

Chemical Loading into Surface Water along a Hydrological, Biogeochemical, and Land Use Gradient: A Holistic Watershed Approach

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Identifying the sources and impacts of organic and inorganic contaminants at the watershed scale is a complex challenge because of the multitude of processes occurring in time and space. Investigation of geochemical transformations requires a systematic evaluation of hydrologic, landscape, and anthropogenic factors. The 1160 km² Boulder Creek Watershed in the Colorado Front Range encompasses a gradient of geology, ecotypes, climate, and urbanization. Streamflow originates primarily as snowmelt and shows substantial annual variation. Water samples were collected along a 70-km transect during spring-runoff and base-flow conditions, and analyzed for major elements, trace elements, bulk organics, organic wastewater contaminants (OWCs), and pesticides. Major-element and trace-element concentrations were low in the headwaters, increased through the urban corridor, and had a step increase downstream from the first major wastewater treatment plant (WWTP). Boron, gadolinium, and lithium were useful inorganic tracers of anthropogenic inputs. Effluent from the WWTP accounted for as much as 75% of the flow in Boulder Creek and was the largest chemical input. Under both hydrological conditions, OWCs and pesticides were detected in Boulder Creek downstream from the WWTP outfall as well as in the headwater region, and loads of anthropogenic-derived contaminants increased as basin population density increased. This report documents a suite of potential endocrine-disrupting chemicals in a reach of stream with native fish populations showing indication of endocrine disruption.

Introduction

Evaluating the flux of chemicals through watersheds is a challenge because of the diversity of chemical inputs, variability of water sources, and diversion of flow for agricultural, industrial, and domestic uses. Spatial and

temporal variability of organic and inorganic streamwater chemistry is controlled by natural and anthropogenic inputs, as well as chemical and biological reactions that influence fate and transport. Understanding complex in-stream chemical transformations requires integrating flow, geology, biology, and anthropogenic factors. Hydrology and the landscape are connected through geochemical processes, and “natural” background concentrations and distributions are modified by anthropogenic influences. Major-element and trace-element chemistry can be used to identify changes that occur in streamwater due to interactions with underlying rocks and soils. Although enriched and redistributed by anthropogenic activities, major-ion and trace-element contaminants have natural sources that must be taken into account. In contrast, identifying contamination by synthetic organic chemicals is more straightforward because they are not naturally occurring. Organic wastewater contaminants (OWCs) including chelating agents, surfactant-degradation products, antioxidants, antimicrobials, steroids, hormones, and pharmaceuticals have been identified in wastewater treatment plant (WWTP) effluents and receiving waters (1–4). Compounds such as ethylenediaminetetraacetic acid (EDTA), which is widely used in domestic and commercial applications to form water-soluble metal complexes, occur at relatively high concentrations ($\mu\text{g/L}$) in the aquatic environment (3, 5, 6) but have limited biological activity. In contrast, synthetic hormones, such as 17 α -ethynylestradiol, are produced in small quantities and occur in the environment at low concentrations (ng/L), but have potent biological effects (7, 8). Other biologically active compounds, such as triclosan (9) and caffeine (10), are ubiquitous in WWTP effluent. Pesticides used to control insects and weeds are another group of biologically active compounds frequently detected in surface waters (11).

This study was initiated to evaluate the spatial chemical loading of a diverse suite of inorganic and organic contaminants at the watershed scale and to identify relations between stream chemistry and the landscape. Water samples were collected during spring-runoff and base-flow conditions to characterize the water chemistry under different flow regimes. The samples encompassed a gradient of topography, geology, ecology, and land use, and were analyzed for major ions, trace elements, OWC, and pesticides. Integrating chemical results with sampling informed by hydrologic processes and landscape gradients provides insight into sources and fates of anthropogenic contaminants.

Methods

Site Description. This study was conducted in the 1160-km² Boulder Creek Watershed (Figure 1) located along the Colorado Front Range (12). The watershed varies in elevation from 4120–1480 m above sea level, and can be divided into the upper basin, defined on the west by the Continental Divide, and the lower basin, defined on the west by the Rocky Mountain foothills (13). The upper basin is underlain by Precambrian igneous and metamorphic rocks (Figure 1A) whereas the lower basin is underlain by Mesozoic and Tertiary sedimentary formations (14–16). Quaternary alluvium covers much of the Boulder Creek flood plain. The elevation gradient in the upper basin (34 m/km) is steeper than that in the lower basin (4 m/km), and the large variation in topography leads to different climatic and ecological zones (17). The upper basin includes alpine, subalpine, montane, and foothills ecotypes consisting of forests and shrubs, whereas the lower basin includes the plains ecotype consisting of moisture-limited grasslands modified by agricultural and

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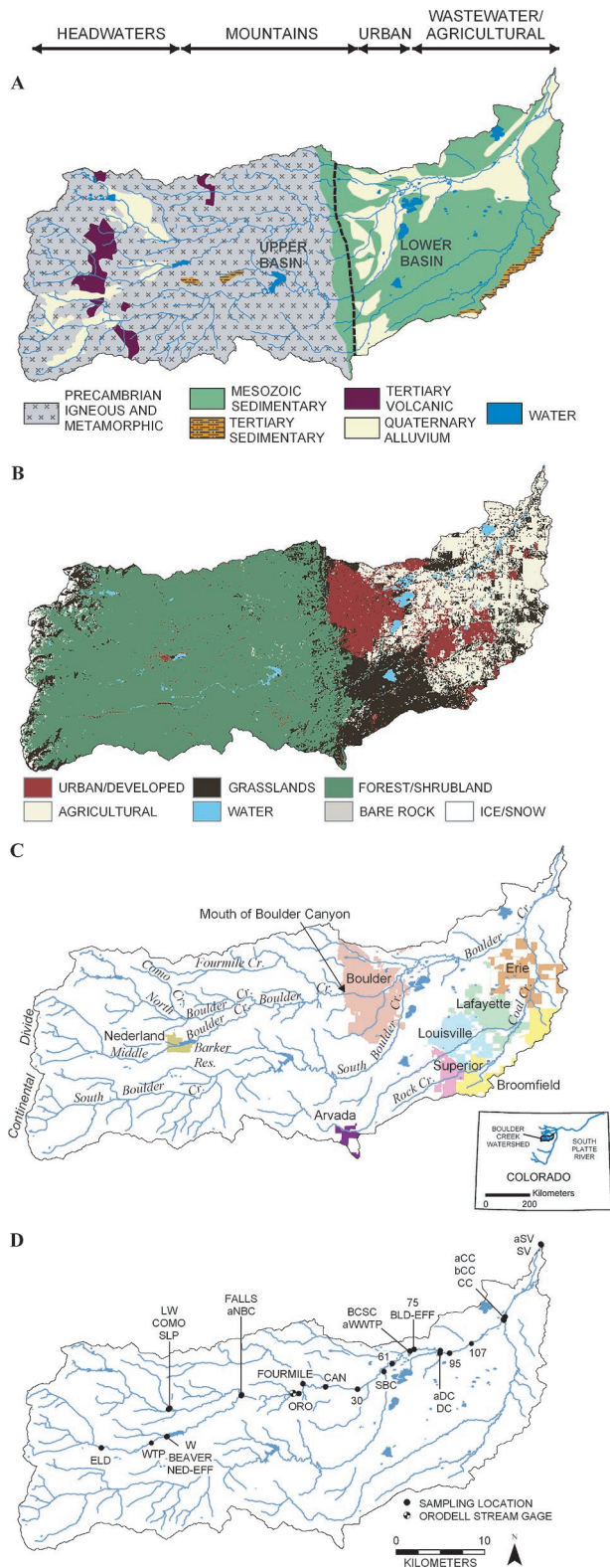


FIGURE 1. Maps of the Boulder Creek Watershed showing (A) geology, (B) land cover, (C) political boundaries and major transportation routes, and (D) sampling site locations (Reprinted from ref 13). [See Table SI-1 for site identifiers].

urban development (Figure 1B). The largest community in the upper basin is Nederland (Figure 1C) which had a population of 1,390 in 2000 (18), and the lower basin includes Boulder (94,670), Louisville (18,940), Lafayette (23,200), Erie (6,290), Superior (9,010), and part of Broomfield (38,270).

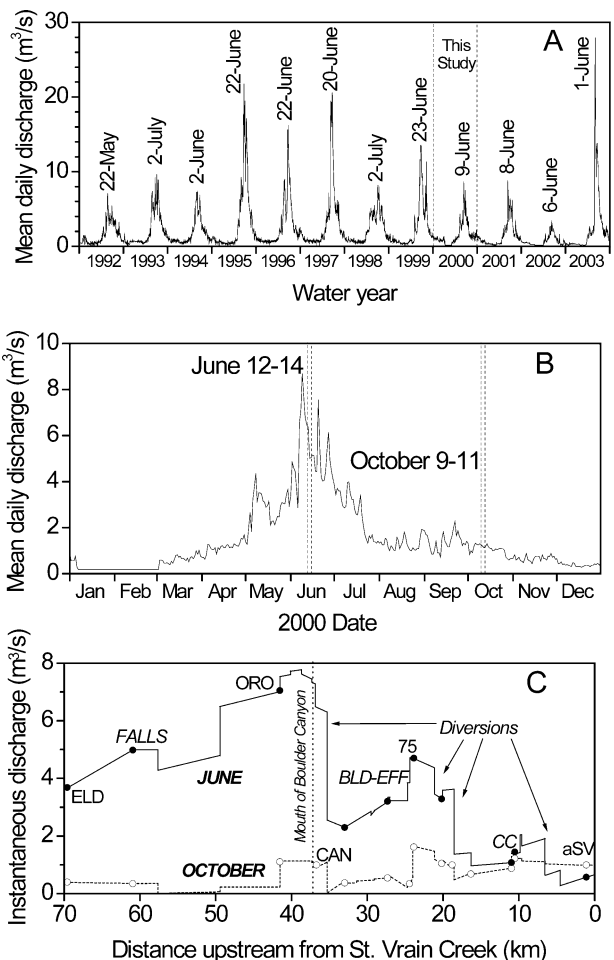


FIGURE 2. Hydrographs for Boulder Creek: (A) at the Orodell stream gage located near the mouth of Boulder Canyon for water years 1992–2003 showing dates of maximum annual flow, (B) at the Orodell stream gage for January 1 to December 31, 2000 showing the sampling periods investigated in this study, and (C) discharge measured along Boulder Creek, June 12–14 and October 9–11, 2000 (Reprinted from ref 13). [See Figure 1D and Table SI-1 for site locations].

Because most precipitation in the watershed falls as snow in the upper basin, snowmelt controls discharge in Boulder Creek and large seasonal fluctuations occur (Figure 2A). Base-flow conditions ($1-2 \text{ m}^3/\text{s}$) occur between August and March, and spring-runoff conditions ($4-28 \text{ m}^3/\text{s}$) occur between April and July. As Boulder Creek flows from mountains to plains it is subjected to a complex water management system. North Boulder Creek and Middle Boulder Creek each provide about 40% of the city of Boulder's drinking water supply (19). The Nederland WWTP discharges $0.008 \text{ m}^3/\text{s}$ (0.18 million gallons per day, MGD, 19) of aerated lagoon-treated wastewater into Middle Boulder Creek upstream from Barker Reservoir. Further downstream, North Boulder Creek converges with Middle Boulder Creek, minor tributaries contribute to flow, and diversion ditches remove water. At the mouth of Boulder Canyon, bedrock geology transitions from igneous and metamorphic to sedimentary rocks, and Boulder Creek enters the urban corridor where it gains water from tributaries (including South Boulder Creek) and groundwater, but loses water to irrigation ditches. A portion of the flow from the headwaters of North and Middle Boulder Creek is diverted through the urban corridor in pipes as treated drinking water (average daily flow $1.1 \text{ m}^3/\text{s}$, 25 MGD, 19) and returned to Boulder Creek as effluent from the Boulder WWTP (average daily flow $0.74 \text{ m}^3/\text{s}$, 17 MGD, 19) after trickling filter/activated sludge treatment. Downstream from the

WWTP, Boulder Creek flows across agricultural land, gains water from groundwater discharge and Coal Creek, and loses water to irrigation ditches. Water is imported into the Boulder Creek Watershed from the west slope of the continental divide, and is delivered sporadically into Boulder Creek from the Boulder Creek Supply Canal just upstream of the WWTP.

Sampling. To link water chemistry to the annual hydrograph, sampling in this study was timed to coincide with spring-runoff (June 12–14, 2000) and base-flow (October 9–11, 2000) conditions. Depth- and width-integrated composite samples (20) were collected along Boulder Creek from 16 mainstem sites and 13 major inflows (Figure 1D, Table SI-1 in the Supporting Information) following USGS National Field Manual (21) protocols. All samples were analyzed for field measurements, major elements, trace elements, and organic carbon, and a subset of samples from 10 sites was analyzed for OWCs and pesticides (22–24). Samples for major- and trace-element determinations were filtered through 0.1- μm membranes, and cation and trace-element samples were preserved with nitric acid. Samples for dissolved organic carbon (DOC), EDTA (also includes nonylphenolethoxycarboxylates acids, NPEC), pharmaceutical compounds, and pesticides were filtered through 0.7- μm glass fiber filters, and the EDTA/NPEC samples were preserved with 1% formalin. Unfiltered samples were collected for nonpharmaceutical OWCs and steroidal hormone analysis.

Analysis. Water temperature, dissolved oxygen, pH, and specific conductance were measured at the time of sample collection. Detailed laboratory analytical methods, quality-assurance data, and complete results for the 216 physical, inorganic, and organic chemical constituents measured are reported elsewhere (22–24). Anions were determined by ion chromatography (25), cations were determined by inductively coupled plasma/optical-emission spectroscopy (26), trace elements were determined by inductively coupled plasma/mass spectrometry (27), and mercury was determined by cold-vapor atomic-fluorescence spectrometry (28). Organic carbon was measured by ammonium persulfate/ultraviolet light oxidation with conductivity detection, and ultraviolet light absorption at 254 nm (UV_{254}) was measured in a 1-cm quartz cell (29). Prior to analysis by gas chromatography/mass spectrometry in the selected-ion monitoring mode, EDTA and NPEC were isolated by evaporation and derivatized to form the propyl esters, nonpharmaceutical OWCs were isolated by liquid–liquid extraction with methylene chloride, and steroids and hormones were isolated by solid-phase extraction and derivatized to form the methoxime/trimethylsilyl ethers (3, 4). Pharmaceuticals were isolated by solid-phase extraction and analyzed by high-performance liquid chromatography with electrospray ionization/mass spectrometry (30). Pesticides were isolated by solid-phase extraction and analyzed by gas chromatography/mass spectrometry or high-performance liquid chromatography (31–33).

Results

Streamflow. Discharge reached the annual daily maximum flow for 2000 (9 m^3/s) 2 days prior to the June sampling (Figure 2B) and exhibited diel variability due to daily differences in snowmelt rates (13, 34). The Boulder WWTP also imparted a diel signal on streamflow, with lowest discharge (0.5 m^3/s , 11 MGD) between 0300 and 0700 and peak discharge (1 m^3/s , 23 MGD) between 0800 and 1200. The combined natural and anthropogenic variations in flow complicate determining percent effluent in Boulder Creek downstream of the Boulder WWTP, and values ranged from 10–26% effluent during spring runoff and 39–74% effluent during base flow.

Discharge measurements taken along Boulder Creek during the spring-runoff and base-flow samplings are shown in Figure 2C. Spring runoff in the upper basin had increased

flow due to snowmelt and tributary inflow. Irrigation diversions near the mouth of Boulder Canyon significantly reduced flow in Boulder Creek, which was replenished by the WWTP discharge. Below the WWTP to the confluence with St. Vrain Creek most of the water was diverted through agricultural ditches. During base flow, discharge at the Orodell stream gage was only about 15% of spring-runoff conditions. Estimated stream velocities ranged from 1.8–2.4 km/hr, resulting in nominal travel times for the 70-km study reach of 30–40 h.

Inorganic Water Chemistry. Complete results of the inorganic chemical analyses (22) are summarized in Table SI-2 in the Supplemental Information. The dominant dissolved ions (up to 200 mg/L) in the upper watershed were bicarbonate, chloride, sulfate, calcium, magnesium, sodium, and silica, which accounted for greater than 90% of the total dissolved solids. Specific conductance (Figure 3A) indicated low dissolved ion concentrations upstream from the mouth of Boulder Canyon, an increase in the urban corridor, and a step increase downstream from the Boulder WWTP. Values were higher during base flow than during spring runoff. Dissolved chloride (Figure 3B), a conservative anion, exhibited stream profiles similar to those of specific conductance, whereas dissolved nitrate (Figure 3C), a nonconservative anion, did not show the same increase across the urban corridor and had a greater decrease downstream from the WWTP. Dissolved boron (Figure 3D), a relatively conservative trace element, exhibited a profile similar to that of chloride, as did lithium (Figure 3E). In contrast to dissolved chloride, boron, and lithium, during spring runoff dissolved gadolinium concentrations (Figure 3F) in the headwaters were elevated relative to base flow, and concentrations decreased downstream. There were step increases in gadolinium below the WWTP and the confluence with Coal Creek, followed by subsequent downstream decreases in concentrations.

Organic Water Chemistry. Complete results for the organic chemical analyses (23) are summarized in Table SI-2 in the Supplemental Information. Dissolved organic carbon profiles (Figure 3G) showed an increase in concentrations from the upper to lower watershed. In contrast to chloride, boron, and lithium, DOC in the upper watershed was greater during spring runoff than during base flow (as was observed for gadolinium). There was a step increase in DOC concentrations downstream from the WWTP as well as a shift in the bulk composition as shown (Figure 3H) by the decrease in specific absorption ($\text{UV}_{254}/\text{DOC}$).

During both sampling events, 77% of the 47 OWCs determined were detected in Boulder Creek at concentrations ranging up to 200 $\mu\text{g}/\text{L}$ (23). Maximum concentrations occurred below the WWTP, and the most abundant OWCs included EDTA, NPEC, and coprostanol (Figure 4A and B). The NPEC compounds are degradation intermediates of nonylphenolethoxylate (NPE) nonionic surfactants (35). The sum of the mono- to tetraethoxycarboxylate NPEC compounds are reported here. Coprostanol, a fecal steroid, was detected throughout the watershed; concentrations increased downstream from the headwater sites, and there was a step increase below the Boulder WWTP. Concentrations of triclosan, caffeine, and nonylphenol (NP) had similar trends (Figure 4C and D). Nonylphenol, nonylphenolmonoethoxylate (NP1EO), and nonylphenoldiethoxylate (NP2EO) are other important NPE degradation products.

Pharmaceutical compounds were detected (55% of the 22 compounds determined) in mainstem Boulder Creek samples, including diltiazem, cotinine, and sulfamethoxazole (Figure 4E and F). Although most pharmaceuticals only occurred downstream from the Boulder WWTP, several (ranitidine, codeine, diltiazem) were detected during spring runoff at the most upstream site (23).

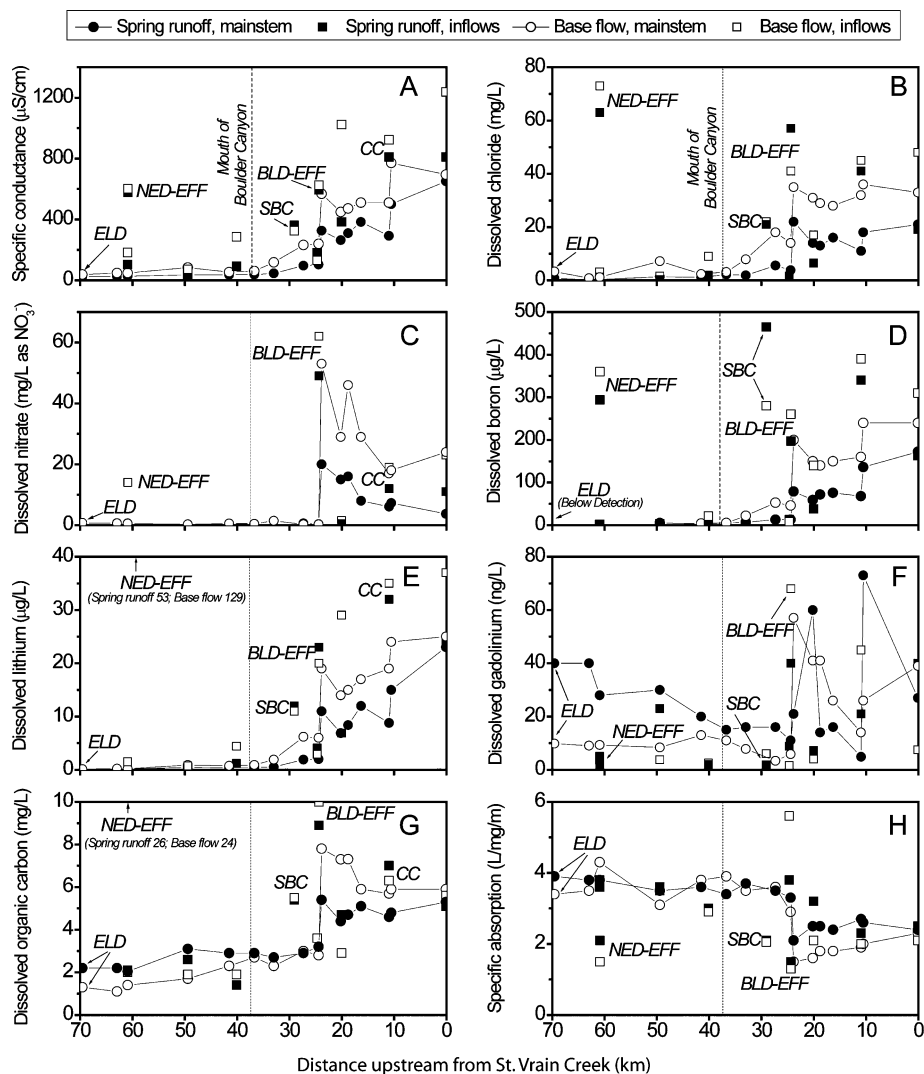


FIGURE 3. Concentration profiles of Boulder Creek showing downstream variations during spring-runoff (June 2000) and base-flow (October 2000) conditions for (A) specific conductance, (B) dissolved chloride, (C) dissolved nitrate, (D) dissolved boron, (E) dissolved lithium, (F) dissolved gadolinium, (G) dissolved organic carbon, and (H) specific absorption (ultraviolet light absorption at 254 nm/dissolved organic carbon). [See Figure 1D and Table SI-1 for site locations].

Pesticides also were detected (11% of the 84 compounds determined) in Boulder Creek (24). Dichlobenil occurred in the upper watershed as well as the wastewater-impacted reach, but not in the WWTP effluents (Figure 4G and H). The herbicide atrazine was detected in the agricultural reach of the watershed, and diazinon was detected in the Boulder WWTP effluent and Boulder Creek.

Discussion

Flow. Although the results presented here represent only two sampling events, the study was linked to the seasonal hydrograph and encompassed the length of the watershed. Consequently, the data represent basic hydrogeochemical relations, source loading concepts, and spatial and temporal trends that may be transferable to other flow regimes. For example, the 2000 hydrograph is slightly below average based on long-term trends (Figure 2A), and the chemical data indicate that maximum contaminant concentrations will occur downstream of the WWTP during the entire base-flow cycle. During the extreme low-flow event of 2002, spring runoff provided little in-stream dilution, and it is likely that WWTP effluent concentrations were greater than those during wetter years because of less commercial and domestic water use due to conservation measures imposed during the drought.

Inorganic Water Chemistry. In the headwater reach, flow originates as precipitation, water has relatively short residence times, and the sites have few potential anthropogenic chemical sources (34, 36–38). Major inorganic constituents at the headwater sites (22) were enriched by an order of magnitude compared to precipitation (36), consistent with local bedrock weathering (39). Although many trace elements are used in industrial, commercial, and domestic activities, their pathways for introduction into the aquatic environment are limited. For example, aluminum used in pans and foil is not a significant source of loading to WWTP, whereas copper, zinc, and lead used in plumbing can be introduced to WWTP through leaching. The relation between concentrations and discharge for select constituents is expressed as loads in Table 1 [load (mass/time) = concentration (mass/volume) × discharge (volume/time)]. Load calculations can be strongly influenced by sample processing, and the amount of chemical in unfiltered samples (dissolved, colloid, particle phases) can be greater than in filtered samples (dissolved phase only). Many of the chemicals used as tracers in this study were selected for their high water solubility characteristics, have little tendency to partition into solids, and occur predominantly in the dissolved form. However, some elements are strongly associated with particles or form precipitates, and total concentrations can be much greater than dissolved

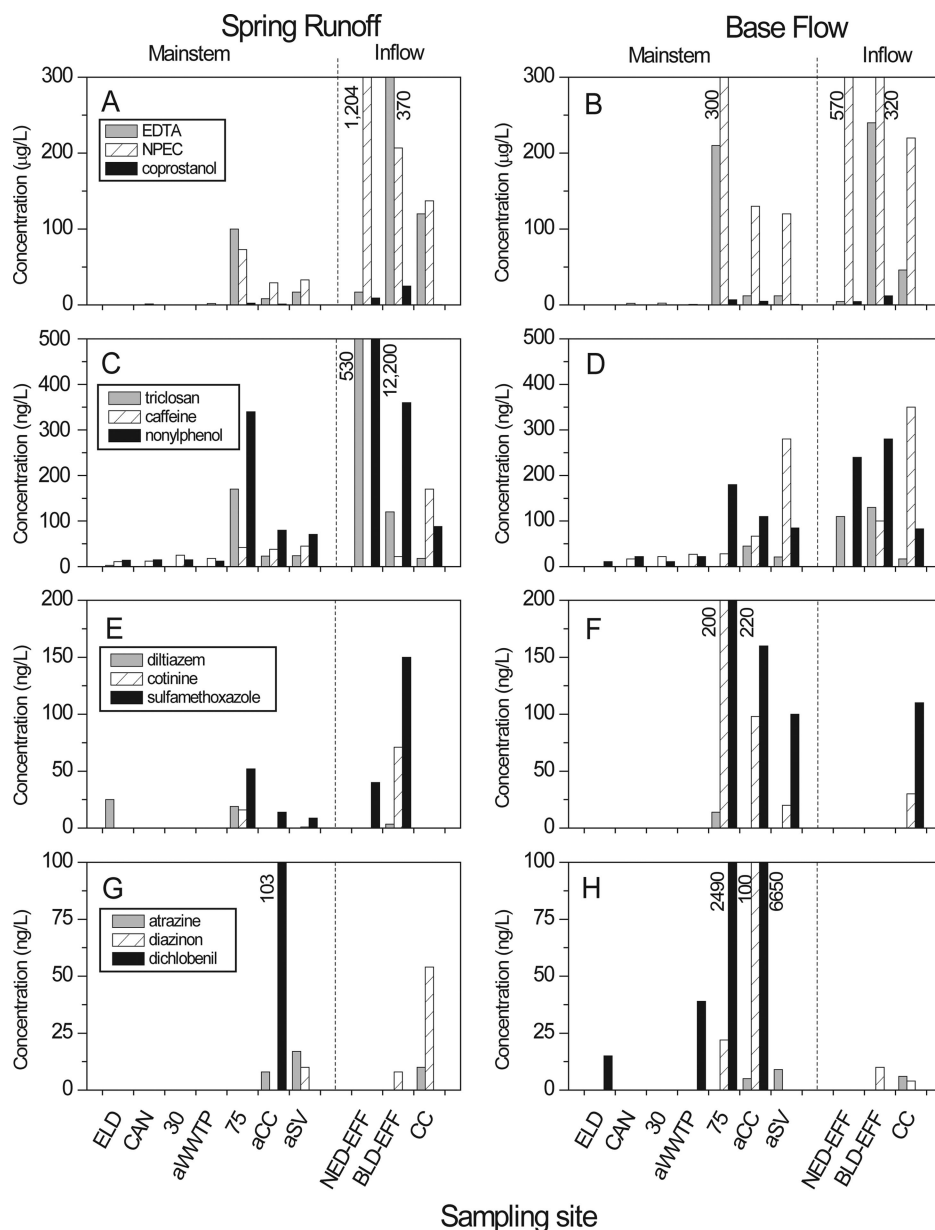


FIGURE 4. Concentration profiles of Boulder Creek showing downstream variations during spring-runoff (June 2000) and base-flow (October 2000) conditions for (A and B) dissolved ethylenediaminetetraacetic acid (EDTA), dissolved nonylphenoethoxycarboxylates (NPEC), and total coprostanol, (C and D) total organic wastewater compounds, (E and F) dissolved pharmaceutical compounds, and (G and H) dissolved pesticides. [Numerical values noted by the bars are the concentrations for sites that are off scale; see Figure 1D and Table SI-1 for site locations].

concentrations. Even for elements that partition strongly to the solid phase, most of the mainstem Boulder Creek load was in the dissolved phase because of the low total suspended sediment concentrations (1–20 mg/L). Load calculations are influenced by both flow and concentration, and in collecting the profiles, flow measurement and sampling occurred at slightly different (± 8 h) times.

As water flows downstream from the headwaters it encounters increasing anthropogenic influences including point-sources, such as the Nederland WWTP, although there was little change in stream chemistry because the WWTP discharge was small compared to the streamflow. Major- and trace-element chemistry of the upper watershed was consistent with progressive weathering of crystalline bedrock, and historical mining had little effect on trace-element loading (22). As Boulder Creek exits the foothills, bedrock composition and potential anthropogenic sources change. Although inorganic solutes increased across the geological/

land use transition, distinguishing natural and anthropogenic sources is difficult because both contribute to stream chemistry. For example, chloride has anthropogenic sources such as road deicers but also is present in marine sediments. Geochemical simulations using the NETPATH model indicate that most of the increase in major- and trace-element concentrations between the mouth of Boulder Canyon and the WWTP reflects rock/water interactions with underlying marine shale deposits (22).

The Boulder WWTP effluent had elevated dissolved inorganic solutes compared to Boulder Creek. Mass balance calculations for boron, chloride, and lithium indicate that during spring runoff effluent accounted for 37–39% of the flow downstream from the outfall, and during base flow effluent accounted for 69–77% of the stream volume. The results are consistent with discharge-based hydrologic mixing calculations. Boron is an indicator of wastewater contamination because it has domestic use as a nonchlorine bleach

TABLE 1. (Continued)

site name	sampling event	flow (m ³ /s)	chloride (kg/d)	nitrate (kg/d)	boron (kg/d)	gadolium (g/d)	lithium (kg/d)	DOC (kg/d)	EDTA (kg/d)	NPEC ^b (kg/d)	coprostanol (g/d)	triclosan (g/d)	caffeine ^c (g/d)	nonylphenol (g/d)	diltiazem (g/d)	cotinine (g/d)	sulfamethoxazole (g/d)	atrazine (mg/d)	diazinon (mg/d)	dichlorobenil (mg/d)
FOURMILE	SR	0.11	18	nd	0.086	0.019	0.011	13	--	--	--	--	--	--	--	--	--	--	--	--
	BF	0.020	16	nd	0.036	0.004	0.008	3.3	--	--	--	--	--	--	--	--	--	--	--	--
SBC	SR	0.020	36	nd	0.80	0.003	0.021	9.3	--	--	--	--	--	--	--	--	--	--	--	--
	BF	0.10	19	nd	0.24	0.005	0.010	4.8	--	--	--	--	--	--	--	--	--	--	--	--
BCSC	SR	0.62	86	nd	0.70	0.47	0.22	190	--	--	--	--	--	--	--	--	--	--	--	--
	BF	0.060	7.8	nd	0.041	0.008	0.015	18	--	--	--	--	--	--	--	--	--	--	--	--
BLD-EFF	SR	0.86	4200	3600	15	3.0	1.7	660	28	15	1900	8.9	1.6	27	0.25 ^d	5.3	11	nd	590	nd
	BF	0.90	3200	4800	20	5.3	1.6	780	19	25	930	10	7.8	22	--	--	--	nd	780	nd
DC	SR	0.37	210	16	1.2	0.23	0.22	150	--	--	--	--	--	--	--	--	--	--	--	--
	BF	0.030	44	3.9	0.36	0.010	0.075	7.5	--	--	--	--	--	--	--	--	--	--	--	--
CC	SR	0.31	1100	320	9.1	0.56	0.86	190	3.2	3.7	13	0.48	4.6	2.4	nd	nd	nd	270	1500	nd
	BF	0.34	1300	560	11	1.3	1.0	190	1.4	6.5	14	0.49	10	2.4	nd	0.88	3.2	180 ^d	120 ^d	nd
SV	SR	3.3	5400	3100	46	11	6.8	1500	--	--	--	--	--	--	--	--	--	--	--	--
	BF	1.9	7900	3800	51	1.2	6.1	910	--	--	--	--	--	--	--	--	--	--	--	--
Outflow																				
12th Street	SR	3.7	700	nd	1.6	4.8	0.14	930	nd	0.46	1.6	nd	3.9	4.8	nd	nd	nd	nd	nd	nd
	BF	0.96	260	36	0.42	0.91	0.075	220	nd	0.18	0.65	nd	1.4	1.8	nd	nd	nd	nd	nd	nd
Leggett	SR	0.91	1100	1200	4.6	4.7	0.86	350	7.9	5.8	180	13	3.3	27	1.5	1.3	4.1	nd	nd	nd
	BF	0.25	750	700	3.6	0.34	0.46	180	5.1	7.3	160	nd	0.68	4.4	0.34	4.8	5.3	nd	530	60000
Lower Boulder	SR	2.3	2600	3200	14	2.8	1.7	930	20	15	460	34	8.4	68	3.8	3.2	10.3	nd	nd	nd
	BF	0.48	1200	1900	5.8	1.7	0.62	300	8.7	12	280	nd	1.2	7.5	0.58	8.3	9.1	nd	910	100000
Idaho Creek	SR	1.3	2000	820	15	8.2	1.7	530	0.92	3.3	140	2.6	4.3	9.0	nd	nd	1.6	900	nd	12000
	BF	0.08	250	124	1.7	0.18	0.17	50	0.081	0.90	34	0.31	0.46	0.76	nd	0.68	1.1	35	690	38000

^a See Figure 1D for site locations and Table SI-1 for site descriptions and reference 13 for flow measurements. Calculations assume instantaneous concentration and discharge measurements equal daily averages. Outflow loads calculated from concentrations at nearest upstream site. Load-based mass balance in the WWTP mixing zone (aWWTP, BLD-EFF, 75), as illustrated by boron, is influenced by differences in flow measurement techniques among the 3 sites and differences between the time of flow measurement and sample collection. Abbreviations: DOC, dissolved organic carbon; EDTA, ethylenediaminetetraacetic acid; NPEC, nonylphenoethoxycarboxylates acids; m³/s, cubic meters per second; kg/d, kilograms per day; g/d, grams per day; mg/d, milligrams per day; μ m, filter pore diameter in micrometers; UF, unfiltered sample; --, sample not analyzed; nd, compound was below method detection level (Table SI-2) and no load was calculated. ^b Concentrations of NPEC is sum of nonylphenolmonoethoxycarboxylate, nonylphenoldiethoxycarboxylate, nonylphenoltriethoxycarboxylate, and nonylphenoltetraethoxycarboxylate. ^c Determined by gas chromatography/mass spectrometry method. ^d Concentration are estimated and load calculations may be overestimated.

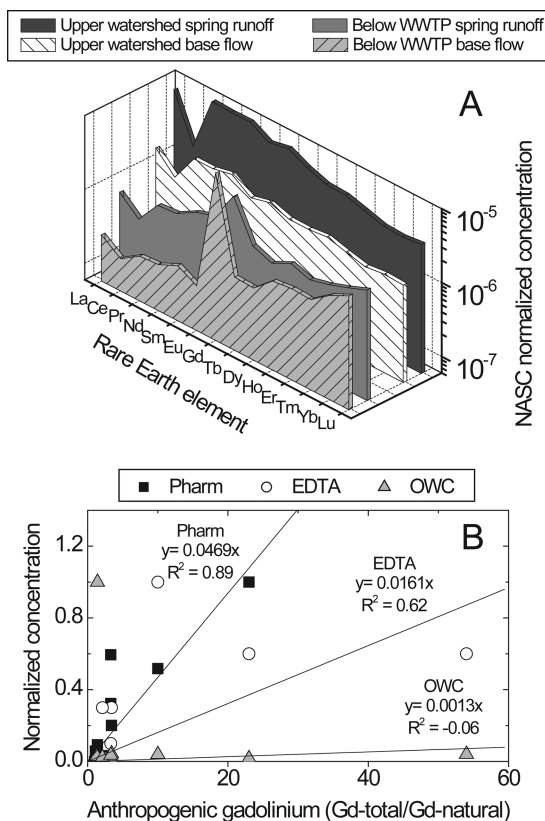


FIGURE 5. (A) Dissolved rare earth element distributions normalized to North American Shale Composite, NASC (48), for the Boulder Creek headwater and wastewater impacted reaches, and (B) correlations between anthropogenic gadolinium and normalized concentrations (relative to maximum measured values) of the sum of dissolved pharmaceuticals (diltiazem, cotinine, sulfamethoxazole), dissolved ethylenediaminetetraacetic acid (EDTA), and the sum of total organic wastewater contaminants (nonylphenol, triclosan, caffeine). [Anthropogenic gadolinium = $Gd/Gd^* = Gd_{SN}/10^{(0.33 \log S_{mSN} + 0.67 \log T_{bSN})}$, where Gd is total dissolved gadolinium, Gd^* is natural gadolinium, Gd_{SN} is NASC normalized dissolved gadolinium, S_{mSN} is NASC normalized dissolved samarium, T_{bSN} is NASC normalized dissolved terbium].

(6, 40–42). However, there are other sources of boron including weathering of marine shale and coal deposits (43) and coal-fired power plant fly ash (44). It is clear from the concentration profiles and load calculations that the major source of boron to Boulder Creek is the Boulder WWTP effluent. Boron concentrations in South Boulder Creek were greater than those in the Boulder or Nederland WWTP effluents, even though there are no major WWTP discharges. A coal-fired power plant located on South Boulder Creek diverts flow for cooling water, and ash leachate is a potential source of the boron.

The 14 rare earth elements (REEs) have similar chemical and physical properties and have been used as tracers of hydrogeologic processes (45–47). Gadolinium is not naturally enriched relative to the other REEs, but has anthropogenic applications that result in a positive anomaly when normalized to geochemical distributions in reference materials such as the North American Shale Composite (48). The gadolinium anomaly provides a WWTP-specific chemical signature attributed to gadopentetic acid used as a paramagnetic contrasting agent in magnetic resonance imaging. Downstream of the Boulder WWTP there was enrichment in dissolved gadolinium compared to its neighboring REEs (Figure 5A), similar to the Boulder WWTP effluent (22, 47). In contrast, the Nederland WWTP effluent did not have a gadolinium anomaly. During spring runoff, the dissolved

gadolinium load in the upper watershed was greater than the load from the Boulder WWTP, but the absence of a positive anomaly indicates geologic rather than anthropogenic sources. Dissolved gadolinium loads in Boulder Creek downstream of the Boulder WWTP (7.4–8.9 g/d) were less than that for the Vltava River (15 g/d) which drains the city of Prague in the Czech Republic (46). However, when normalized to population, the per capita load was higher for Boulder (44 mg/person/d) than for Prague (13 mg/person/d). Even specific trace-element indicators such as gadolinium are confounded by natural sources that contribute to stream chemistry. The gadolinium anomaly has been suggested as a surrogate for other medically related compounds that are more difficult to determine (47). Figure 5B shows associations between anthropogenic gadolinium and EDTA, the sum of OWCs, and the sum of pharmaceutical compounds (note the regression is forced through the origin). The best correlation ($r^2 = 0.89$) was between anthropogenic gadolinium and the summed pharmaceutical compounds. This relatively robust correlation likely reflects a more specific source (i.e., human excretion of synthetic pharmaceuticals into domestic wastewater) for gadolinium and the summed pharmaceuticals than either EDTA or the summed OWCs. EDTA has substantial sources to wastewater that differ from gadolinium and the summed pharmaceuticals. The summed OWCs include caffeine, triclosan, and NP which would not be expected to co-vary with pharmaceutical concentrations. Co-occurrence of the related antimicrobials triclosan and triclocarban (49), and associations between pharmaceuticals of differing classes and physical properties (50) have been reported for surface waters with substantial inputs of WWTP effluent.

Lithium had elevated concentrations in the Nederland and Boulder WWTP effluents relative to the streamwater, and is another inorganic indicator with a medically derived source. Lithium carbonate ranks in the top 250 pharmaceutical compounds prescribed in the United States during 2004 (51), with 3.2 million prescriptions written for treatment of bipolar disorder. Optimal therapeutic response is typically achieved at a lithium dose of ~1800 mg/day, suggesting that the observed elevated WWTP concentrations could result from pharmaceutical use. The average load of 1.65 kg/day of dissolved lithium in the Boulder WWTP effluent would represent approximately 900 daily users of lithium carbonate taking the optimal therapeutic amount. This estimate is similar to the projected occurrence of individuals with bipolar disorder (1140) in the Boulder Creek watershed population, assuming the National Institutes of Mental Health estimate of a 1.2% rate of occurrence in the general U.S. population (52). A number of other pharmaceutical compounds are prescribed to treat bipolar disorder, including carbamazepine, which has been detected in subsequent analyses of the Boulder WWTP effluent. The similarity in magnitude between the potential loading of pharmaceutical lithium to the effluent and the population segment in the watershed expected to use lithium suggests that the lithium in Boulder Creek below the WWTP discharge has a pharmaceutical source. The primary industrial and commercial uses of lithium also suggest that other contributions to wastewater are unlikely to contribute significantly to dissolved lithium concentrations (53). Although the lithium source signal is not as specific as the gadolinium anomaly because lithium has other anthropogenic uses and natural sources, dissolved lithium (Figure 3E) is a more conservative hydrological tracer than natural (uncomplexed) dissolved gadolinium (Figure 3F) which undergoes in-stream removal.

Organic Water Chemistry. Dissolved organic carbon loading in the upper watershed reflects biogeochemical interactions between the native flora and fauna and the hydrosphere (54). During spring runoff, DOC concentrations

in the upper basin were greater than those during base flow due to flushing of natural organic matter from the soil and shallow groundwater system. As was the case for water-soluble elements (chloride, boron, lithium), greater than 95% of the organic carbon in Boulder Creek occurs in the dissolved phase. Carbon flux has water-resource implications, in particular the relation between DOC and disinfection by-product formation during drinking-water treatment (55). Although DOC concentrations downstream from the Boulder WWTP were higher than those in the upper watershed, the potential for WWTP-derived DOC to form disinfection byproducts is less than that for natural DOC (56). Disinfection byproduct formation potential is correlated with specific absorbance (a measure of DOC aromaticity, 29), and the lower specific absorbance below the WWTP indicates that the DOC had a more aliphatic character and a lower disinfection byproduct formation potential.

Although the upper watershed is relatively pristine, it receives recreational use and has scattered residential development. Anthropogenic impacts can be distinguished using specific compound analysis, and several OWCs and pesticides (triclosan, caffeine, bisphenol A, nonylphenol, cholesterol, coprostanol, cimetidine, ranitidine, codeine, diltiazem, dichlobenil) were detected at the most upstream site. In contrast to the Boulder and Nederland WWTP effluents, which had relatively constant flow and composition, OWCs detected in the upper watershed indicate flushing from the landscape-derived sources.

As Boulder Creek traverses the population and land-use gradient, concentrations of OWCs increase. The most abundant OWCs detected in Boulder Creek were EDTA and NPEC, which had concentrations (up to 200 $\mu\text{g/L}$) orders of magnitude greater than the other OWCs, reflecting their high production volumes (annual U.S. production of EDTA = 5×10^7 kg/yr (5); annual U.S. production of NPE = 1×10^8 kg/yr (57)) and relative resistance to removal during wastewater treatment and stream transport. The per capita load of dissolved EDTA discharged from the Boulder WWTP was 250 mg/person/d, greater than the 50 mg/person/d reported for a Swiss WWTP (58). The per capita dissolved NPEC load was 210 mg/person/d, although it is difficult to evaluate NPEC removal because it is both a product and reactant in the degradation of NPE surfactants (35). Concentrations of NPEC and the associated NP, NP1EO, and NP2EO degradates in the wastewater-impacted reach of Boulder Creek were similar to those reported elsewhere (3, 4, 59–61). Greater than 95% of the total NPE degradation products were in the NPEC form. The ratio of NPEC to EDTA in Boulder Creek immediately downstream from the WWTP outfall was similar to that in the effluent, although spring runoff concentrations were lower than those during base flow reflecting greater dilution by streamwater. In other studies (3) comparison of EDTA and NPEC concentrations in filtered and unfiltered WWTP effluent gave nearly identical results as would be expected for water soluble compounds that occur predominantly in the dissolved phase. Coprostanol, another high abundance compound, was detected throughout the watershed but showed a step increase below the WWTP outfall. Coprostanol is an indicator of contamination by human and other animal fecal matter (62–64), and is produced by the transformation of dietary cholesterol during digestion in the gut. Cholesterol has additional nonfecal sources, and as a consequence, occurs at higher concentrations than coprostanol. Because of their affinity for solids, steroids and hormones were measured in unfiltered rather than filtered samples.

Unique source characteristics and widespread use make caffeine a good indicator of anthropogenic contamination (3–5, 10). Low concentrations of caffeine were detected in the urban corridor upstream from the Boulder WWTP, and

typically co-occurred with the metabolite 1,7-dimethylxanthine. The per capita caffeine load (unfiltered) discharged from the WWTP (0.06 mg/person/d) was similar to the average value of 0.06 ± 0.03 mg/person/d reported for several Swiss WWTPs (10). Triclosan, a widely used antimicrobial compound, is another source-specific OWC (3, 4, 9) detected in the upper watershed during spring runoff. In contrast to caffeine, additional detections of triclosan in Boulder Creek only occurred downstream from the Boulder WWTP, which had a per capita load of 0.11 mg/person/d, within the range of 0.03–0.43 mg/person/d reported for several Swiss WWTPs (9).

Pharmaceutical concentrations in Boulder Creek were generally lower than for the other OWCs, similar to results from a national survey of the United States (4). The presence of pharmaceutically active agents in surface waters reflects the combined impacts of contemporary healthcare practices and incomplete removal during wastewater treatment (2, 65). Per capita dissolved mass loading of the antimicrobial sulfamethoxazole into Boulder Creek from the WWTP was 0.27 mg/person/d, higher than the median value of 0.15 mg/person/d reported for several Canadian WWTPs (66). Trimethoprim, which is co-prescribed with sulfamethoxazole also co-occurs in the WWTP effluent and Boulder Creek samples. Other prescription drugs including diltiazem, used to treat high blood pressure, were detected in Boulder Creek. As was the case for caffeine, which co-occurred with its metabolite 1,7-dimethylxanthine, cotinine, the metabolite of nicotine was frequently detected.

Estimates of agricultural pesticide use in Boulder County (24) indicate that 7900 kg of total active ingredient (top 50 compounds) are applied annually. By comparison, the estimated load of dissolved sulfamethoxazole from the Boulder WWTP was 9.5 kg/yr and dissolved EDTA was 13 000 kg/yr. There was little correlation between pesticide concentrations in Boulder Creek and estimated use. Atrazine and methyl-parathion are among the top 10 pesticides used in the region and were detected in Boulder Creek, but other high-use pesticides were not detected. The average atrazine load from the agricultural reach was 0.24 kg/yr versus the 1200 kg/yr applied in Boulder County. Additional pesticides including diazinon, dichlobenil, lindane, and picloram were detected (24). Dichlobenil, used to control weeds and tree-root growth in sewers, was the only pesticide detected in the upper watershed, and was the highest concentration pesticide detected at the downstream Boulder Creek sites during both sampling events, but was not detected in either WWTP effluent. The herbicide atrazine and the degradate desethyl-atrazine were detected in the agricultural reach. Comparison of data normalized to population density indicates fewer pesticides were detected at lower frequency in Boulder Creek than in nearby urban streams (11, 24), possibly due to local pesticide-use practices. Of the compound classes evaluated in this investigation, pesticides were lowest in percent detection, illustrating different impacts on Boulder Creek stream chemistry from different introduction pathways—landscape runoff versus wastewater discharge.

In-Stream Processes. The Boulder WWTP discharge increased the chemical load of Boulder Creek from the biogeochemistry of human activity as well as chemicals used in domestic and commercial applications. Once inorganic and organic chemicals are introduced into Boulder Creek, they are subject to physical processes (mixing, dilution, diversion) as well as environmental removal pathways (volatilization, sorption, precipitation, biodegradation, photolysis). In-stream degradation can be affected by hydraulic residence time, temperature, sunlight, and biota. Certain elements, such as boron, chloride, and lithium, exhibited relatively conservative behavior and primarily were attenuated by dilution. Other constituents had nonconservative

behavior, resulting from different removal mechanisms. For example, nitrate is removed by plant uptake and microbial denitrification (67), whereas gadolinium is removed by sorption and precipitation (47). Estimates of removal based on concentrations as a function of transport distance in managed streams such as Boulder Creek can be more reliable than calculations using loads, as illustrated by the decrease in load along the flow path due to export of mass out of the stream. Of course, all input flows also must be taken into account. Lagrangian sampling techniques, which were not conducted as part of this study, are required to obtain the most accurate load-based mixing and in-stream attenuation data.

During both spring runoff and base flow, the NPEC to EDTA ratio shifted after 13 km of transport, indicating preferential loss of dissolved EDTA (92–94% in-stream attenuation) relative to dissolved NPEC (57–59% decrease). The most likely process for selective removal of EDTA is direct photolysis of the Fe(III)–EDTA complex (68). Photolysis also is a primary removal mechanism for triclosan and caffeine, although degradation rates are lower than for EDTA (9, 10), consistent with their observed minimal removal in Boulder Creek. Other compounds such as NP, which has much lower water solubility than NPEC, are removed by sorption and volatilization (59). During spring runoff, concentrations of the antimicrobial sulfamethoxazole decreased 73% after 13 km of transport whereas under base-flow conditions concentrations decreased 27%, consistent with results from another Colorado Front Range watershed (69). Concentrations of the co-prescribed compound trimethoprim decreased 80% during spring runoff and 58% during base flow.

Ecological Effects. Water quality standards have not been set for most of the trace elements and OWCs evaluated in this study, although compounds such as NP are potentially toxic (57) and endocrine disrupting (70–73). The maximum concentration of NP (0.34 $\mu\text{g/L}$) in Boulder Creek was below the range reported to cause endocrine disruption in fish (~10 $\mu\text{g/L}$) and lower than toxicity-based guidelines (~6 $\mu\text{g/L}$). The maximum triclosan concentration in Boulder Creek (0.17 $\mu\text{g/L}$) approached the no observable effect concentrations (NOEC) for sensitive aquatic species (0.69 $\mu\text{g/L}$, 74). Of the pesticides detected, only diazinon and lindane exceeded water quality criteria (24). Because of the complexity of the chemical mixture in the wastewater-impacted reach of Boulder Creek, it is possible that the additive effects of multiple chemical agents below the individual compound NOEC can have an impact.

Studies on native fish populations in Boulder Creek by Vajda and colleagues (75) indicate significant endocrine disruption in the wastewater-impacted reach. Upstream from the WWTP outfall the gender ratio (male/female) for white sucker (*Catostomus commersoni*) ranged from 0.7–0.9, whereas below the outfall the ratio ranged from 0.2–0.3. Other indicators of endocrine disruption, including gonadal intersex and vitellogenin induction in juvenile and male fish, also were observed. These reported biological effects occur in the reach where a step change in concentration and composition occurs for a variety of trace element, OWCs, and pesticide contaminants.

Although known endocrine-disrupting chemicals such as NP and bisphenol A were detected in the wastewater-impacted reach of Boulder Creek, the composition of the streamwater is very complex. For example, endogenous human steroidal hormones (17 β -estradiol, estrone, estriol, testosterone) and synthetic ovulating inhibiting hormones (17 α -ethynylestradiol, 19-norethisterone) were not detected in Boulder Creek above the method detection limit of ~1 ng/L, but the nonhuman biogenic estrogens 17 α -estradiol and equilenin were detected (Table SI-2 in the Supplemental Information). Equilenin is a component of post-menopausal

hormone replacement therapy formulations (7), with nearly 20 million prescriptions in 2004 (51), but the Boulder Creek detections were attributed to horse-boarding facilities with direct access to Boulder Creek. Likewise, 17 α -estradiol is likely coming from livestock or other nonhuman animal sources rather than WWTP effluent. Although concentrations of the biologically active steroidal hormones were below detection, NOEC values of less than 10 ng/L have been reported for sensitive endocrine disruption endpoints and the combined effects of multiple low dose estrogens on the estrogen receptor can be additive (76). The location of the chemical gradient and shift in fish gender occurs in the transition zone from the cold-water aquatic habitat of the mountain ecosystems to the warm-water aquatic habitat of the plains, a reach of Boulder Creek where the ecosystem structure is changing. Ecological and hydrological dynamics should be considered in addition to water quality when evaluating causative factors affecting natural organism populations. For example, maximum chemical concentrations, thus maximum aquatic organism exposures, occur in the wastewater-impacted reach of Boulder Creek during base-flow conditions, which coincides with the period of greatest susceptibility to impact on fish sexual differentiation and reproductive development.

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Supporting Information Available

Tables SI-1 (information on specific sampling site locations) and SI-2 (summary of the complete analytical results (22–24) for the 216 measurements made on mainstem Boulder Creek samples collected during spring-runoff and base-flow conditions). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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