	0.011	-	-
Metolachlor	20	10	0	0	0	0.008	70 (HAL)	8 (CAN)
Prometon	20	35	30	0	0	0.017	100 (HAL)	-
Dichlobenil	20	25	25	15	15	8.969	-	-
Picloram	20	5	5	0	0	0.042	-	-
Insecticides								
Carbaryl	20	15	10	5	0	0.092	700 (MCL)	-
Diazinon	20	35	20	10	5	0.107	0.6 (HAL)	0.08 (IJC)
Lindane	20	5	5	0	0	0.031	0.02 (MCL)	0.08 (USEPA)
Malathion	20	5	5	0	0	0.020	200(HAL)	0.1 (USEPA)
Parathion-methyl	20	15	15	15	5	0.126	2 (HAL)	-

Table 6.7. Spatial distribution of pesticide detections greater than 0.01 µg/L in Boulder Creek samples in June and October 2000

[Site locations are shown in fig. 6.1; 1 indicates detection in either June or October, 2000; 2 indicates detections in both June and October 2000]

Pesticide	Mainstem sites (in downstream order)							Inflow sites (in downstream order)			Number of sites where pesticide was found
	MBC-ELD	BC-CAN	BC-30	BC-aWWTP	BC-75	BC-aCC	BC-aSV	NED-EFF	BLD-EFF	CC	
Herbicide											
Dichlobenil	1			1	1	2					4
Prometon						1	1		2	2	4
Atrazine							1				1
Desethylatrazine							1				1
Picloram						1					1
Insecticide											
Diazinon					1	1	1			1	4
Parathion-methyl						1	1			1	3
Carbaryl										2	1
Lindane						1					1
Malathion								1			1
Number of pesticides detected at site	1	0	0	1	2	6	5	1	1	4	

related to non-agricultural use on treatment of timber or use on pets. The insecticide malathion, although used in agriculture in the basin (table 6.1), was only found in the effluent from the Nederland WWTP (NED-EFF), in the mountain corridor. This pesticide also was found in the urban sites in the South Platte River Basin (Kimbrough and Litke, 1998) and in the NAWQA national pesticide study (Larson and others, 1999).

The spatial and temporal distributions of the more commonly detected pesticides are shown in figures 6.2 to 6.5. Nondetections are plotted with open symbols. The LRLs were different for the two sampling times, so the nondetections are plotted at different concentrations. The names of the mainstem sites are listed along the top of the plots, and the names of the tributaries are listed next to the data points. Note that figures 6.2 and 6.3 have arithmetic concentration scales while figures 6.4 and 6.5 have log scales.

Seasonal Variations

There were seasonal differences in the detection frequency and distribution of pesticides in Boulder Creek samples. During high-flow conditions in June, three herbicides and four insecticides were found (tables 6.3 and 6.4). During low-flow conditions in October, four herbicides and three insecticides were found. In June, pesticides were only detected at concentrations greater than 0.01 µg/L in BC-aCC and Boulder Creek upstream of Saint Vrain Creek (BC-aSV) and in inflows. The herbicide picloram (table 6.4) and insecticides parathion-methyl and malathion (fig. 6.4) were only found in June. In October, the herbicide dichlobenil was found in samples from MBC-ELD, BC-aWWTP, BC-75 and BC-aCC (fig. 6.5). It was not found in any of the inflows. Other herbicides used in agriculture, including atrazine and its degradate desethylatrazine, and metolachlor, were found only in October (fig. 6.2 and 6.3). These herbicides are probably transported to surface water through infiltration of ground water,

because higher concentrations of the herbicides are typically found in spring storm runoff (Larson and others, 1999). The presence of desethylatrazine at concentrations comparable to atrazine (fig. 6.2) also suggests ground water rather than overland flow transport (Kimbrough and Litke, 1998). Dichlobenil, carbaryl, and prometon were found at some sites during both sampling times.

Pesticide Concentrations

Concentrations of herbicides generally were less than 0.02 µg/L, while the insecticides diazinon and methyl parathion were found in concentrations ranging from 0.05 to 0.126 µg/L (tables 6.3 and 6.4). With the exception of dichlobenil, concentrations of herbicides were less than 0.01 µg/L, whereas diazinon ranged from 0.02 to 0.09 µg/L, and lindane was 0.03 µg/L.

Dichlobenil was the pesticide identified at the highest concentration, up to 9 µg/L, and had the highest frequency of detections greater than 0.1 µg/L (15 percent). Dichlobenil concentrations increased from 0.04 to 2.49 µg/L from BC-aWWTP to BC-75, although no dichlobenil was detected in the Boulder 75th Street WWTP effluent (BLD-EFF), which enters the creek 500 m upstream of BC-75. However, the effluent was sampled about a week after the creek samples were collected.

Concentrations of individual pesticides found in the surface-water samples generally were lower than human-health and aquatic-life criteria (table 6.6). The aquatic-life criteria for diazinon was exceeded in October in Boulder Creek above Coal Creek. At the same site the human-health advisory level for drinking water was exceeded for lindane (*gamma*-HCH).

Inflow Concentrations

Effluent from wastewater treatment plants contributed few pesticides, and at concentrations less than 0.05 µg/L. Malathion and carbaryl were

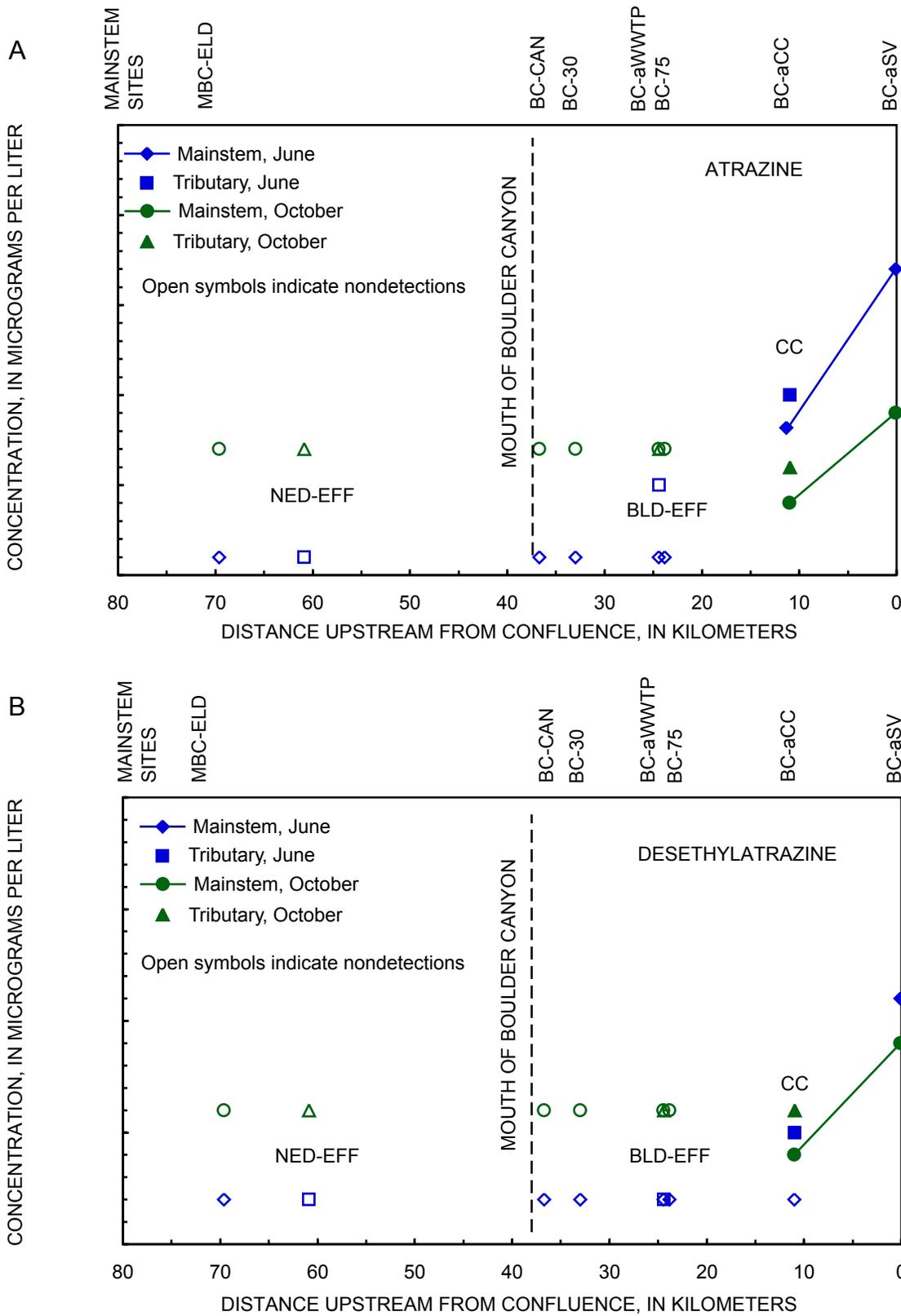


Figure 6.2. Graph showing downstream variation in concentrations of (A) atrazine and (B) desethylatrazine for Boulder Creek and its inflows.

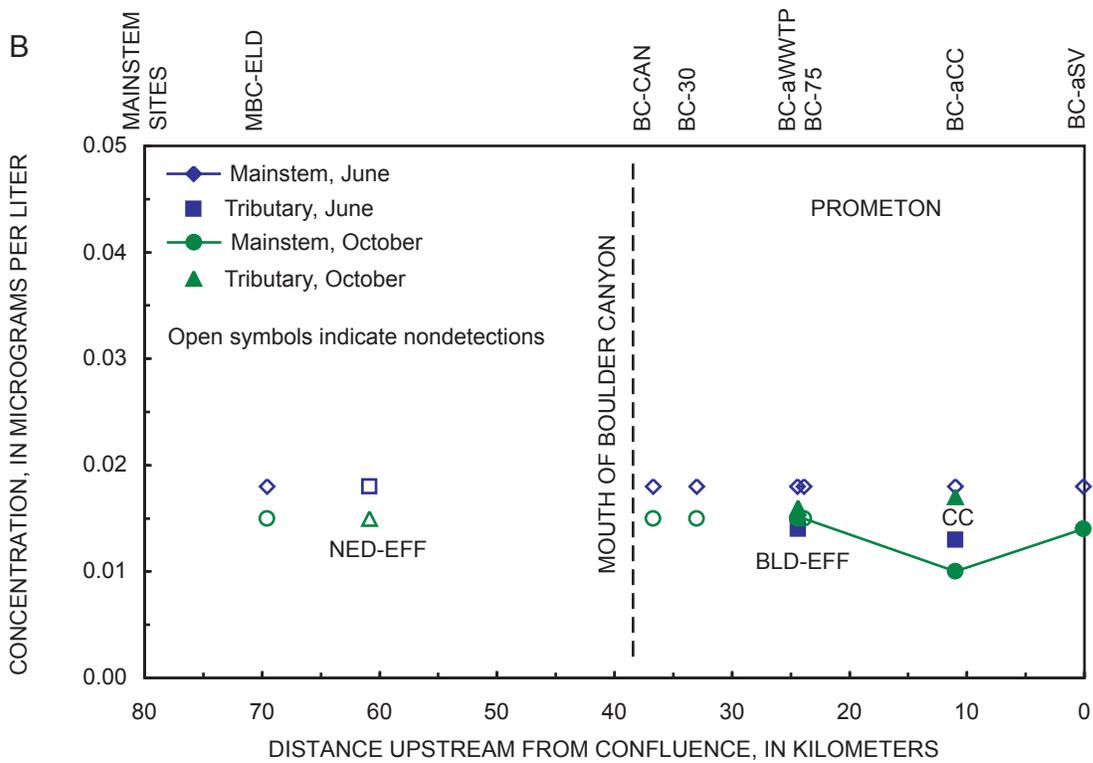
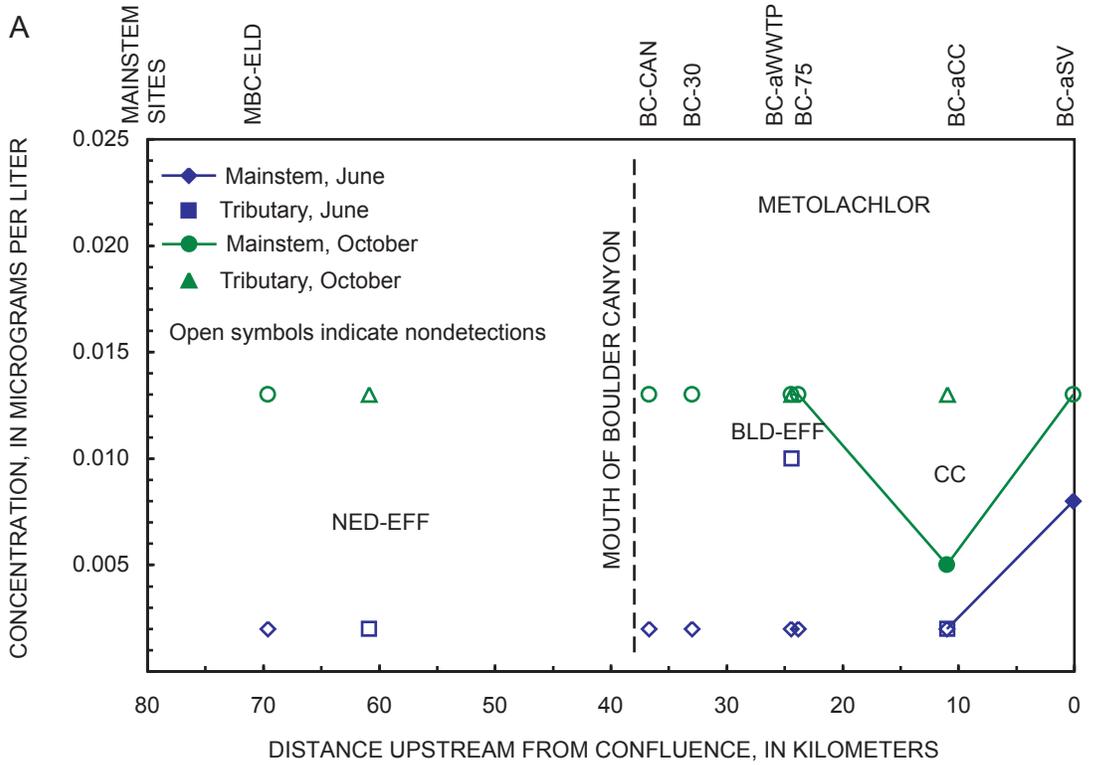


Figure 6.3. Graph showing downstream variation in concentrations of (A) metolachlor and (B) prometon for Boulder Creek and its inflows.

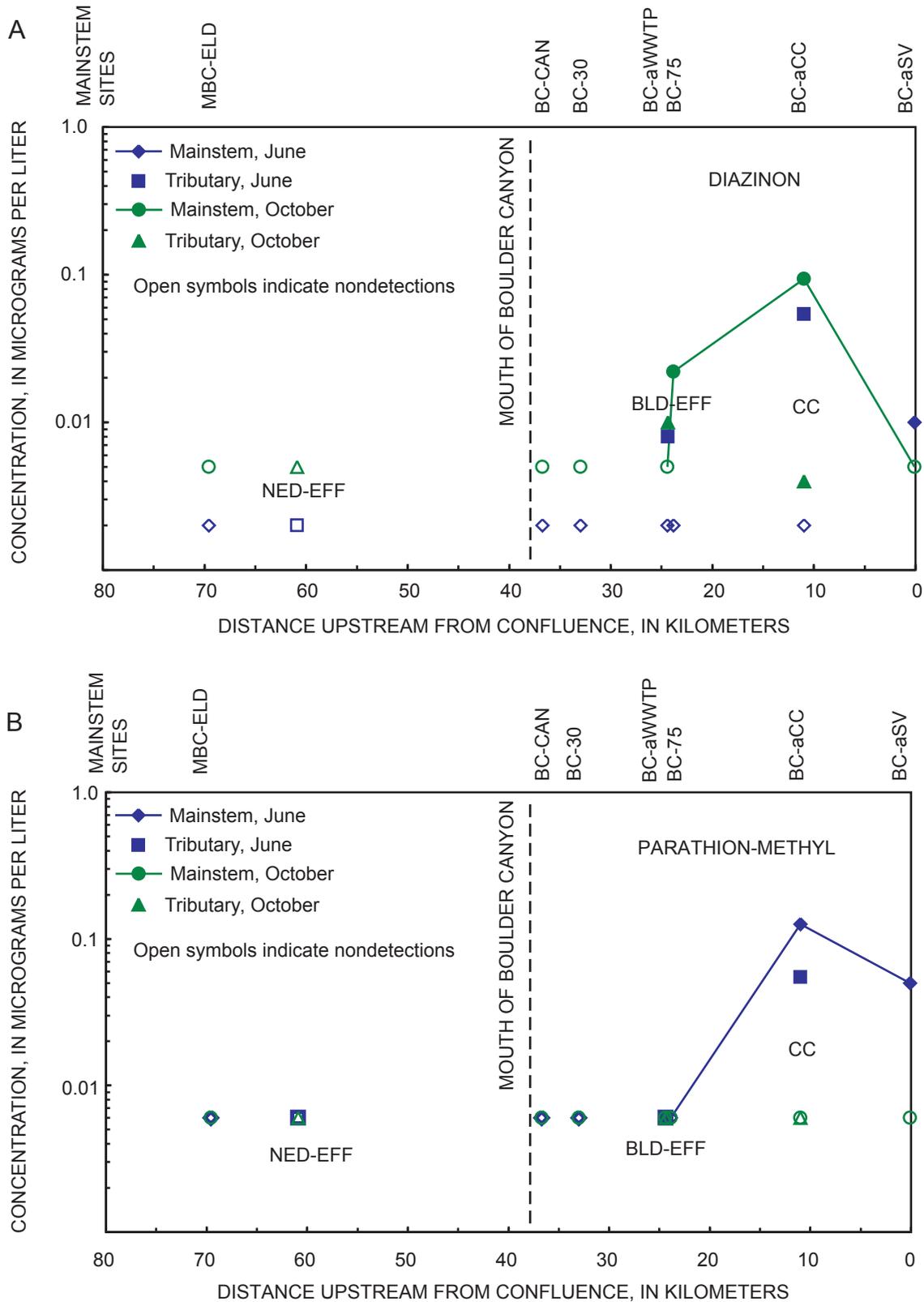


Figure 6.4. Graph showing downstream variation in concentrations of (A) diazinon and (B) parathion-methyl for Boulder Creek and its inflows.

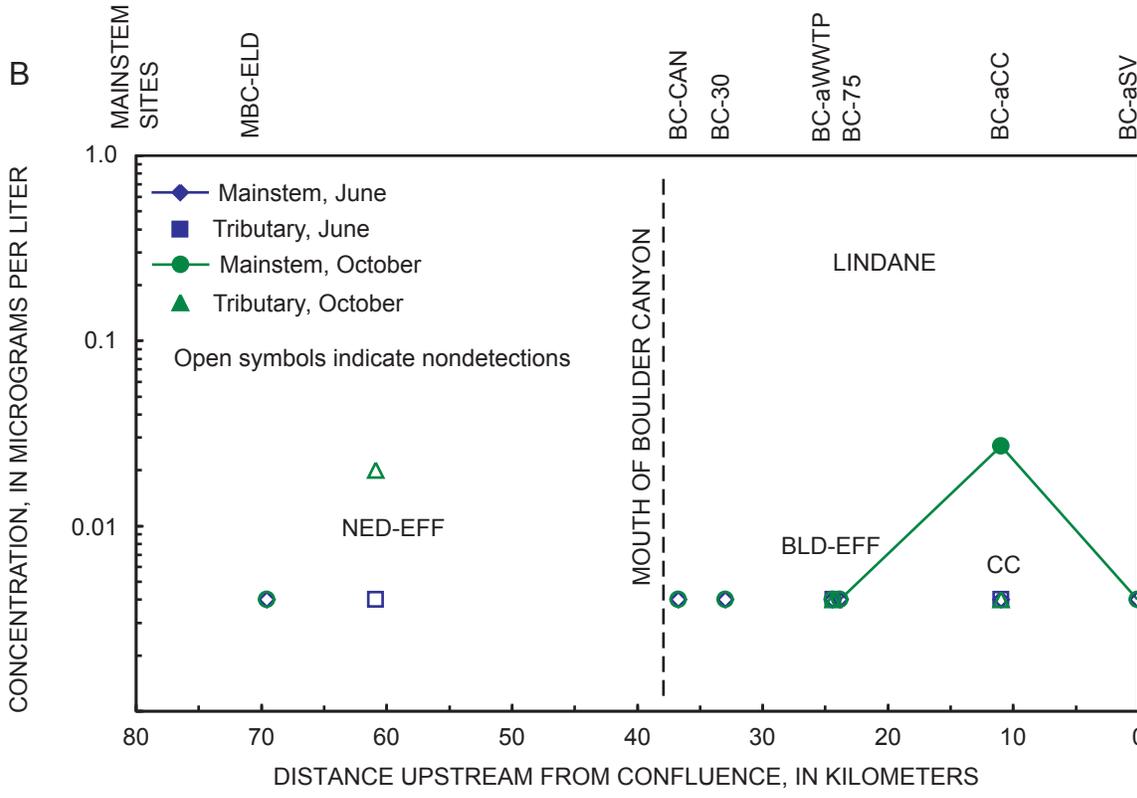
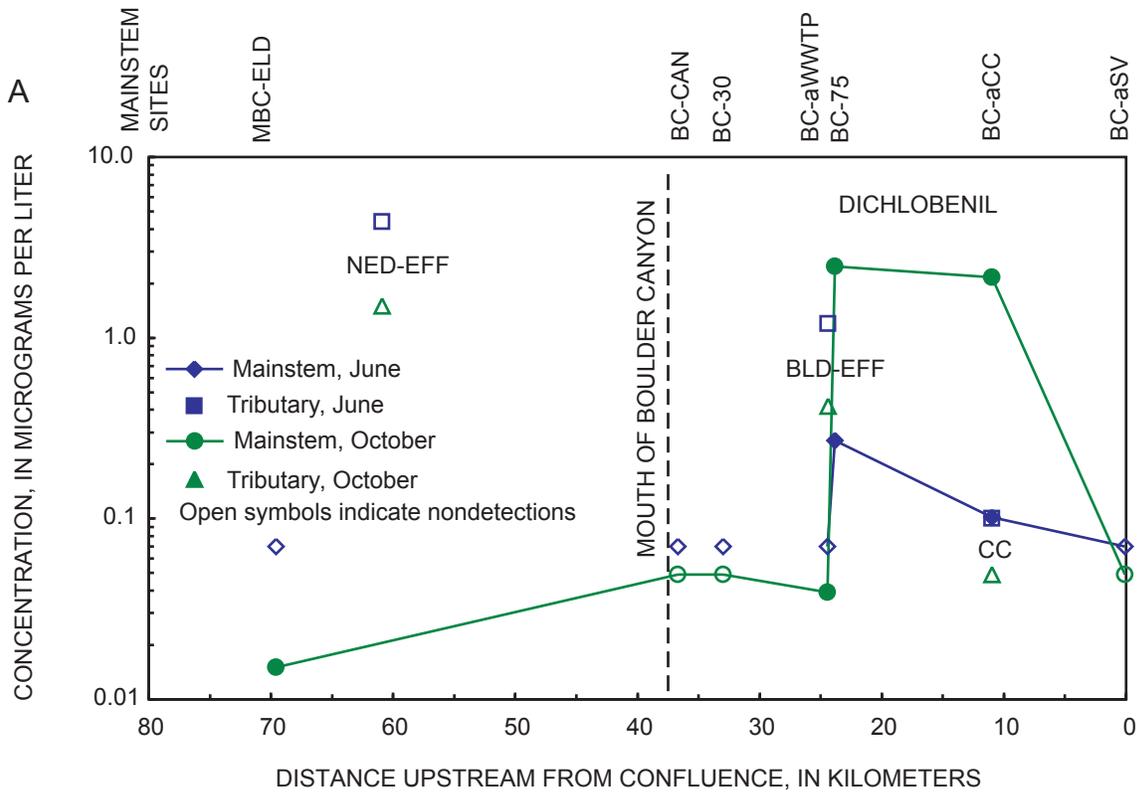


Figure 6.5. Graph showing downstream variation in concentrations of (A) dichlobenil and (B) lindane for Boulder Creek and its inflows.

the only pesticides detected in effluent from the Nederland WWTP (NED-EFF; table 6.3). Neither of these pesticides was detected in any of the downstream Boulder Creek samples. Prometon and diazinon were the only pesticides found in effluent from the Boulder 75th Street WWTP (BLD-EFF), and were found in June and October. Effluent from the Boulder 75th Street WWTP is treated using a trickling filter/solids contact and nitrification process (Murphy and others, 2003). It is noteworthy that low concentrations of these pesticides persisted after the treatment process. These pesticides also were frequently detected in sites downstream from the WWTP, at comparable concentrations.

Up to six pesticides or pesticide degradates were detected in Coal Creek during June and October; four pesticides were found at concentrations greater than 0.1 µg/L. The herbicides atrazine, desethylatrazine, and prometon and the insecticides diazinon and carbaryl were present during June and October. Parathion-methyl also was present in June.

Pesticide Presence in Relation to Estimated Application

Estimates of pesticides used on crops in Boulder County in 1997 are listed in table 6.1. Although the Boulder Creek Watershed only contains about half of the agricultural land use in Boulder County, the pesticide-use data provides an estimate of the relative amounts of the different pesticides used in agriculture in the basin. About 7890 kilograms of pesticides (active ingredient) are applied annually to agricultural land in Boulder County. The most commonly used pesticides are the herbicides atrazine, 2,4-D, dicamba, metolachlor, and glyphosate, and the insecticides terbufos, carbofuran, and chlorpyrifos. There was little correlation between pesticides found in Boulder Creek and estimated agricultural pesticide use. Atrazine, metolachlor, and parathion-methyl are among the top ten most abundantly used pesticides in the region and were detected in Boulder Creek, but not as frequently

as other pesticides. None of the other commonly used pesticides were detected. This might be explained by differences in actual pesticide use in the Boulder Creek Watershed and County-wide estimates, as well as differences in time of application, persistence, and mobility of the pesticides.

The estimates in table 6.1 are for agricultural use only, and do not include pesticides used in the watershed for nonagricultural purposes, including use by commercial applicators and homeowners in urban areas. Quantitative pesticide-use data are not available for Boulder Creek non-agricultural uses. Informal surveys of pesticides used by commercial lawn applicators and available at garden stores in Denver found the herbicides glyphosate, trifluralin, and 2,4-D and the insecticides carbaryl, chlorpyrifos, and diazinon (Kimbrough and Litke, 1998). Diazinon was detected in Boulder Creek, while diazinon and carbaryl were detected in Coal Creek.

Comparisons of pesticides in watersheds with high urban land use are made to population density because pesticide-use data are not available for urban land use as in the case of agricultural land use (Hoffman and others, 2000). For the Boulder Creek Watershed, the number of pesticides found and detection frequency were compared with population density in the sub-watersheds (table 6.8). Similar information is given for the nearby Cherry Creek Watershed, which was studied during 1993-94 (Kimbrough and Litke, 1998). Population density and land-use estimates for the Boulder city and Cherry Creek sub-watersheds were comparable. However, only 2 pesticides were found in Boulder Creek, while 25 pesticides were found in Cherry Creek. In addition, pesticide detection frequency was 8 percent in Cherry Creek samples, compared to less than 1 percent in Boulder Creek city sub-watershed. Part of this difference might be caused by the greater number of samples (18) and length (2 yrs) of the Cherry Creek study compared to the snapshot study of Boulder Creek. In addition, the Cherry Creek study included storm-runoff samples, where pesticide detections were more

Table 6.8. Number of pesticides found, detection frequency, and population density in Boulder Creek and Cherry Creek watersheds

[Population from U.S. Census Bureau, 2001; Land use in Boulder Creek Watershed based on aerial photographs from 1989-1994 (Kinner, 2003); person/km², persons per square kilometer; kilometer; km², square kilometer; %, percent; Agr., agricultural; number of analyses, number of individual pesticides in each method multiplied by number of sites multiplied by number of events sampled; H, number of herbicides found; I, number of insecticides found; MDL, method detection level; >, greater than; <, less than]

Watershed	2000 population	2000 population density (person/km ²)	Area (km ²)	Urban land use (%)	Agr. land use (%)	Number of analyses	H	I	Number of detections greater than MDL	Detection frequency (%)
Boulder city ¹	94,673	1563	60	>90	0	688	1	1	2	0.3
Cherry Creek, Denver ²	111,912	1830	61	96	0	1457	16	9	125	8.5
Lower Boulder Creek ³	114,021	426	269	16	30	860	5	3	9	1
Coal Creek	79,364	529	208	10-20	<28	172	3	3	8	5

¹ Includes four mainstem sites- BC-CAN, BC-30, BC-aWWTP, and BC-75

² Cherry Creek data from Kimbrough and Litke (1998); includes 1990 population data.

³ Lower Boulder Creek above Coal Creek; includes five mainstem sites- BC-CAN, BC-30, BC-aWWTP, BC-75, and BC-aCC.

frequent than for nonstorm samples. Other nonhydrologic factors include local pesticide-use practices within the basin. The city of Boulder has an Integrated Pest Management program that includes a pesticide notification system intended to minimize excessive use of urban pesticides (City of Boulder, 2003). Additional sampling of the Boulder Creek watershed during storm runoff might provide more information about the importance of hydrologic and pesticide-use practices in relation to pesticides in streams.

Similar comparisons can be made for the Coal Creek and Lower Boulder Creek sub-watersheds, which have comparable population density and mixed urban and agricultural land use (table 6.8). Eight pesticides were found in the Lower Boulder Creek sub-watershed and 6 pesticides were found in Coal Creek. Atrazine, desethylatrazine, diazinon, parathion-methyl, and prometon were found in both watersheds, while dichlobenil, lindane, and metolachlor were found only in Lower Boulder Creek, and carbaryl was found only in Coal Creek. The number of detections in Coal Creek was comparable to Lower Boulder Creek, even though one site was sampled in Coal Creek compared to five sites in Lower Boulder Creek. Carbaryl and diazinon are used to control insects in turfgrasses and gardens in urban areas, and also were the most frequently detected insecticides in the national study of urban pesticides (Hoffman and others, 2000).

SUMMARY

Pesticide data were collected at surface-water sites from Boulder Creek and selected inflows during June and October, 2000. The purpose of the study was to document the presence and spatial distribution of pesticides in surface water along Boulder Creek during two seasons, spring runoff and fall baseflow, as part of a larger study of the water quality of Boulder Creek. Water samples were collected at six sites along Middle Boulder Creek and Boulder Creek, at the mouth of a major tributary, and from the effluents of two wastewater treatment plants. One of the unique aspects of this study was the use of analytical methods that provide a broader range of pesticides and lower detection levels than any previous studies in the Boulder Creek Watershed.

The main crops grown in the agricultural areas in the eastern downstream part of the watershed are corn, wheat, barley and alfalfa. About 7890 kilograms of pesticides (active ingredient) are applied annually to agricultural land in Boulder County. The most commonly used pesticides are the herbicides 2,4-D, atrazine, dicamba, glyphosate, and metolachlor, and the insecticides carbofuran, chlorpyrifos, and terbufos.

During sampling in 2000, 11 of the 84 pesticides determined in the study were found at one or more sites in Boulder Creek or the inflows.

Pesticides were detected mainly in the eastern (downstream) part of the watershed, and included pesticides used on agricultural and urban land. Pesticides were detected in both June and October, with more pesticides detected in October. The most frequently detected pesticide was diazinon, which was found at three Boulder Creek sites and two inflows. Dichlobenil was the pesticide found at highest concentration, up to 9 µg/L. Atrazine, metolachlor, and parathion-methyl, used mainly in corn production, were found in Boulder Creek, but none of the other pesticides commonly used in agriculture were detected.

REFERENCES CITED

- City of Boulder, 2003, Pesticide use— Chapter 10, title 6 *in* Boulder Revised Code, 1981: accessed June 23, 2003, at <http://www.ci.boulder.co.us/cao/brc/6-10.html>
- Dennehy, K.F., Litke, D.W., McMahon, P.B., Heiny, J.S., and Tate, C.M., 1995, Water-quality assessment of the South Platte River Basin Colorado, Nebraska, and Wyoming— Analysis of available nutrient, suspended sediment, and pesticide data, water years 1980-92: U.S. Geological Survey Water-Resources Investigations Report 94-4095, 145 p.
- Hoffman, R.S., Capel, P.D., and Larson, S.J., 2000, Comparison of pesticides in eight US urban streams: *Environmental Toxicology and Chemistry*, v. 19, no. 9, p. 2249-2258.
- Kimbrough, R.A. and Litke, D.W., 1998, Pesticides in surface water in agricultural and urban areas of the South Platte River Basin, from Denver, Colorado, to North Platte, Nebraska, 1993-94: U.S. Geological Survey Water-Resources Investigations Report 97-4230, 66 p.
- Kinner, D.A., 2003, Delineation and characterization of the Boulder Creek Watershed and its sub-watersheds— Chapter 2 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 27-39.
- Larson, S.J., Capel, P.D., and Gilliom, R.J., 1999, Pesticides in streams of the United States— Initial results from the National Water-Quality Assessment Program: U.S. Geological Survey Water-Resources Investigations Report 98-4222, 99 p. [Available at <http://water.wr.usgs.gov/pnsp/rep/wrir984222/>]
- Murphy, S.F., Barber, L.B., Verplanck, P.L., and Kinner, D.A., 2003, Environmental setting and hydrology of the Boulder Creek Watershed— Chapter 1 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 5-26.
- National Center for Food and Agricultural Policy, 2001, Pesticide use in crop production by crop and state— Colorado: accessed August. 24, 2001, at <http://www.ncfap.org/pesticidedb.htm>
- Sandstrom, M.W., 1995, Filtration of water-sediment samples for the determination of organic compounds: U.S. Geological Survey Water-Resources Investigations Report 95-4105, 13 p.
- Thelin, G.P. and Gianessi, L.P., 2000, Method for estimating pesticide use for county areas of the conterminous United States: U.S. Geological Survey Open-File Report 00-250, 62 p.
- U.S. Census Bureau, 2001, Census 2001 Summary File 1. [Available from U.S. Census Bureau, Washington, D.C. 20233, and on the internet at <http://www.census.gov/>]
- U.S. Department of Agriculture, 2000, 1997 census of agriculture— Colorado: U.S. Department of Agriculture, National Agricultural Statistics Service, accessed December 3, 2000 at <http://www.nass.usda.gov/co>
- Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96-216, 49 p.
- Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., 1999, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations Book 9, A1, variously paged.
- Winfield, T.W., Bashe, W.J., and Baker, T.V., 1990, Method 547— Determination of glyphosate in drinking water by direct-aqueous-injection HPLC, post-column derivatization, and fluorescence detection, *in* Methods for the determination of organic compounds in drinking water, supplement I: Cincinnati, Ohio, Office of Research and Development, U.S. Environmental Protection Agency, EPA/600/4-90/020, 16 p.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory— Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 p.

Chapter 7 - Quantitative Mineralogy and Particle-Size Distribution of Bed Sediments in the Boulder Creek Watershed

By Daniel E. Kile and Dennis D. Eberl

Abstract

Twenty-four bed-sediment samples were collected from Boulder Creek and several of its tributaries to assess particle-size distribution and mineralogical composition. Changes in particle-size distribution were correlated with stream gradient, and also with stream mixing. Samples were analyzed by X-ray diffraction, and their quantitative mineralogy was determined with a recently-developed computer program. Mineralogical changes are evidenced in post-confluence stream mixing, and correlated with the underlying rock type of the surrounding drainage and stream channel.

INTRODUCTION

This study was undertaken to assess the mineralogy of stream bed sediments in the Boulder Creek Watershed. A knowledge of the mineralogical composition of these sediments can permit an assessment of: (1) a relation between mineralogy and sediment size fraction, (2) mineralogical differences in sediment samples that originate from different geological provinces, (3) the influence of tributary input on mineralogy, (4) downstream trends of the sediment mineralogy, and (5) the possible effect of mineralogy on water chemistry.

Determination of quantitative mineralogy by X-ray diffraction (XRD) methods has been problematic because a given mineral can generate variable peak intensities as measured by the XRD detector. This variation is due in part to compositional variability of the minerals (such as can occur within a mineral solid solution series) or by variable grain orientation (e.g., as controlled by cleavage and sample preparation);

additional variation can also be caused by sample heterogeneity.

New methods for sample preparation have largely eliminated signal variability caused by non-randomness of the sample mounts, while revised protocols for internal standard addition, external standards preparation, and a recently-developed computer program that provides a detailed fitting of specific 2θ regions have facilitated an accurate quantification of mineralogical components of heterogeneous samples.

METHODS

Sample Collection

Bed sediment samples were collected at 17 sites in June 2000 (high flow), and at 6 sites in October 2000 (low flow; fig. 7.1, tables 7.1 and 7.2). Site descriptions are provided in Murphy and others (2003). From 0.5 to 1 kg of sample was collected from each site near the stream bank in areas where finer-grained particle sizes were more likely to predominate (in eddies, behind rocks, etc.) and stored in plastic Ziplock™ bags. At the BC-aSV site, two samples from different locations were collected.

Sample Preparation

Samples were dried at 85°C for 18 hours and sieved using a Rototap shaker for 12 to 15 minutes. Eight fractions were collected, using mesh sizes of 2.5, 5, 10, 18, 35, 60, 120, and 230 (corresponding to 8, 4, 2, 1, 0.5, 0.25, 0.125, and 0.063 mm respectively). Weights for each size fraction were recorded (tables 7.1 and 7.2).

Samples from three particle sizes, <0.063, 0.063-0.125, and 0.125-0.250 mm, were analyzed

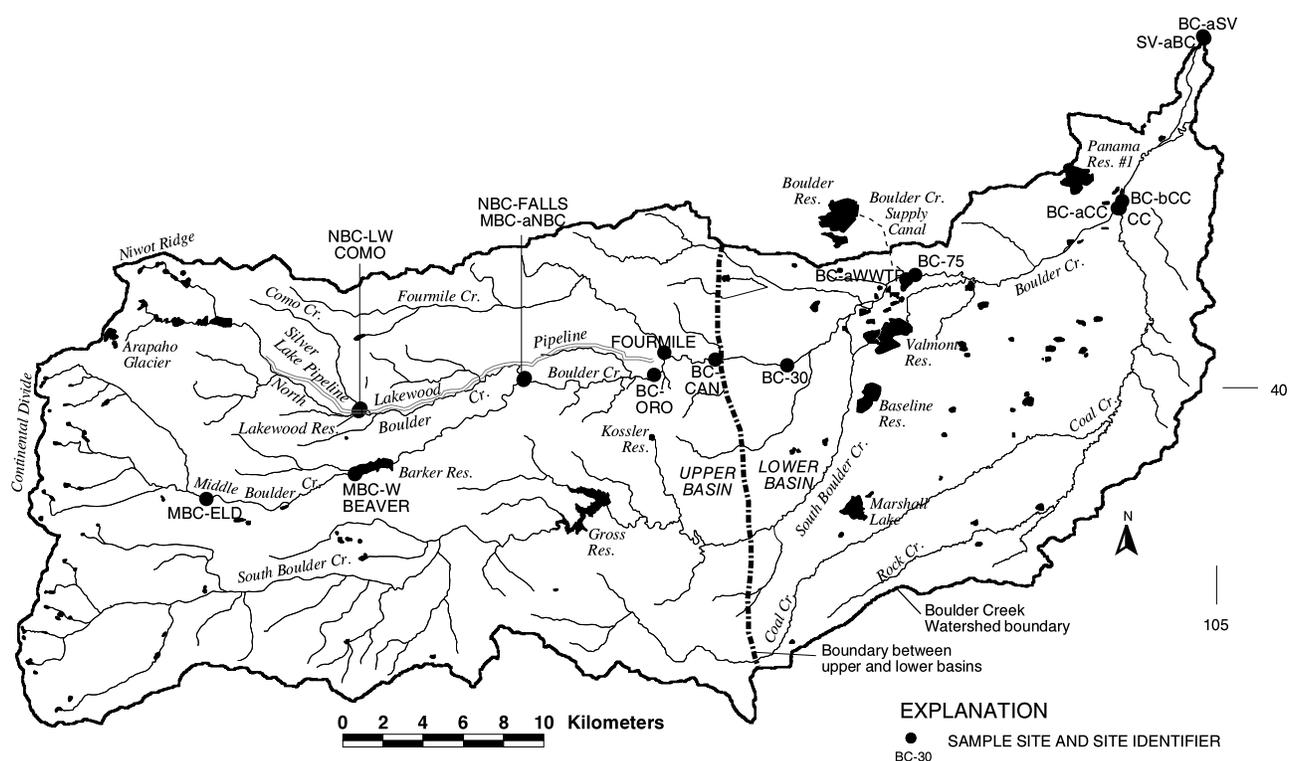


Figure 7.1. Map showing Boulder Creek Watershed and sampling sites.

with XRD, as it was presumed that these sizes best represent the clay-size minerals and overall mineralogy (including accessory minerals) of the sediment (Barber and others, 1992; Barber, 1994).

Samples were prepared for quantitative XRD analysis by weighing 3.0 g sediment and adding to it 0.333 g zinc oxide (U.S.P., J.T. Baker), which constituted a 10 weight percent internal standard for quantification. This mixture was ground with 4 mL methanol for 5 minutes in a McCrone Micronizing Mill using cylindrical corundum elements; the grinding step reduces particle size to less than 20 μm , and provides a narrow particle-size distribution, which maximizes random grain orientation. The slurry was oven-dried at 80°C, sieved through a 0.38-mm sieve (McCrone), and then side-packed in an XRD holder using a frosted glass slide (Ward's Natural Science) on the open side of the holder during packing to assure random orientation.

Qualitative analyses for smectite, vermiculite and chlorite were done from oriented preparations using the <63 μm sediment fractions. A sample slurry (~80 mg sample in 2 mL distilled water) was prepared from each sample, overlaid on glass slides, and air dried under a heat lamp for routine scanning. These preparations were subsequently saturated in ethylene glycol (85°C, 18 hours) to verify the presence of smectite, and heated to 250°C to differentiate vermiculite from chlorite.

X-Ray Analysis

Samples were analyzed on a Siemens D-500 diffractometer equipped with a copper radiation source, a graphite monochromator, and a scintillation detector. Quantitative scans were run at 40 kV and 30 mA. Detector slits were set at 1°, with a 2.3° Soller slit between the X-ray tube and the detector. Scans were run from 2 to 65°, with 2 seconds/step and 0.02 degrees per 2 θ step. Qualitative scans were run at 2 to 35°, one

Table 7.1. Sediment particle-size fractionation data, June 2000

[>, greater than; <, less than; bold font indicates that X-ray diffraction was performed on sample. For site descriptions, see Murphy and others, 2003]

Site	Weight (in grams) of fraction within indicated particle-size interval (in millimeters)									Sum
	>8	4-8	2-4	1-2	0.5-1	0.25-0.5	0.125-0.25	0.063-0.125	<0.063	
Middle Boulder Creek/Boulder Creek										
MBC-ELD	26.74	4.25	7.46	37.45	149.89	251.74	49.76	3.29	0.73	531.31
MBC-W	5.27	67.65	94.64	52.33	20.87	43.76	20.00	3.61	0.98	309.11
MBC-aNBC	8.86	8.67	25.67	32.51	48.36	60.56	25.94	10.68	3.38	224.63
BC-ORO	1.00	3.67	45.34	82.73	59.99	51.27	24.97	6.52	1.20	276.69
BC-CAN	2.00	24.90	130.10	157.23	109.25	57.76	10.48	1.10	0.23	493.05
BC-30	3.96	10.69	36.28	62.20	63.10	58.31	30.65	19.52	9.08	293.79
BC-aWWTP	4.14	10.88	16.10	14.77	15.83	18.21	15.55	15.33	18.13	128.94
BC-75	38.14	5.52	3.34	14.69	47.63	66.20	13.25	3.46	1.21	193.44
BC-aCC	54.28	41.28	38.05	22.04	11.91	30.95	21.88	4.60	0.93	225.92
BC-bCC	0.00	0.00	0.00	0.07	0.68	4.21	25.35	53.91	54.70	138.92
BC-aSV #1	8.68	0.00	5.63	45.20	113.10	35.21	1.72	0.28	0.09	209.91
BC-aSV #2	16.54	8.86	8.33	9.83	15.02	21.20	31.10	33.44	14.46	158.78
Tributaries										
NBC-LW	2.37	8.19	19.02	35.67	48.14	38.76	24.38	11.47	7.73	195.73
NBC-FALLS	6.24	4.76	11.28	27.70	65.68	109.24	46.55	14.26	6.37	292.08
BEAVER	0.00	3.61	1.90	6.91	39.34	93.16	40.75	11.38	5.52	202.57
FOURMILE	0.00	9.92	93.33	163.83	157.80	93.02	18.54	2.69	2.26	541.39
CC	0.00	1.56	1.47	6.34	20.97	17.68	29.57	79.97	93.12	250.68
SV-aBC	14.53	0.00	4.94	9.04	15.17	78.80	135.59	84.84	26.97	369.88
Site	Percentage within indicated particle-size interval (in millimeters)									Sum
	>8	4-8	2-4	1-2	0.5-1	0.25-0.5	0.125-0.25	0.063-0.125	< 0.063	
Middle Boulder Creek/Boulder Creek										
MBC-ELD	5.03	0.80	1.40	7.05	28.21	47.38	9.37	0.62	0.14	100
MBC-W	1.70	21.89	30.62	16.93	6.75	14.16	6.47	1.17	0.32	100
MBC-aNBC	3.94	3.86	11.43	14.47	21.53	26.96	11.55	4.75	1.50	100
BC-ORO	0.36	1.33	16.39	29.90	21.68	18.53	9.02	2.36	0.43	100
BC-CAN	0.41	5.05	26.39	31.89	22.16	11.71	2.13	0.22	0.05	100
BC-30	1.35	3.64	12.35	21.17	21.48	19.85	10.43	6.64	3.09	100
BC-aWWTP	3.21	8.44	12.49	11.45	12.28	14.12	12.06	11.89	14.06	100
BC-75	19.72	2.85	1.73	7.59	24.62	34.22	6.85	1.79	0.63	100
BC-aCC	24.03	18.27	16.84	9.76	5.27	13.70	9.68	2.04	0.41	100
BC-bCC	0.00	0.00	0.00	0.05	0.49	3.03	18.25	38.81	39.38	100
BC-aSV #1	4.14	0.00	2.68	21.53	53.88	16.77	0.82	0.13	0.04	100
BC-aSV #2	10.42	5.58	5.25	6.19	9.46	13.35	19.59	21.06	9.11	100
Tributaries										
NBC-LW	1.21	4.18	9.72	18.22	24.60	19.80	12.46	5.86	3.95	100
NBC-FALLS	2.14	1.63	3.86	9.48	22.49	37.40	15.94	4.88	2.18	100
BEAVER	0.00	1.78	0.94	3.41	19.42	45.99	20.12	5.62	2.72	100
FOURMILE	0.00	1.83	17.24	30.26	29.15	17.18	3.42	0.50	0.42	100
CC	0.00	0.62	0.59	2.53	8.37	7.05	11.80	31.90	37.15	100
SV-aBC	3.93	0.00	1.34	2.44	4.10	21.30	36.66	22.94	7.29	100

Table 7.2. Sediment particle-size fractionation data, October 2000

[>, greater than; <, less than; bold font indicates that X-ray diffraction was performed on sample. For site descriptions, see Murphy and others, 2003]

Site	Weight (in grams) of fraction within indicated particle-size interval (in millimeters)									
	>8	4-8	2-4	1-2	0.5-1	0.25-0.5	0.125-0.25	0.063-0.125	<0.063	Sum
Middle Boulder Creek/Boulder Creek										
MBC-ELD	149.23	82.01	55.49	51.03	49.89	25.55	5.60	1.60	1.11	421.51
MBC-W	42.99	90.91	108.09	80.54	47.41	64.98	30.10	6.00	1.68	472.70
BC-aSV	117.71	21.10	44.57	87.46	130.09	71.89	13.05	2.03	0.53	488.43
Tributaries										
NBC-LW	0.00	1.47	11.47	26.10	56.57	80.17	51.75	19.54	6.72	253.79
COMO	31.49	3.16	1.88	0.78	1.85	31.44	60.78	19.88	8.27	159.53
SV-aBC	150.10	41.14	30.96	33.29	42.90	38.06	14.39	7.71	4.70	363.25
Site	Percentage within indicated particle-size interval (in millimeters)									
	>8	4-8	2-4	1-2	0.5-1	0.25-0.5	0.125-0.25	0.063-0.125	<0.063	Sum
Middle Boulder Creek/Boulder Creek										
MBC-ELD	35.40	19.46	13.16	12.11	11.84	6.06	1.33	0.38	0.26	100
MBC-W	9.09	19.23	22.87	17.04	10.03	13.75	6.37	1.27	0.36	100
BC-aSV	24.10	4.32	9.13	17.91	26.63	14.72	2.67	0.42	0.11	100
Tributaries										
NBC-LW	0.00	0.58	4.52	10.28	22.29	31.59	20.39	7.70	2.65	100
COMO	19.74	1.98	1.18	0.49	1.16	19.71	38.10	12.46	5.18	100
SV-aBC	41.32	11.33	8.52	9.16	11.81	10.48	3.96	2.12	1.29	100

second/step, and 0.1° per 2θ step. Other procedural details are given in Środoń and others (2001). Results were quantified by comparison of the sample XRD patterns against known mineral standards, from which mineral intensity factors (MIFs) were computed using the RockJock computer program (Środoń and others, 2001; Eberl, 2003). Non-clay minerals scanned include the plagioclase feldspars (albite, oligoclase, labradorite), alkali feldspars (e.g., microcline), and iron oxides (magnetite, hematite), in addition to amphibole group minerals, dolomite, and quartz. Clay and mica-group minerals scanned, comprising the phyllosilicates, include phlogopite, $1M_d$ illite + smectite + vermiculite, and $2M_l$ illite; $1M_d$ and $2M_l$ are polytypes that are related to the stacking orientation of the tetrahedral-octahedral-tetrahedral layers of phyllosilicates, which include most of the common illite and muscovite minerals.

RESULTS

Size Fractionation

Size-fractionation data for samples collected in June and October, 2000, are given in tables 7.1 and 7.2 and displayed in figures 7.2 and 7.3. Particle-size classification is adapted from Tickell (1965). Additionally, the particle-size distribution data for all samples have been smoothed using a cubic spline method (R. F. Stallard, U.S. Geological Survey, oral commun., 2001; values for phi taken from Office of Water Data Coordination, 1977) to represent the data as a continuous distribution (figs. 7.4 and 7.5). The “percent per phi interval” (Krumbein and Pettijohn, 1938, p. 76-90) is a measure of the weight-based percent of particles within a given range of mesh sizes. Figure 7.6 presents a comparison of particle-size distributions for bed sediment samples from 5 sites collected in both June and October, 2000.

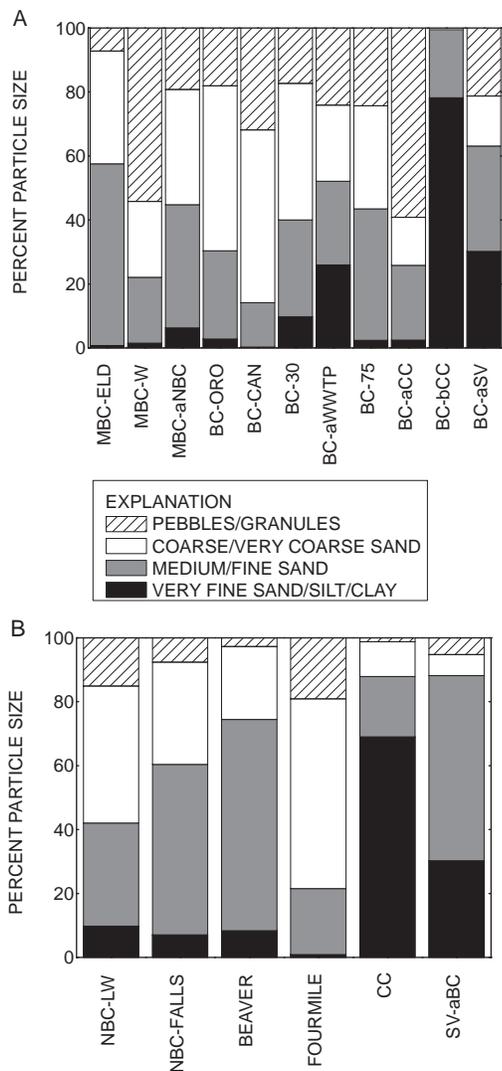


Figure 7.2. Sediment particle-size fractionation data for (A) Middle Boulder Creek/Boulder Creek sampling sites and (B) tributary sampling sites, June 2000.

Several factors can render an assessment of particle-size distribution ambiguous, and conclusions must therefore be regarded with caution. For example, differences in particle-size distributions are highly dependent on the exact depositional environment in the river channel from which the sample was taken. This is clearly evidenced by the two samples collected at site BC-aSV (table 7.1), where the percentages in the respective size fractions differ significantly. Moreover, clay-size minerals are sometimes found in abundance in some of the “non-clay” size fractions. This is likely due to adhesion to grain surfaces, and also to the weathering and

alteration of feldspar minerals that results in the formation of clays as an integral constituent. Despite these uncertainties, some observations of a general nature can nevertheless be made.

There are no significant trends in particle-size distribution (within limits of variability for sample collection) along the course of Boulder Creek for the larger size fractions, whereas there are some definite differences noted (table 7.1, figs. 7.2 and 7.3) in some sediments for the smallest size fractions (<0.063 and 0.063-0.125 mm). The smaller-size fractions constitute a negligible portion of the samples from upper Boulder Creek; in contrast, the sample from Coal Creek is composed predominantly of particles less than 0.125 mm (fig. 7.2). This observation is likely due to minimal clay content in the igneous and metamorphic source rocks in the upper Boulder Creek Watershed, and partly due to a higher stream gradient (and therefore higher flow rates) in the mountainous terrain. Moreover, spline curves for BC-ORO, BC-CAN, and BC-30 (fig. 7.4) show downstream trends of decreasing particle size. Two sediment samples from upper Middle Boulder Creek (MBC-ELD and MBC-W) show a bimodal particle-size distribution,

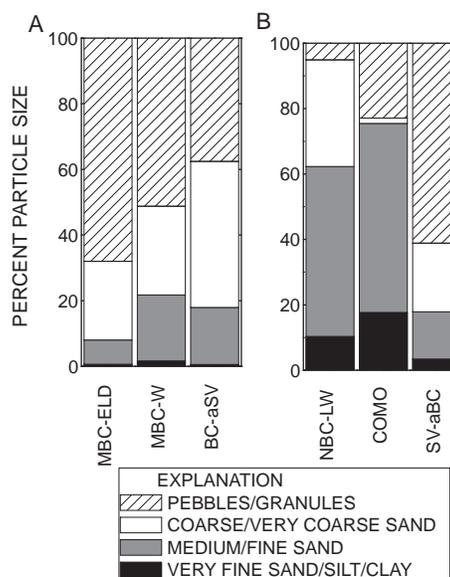


Figure 7.3. Sediment particle-size fractionation data for (A) Middle Boulder Creek/Boulder Creek sampling sites and (B) tributary sampling sites, October 2000.

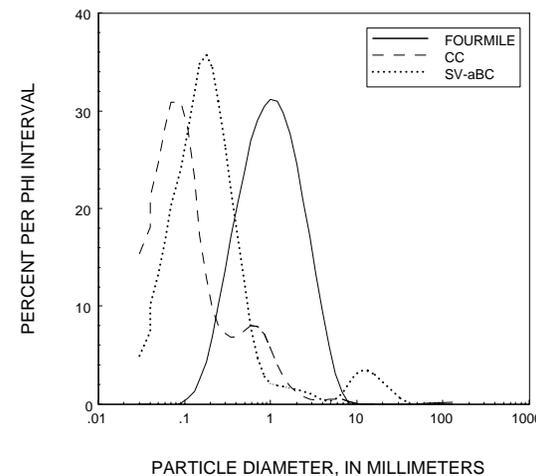
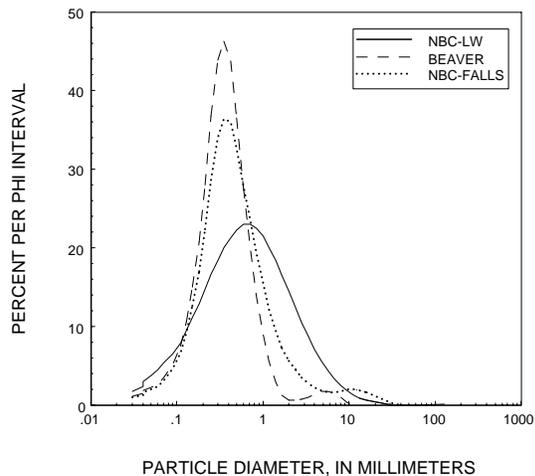
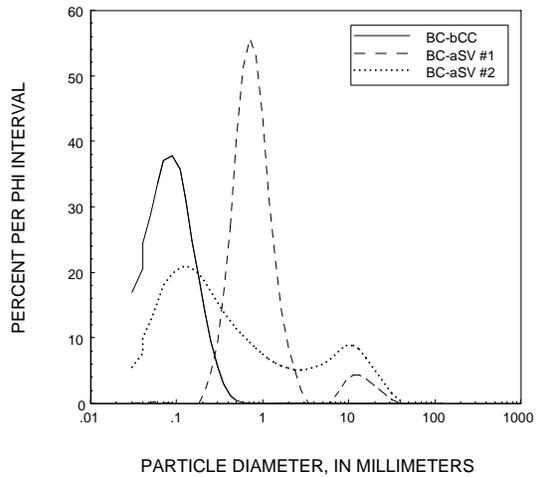
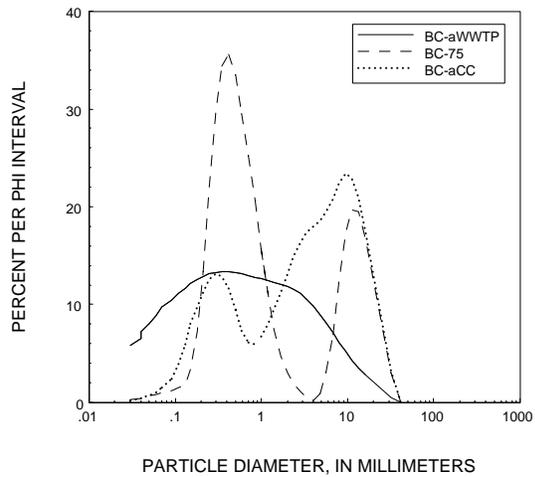
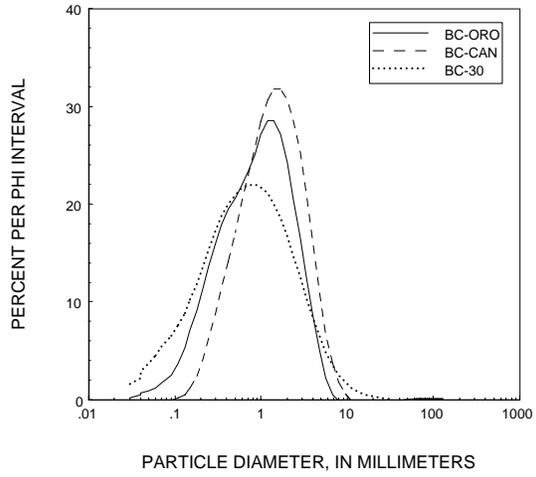
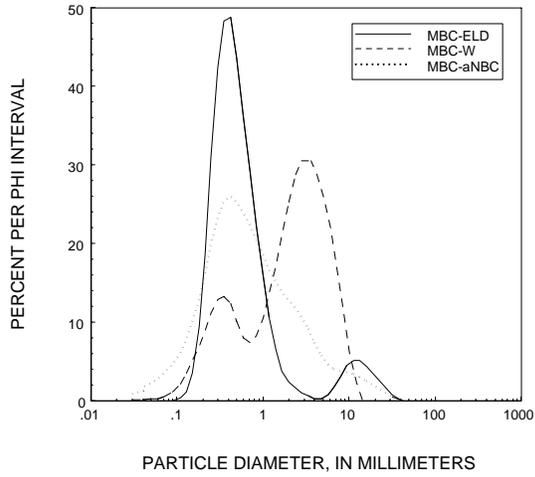


Figure 7.4. Particle-size distributions of bed sediments for Middle Boulder Creek/Boulder Creek and tributaries, June 2000.

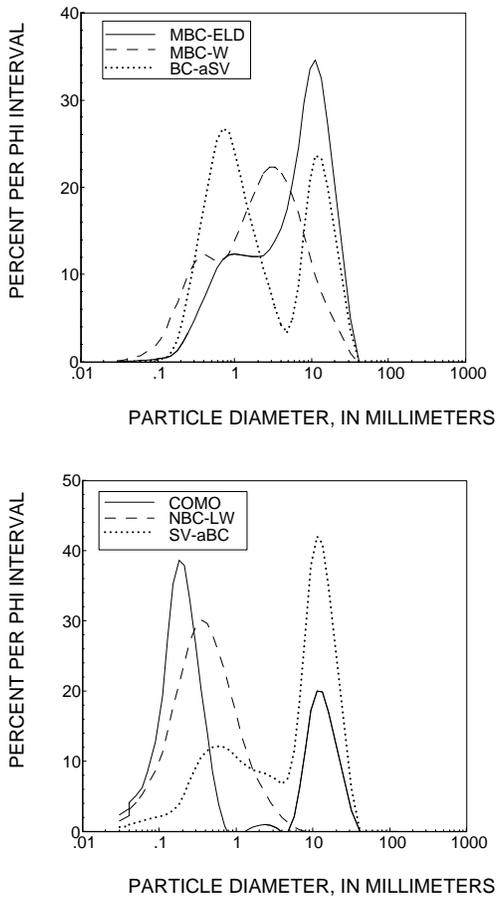


Figure 7.5. Particle-size distributions of bed sediments for Middle Boulder Creek/Boulder Creek and tributaries, October 2000.

whereas a sample collected farther downstream (MBC-aNBC) shows a unimodal distribution (fig. 7.4).

The high silt load carried by Coal Creek is likely a manifestation of its low gradient and its lengthy traverse through sedimentary rocks. Boulder Creek shows comparatively higher levels of the very fine sand and silt (<0.063 and 0.063-0.125 mm) fractions at sites above the Boulder Wastewater Treatment Plant (BC-aWWTP) and below Coal Creek (BC-bCC; fig 7.2). The higher fine particulate load at the BC-aWWTP site is likely a result of its traverse through sedimentary rocks (predominantly the Cretaceous Pierre Shale) following its exit from the foothills at the mouth of Boulder Canyon (Colton, 1978; Trimble and Machette, 1979; Hall and others, 1980;

Bilodeau and others, 1987). In contrast, the very high levels of the smaller size fractions at the BC-bCC site are due to the mixing of Coal Creek and Boulder Creek. Boulder Creek shows a 10-fold increase in fine particulates (<0.25 mm between the samples above and below the Coal Creek confluence (BC-aCC and BC-bCC, respectively). The Boulder Creek samples also show significant differences in mineralogy above and below the confluence with Coal Creek (see below).

There were no distinct trends in particle-size distribution between samples collected in June and October (fig. 7.6). As discussed above, variability in sediment collection may have obscured any differences that might have been present.

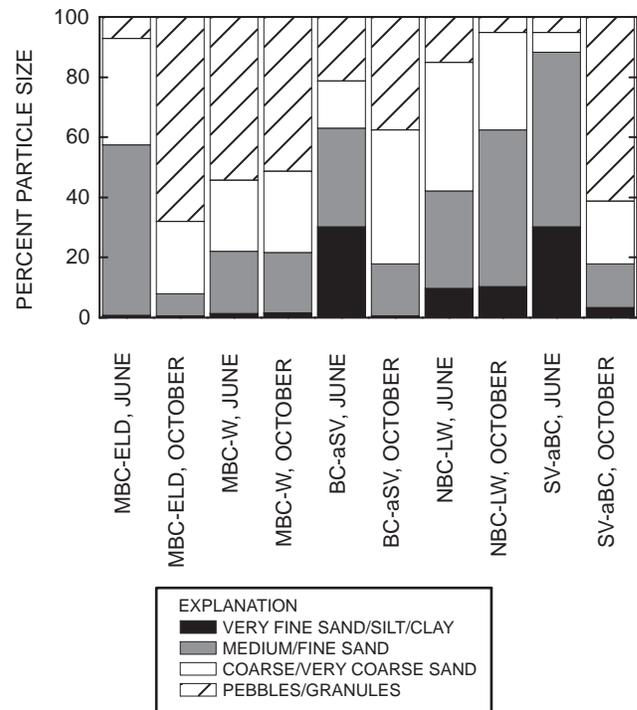


Figure 7.6. Comparison of sediment particle-size fractionation data, June and October 2000.

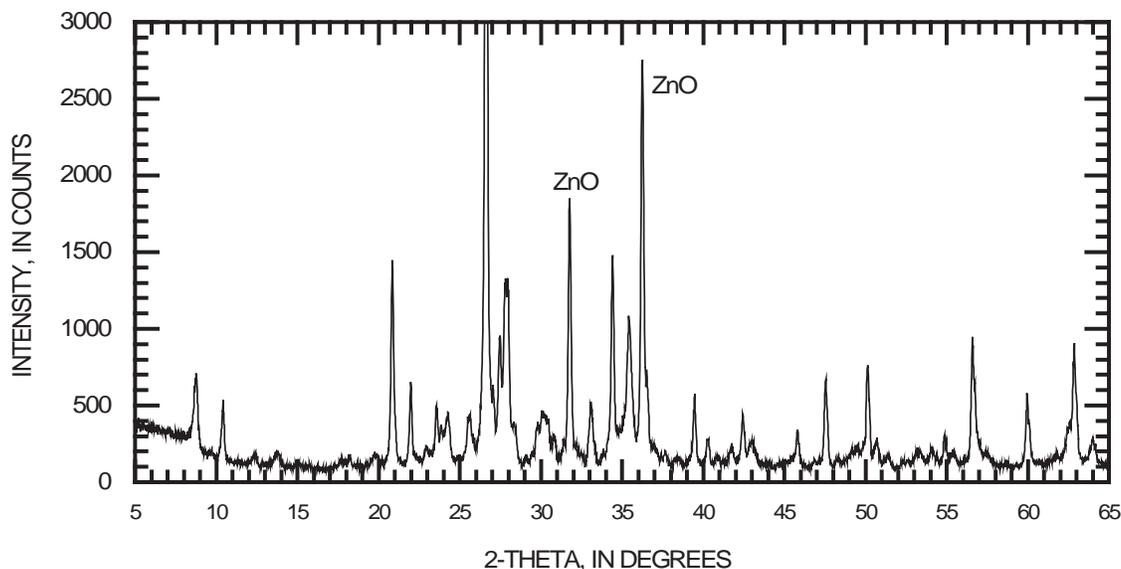


Figure 7.7. X-ray diffraction pattern for 0.063-0.125 mm fraction of sample from site BC-ORO (random mount with zinc oxide [ZnO] internal standard).

Mineralogy

Figure 7.7 shows a representative XRD pattern of a sample in a random mount with the internal zinc oxide standard added. This pattern shows peaks from all the major mineral phases present in the sediment. Several points need to be considered in interpreting XRD data. While analysis by XRD can be very accurate in quantifying major components within a mixture, it is not very good at detecting constituents that are present in trace amounts (less than about 2 percent). Thus, while small amounts of minerals, such as garnet, titanite, and zircon, may be expected to be present in a given sediment (particularly those collected in the upper drainages where Boulder Creek traverses igneous rocks), such minor constituents will not be evident on the XRD pattern. Furthermore, speciation of plagioclase by XRD analysis will not necessarily correspond to a petrologic examination by polarized-light microscopical methods, because XRD will detect the entire compositional range of plagioclase, whereas analysis by polarized-light microscopy speciates only the most sodic member in the plagioclase series (e.g., by using the Michel-Lévy method for determining the extinction angle). The cumulative

percent of the minerals for a given sample will vary on either side of an ideal 100 percent because of experimental error, e.g., the mineral standard for a given species may not be exactly identical to that in the sample, resulting in an error in the corresponding mineral intensity factor or in the integrated intensities that are used to calculate the percent total. Quantitative mineralogy of sediment samples from Middle Boulder Creek, Boulder Creek, Fourmile Creek, Coal Creek, and Saint Vrain Creek is provided in table 7.3 and figure 7.8.

Figure 7.9 shows superimposed XRD patterns for clay minerals (0.063-0.125 mm fraction) from a single sample that was (1) an air-dried oriented preparation, (2) saturated in ethylene glycol, and (3) heated to 250°C. This protocol allows a qualitative assessment of smectite, vermiculite, and chlorite. Treating samples with ethylene glycol will shift the 12- to 14-Å smectite peak to 17 Å, differentiating smectite clays from vermiculite and chlorite, whereas heating the samples to 250°C collapses the vermiculite structure, shifting a peak from 14.5 to 10 Å, thus differentiating vermiculite from chlorite (chlorite spacing remains at 14.5 Å). Smectite was present in all samples. Vermiculite was minimal in Coal Creek, and

Table 7.3. Quantitative mineralogy data for bed sediments collected during June and October, 2000

[All samples were collected in June 2000 except MBC-ELD, which was collected in October 2000]

Mineral	Percentage within the indicated particle-size interval (in millimeters) for the indicated sample																			
	MBC-ELD		BC-ORO		BC-aCC		BC-bCC		BC-aSV		FOURMILE		CC		SV-aBC					
	0.063-0.125-0.125	0.125-0.250	0.063-0.125-0.125	0.125-0.250	0.063-0.125-0.125	0.125-0.250	<0.063	0.063-0.125-0.125	0.125-0.250	<0.063	0.063-0.125-0.125	0.125-0.250	<0.063	0.063-0.125-0.125	0.125-0.250	<0.063	0.063-0.125-0.125			
Non-clay minerals																				
Amphibole	5	5	8	7	4	7	1	1	2	2	2	7	5	7	1	2	1	2	2	1
Microcline	16	17	15	17	13	21	10	13	14	11	13	12	12	12	9	11	13	11	14	19
Albite	6	4	2	5	0	6	5	5	2	5	6	12	7	12	4	2	4	9	8	8
Oligoclase	9	15	12	11	10	13	3	5	10	7	7	8	6	8	4	7	6	5	7	11
Labradorite	9	10	11	12	4	7	3	5	3	5	5	9	7	9	4	4	4	6	6	6
Magnetite	8	5	9	4	10	5	1	1	0	1	1	2	6	2	1	0	1	2	1	1
Hematite	4	1	3	2	5	5	1	1	0	1	1	2	4	2	0	0	1	1	1	0
Dolomite	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	1	0
Quartz	27	39	29	33	42	39	52	58	59	48	56	35	27	35	49	56	59	45	50	47
Total non-clay minerals	85	95	90	91	88	102	76	88	91	79	90	86	74	86	73	83	88	81	89	92
Clay-phylosilicate minerals																				
Phlogopite	6	1	5	5	5	1	4	4	5	4	3	5	9	5	3	5	4	3	2	3
Illite (IM_d)+smectite+vermiculite	0	0	8	2	7	0	21	13	10	17	12	6	6	6	25	23	12	15	6	6
Illite ($2M_1$)	8	5	1	6	2	4	0	2	2	3	3	8	7	8	0	0	2	2	5	5
Total clay minerals	14	6	14	13	14	6	25	18	17	23	18	19	23	19	29	28	18	20	13	14
Total all minerals	99	101	104	104	102	109	101	106	108	102	108	105	97	105	102	111	106	101	102	106

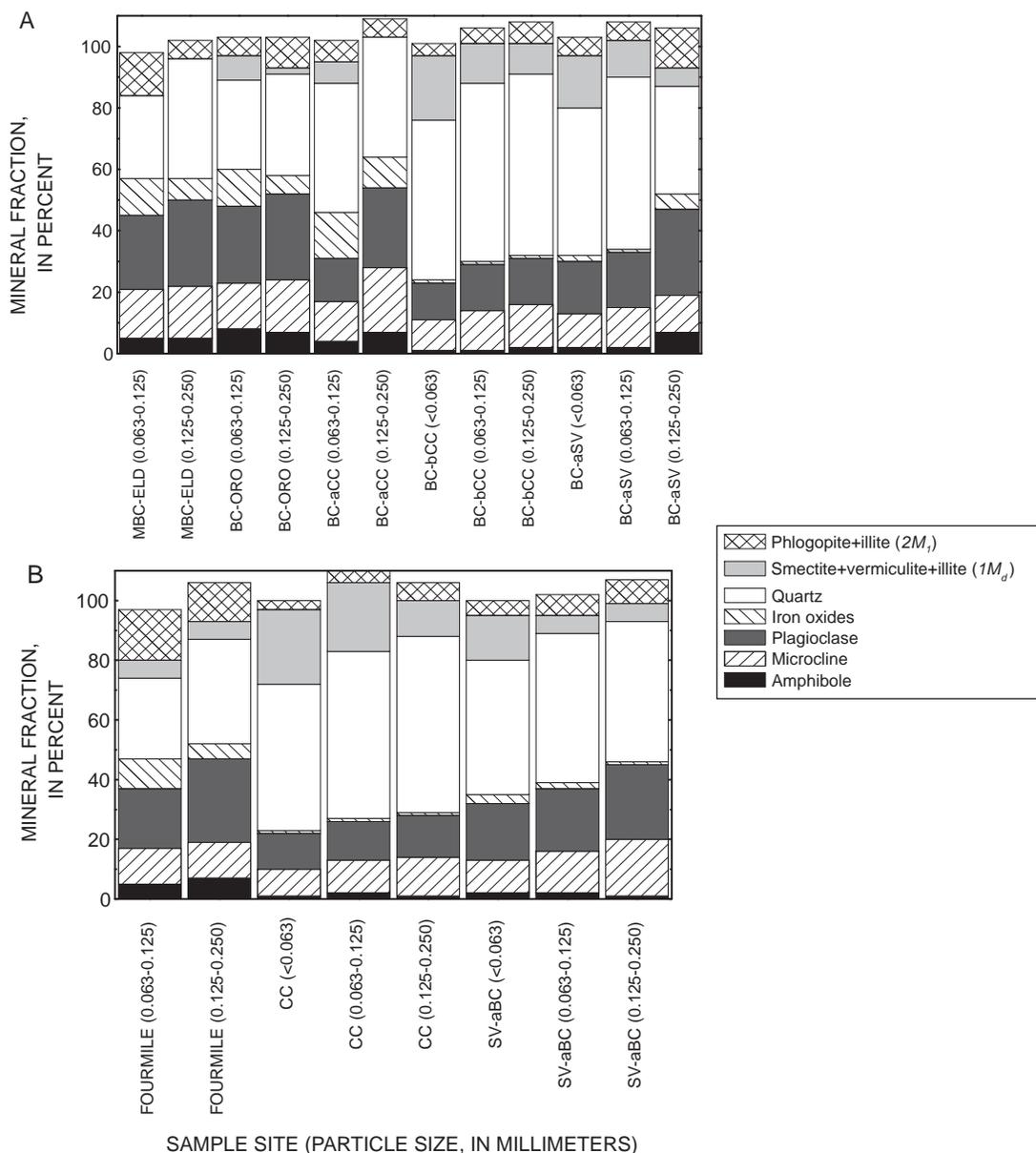


Figure 7.8. Quantitative mineralogy of sediment samples from (A) Middle Boulder Creek/Boulder Creek and (B) Fourmile Creek, Coal Creek, and Saint Vrain Creek.

absent in Boulder Creek below the Coal Creek confluence. Chlorite was not detected. Qualitative XRD data for the expandable clays are presented in table 7.4.

The relation between mineralogy and size fraction observed in this study is mostly expected. For example, clay minerals are more abundant in the smaller size fractions, whereas other minerals (such as mica and feldspar) tend to be present at higher concentrations in the larger size fractions.

The iron oxides show a distinct inverse relation with respect to particle size. Quartz is the major component in all samples, followed by plagioclase and microcline. Quartz and the feldspars remained relatively consistent throughout the Boulder and Middle Boulder Creek sediments, although quartz does become a more prominent constituent below the confluence of Boulder Creek and Coal Creek.

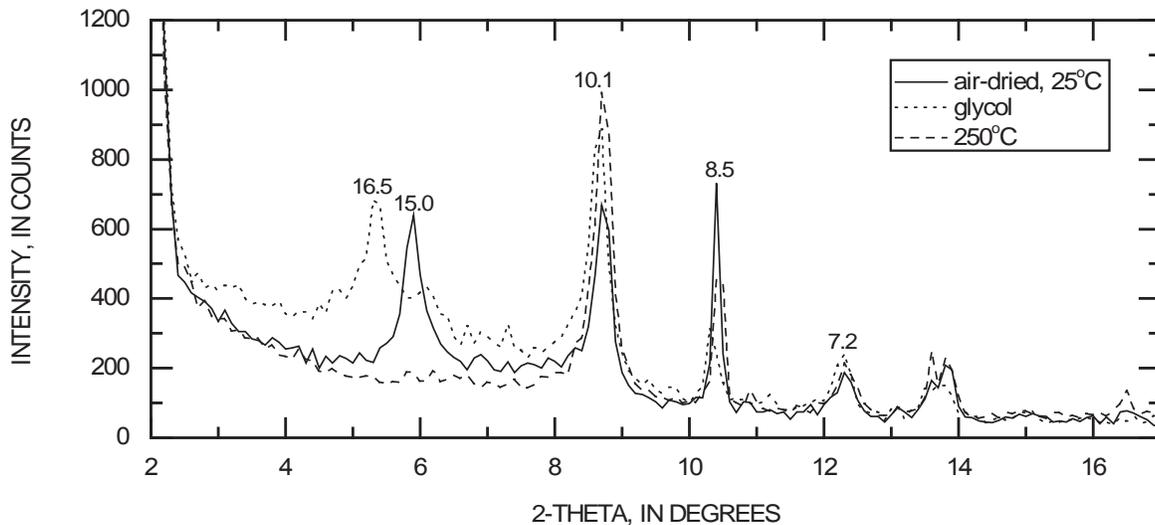


Figure 7.9. X-ray diffraction pattern for 0.063-0.125 mm fraction of sample from site BC-ORO with air drying, glycolation, and heating to 250 C. (Peaks are labeled in angstroms. Pattern shows smectite and vermiculite components.)

The Precambrian rocks and corresponding minerals that compose the upper Boulder Creek Watershed are predominantly the Boulder Creek Granodiorite (microcline, plagioclase, quartz, biotite, and hornblende, with accessory magnetite, ilmenite, hematite, allanite and sphene), the Silver Plume Quartz Monzonite (microcline, plagioclase, biotite, and muscovite), and Precambrian gneisses (with accessory cordierite, magnetite, sillimanite, garnet, and biotite). In addition, Tertiary intrusive alkali feldspar syenite and quartz syenite of Eocene age is common (Colton, 1978; Gable, 1980). As expected, the overall mineralogy of the bed sediments in the Boulder Creek Watershed, particularly for samples above the confluence with Coal Creek, is consistent with these source rocks, being composed predominantly of quartz, plagioclase, and microcline, with amphibole, magnetite and hematite present in smaller amounts.

Predictably, magnetite, hematite, and amphibole-group minerals in Boulder Creek drop off noticeably once the creek flows out of igneous source rocks and into sedimentary rocks. This is likely due to: (1) physical size reduction (as would be expected for a highly cleavable mineral

such as an amphibole); (2) weathering and chemical alteration (e.g., alteration of magnetite and hematite to limonite); and (3) gravitational settling due to a reduced stream gradient and concomitant diminished flow rate. Much of the hematite in these samples likely occurs as a relatively stable martitic intergrowth with magnetite (as formed by a process of martitization, whereby primary magnetite is altered to hematite along crystallographic planes, resulting in distinctive textures), rather than as a separate phase (e.g., limonitic). Amphiboles and feldspars (microcline and plagioclase) were generally present in higher amounts in Boulder Creek above its confluence with Coal Creek; below the confluence, quartz becomes a more significant constituent.

The increased proportion of quartz in Coal Creek may be a reflection of its traverse through predominantly sandstone-bearing sediments of the Laramie and Fox Hills formations. Magnetite and amphibole-group minerals are absent from the Coal Creek sediments; these sediments are also noticeably poor in the mica $2M_1$ polytype (e.g., muscovite and illite). The reduction in these constituents in Boulder Creek sediments after the Coal Creek confluence is also noteworthy,

Table 7.4. Qualitative mineralogy of expandable clays in size fraction below 0.063 millimeters

Site	Clay(s)
MBC-ELD	smectite, vermiculite
BC-ORO	smectite, vermiculite
BC-aCC	smectite, vermiculite
BC-bCC	smectite
BC-aSV	smectite, vermiculite
FOURMILE	smectite, trace vermiculite
CC	smectite, trace vermiculite
SV-aBC	smectite, vermiculite

suggesting that Coal Creek is a major sediment source to the lower Boulder Creek system.

SUMMARY

Although there is a distinct heterogeneity in particle-size distribution and mineralogy throughout the Boulder Creek Watershed, some trends are nonetheless evident. Differences in mineralogy are also noted within a given river system (e.g., Boulder Creek), and from upstream to downstream sample sites. These changes are mostly attributable to a change in the rock type (from igneous to sedimentary) over which the creek flows. For example, there is a significant increase from upstream to downstream in particle size for the < 0.25 mm fractions, as well as a decrease in the relative amounts of iron oxide minerals. The presence of amphibole-group minerals and iron oxides in the Boulder Creek system, and their absence in the Coal Creek drainage, is also likely manifest of the geology of the terrain through which the creek travels. The sediments downstream of the confluence of Boulder Creek and Coal Creek show the expected effects of dilution for these constituents.

REFERENCES CITED

Barber, L.B., Thurman, E.M., and Runnells, D.D., 1992, Geochemical heterogeneity in a sand and gravel aquifer— Effect of sediment mineralogy and particle size on the sorption of chlorobenzenes: *Journal of Contaminant Hydrology*, v. 9, p. 35-54.

- Barber, L.B., 1994, Sorption of chlorobenzenes to Cape Cod aquifer sediments: *Environmental Science and Technology*, v. 28, p. 890-897.
- Bilodeau, S.W., Van Buskirk, Donald, and Bilodeau, W.L., 1987, *Geology of Boulder, Colorado, United States of America: Bulletin of the Association of Engineering Geologists*, v. 24, p. 289-332.
- Colton, R.B., 1978, *Geologic map of the Boulder-Fort Collins-Greeley area, Colorado: U.S. Geological Survey Miscellaneous Investigations Series I-855G*.
- Eberl, D.D., 2003, *User's guide to RockJock— A program for determining quantitative mineralogy from powder X-ray diffraction data: U.S. Geological Survey Open-File Report 03-78*, 37 p.
- Gable, D.J., 1980, *Geologic map of the Gold Hill quadrangle, Boulder County, Colorado: U.S. Geological Survey Geologic Quadrangle Map GQ-1525*.
- Hall, D.C., Hillier, D.E., Cain, Doug, and Boyd, E.L., 1980, *Water resources of Boulder County, Colorado: Denver, Colo., Colorado Department of Natural Resources, Bulletin 42*, 97 p.
- Krumbein, W.C. and Pettijohn, F.J., 1938, *Manual of sedimentary petrography: New York, Appleton-Century Crofts, Inc.*, 549 p.
- Murphy, S.F., Barber, L.B., Verplanck, P.L., and Kinner, D.A., 2003, *Environmental setting and hydrology of the Boulder Creek Watershed— Chapter 1 in Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045*, p. 5-26.
- Office of Water Data Coordination, 1977, *National handbook of recommended methods for water-data acquisition, U.S. Geological Survey*.
- Środoń, J., Drita, V.A., McCarty, D.K., Hsieh, J.C.C., and Eberl, D.D., 2001, *Quantitative mineral analysis by powder X-ray diffraction from random preparations: Clays and Clay Mineralogy*, v. 149, p. 514-528.
- Tickell, F.G., 1965, *The techniques of sedimentary mineralogy: New York, Elsevier Publishing Co.*, 220 p.
- Trimble, D.E. and Machette, M.N., 1979, *Geologic map of the Greater Denver Area, Front Range urban corridor, Colorado: U.S. Geological Survey Miscellaneous Investigations Series I-856-H*.

Chapter 8- Headwater Catchments of North Boulder Creek, Colorado

By Mark W. Williams*, Eran W. Hood*, and Nel Caine*

Abstract

Streamflows from the Colorado alpine are an important contribution to the water resources of the Boulder Creek Watershed and are generated almost entirely by melting of seasonal snow cover. Water quality in this high-elevation ecosystem is relatively sensitive to changes in the flux of energy, chemicals, and water compared to downstream ecosystems, because of extensive areas of exposed and unreactive bedrock, rapid hydrologic flushing rates during snowmelt, limited extent of vegetation and soils, and short growing seasons. With specific conductance values below 10 microsiemens per centimeter, surface waters in North Boulder Creek are among the most sensitive to perturbation in the world. Alkalinity values below 3 milligrams per liter show that these surface waters are extremely sensitive and that even small increases in the atmospheric deposition of sulfate and nitrate may cause acidification, particularly during snowmelt runoff. High nitrate concentrations in these headwater basins relative to more pristine areas on the western slope of the Rocky Mountains and other high elevation mountain ranges suggest that atmospheric deposition of nitrogen is causing changes in ecosystem function within the headwater catchments of North Boulder Creek. These results suggest that water quality in North Boulder Creek is being degraded at present levels of nitrogen deposition in wetfall, and may serve as an early warning system for other high-elevation catchments in the Colorado Front Range and for downstream ecosystems within the North Boulder Creek drainage.

INTRODUCTION

Streamflows generated in the Colorado alpine are an important contribution to the flow of Boulder Creek. Discharge in headwater catchments of the Boulder Creek Watershed are generated almost entirely by melting of seasonal snow cover. As such, they are remarkably predictable, following the temporal patterns of solar radiation, which drives snowmelt. Within the Green Lakes Valley, the diurnal flow cycle is most consistently developed in headwater subbasins and is superimposed upon the predominant annual cycle. Together, these snowmelt-driven cycles account for up to 90 percent of the variability in streamflow. Summer rainfall, though occasionally intense, has relatively little hydrologic influence (Williams and Caine, 2001).

The quantity and quality of stream waters in the headwaters of Boulder Creek are protected by a variety of administrative actions. The city of Boulder owns the upper reaches of North Boulder Creek and limits access by the public. Much of the high-elevation area is encompassed by the Indian Peaks Wilderness Area. Nonetheless, these protected, high-elevation areas are within the “airshed” of the greater Denver Metropolitan area. The airshed connection means that the chemical and nutrient content of this headwater region can be changed by downstream activities resulting in the emission of pollutants which are then transported to this area. Many high-elevation ecosystems are relatively sensitive to changes in the flux of energy, chemicals and water compared to downstream ecosystems, because of extensive areas of exposed and unreactive bedrock, rapid hydrologic flushing rates during snowmelt, limited extent of vegetation and soils,

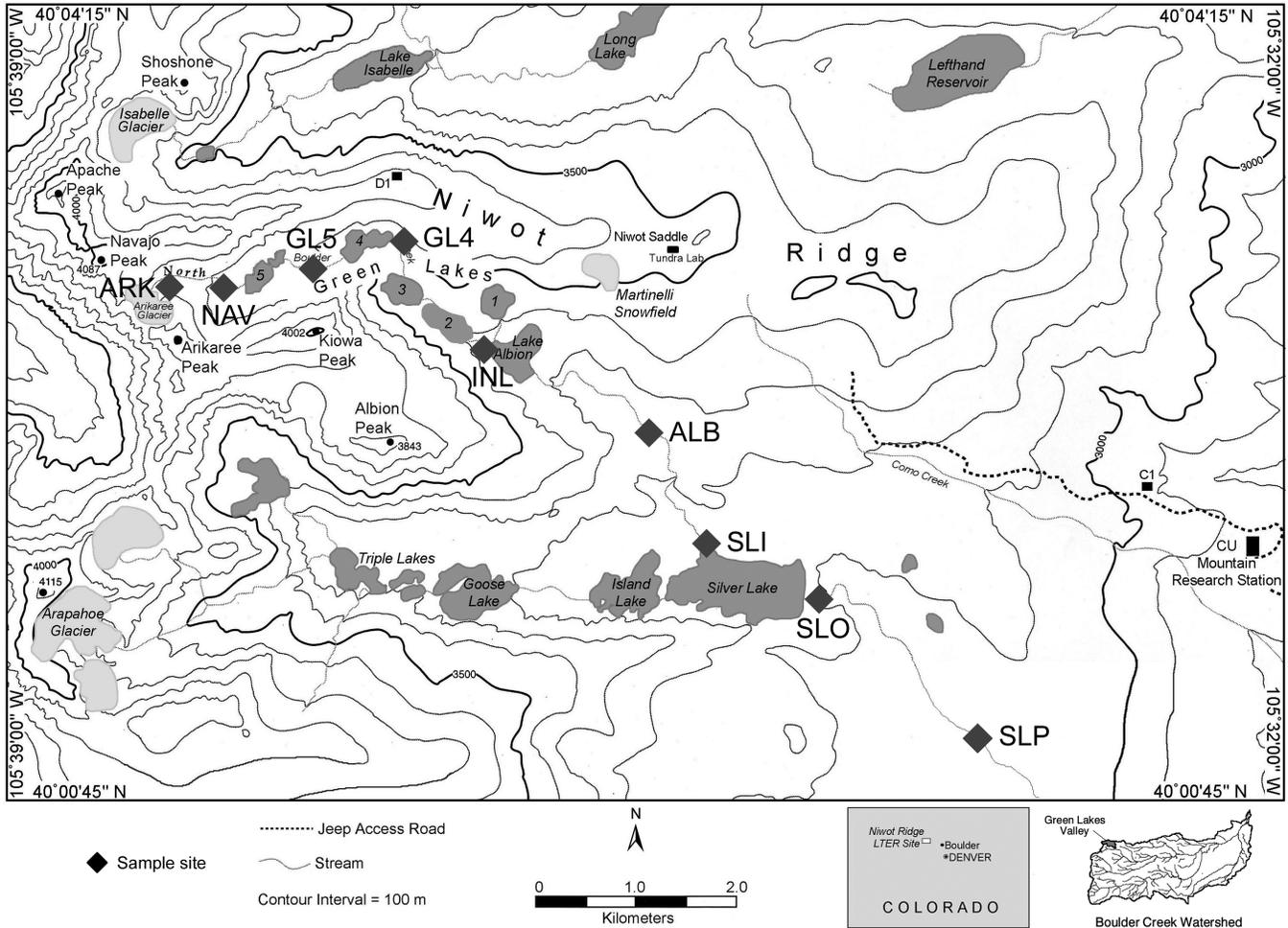


Figure 8.1. Map of study area.

and short growing seasons. Small changes in atmospheric deposition can cause large changes in ecosystem dynamics and water quality. Furthermore, these ecosystem changes may occur in alpine areas before they occur in downstream ecosystems.

STUDY SITE

Green Lakes Valley is an east-facing headwater catchment, 27 km² in area, extending from Silver Lake (elevation 2963 m) to the crest of the Continental Divide (over 4000 m) in the Colorado Front Range (fig. 8.1).

The Green Lakes Valley is characterized by a continental climate, with a mean annual temperature of -3.8°C and an average annual precipitation of 1000 mm (Williams, Losleben,

and others, 1996), 80 percent of which is in the form of snow (Caine, 1996). The valley is located within a protected area owned by the city of Boulder (Murphy and others, 2003) and public access has been restricted since the 1930s. As a result, the hydrologic and biogeochemical systems are protected from recreational and commercial perturbations.

The 5 km² of the catchment above Lake Albion is unforested and alpine in nature, and is underlain by crystalline bedrock. Steep rock walls and talus slopes are the dominant landforms and vegetation is sparse. In the upper valley, soils are limited in extent, depth, and development as a result of late-Pleistocene glaciation (Madole, 1982). Catchment soils are a mixture of Cryic Inceptisols and Entisols with Histosols in wetter areas on the valley floor (Burns, 1980).

Below Lake Albion, the catchment is dominated by a mixed conifer forest composed primarily of subalpine fir (*Abies lasiocarpa*) and Engelmann spruce (*Picea engelmannii*), with some limber pine (*Pinus flexilis*) at treeline and regrowth lodgepole pine (*Pinus contorta*) lower in the basin. This portion of the catchment is typified by extensive vegetative cover and developed soils on glacial till and moraine deposits. Watershed soils overlie granitic and metamorphic parent material. Soils are Inceptisols and intermixed Alfisols with Histosols in wet meadow areas. Soil depths range from 30 to 100 cm with the deeper soils located on well-drained glacial moraines. Soil pH values range from 4.5 to 6.0.

Above Silver Lake, the Green Lakes Valley consists of a linear cascade of 5 lakes (fig. 8.1). There are 5 alpine sample sites (ARK, NAV, GL5, GL4, and INL) which range in elevation from 3345 to 3785 m and in catchment area from 0.9 to 3.5 km². There are 4 forested sample sites (ALB, SLI, SLO, and SLP) ranging in elevation from 2963 to 3250 m and in basin area from 7 to 27 km². The highest site sampled (ARK) was outflow from the Arikaree Glacier at 3785 m. The ALB site, located at treeline, represents the transition from an alpine ecosystem to a forested subalpine ecosystem. The lowest-elevation (2963 m) sampling site (SLP) was located 3 kilometers downstream from the outflow of Silver Lake at the intake for the Silver Lake Pipeline. This pipeline diverts water from North Boulder Creek to the Lakewood Reservoir. The Lakewood Pipeline then diverts water to the city of Boulder's Betasso Water Treatment Plant (Murphy and others, 2003). The North Boulder Creek watershed provides about 40 percent of the city of Boulder's water supply (City of Boulder, 2001).

METHODS

Stream samples were collected as grab samples following the protocol of Williams, Brooks, and others (1996). Polyethylene bottles

were soaked with deionized water overnight and then rinsed copiously with deionized water. Bottles were further rinsed three times with sample water at the time of collection. Samples were transported within a few hours of collection to a wet chemistry laboratory located at the University of Colorado's Mountain Research Station. Subsamples were immediately filtered through glass fiber filters with a nominal pore size of 1.0 µm and stored in the dark at 4°C for subsequent analysis. Samples for dissolved organic carbon (DOC) analysis were collected in precombusted amber glass bottles. DOC samples were filtered (at the time of collection) through precombusted Gelman A/F glass fiber filters with an approximate pore size of 1.0 µm.

All water samples were analyzed for pH, alkalinity, specific conductance, and major ions. The pH measurements were made with combination electrodes suitable for use in dilute waters (Sargent Welch S-30072-15 or Ross 8104) and a Fisher Acumet 805 pH meter. For each series of measurements the electrode was calibrated with pH 7.00 and pH 4.00 reference buffers and washed twice for 3 minutes with stirred deionized water. The pH calibration was then verified with low ionic strength solutions of hydrochloric acid (HCl; 10⁻⁵ and 10⁻⁴ N); calibration was repeated if the measured pH values of these solutions differed from the expected values by more than 0.1 units. The electrode was rinsed with an aliquot of sample, and the temperature-compensated pH determination made on a fresh, quiescent sample after five minutes. Specific conductance was measured with a Yellow Springs Instruments Model 32 and a glass electrode with a 0.1 cell constant. Simultaneous temperature measurements were made, and conductivity was standardized to 25°C using a coefficient of 2 percent per degree C. The conductivity cell was calibrated with dilute solutions of potassium chloride. Alkalinity was measured as acid neutralizing capacity (ANC) and is considered to equal bicarbonate (HCO₃⁻) for these dilute waters.

Subsets of all samples were immediately filtered through pre-rinsed (300 mL) 47-mm Gelman A/E glass fiber filters with a nominal pore size of 1.0 μm . Nitrate was analyzed using a Dionex DX 500 ion chromatograph with an IonPac AS4A-SC Analytical Column. The detection limit was 0.00042 mg/L and precision was 1.1 percent. Ammonium was measured on a Lachat QuikChem 4000 Flow Injection Analyzer using a method based on the Berthelot reaction. The detection limit was 0.00462 $\mu\text{g/L}$ and precision was 0.91 percent. Total N (TN) concentrations were determined by using potassium persulfate digestion to oxidize all forms of N into $\text{NO}_3\text{-N}$ on both unfiltered and filtered samples. Nitrate was then measured on a Lachat QuikChem 4000 Flow Injection Analyzer as described above. Detection limits for TN were 0.0098 mg/L and precision was 1.62 percent. DON was calculated by subtracting measured inorganic N from total N on filtered samples. DOC was analyzed at the Institute of Arctic and Alpine Research (INSTAAR) in Boulder using a Dohrman high-temperature combustion instrument. Three replicate DOC analyses were done for each sample. The standard deviation for these analyses was typically 0.05 mg/L with a range of 0.01 to 0.12 mg/L.

RESULTS

Specific conductance provides an estimate of the amount of dissolved solutes in stream waters and hence the magnitude of geochemical weathering in a catchment. In June, specific conductance more than doubled from about 7 microsiemens per centimeter ($\mu\text{S/cm}$) near the Continental Divide to about 20 $\mu\text{S/cm}$ at the lowest-elevation site, SLP (table 8.1 and fig. 8.2a). The increase in specific conductance with distance downstream reflects longer residence time in ground-water reservoirs and enhanced geochemical weathering.

Specific conductance values measured in October were much higher than in June above Lake Albion (table 8.1 and fig. 8.2a). These

higher specific conductance values in October reflect longer residence times in ground-water reservoirs and increased geochemical weathering before waters contribute to stream flow. Below Lake Albion there was little difference in specific conductance between June and October values. Most likely the similarity in values between June and October is because of the storage and release of water from reservoirs on North Boulder Creek.

Calcium concentrations mirror specific conductance values (fig. 8.2b). The correlation between measurements of calcium and specific conductance suggest that specific conductance values are dominated by the amount of base cations in solution. In turn, concentrations of base cations in stream flow are primarily driven by residence time and geochemical weathering processes in subsurface reservoirs before water contributes to stream flow. As residence time in the subsurface decreases during snow melt runoff, base cation concentrations in surface waters are diluted and concentrations decrease.

Alkalinity values during snowmelt runoff were as low as 1.5 mg/L at the highest elevation sites closest to the Continental Divide, such as Arikaree (table 8.1 and fig. 8.2c). The low values of alkalinity at this time are driven in part by dilution of geochemical weathering products with snowmelt runoff. Values of alkalinity then increased downstream to about 9.15 mg/L at the lowest elevation site. In October, alkalinity values increased by 0.6 to 1.2 mg/L compared to values during snowmelt runoff. The higher values in the autumn sampling are the result of both the lack of dilute snowmelt runoff and increased residence time before contributing to stream flow.

The value of pH during the June synoptic survey was about 5.4 at Arikaree near the Continental Divide and then increased downstream to values near 7.0 (table 8.1 and fig. 8.3a). The pH values were greater in October compared to June values in the upper end of North Boulder Creek. To illustrate, the lowest pH values of 6.0 at the high-elevation Arikaree site was more than one-half of a pH unit greater than June. The low pH values during June may be due

Table 8.1. Results of water quality analyses for headwaters of North Boulder Creek, June and October 2000

[S/cm, micromoles per centimeter; mg/L, milligrams per liter; N, nitrogen; C, carbon; --, not analyzed; all inorganic samples analyzed at Kiowa Environmental Chemistry Laboratory, Mountain Research Station, University of Colorado; organic samples (dissolved organic N and dissolved organic C) analyzed at the Institute of Arctic and Alpine Research]

Site	Site description	Elevation (meters)	Date	Time	Specific conductance (S/cm)	pH (units)	Alkalinity* (mg/L)	Calcium (mg/L)	Ammonium (mg/L as N)	Nitrate (mg/L as N)	Dissolved organic nitrogen (mg/L as N)	Dissolved organic carbon (mg/L as C)
JUNE 2000												
ARK	Arikaree glacier outflow	3785	6/15/00	1125	7.11	5.34	1.39	0.50	0.147	1.37	0.031	--
NAV	Navajo site	3720	6/15/00	1210	7.92	5.78	1.47	0.83	0.004	1.87	0.027	--
GL5	Green Lake 5	3620	6/15/00	1330	9.37	6.09	2.74	1.20	0.005	1.13	0.022	--
GL4	Green Lake 4	3550	6/15/00	0945	12.7	6.30	3.93	1.74	0.005	0.90	0.000	0.55
INL	Inlet to Lake Albion	3400	6/15/00	0900	17.9	6.56	4.99	2.33	0.007	0.81	0.036	1.45
ALB	Downstream of Lake Albion	3250	6/15/00	1530	20.7	6.54	7.98	3.02	0.008	0.20	0.014	1.71
SLI	Inlet to Silver Lake	3122	6/15/00	1200	20.2	6.76	8.29	2.85	0.007	0.14	0.036	1.61
SLO	Outlet of Silver Lake	3100	6/15/00	1230	20.5	6.72	8.78	2.91	0.013	0.21	0.058	2.16
SLP	Silver Lake Pipeline intake	2963	6/15/00	1330	21.1	6.83	9.27	2.91	0.000	0.20	0.045	2.34
OCTOBER 2000												
ARK	Arikaree glacier outflow	3785	9/21/00	0955	8.60	6.03	2.29	0.88	0.254	1.08	--	--
NAV	Navajo site	3720	10/5/00	1030	18.2	6.13	3.27	2.07	0.016	3.45	--	--
GL5	Green Lake 5	3620	10/5/00	1050	27.1	6.37	4.00	3.68	0.006	1.81	--	--
GL4	Green Lake 4	3550	10/5/00	0850	26.9	6.61	4.86	3.70	0.027	1.07	--	0.62
INL	Inlet to Lake Albion	3400	10/5/00	1255	17.8	6.71	6.35	2.36	0.035	0.11	0.009	0.89
ALB	Downstream of Lake Albion	3250	10/5/00	1325	20.8	6.76	9.16	3.02	0.006	0.05	0.052	1.08
SLI	Inlet to Silver Lake	3122	10/26/00	1140	24.8	6.68	11.2	3.39	0.000	0.12	--	0.96
SLO	Outlet of Silver Lake	3100	10/26/00	1215	18.7	6.61	8.83	2.72	0.005	0.00	--	1.28
SLP	Silver Lake Pipeline intake	2963	10/26/00	1300	21.6	6.87	11.2	3.02	0.000	0.00	--	1.42

*Alkalinity was measured as Acid Neutralizing Capacity, considered as equivalent to bicarbonate (HCO₃⁻) for these waters.

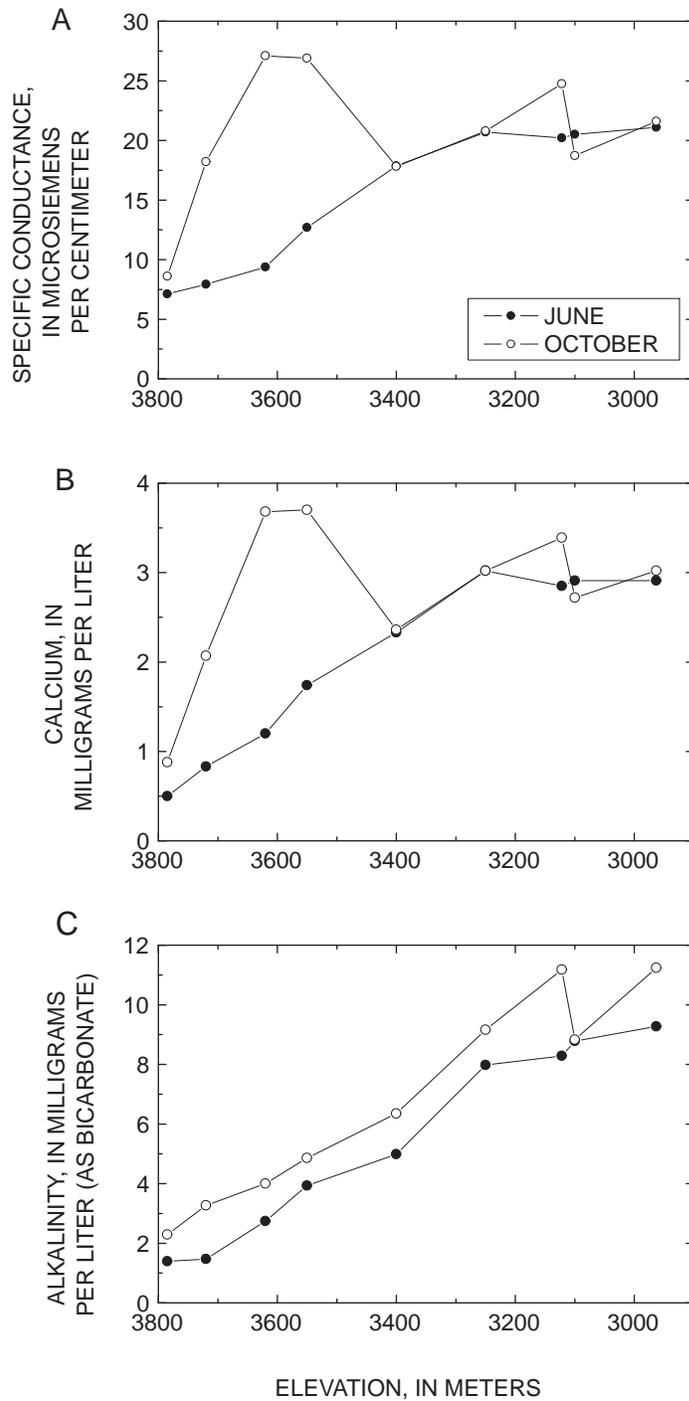


Figure 8.2. Graphs showing (A) specific conductance values, (B) calcium concentrations, and (C) alkalinity values as a function of elevation.

to dilution of geochemical weathering products by snowmelt runoff.

Ammonium (NH_4^+) concentrations were generally at or near detection limits of 0.0004 mg/L (table 8.1 and fig. 8.3b). The one exception was the Arikaree sampling site, with values in the 0.15 to 0.25 mg/L range. However, below this site, NH_4^+ values in stream water quickly decreased towards detection limits.

Nitrate (NO_3^-) concentrations were relatively high in stream waters compared to NH_4^+ concentrations (tables 8.1; fig. 8.3c). During snowmelt runoff in June, NO_3^- concentrations at the headwater areas ranged from 1.24 to 1.86 mg/L. Nitrate concentrations in June remained above 0.62 mg/L at all alpine sites. At treeline (below 3400 m), concentrations decreased to about 0.3 mg/L. In October, NO_3^- concentrations in the high-elevation areas above treeline were as high as 3.4 mg/L.

Dissolved organic nitrogen (DON) behaves very differently than NO_3^- . Concentrations of DON were always lower than 0.6 mg/L and at times below detection limits of 0.0098 mg/L (table 8.1 and fig. 8.4a). There was a tendency for DON concentrations to increase downstream.

Dissolved organic carbon (DOC) generally increased downstream (table 8.1 and fig. 8.4b) from about 0.5 mg/L in the alpine catchments to 2.5 mg/L in the forested catchments. Concentrations of DOC in June were about 1 to 2 mg/L greater than DOC concentrations at the same sites measured in October.

DISCUSSION

Surface waters in headwater catchments of North Boulder Creek are among the most pristine and sensitive streams in the world. Specific conductance values below 10 $\mu\text{S}/\text{cm}$ are very low. To place the values in perspective, high-quality distilled water has a specific conductance value around 2 $\mu\text{S}/\text{cm}$. The specific conductance of stream water during snow melt runoff in this high-elevation catchment is near that of distilled water. Thus, surface waters at high-elevation in

North Boulder Creek, with the low amount of solutes in the stream and the low amount of geochemical weathering in the basin relative to downstream locations such as within the city of Boulder, are very sensitive to pollutants of any kind.

Stream waters with low alkalinity values show extreme sensitivity to acidification. The U.S. Environmental Protection Agency has defined surface waters with alkalinity values less than 3.0 mg/L as sensitive to acidification (Herlihy and others, 1996). Acidification of surface waters has occurred in the northeastern United States as a result of emissions from coal-fired power plants and other sources. These gaseous emissions are converted to strong acid anions such as sulfate (SO_4^{2-}) and NO_3^- in rain and snow (Driscoll and Schafran, 1984). The very low alkalinity values in headwater catchments of North Boulder Creek suggest that even small increases in the atmospheric deposition of SO_4^{2-} and NO_3^- may cause acidification of these surface waters, particularly during snowmelt runoff.

Moreover, alkalinity values appear to be decreasing over time. A simple linear regression of alkalinity versus time shows that alkalinity in GL4 has been decreasing at the rate of 0.15 mg/L per year since the early 1980s (Caine, 1995). While the R^2 of 0.24 is low, the slope is significant at the $\alpha = 0.05$ level (Williams and Tonnessen, 2000). In Caine's (1995) extensive analysis of temporal trends in water quality in the Green Lakes Valley, he reports on earlier records in the Green Lakes Valley that were summarized in Caine and Thurman (1990). At GL4, records of alkalinity measured in summer from 1969 to 1971 have an arithmetic mean of 4.9 mg/L, about the same as that predicted for the year 1980 by the regression trend at GL4. This analysis suggests that the decline in alkalinity at GL4 was initiated in the early 1980s.

Williams, Losleben, and others (1996) have shown that episodic acidification (alkalinity < 0 mg/L) of surface waters is now occurring in the headwater catchments above GL4, perhaps as a result of the increase of inorganic N deposition in

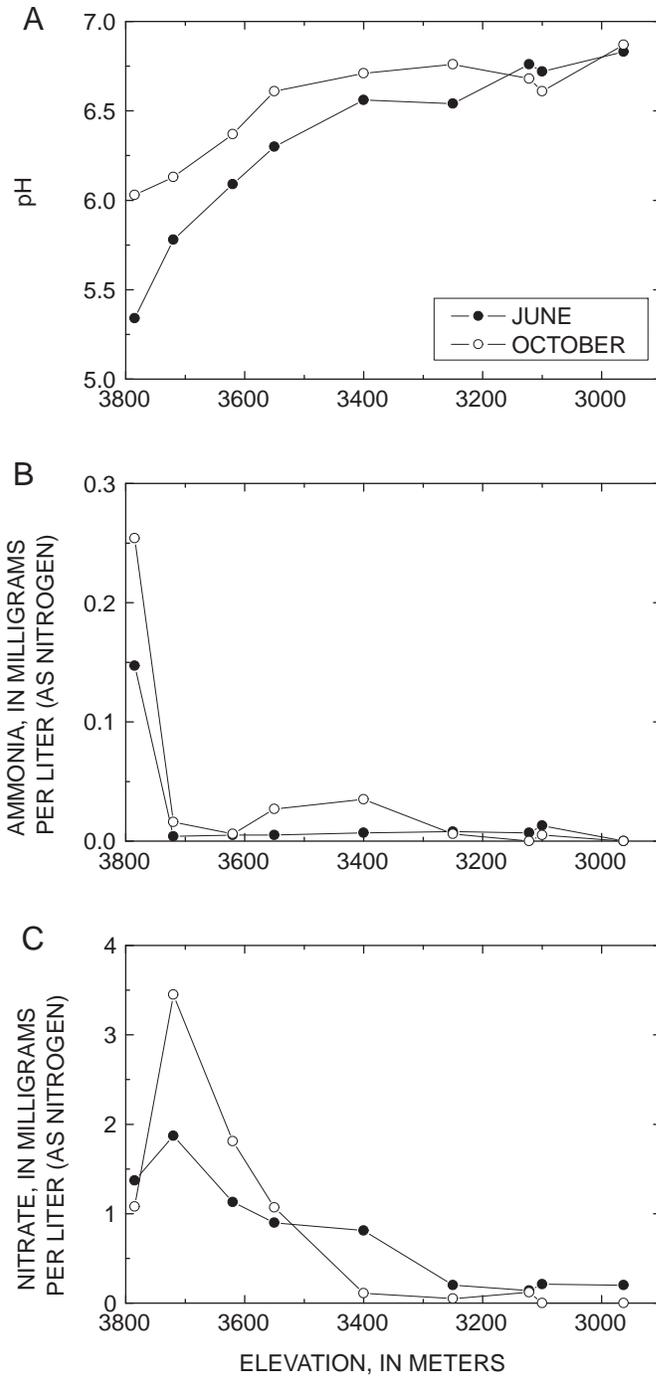


Figure 8.3. Graphs showing (A) pH, (B) ammonium concentrations, and (C) nitrate concentrations as a function of elevation.

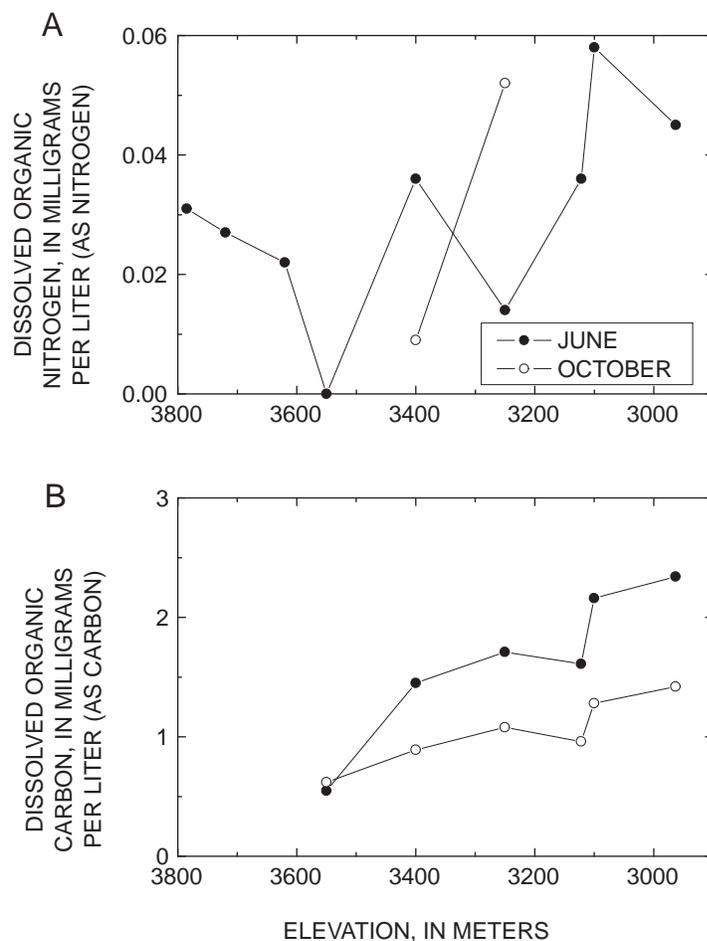


Figure 8.4. Graphs showing (A) dissolved organic nitrogen concentrations and (B) dissolved organic carbon concentrations as a function of elevation.

wetfall (Williams and Tonnessen, 2000). In 1994, alkalinity concentrations in surface waters draining the 0.09-km² Arikaree catchment were less than 0 mg/L for three weeks on the rising limb of the hydrograph during the initiation of snowmelt runoff, with the negative alkalinity values ranging from -0.2 to -0.4 mg/L.

The observed episodic acidification and decrease in alkalinity of surface waters was predicted in the early 1980s by Kling and Grant (1984). At that time there were no reports of acidification of surface waters (alkalinity < 0

mg/L) in the Rocky Mountains, but there was evidence that precipitation was becoming more acidic (Lewis and others, 1984). Kling and Grant (1984) predicted that acidification of surface waters in the Rocky Mountains would be detected first at the highest elevations in the Colorado Front Range, because of limited soil extent and flashy hydrographs at these high elevation sites, consistent with the results presented here.

The acidification of surface waters and resulting decrease in pH can cause changes in the aquatic resources of high-elevation catchments.

Zooplankton species, such as the dominant *Daphnia rosea*, begin decreasing below pH 5.5 to 5.8 and virtually disappear below pH 5.0 (Barmuta and others, 1990). In turn, decreases in the population of *Daphnia rosea* result in increases of more acid-tolerant species such as *Bosmina* spp., resulting in a restructuring of the natural zooplankton assemblages when pH decreases to about 5.5. Among the benthic invertebrates found in western streams, the mayfly larva (*Baetis* spp.) is very sensitive to acidic episodes, with populations decreasing rapidly once pH drops below 5.5 (Kratz and others, 1994). These species are important as food sources for native fish in high-elevation aquatic systems. Native fish species, such as the greenback cutthroat trout (*Oncorhynchus clarkii stomias*) have sensitivity to acidic waters depending on the life stage exposed to acidic episodes. In general, fish population viability is expected to be reduced below pH 6 (Baker and others, 1990). In the eastern United States, streams with low ANC in Shenandoah National Park (Virginia) showed fish populations with decreased species richness, population density, condition factor, age distribution, and size compared to streams with higher ANC (Bulger and others, 1995; Dennis and others, 1995; MacAvoy and Bulger, 1995). Furthermore, a study of 13 streams in the Adirondack and Catskill Mountains in New York and the northern Appalachian Plateau in Pennsylvania showed long-term adverse effects on fish populations from episodic reductions in alkalinity similar to those we report for the Green Lakes Valley (Wigington and others, 1996). Fish populations in high-elevation catchments of the Colorado Front Range are at risk of reduced viability as a result of increasing amounts of inorganic N in wetfall.

In general, water quality of lakes in the Rocky Mountains are pristine compared to the global distribution of alpine/subalpine lakes, with the median value of NO_3^- concentrations less than 0.06 mg/L (Psenner, 1989). Similarly, NO_3^- values in high-elevation catchments in the Sierra Nevada are generally below 0.30 mg/L (Williams

and others, 1995). However, these high-elevation ecosystems are relatively sensitive to changes in the flux of energy, chemicals, and water compared to downstream ecosystems, because of extensive areas of exposed and unreactive bedrock, rapid hydrologic flushing rates during snowmelt, limited extent of vegetation and soils, and short growing seasons (Williams and others, 1993; National Acid Precipitation Assessment Program, 1998). Hence, small changes in atmospheric deposition have the potential to result in significant changes in ecosystem dynamics and water quality (Williams, Baron, and others, 1996). The high NO_3^- concentrations in North Boulder Creek relative to more pristine areas on the western slope of the Rocky Mountains and other high elevation mountain ranges suggest that atmospheric deposition of N is causing changes in ecosystem function within the headwater catchments of North Boulder Creek (Williams and Tonnesson, 2000).

Atmospheric deposition of inorganic N in wetfall to the central Rocky Mountains is relatively modest but greater than background levels. Agriculture, combustion of fossil fuels, and other human activities have altered the global cycle of N substantially, generally increasing both the availability and mobility of N over large regions of the Earth (Vitousek and others, 1997). Inorganic N deposition in annual wetfall from unpolluted regions of the world generally ranges from 0.1 to 0.7 kilogram per hectare per year ($\text{kg ha}^{-1} \text{yr}^{-1}$), based on extensive measurements of precipitation chemistry in remote areas of the southern hemisphere (Galloway and others, 1982, 1996; Likens and others, 1987; Hedin and others, 1995). The 2.5 to 3.5 $\text{kg ha}^{-1} \text{yr}^{-1}$ of inorganic N deposition in wetfall to the Colorado Front Range is about five- to ten-fold greater than background amounts (Williams and Tonnesson, 2000). Compared to the northeastern United States, deposition of inorganic N in wetfall to the Rocky Mountains is similar to the 3.7 $\text{kg ha}^{-1} \text{yr}^{-1}$ at Acadia National Park and about half of the 5.1 $\text{kg ha}^{-1} \text{yr}^{-1}$ at the Hubbard Brook Experimental Forest as measured over the last ten years by the

National Atmospheric Deposition Program (Williams and others, 1998).

Orographic precipitation in the Rocky Mountains compounds the N-loading problem. In the northeastern United States, increases in NO_3^- leaching losses have been associated with high-elevation sites because of higher amounts of N deposition in wetfall (Driscoll and others, 1987). It is well documented that many high-elevation ecosystems receive higher doses of nutrients and pollutants than adjacent low-elevation ecosystems in the northeastern United States (Lovett and Kinsman, 1990; Lovett, 1994). The Continental Divide in the Colorado Rocky Mountains is generally higher than 4000 m in elevation, with 58 peaks in Colorado exceeding 4,267 m (14,000 feet) in elevation. As air masses rise to over 4000 m from surrounding lowlands, they cool adiabatically with resulting precipitation as air temperatures decrease below the dew point. Consequently, annual precipitation generally increases with increasing elevation in the Rocky Mountains (Barry, 1973). In turn, this increase in orographic precipitation with increasing elevation results in more N deposition in mountain areas compared to surrounding lowlands (Williams and Tonnesson, 2000). As in the northeastern United States, the highest rates of N deposition in the Rocky Mountains occur at the highest elevations. This orographic effect is much greater than in the northeastern United States, since the Rocky Mountains are generally two to three times the height of mountains in the northeast. Consequently, in high-elevation areas of the Rocky Mountains, even modest increases in the atmospheric content of anthropogenically-produced N will result in much greater deposition in wetfall of inorganic N compared to the northeastern United States.

Nitrate leaching to surface waters in the northeastern United States has been associated with catchments characterized by shallow soils and sites which have received little human disturbance (which presumably were close to input-output balance prior to receiving enhanced N deposition; Stoddard and Murdoch, 1991; Kahl

and others, 1993). In general, Pleistocene glaciation has resulted in catchments of the Colorado Front Range having soils that are limited in area and very shallow when present (Kling and Grant, 1984; Caine and Thurman, 1990; Baron, 1992). Moreover, these high-elevation areas have received little human disturbance compared to the eastern United States and Europe. The short growing season, location above treeline, and limited soil development result in little agricultural use, no logging, only limited grazing, and little development. Consequently, it appears that these high-elevation ecosystems were close to input-output balance prior to the enhanced N deposition that we report. Furthermore, the increases of anthropogenically-fixed N in the ambient atmosphere of the Colorado Front Range and resulting increases in the deposition of inorganic N in wetfall result in an uncontrolled experiment of N fertilization at the catchment level similar to controlled experiments in the northeastern United States (Kahl and others, 1993; Williams, Brooks, and others, 1996; Williams, Losleben, and others, 1996). As in the northeastern United States, limited extent of soils combined with little human disturbance results in the high-elevation catchments of the Rocky Mountains having little capacity to assimilate increases in atmospheric deposition of inorganic N.

Additionally, the storage and release of solutes from the seasonal snowpack in the form of an ionic pulse magnifies the aquatic problems caused by pollutants in wetfall. Here we define an ionic pulse as occurring when the initial fraction of snowmelt has ionic concentrations greater than the bulk average for the snowpack (Johannessen and Henriksen, 1978; Colbeck, 1981). Williams, Brooks, and others (1996) have shown that on Niwot Ridge, initial concentrations of NO_3^- in snowmelt at the plot scale (1 m^2) may be as high as 20 times those of bulk snowpack concentrations. At the ARIK site, the elevated NO_3^- and H^+ concentrations in surface waters at the onset of snowmelt are consistent with the storage and release of solutes from the seasonal

snowpack in the form of an ionic pulse. Storage and release of solutes from the snowpack in the form of an ionic pulse at the 0.09-km² ARIK site magnifies the concentration of pollutants in wetfall about 5-fold. The relatively high concentrations of NH₄⁺ at the ARIK site suggest that the snowpack on the small glacier essentially acts as a giant snow lysimeter, providing information on the chemical content of snow and ice melt. Immediately below the Arikaree glacier, the NH₄⁺ in streamwater is immobilized by biotic (microbial assimilation) and abiotic (adsorption by ion exchange on soil particles) processes. Thus, even during snowmelt runoff, much of the melted snow flows through the subsurface before contributing to stream flow.

Our results suggest that water quality in North Boulder Creek is being degraded at present levels of N deposition in wetfall (Williams and Tonnessen, 2000). These results may serve as an early warning system for high-elevation catchments in the Colorado Front Range. Protected areas such as national parks and wilderness areas with elevated amounts of N deposition are susceptible to N leakage because of stand maturity where forested, accumulation of N in soil, and particularly in high-elevation sites, low N retention capacity of soils and vegetation. All of these factors suggest that reductions of N emissions are needed to protect these environments (Fenn and others, 1998; Williams and Tonnessen, 2000).

SUMMARY

Our results demonstrate strong longitudinal trends in water quality in headwater streams of North Boulder Creek. The increase in specific conductance with distance downstream reflects longer residence time in ground-water reservoirs and enhanced geochemical weathering with distance downcanyon. Specific conductance values measured above Lake Albion were much higher in October than in June. The higher values in October reflect longer residence times in ground-water reservoirs and increased

geochemical weathering before waters contribute to stream flow. Alkalinity values during snowmelt runoff were as low as 1.5 mg/L at the highest elevation sites closest to the Continental Divide, such as ARIK. The low values of alkalinity at this time are driven in part by dilution of geochemical weathering products with snowmelt runoff. Values of alkalinity then increased downstream to about 9.15 mg/L at the lowest elevation site. In October, alkalinity values increased by 0.6 to 1.2 mg/L compared to values during snowmelt runoff. The higher values in the autumn sampling are the result of both the lack of dilute snowmelt runoff and increased residence time before contributing to stream flow. The low values of alkalinity at the headwaters of North Boulder Creek are a good indicator that this area is sensitive to acidification.

The value of pH during the June synoptic survey was about 5.4 at ARIK and then increased downstream to values near 7.0. As with specific conductance and alkalinity, pH values in the upper end of North Boulder Creek were much greater in October than in June. To illustrate, the lowest pH values of 6.0 at the high-elevation ARIK site was more than one-half of a pH unit greater than in June. The low pH values during June represent two processes: (a) dilution of geochemical weathering products by snowmelt runoff; and (b) possible titration by strong acid ions such as sulfate and nitrate. The pH values below 6.0 are in the range where biological damage may be occurring.

In contrast, nitrate (NO₃⁻) concentrations were generally highest near the Continental Divide and decreased downstream. During snowmelt runoff in June, NO₃⁻ concentrations at the headwater areas ranged from 1.24 to 1.86 mg/L. Nitrate concentrations in June remained above 0.62 mg/L at all alpine sites. At treeline (below 3400 m), concentrations decreased to about 0.3 mg/L. In October, NO₃⁻ concentrations in the high-elevation areas above treeline were as high as 3.4 mg/L. These high NO₃⁻ concentrations in North Boulder Creek relative to more pristine areas on the western slope of the Rocky

Mountains and other high elevation mountain ranges suggest that atmospheric deposition of nitrogen is causing changes in ecosystem function within the headwater catchments of North Boulder Creek.

REFERENCES CITED

- Baker, J.P., Bernard, D.P., Christensen, S.W., and Sale, M.J., 1990, Biological effects of changes in surface water acid-base chemistry: National Acid Precipitation Assessment Program, Report no. 13.
- Barmuta, L.A., Cooper, S.D., Hamilton, S.K., Kratz, K.W., and Melack, J.M., 1990, Responses of zooplankton and zoobenthos to experimental acidification in a high-elevation lake (Sierra Nevada, California, U.S.A.): *Freshwater biology*, v. 23, p. 571-586.
- Baron, J.S., 1992, Biogeochemical fluxes, *in* J.S. Baron, ed., *Biogeochemistry of a subalpine ecosystem—Loch Vale Watershed*: New York, Springer-Verlag, Ecological Studies ser. 90, p. 247.
- Barry, R.G., 1973, A climatological transect on the east slope of the Front Range, Colorado: *Arctic and Alpine Research*, v. 5, p. 89-110.
- Bulger, A.J., Dolloff, C.A., Cosby, B.J., Eshleman, K.N., Webb, J.R., and Galloway, J.N., 1995, The Shenandoah National Park—Fish in sensitive habitats (SNP:FISH) project—An integrated assessment of fish community responses to stream acidification: *Water, Air, and Soil Pollution*, v. 85, p. 309-314.
- Burns, S.F., 1980, Alpine soil distribution and development, Indian Peaks, Colorado Front Range: Boulder, University of Colorado, Ph.D. dissertation, 360 p.
- Caine, Nel, 1995, Temporal trends in the quality of streamwater in an alpine environment—Green Lakes Valley, Colorado Front Range, USA: *Geografiska Annaler*, v. 77a, p. 207-220.
- _____, 1996, Streamflow patterns in the alpine environment of North Boulder Creek, Colorado Front Range: *Zeitschrift fur Geomorphologie*, v. 104, p. 27-42.
- Caine, Nel and Thurman, E.M., 1990, Temporal and spatial variations in the solute content of an alpine stream, Colorado Front Range: *Geomorphology*, v. 4, p. 55-72.
- City of Boulder, 2001, Drinking water quality report number 3: Boulder, Colo., Boulder Public Works Department, accessed May 10, 2002, at http://www.ci.boulder.co.us/publicworks/depts/utilities/water_quality/drinking/report01/index.htm
- Colbeck, S.C., 1981, A simulation of the enrichment of atmospheric pollutants in snow cover runoff: *Water Resources Research*, v. 17, p. 1383-1388.
- Dennis, T.E., MacAvoy, S.E., Steg, M.B., and Bulger, A.J., 1995, The association of water chemistry variables and fish condition in streams of Shenandoah National Park (USA): *Water, Air, and Soil Pollution*, v. 85, p. 365-370.
- Driscoll, C.T. and Schafran, G.C., 1984, Short-term changes in the base neutralizing capacity of an acid Adirondack lake, New York: *Nature*, v. 310, p. 308-310.
- Driscoll, C.T., Wyskowski, B.J., Cosentini, C.C., and Smith, M.E., 1987, Processes regulating temporal and longitudinal variations in the chemistry of a low-order woodland stream in the Adirondack region of New York: *Biogeochemistry*, v. 3, p. 225-241.
- Fenn, M.E., Poth, M.A., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.F., and Stottlemeyer, Robert, 1998, Nitrogen excess in North American ecosystems—Predisposing factors, ecosystem responses, and management strategies: *Ecological Applications*, v. 8, p. 706-733.
- Galloway, J.N., Keene, W.C., and Likens, G.E., 1996, Processes controlling the composition of precipitation at a remote southern hemisphere location—Torres del Paine National Park, Chile: *Journal of Geophysical Research*, v. 101, p. 6883-6897.
- Galloway, J.N., Likens, G.E., Keene, W.C., and Miller, J.M., 1982, The composition of precipitation in remote areas of the world: *Journal of Geophysical Research*, v. 87, p. 8771-8786.
- Hedin, L.O., Armesto, J.J., and Johnson, A.H., 1995, Patterns of nutrient loss from unpolluted, old-growth temperate forests—Evaluation of biogeochemical theory: *Ecology*, v. 76, p. 493-509.
- Herlihy, A.T., Kaufmann, P.R., Stoddard, J.L., Eshleman, K.N., and Bulger, A.J., 1996, Effects of acidic deposition on aquatic resources in the Southern Appalachians with a special focus on Class I Wilderness Areas: Prepared for the Southern Appalachian Mountain Initiative, 91 p.
- Johannessen, M. and Henriksen, A., 1978, Chemistry of snow meltwater—Changes in concentration during melting: *Water Resources Research*, v. 14, p. 615-619.
- Kahl, J.S., Norton, S.A., Fernandez, I.J., Nadelhoffer, K.J., Driscoll, C.T., and Aber, J.D., 1993, Experimental inducement of nitrogen saturation at the watershed scale: *Environmental Science and Technology*, v. 27, p. 565-568.

- Kling, G.W. and Grant, M.C., 1984, Acid precipitation in the Colorado Front Range— An overview with time predictions for significant effects: *Arctic and Alpine Research*, v. 16, p. 321-329.
- Kratz, K.W., Cooper, S.D., and Melack, J.M., 1994, Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream: *Freshwater Biology*, v. 32, p. 161-183.
- Lewis, W.M., Jr., Grant, M.C., and Saunders, J.F., III, 1984, Chemical patterns of bulk atmospheric deposition in the state of Colorado: *Water Resources Research*, v. 20, p. 1691-1704.
- Likens, G.E., Keene, W.C., Miller, J.M., and Galloway, J.N., 1987, Chemistry of precipitation from a remote, terrestrial site in Australia: *Journal of Geophysical Research*, v. 92, p. 13299-13314.
- Lovett, G.M., 1994, Atmospheric deposition of nutrients and pollutants in North America— An ecological perspective: *Ecological Applications*, v. 4, p. 629-650.
- Lovett, G.M. and Kinsman, J.D., 1990, Atmospheric pollutant deposition to high-elevation ecosystems: *Atmospheric Environment*, v. 24A, p. 2767-2786.
- MacAvoy, S.E. and Bulger, A.J., 1995, Survival of brook trout (*Salvelinus fontinalis*) embryos and fry in streams of different acid sensitivity in Shenandoah National Park, USA: *Water, Air, and Soil Pollution*, v. 85, p. 445-450.
- Madole, R.F., 1982, Possible origins of till-like deposits near the summit of the Front Range in north-central Colorado: U.S. Geological Survey Professional Paper no. 1243, 31 p.
- Murphy, S.F., Barber, L.B., Verplanck, P.L., and Kinner, D.A., 2003, Environmental setting and hydrology of the Boulder Creek Watershed— Chapter 1 in Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., *Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000*: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 5-26.
- National Acid Precipitation Assessment Program, 1998, Biennial report to Congress— An integrated assessment: Silver Spring, Md., 118 p.
- Psenner, R., 1989, Chemistry of high mountain lakes in siliceous catchments of the Central Eastern Alps: *Aquatic Sciences*, v. 51, p. 108-128.
- Stoddard, J.L. and Murdoch, P.S., 1991, Catskill Mountains, in Charles, D.F., ed., *Acidic deposition and aquatic ecosystems*: New York, Springer-Verlag, p. 237-271.
- Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., and Tilman, D.G., 1997, Human alteration of the global nitrogen cycle— Sources and consequences: *Ecological Applications*, v. 7, p. 737-750.
- Wigington, P.J., Jr., DeWalle, D.R., Murdoch, P.S., Kretser, W.A., Simonin, H.A., Van Sickle, J., and Baker, J.P., 1996, Episodic acidification of small streams in the northeastern United States— Ionic controls of episodes: *Ecological Applications*, v. 6, p. 389-407.
- Williams, M.W., Bales, R.C., Brown, A.D., and Melack, J.M., 1995, Fluxes and transformations of nitrogen in a high-elevation catchment: *Biogeochemistry*, v. 28, p. 1-31.
- Williams, M.W., Bardsley, Tim, and Ridders, Mark, 1998, Overestimation of snow depth and inorganic nitrogen wetfall using NADP data, Niwot Ridge, Colorado: *Atmospheric Environment*, v. 32, p. 3827-3833.
- Williams, M.W., Baron, J.S., Caine, Nel, Sommerfeld, Richard, and Sanford, Robert, Jr., 1996, Nitrogen saturation in the Colorado Front Range: *Environmental Science and Technology*, v. 30, p. 640-646.
- Williams, M.W., Brooks, P.D., Mosier, Arvin, and Tonnessen, K.A., 1996, Mineral nitrogen transformations in and under seasonal snow in a high-elevation catchment in the Rocky Mountains, United States: *Water Resources Research*, v. 32, p. 3161-3171.
- Williams, M.W., Brown, A.D., and Melack, J.M., 1993, Geochemical and hydrological controls on the composition of surface water in a high-elevation basin, Sierra Nevada, California: *Limnology and Oceanography*, v. 38, p. 775-797.
- Williams, M.W. and Caine, Nel, 2001, Hydrology and hydrochemistry, in Bowman, W. and Seastedt, T.R., eds., *Alpine dynamics— The structure and function of an alpine ecosystem— Niwot Ridge, Colorado*: New York, Oxford University Press, p. 75-98.
- Williams, M.W., Losleben, M.V., Caine, Nel, and Greenland, D.E., 1996, Changes in climate and hydrochemical responses in a high-elevation catchment in the Rocky Mountains: *Limnology and Oceanography*, v. 41, p. 939-946.
- Williams, M.W. and Tonnessen, K.A., 2000, Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA: *Ecological Applications*, v. 10, p. 1648-1665.

