

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 (UV_{254}) 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

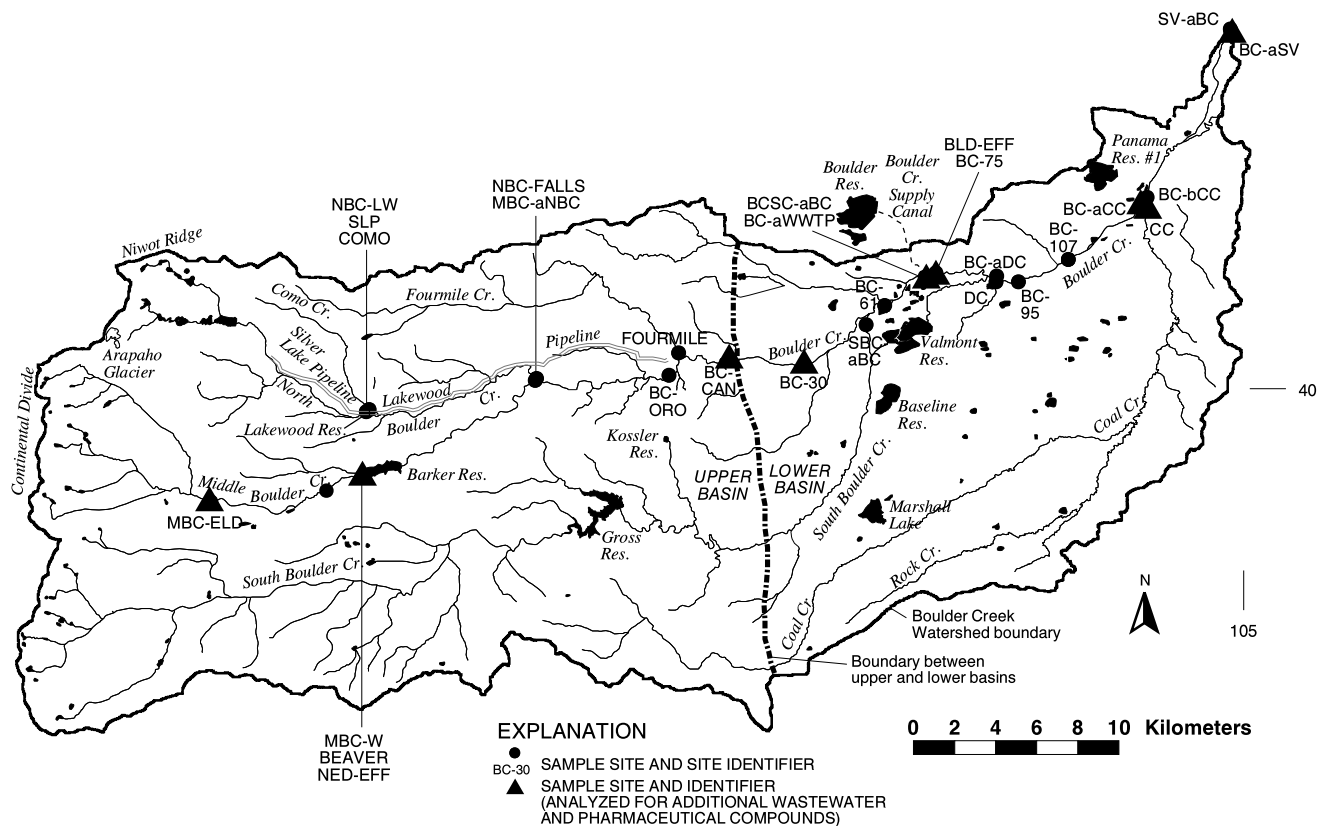


Figure 5.1. Map of Boulder Creek Watershed and sampling sites.

of wastewater-derived contaminants were evaluated in this study, including metal complexing agents, surfactant degradation products, antioxidants, caffeine, antimicrobials, steroids, hormones, prescription drugs, and nonprescription pharmaceuticals. Detailed descriptions of these “emerging contaminants” are given in Halling-Sorensen and others (1998) and Daughton and Ternes (1999).

The rationale for selection of compounds evaluated in this study (table 5.1) is based on the hierarchical analytical approach (Barber, 1992) and includes a range of compounds covering a spectrum of uses and effects. For example, ethylenediaminetetraacetic acid (EDTA) is a low-toxicity, high production-volume chemical used in a multiplicity of domestic, commercial, and industrial applications to form stable, water-soluble complexes with trace metals. Because of its uses and chemical characteristics, EDTA

occurs at relatively high concentrations and can persist in the aquatic environment (Barber and others, 1996; Barber and others, 2000; Leenheer and others, 2001). In contrast, prescription drugs such as 17- α -ethynylestradiol (EE2), although prescribed to a large number of people, are produced in small quantities (Arcand-Hoy and others, 1998) and occur in the environment at very low concentrations (Huang and Sedlak, 2001), but can have potent effects on biological systems (Desbrow and others, 1998; Johnson and Sumpter, 2001). Likewise, other pharmaceutical compounds are included because of their widespread use. Additional compounds such as caffeine (CAFF) and triclosan (TRI) are included because their ubiquitous nature makes them general indicators of municipal wastewater effluent contamination and they also are biologically active.

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 (UV₂₅₄) from all 29 sites. Samples for additional wastewater and pharmaceutical analysis were collected at 10 sites.

Samples for analysis of DOC and UV₂₅₄ were filtered through 0.7- μ m 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- μ m 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 μ L under a stream of nitrogen for GC/MS analysis.

Hormones were extracted by solid-phase extraction (SPE) using octadecyl surface-modified-silica (C₁₈) ENVI-Disk™ (47 mm, 5 μ m 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 μm 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/ μL) 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 C_{18} reverse-phase HPLC column (Metasil Basic, 3 μm , 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	EQU1 (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	--	--	--	--	--	--	<LRL	200	<LRL	<LRL
BC-aDC	<0.5	<0.5	<0.5	<0.5	6700	6500	--	--	--	--
BC-95	--	--	--	--	--	--	--	--	--	--
BC-107	--	--	--	--	--	--	--	--	--	--
BC-aCC	--	--	--	--	--	--	<LRL	98	<LRL	11
BC-bCC	<0.5	<0.5	<0.5	<0.5	4900	5800	--	--	--	--
BC-aSV	--	--	--	--	--	--	<LRL	E20	<LRL	14
	3.8	<0.5	<0.5	<0.5	680	2000	--	--	--	--
COMO	--	--	--	--	--	--	--	--	--	--
NBC-LW	--	--	--	--	--	--	--	--	--	--
SLP	--	--	--	--	--	--	--	--	--	--
BEAVER	--	--	--	--	--	--	--	--	--	--
NED-EFF	--	--	--	--	--	--	--	--	--	--
NBC-FALLS	<0.5	<0.5	<0.5	<0.5	4400	11000	--	--	--	--
FOURMILE	--	--	--	--	--	--	--	--	--	--
SBC-aBC	--	--	--	--	--	--	--	--	--	--
BCSC-aBC	--	--	--	--	--	--	--	--	--	--
BLD-EFF	--	--	--	--	--	--	--	--	--	--
DC	<0.5	<0.5	<0.5	<0.5	12000	9000	--	--	--	--
CC	--	--	--	--	--	--	<LRL	30	<LRL	74
SV-aBC	<0.5	<0.5	<0.5	<0.5	460	1400	--	--	--	--
	--	--	--	--	--	--	--	--	--	--
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

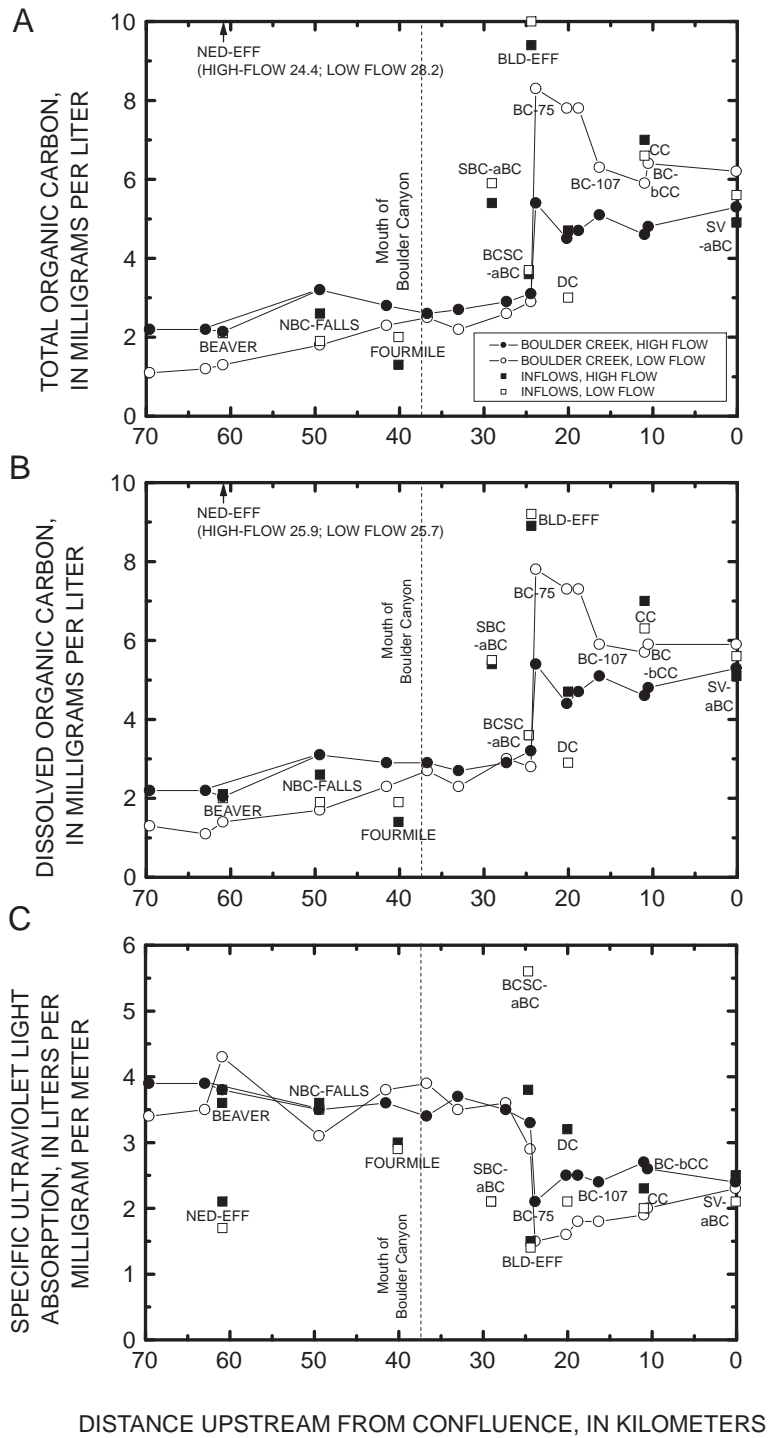


Figure 5.2. Concentrations of (A) total organic carbon, (B) dissolved organic carbon, and (C) specific absorbance for Middle Boulder Creek/Boulder Creek, inflows, and other flows, June and October 2000.

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

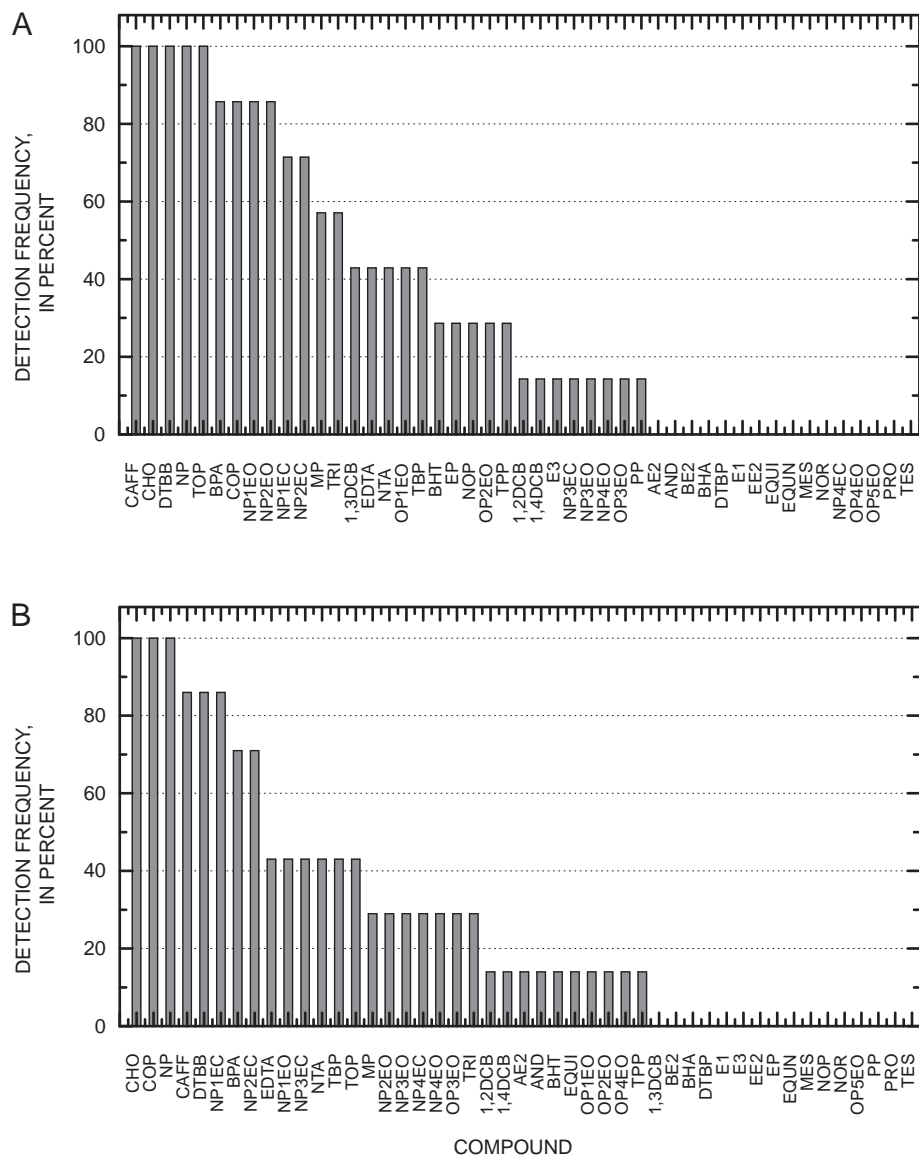


Figure 5.3. Wastewater compound detection frequency, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

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

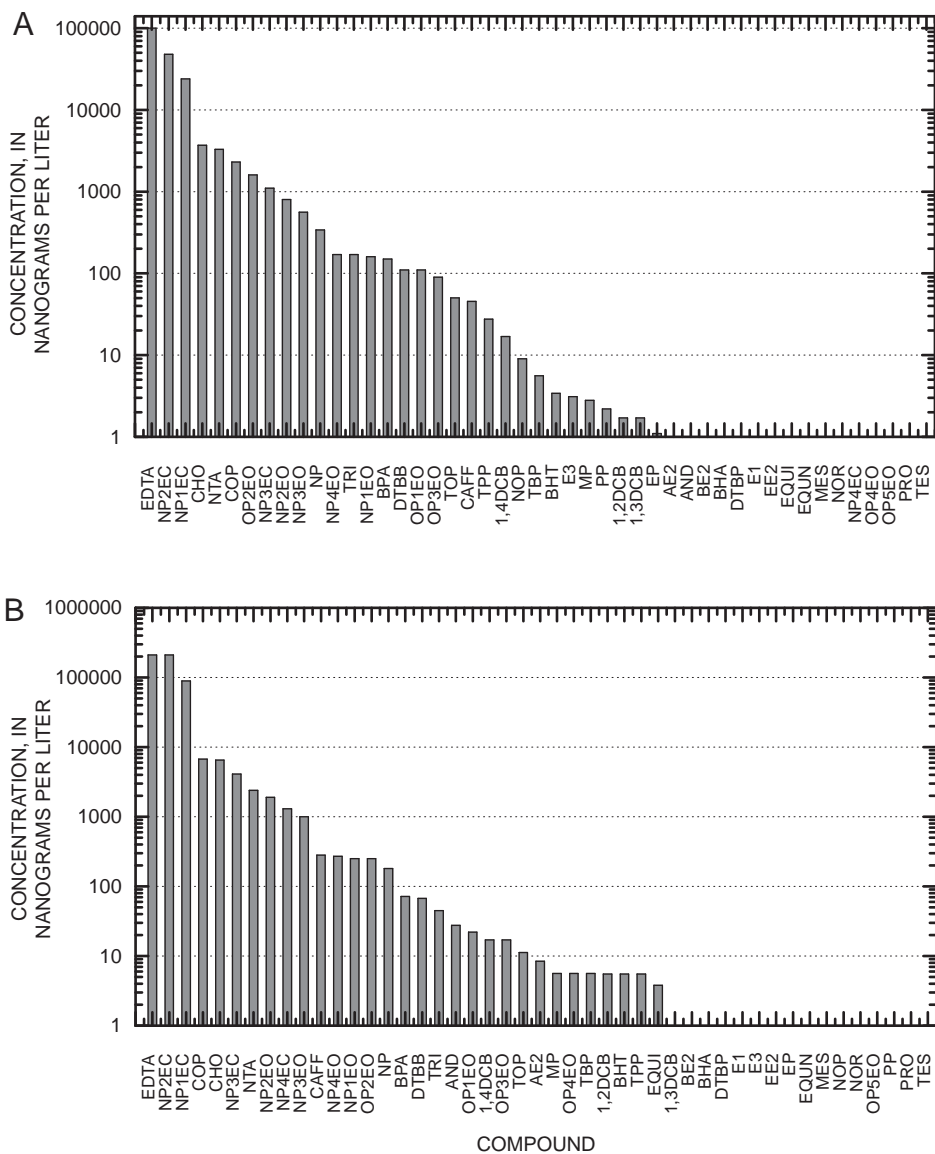


Figure 5.4. Wastewater compound maximum concentrations, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

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

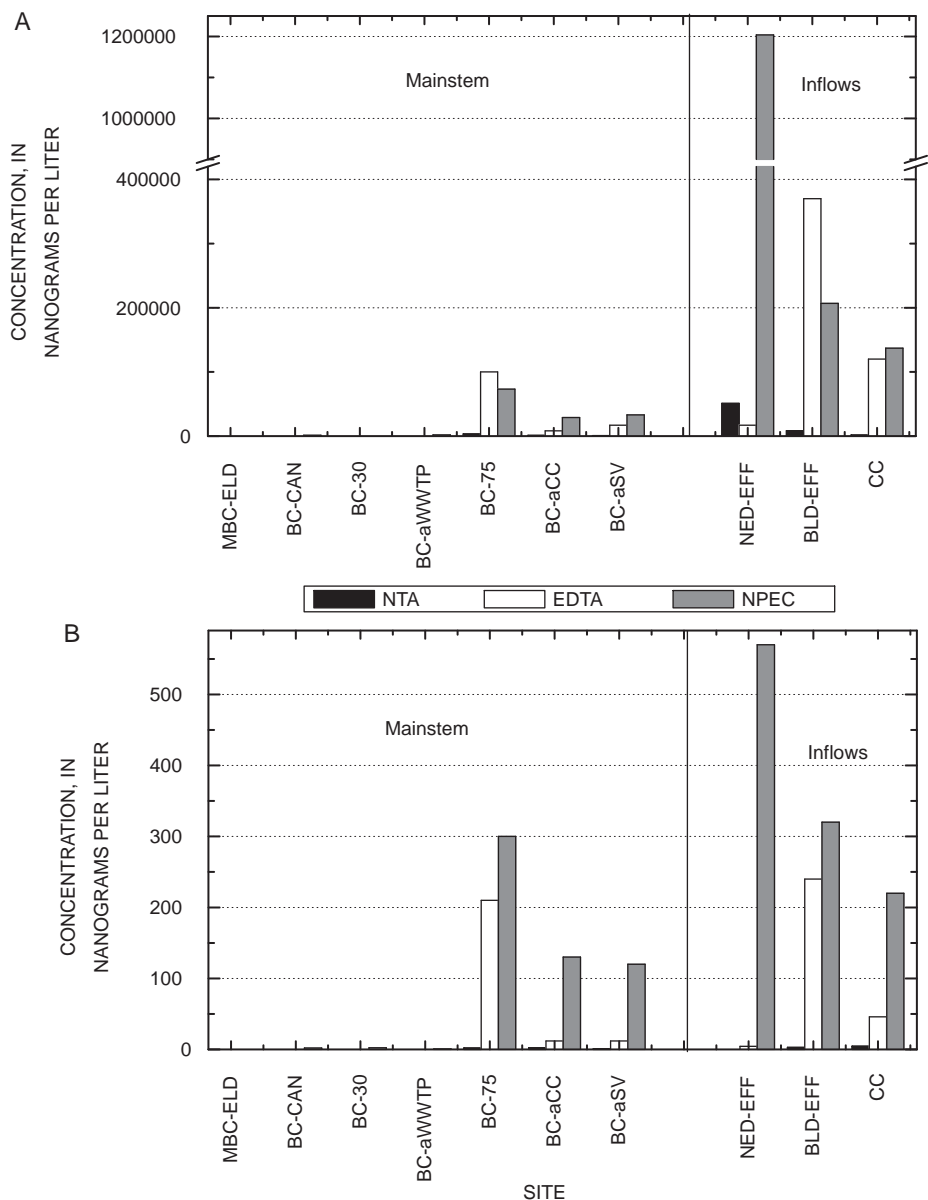


Figure 5.5. Concentrations of nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and total nonylphenolethoxycarboxylates (NPEC), Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000.

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

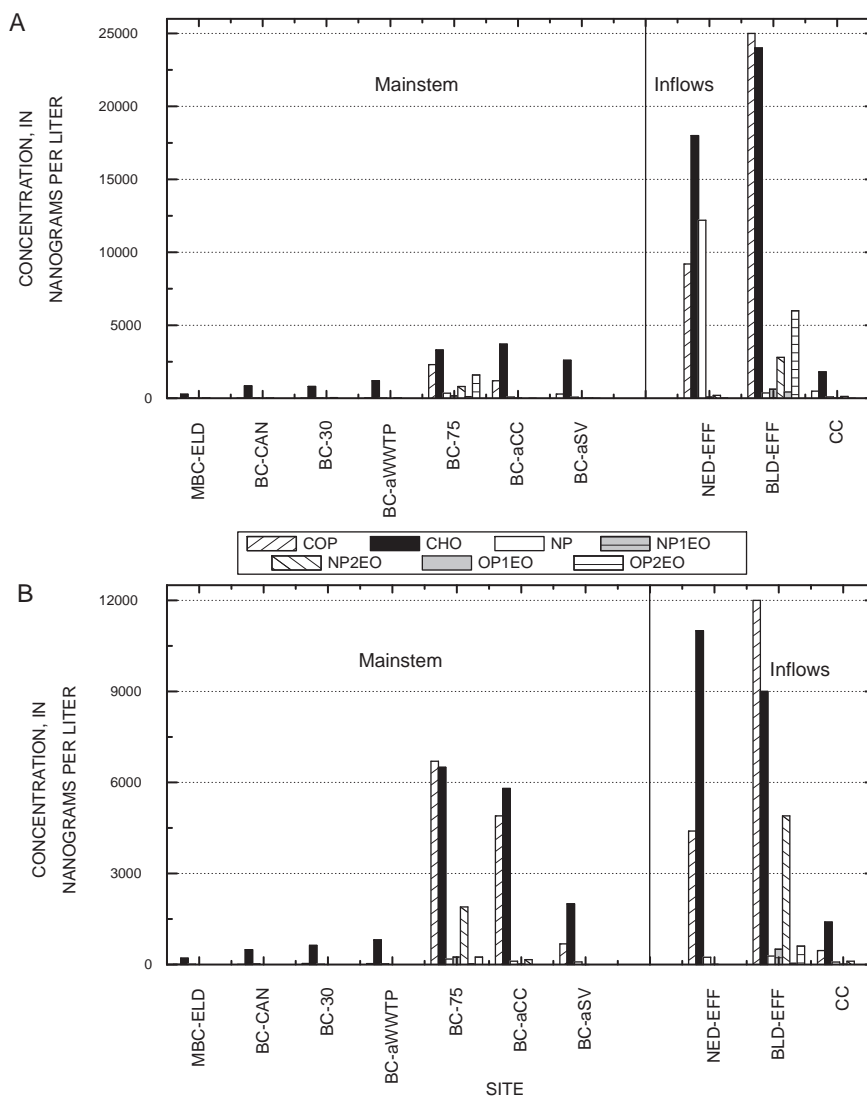


Figure 5.6. Concentrations of wastewater compounds with maximum concentrations greater than 200 nanograms per liter, Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

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

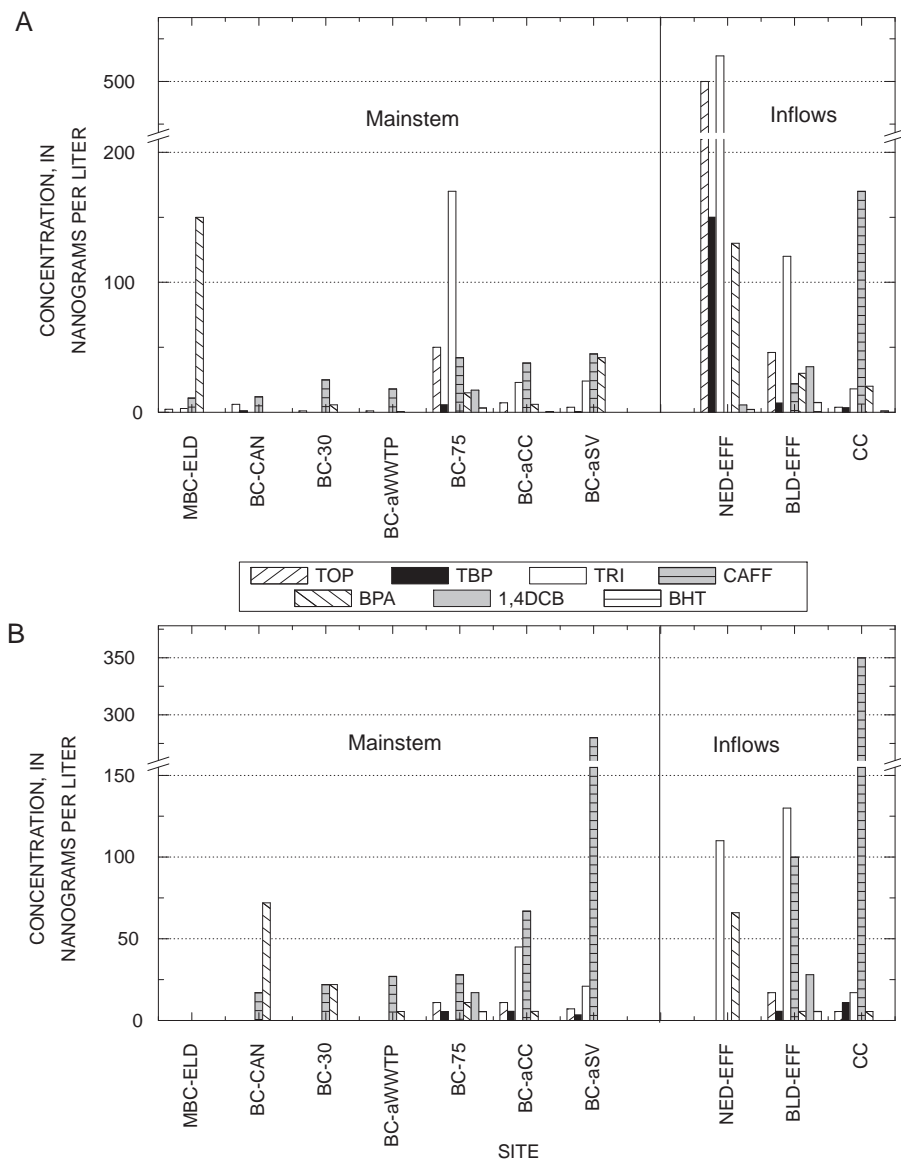


Figure 5.7. Concentrations of wastewater compounds with maximum concentrations less than 200 nanograms per liter, Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

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.

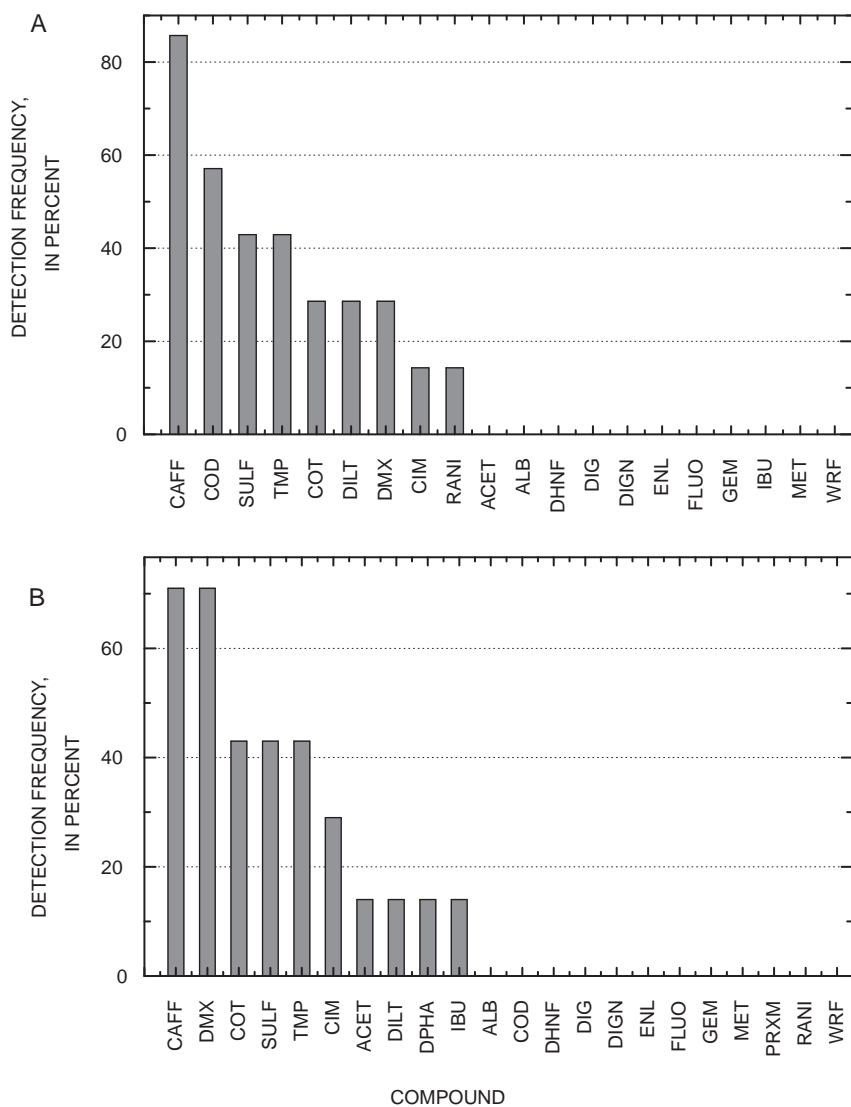


Figure 5.8. Pharmaceutical compound detection frequency, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

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

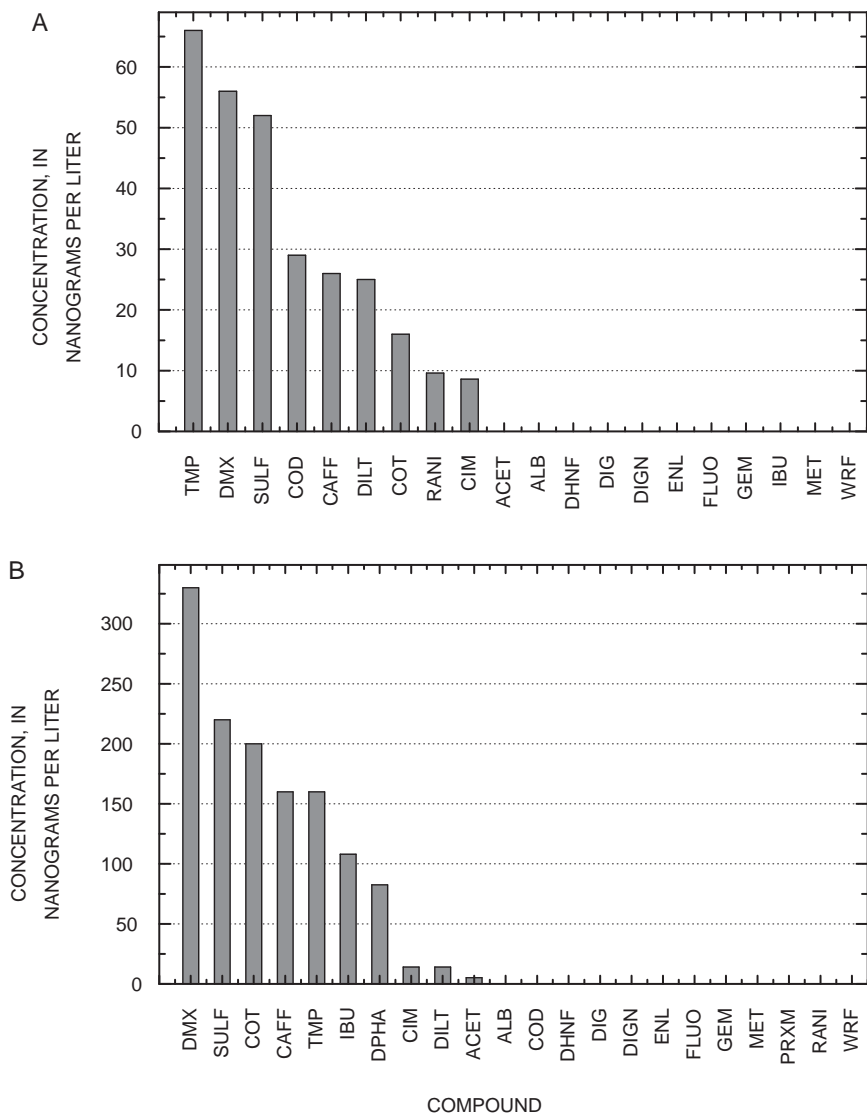


Figure 5.9. Pharmaceutical compound maximum concentrations, Middle Boulder Creek/Boulder Creek, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

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

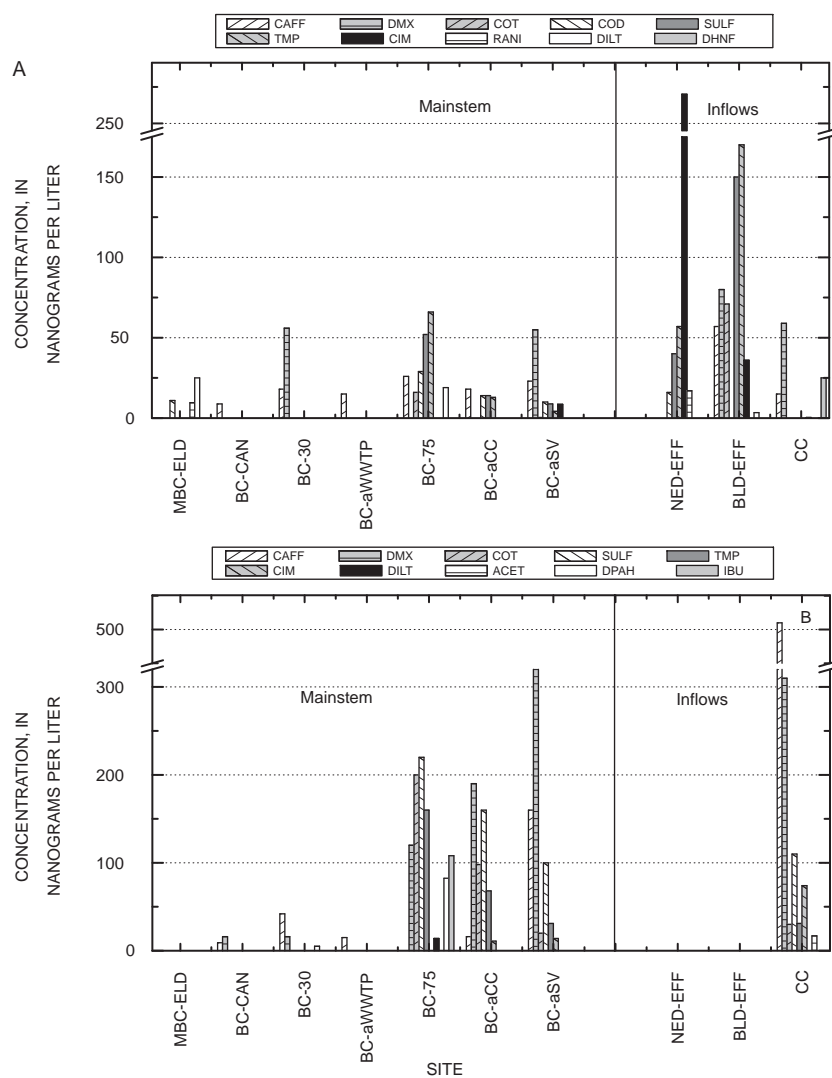


Figure 5.10. Concentrations of individual pharmaceutical compounds, Middle Boulder Creek/Boulder Creek and major inflows, during (A) June 2000 and (B) October 2000. See table 5.1 for compound abbreviations.

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 Wasterwater 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.

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