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

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Abstract

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

INTRODUCTION

This report describes the presence and distribution of selected dissolved pesticides in the Boulder Creek Watershed during June and October, 2000. The study of pesticides was part of a collaborative effort of the U.S. Geological Survey (USGS) and the city of Boulder (Murphy and others, 2003). The study was designed to provide a comprehensive analysis of Boulder Creek water quality. High-flow (June) and low-flow (October) water-quality sampling of Boulder Creek from upstream of the town of Eldora to the confluence with Saint Vrain Creek, along with several inflows, was carried out to determine natural and human influences on water chemistry. Samples from ten sites were analyzed for pesticides using gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC).

Purpose and Scope

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

Previous Studies

Little information on the presence of pesticides in Boulder Creek and its inflows is available. In 1991, a water-quality investigation of the South Platte River Basin was started as part of the USGS National Water-Quality Assessment (NAWQA) program. The Boulder Creek Watershed is a subbasin of the South Platte River. One of the first tasks of the assessment was a compilation, screening, and interpretation of available nutrient, suspended-sediment, and pesticide data collected from surface- and ground-water sites in the basin. A total of 3484 samples from 54 surface-water sites and 107 wells were used in the analysis from water years 1980 to 1992. Most pesticide concentrations were less than laboratory-reporting levels. The pesticides with the highest percentage detections in surface water among the six land uses studied were atrazine in agricultural areas and picloram in mixed agricultural and urban land use. Only one surface-water site, in the mixed agricultural and urban land-use area, had a pesticide (parathion) concentration that exceeded water-quality criteria (Dennehy and others, 1995).

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

Approach

This study was developed from an existing network used by the city of Boulder in its routine water-quality monitoring. Individual sites were selected based on city of Boulder sampling sites (Murphy and others, 2003) and at locations downstream of major tributary inputs. The spatial distribution of the sites across the watershed reflects the different land-use characteristics across the basin, namely forested and semirural in the mountains in the west, urban and suburban along the Front Range, and more rural and agricultural in the eastern part of the basin. Water samples were collected over a 3-day period in June and October, which represent high-flow and low-flow conditions in the streams. In addition, these different periods reflect different applications and uses of pesticides in the basin.

DESCRIPTION OF STUDY AREA

Location

The Boulder Creek Watershed covers about 1160 km^2, primarily in Boulder County, Colorado. The Boulder Creek Watershed consists of two physiographic provinces: the upper basin, defined on the west by the Continental Divide, and the lower basin, defined on the west by the foothills of the Rocky Mountains (fig. 6.1; table 1.1, Murphy and others, 2003). The watershed begins at the Continental Divide, and extends east from the headwaters in the mountains to the plains and finally to its confluence with Saint Vrain Creek. The watershed is nested between the Clear Creek Watershed to the south, the Saint Vrain Creek Watershed to the north, and the South Platte River Watershed to the east.

Land use

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

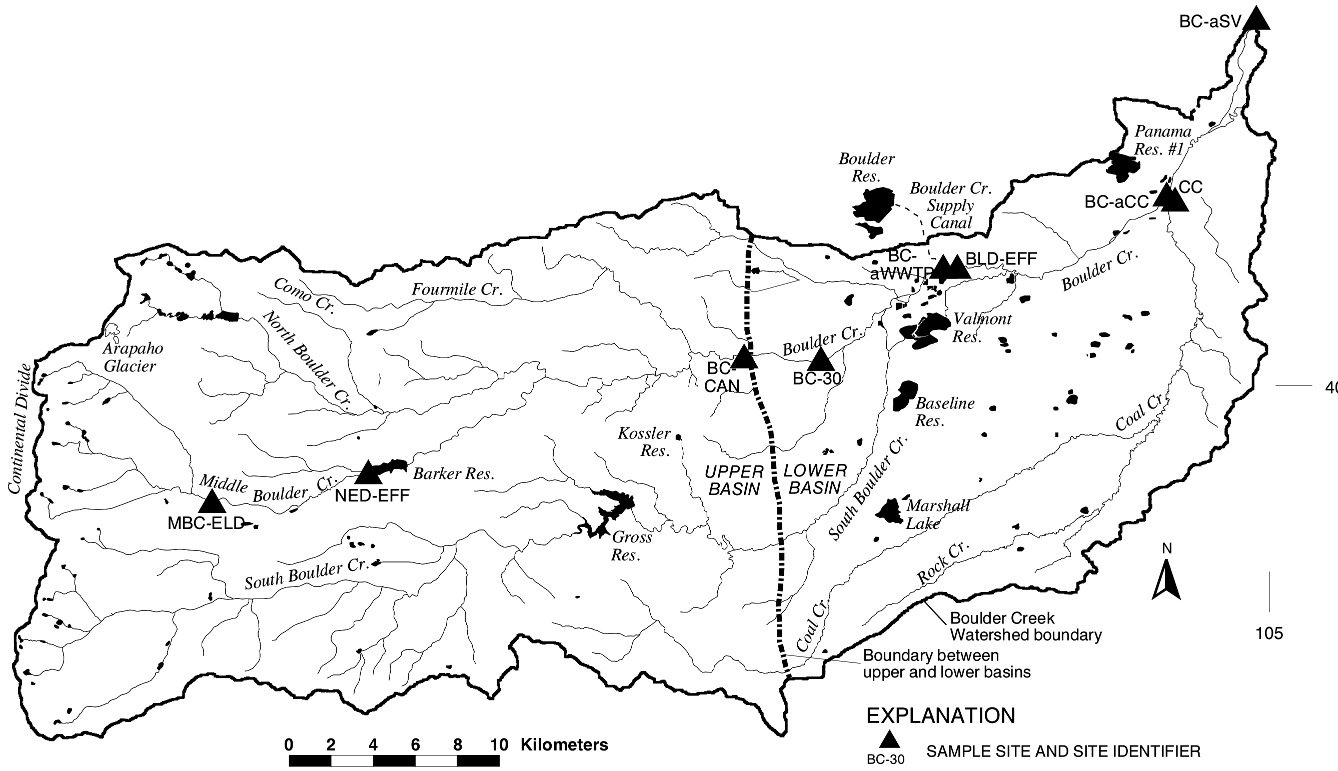


Figure 6.1. Map of Boulder Creek Watershed and sampling sites.

headwater region. The mountain corridor is characterized by a low density of homes, the town of Nederland, and two highways, one of which (Highway 119) runs alongside Middle Boulder Creek. The Nederland Wastewater Treatment Plant (WWTP) discharges effluent into Middle Boulder Creek upstream of Barker Reservoir. East of the mouth of Boulder Canyon, Boulder Creek enters the main urban corridor of the city of Boulder, which had a population of 94,673 in the year 2000 (Murphy and others, 2003). The Boulder 75th Street WWTP discharges effluent into Boulder Creek east of the corridor, and during low-flow conditions it can contribute a substantial portion of the total streamflow in lower Boulder Creek. The eastern region consists of less populated suburban areas and agricultural fields, pasture and open space. Coal Creek, a tributary that flows through the urban regions of Erie, Lafayette, Louisville, and Superior, enters Boulder Creek about 11 km upstream of the confluence with Saint Vrain Creek.

Pesticide Use

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

STUDY METHODS

Sampling-Site Selection

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

Estimation of Pesticide Use in Boulder County

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

Sample Collection

The distribution of pesticides in Boulder Creek and inflows was studied during June and October, 2000. The June sampling was designed to coincide with high-flow conditions caused by snowmelt runoff, as well as early application of pesticides during the growing season. Agricultural pre-plant herbicides and insecticides generally are applied during March and April. The October sampling was designed to sample when discharge was characteristically lower, and different types of pesticides are expected to be applied. Throughout spring and summer, insecticides are applied to agricultural crops, and on lawns and gardens in urban areas.

Sampling Protocols

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

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

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

Quality Assurance and Quality Control

Quality-control samples used to estimate bias and variability in sampling and laboratory procedures included field blanks (bias) and replicate samples (variability). In addition, the laboratory analyses included laboratory blanks (bias) and reagent water fortified samples (bias and variability), and surrogates added to every sample (bias) as part of the routine quality-assurance (QA) program. Field equipment blanks were prepared by processing pesticide-grade water through all sample collection and filtration equipment at the collection site, and then analyzing the sample in the laboratory along with environmental samples. Replicate samples consisted of two samples taken from the stream composite sample.

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

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

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

Sample Analysis

Pesticide samples were analyzed by two different analytical methods: GC/MS and HPLC. Details of the analytical methods are described by Zaugg and others (1995) for GC/MS, and by Werner and others (1996) for HPLC. The 83 pesticides determined by the two methods are listed in tables 6.3 and 6.4. For four samples collected in June, glyphosate was determined by an HPLC method (Winfield and others, 1990; table 6.5).

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

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

PESTICIDES IN SURFACE WATER

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

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

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

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

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

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

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

The pesticides detected most frequently at concentrations greater than 0.01 µg/L (table 6.6) were prometon (6 samples, or 30 percent), dichlobenil (25 percent), and diazinon (20 percent). Diazinon is an organophosphate insecticide commonly used in urban areas for control of insects in commercial and home gardens. Prometon and dichlobenil are primarily used for nonselective weed control in nonagricultural areas. Atrazine, desethylatrazine, and metolachlor also were detected frequently, but at much lower concentrations. Atrazine and metolachlor are herbicides commonly used in agricultural practices in the study area (table 6.1). Desethylatrazine (2-chloro-4-amino-6-isopropylamino-5-triazine) is a degradate of atrazine.

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

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

[Sample site Boulder Creek above Coal Creek (BC-aCC); values reported in micrograms per liter; <, less than; nc, not calculated; E, estimated concentration; relative percent difference for two samples = [R1 –R2]/[(R1+R2)/2] x100, where R1= sample 1 result and R2 = sample 2 result]

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

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

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

Site	Date	Time	Medium	2,6-Diethylaniline 579-66-8 82660E	Acetochlor 34256-82-1 49260E	Alachlor 15972-60-8 46342E	alpha-HCH 319-84-6 34253E	Atrazine 1912-24-9 39632E	Azinphos-methyl 86-50-0 82686E	Benfluralin 1861-40-1 82673E	Butylate 2008-41-5 04028E
Middle Boulder Creek/Boulder Creek											
MBC-ELD	6/12/00	0820	9	<0.003	<0.002	<0.002	<0.002	<0.001	<0.001	<0.002	<0.002
MBC-ELD	10/9/00	0830	9	<.002	<.004	<.002	<.005	<.007	<.05	<.01	<.002
BC-CAN	6/13/00	1330	9	<.003	<.002	<.002	<.002	<.001	<.001	<.002	<.002
BC-CAN	10/10/00	1236	9	<.002	<.004	<.002	<.005	<.007	<.05	<.01	<.002
BC-30	6/12/00	1430	9	<.003	<.002	<.002	<.002	<.001	<.001	<.002	<.002
BC-30	10/ 10/00	1345	9	<.002	<.004	<.002	<.005	<.007	<.05	<.01	<.002
BC-aWWTP	6/13/00	1910	9	<.003	<.002	<.002	<.002	<.001	<.001	<.002	<.002
BC-aWWTP	10/11/00	0815	9	<.002	<.004	<.002	<.005	<.007	<.05	<.01	<.002
BC-75	6/13/00	2000	9	<.003	<.002	<.002	<.002	<.001	<.001	<.002	<.002
BC-75	10/ 11/00	0900	9	<.002	<.004	<.002	<.005	<.007	<.05	<.01	<.002
BC-aCC	6/13/00	1720	9	<.003	<.002	<.002	<.002	<.001	<.001	<.002	<.002
BC-aCC	6/13/00	1725	R	<.003	<.002	<.002	<.002	**0.008**	<.001	<.002	<.002
BC-aCC	10/10/00	1630	9	<.002	<.004	<.002	<.005	**E.004**	<.05	<.01	<.002
BC-aCC	10/10/00	1635	R	<.002	<.004	<.002	<.005	**E.005**	<.05	<.01	<.002
BC-aSV	6/12/00	1700	9	<.003	<.002	<.002	<.002	**0.017**	<.001	<.002	<.002
BC-aSV	10/9/00	1545	9	<.002	<.004	<.002	<.005	**0.009**	<.05	<.01	<.002
Inflows											
CC	6/ 13/00	1615	9	<.003	<.002	<.002	<.002	**0.01**	<.001	<.002	<.002
CC	10/ 10/00	1600	9	<.002	<.004	<.002	<.005	**E.006**	<.05	<.01	<.002
NED-EFF	6/12/00	1330	9	<.003	<.002	<.018	<.002	<.001	<.001	<.002	<.002
NED-EFF	10/17/00	1345	9	<.002	<.004	<.002	<.005	<.007	<.05	<.01	<.002
BLD-EFF	6/13/00	2030	9	<.003	<.002	<.002	<.002	<.005	<.02	<.002	<.002
BLD-EFF	10/17/00	1600	9	<.002	<.004	<.01	<.005	<.007	<.05	<.01	<.002

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

Site	Carbaryl 63-25-2 82680E	Carbofuran 1563-66-2 82674E	Chlorpyrifos 2921-88-2 38933E	cis-Permethrin 54774-45-7 82687E	Cyanazine 21725-46-2 04041E	Dacthal 1861-32-1 82682E	Desethyl-atrazine 6190-65-4 04040E	Diazinon 333-41-5 39572E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.003	<0.003	<0.004	<0.005	<0.004	<0.002	<0.002	<0.002
MBC-ELD	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-CAN	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-CAN	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-30	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-30	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-aWWTP	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-aWWTP	<.041	<.02	<.005	<.006	<.018	<.003	<.006	<.005
BC-75	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-75	<.041	<.02	<.005	<.006	<.018	<.003	<.006	**0.022**
BC-aCC	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-aCC	<.003	<.003	<.004	<.005	<.004	<.002	<.002	<.002
BC-aCC	<.041	<.02	<.005	<.006	<.018	<.003	**E.004**	**0.094**
BC-aCC	<.041	<.02	<.005	<.006	<.018	<.003	**E.006**	**0.107**
BC-aSV	<.003	<.003	<.004	<.005	<.004	<.002	**E.011**	**0.01**
BC-aSV	<.041	<.02	<.005	<.006	<.018	<.003	**E.009**	<.005
Inflows								
CC	**E.092**	<.003	<.004	<.005	<.004	<.002	**E.005**	**0.054**
CC	**E.018**	<.02	<.005	<.006	<.018	<.003	**E.006**	**E.004**
NED-EFF	**E.009**	--	<.004	<.005	<.004	<.002	<.002	<.002
NED-EFF	<.041	<.075	<.005	<.006	<.018	<.003	<.006	<.005
BLD-EFF	<.02	<.003	<.004	<.005	<.004	<.002	<.002	**0.008**
BLD-EFF	<.041	<.075	<.005	<.006	<.018	<.003	<.006	**0.01**

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

Site	Dieldrin 60-57-1 39381E	Disulfoton 298-04-4 82677E	EPTC 759-94-4 82668E	Ethalfluralin 55283-68-6 82663E	Ethoprophos 13194-48-4 82672E	Fonofos 944-22-9 04095E	Lindane 58-89-9 39341E	Linuron 330-55-2 82666E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.001	<0.017	<0.002	<0.004	<0.003	<0.003	<0.004	<0.002
MBC-ELD	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-CAN	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-CAN	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-30	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-30	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-aWWTP	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aWWTP	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-75	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-75	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
BC-aCC	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aCC	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aCC	<.005	<.021	<.002	<.009	<.005	<.003	**0.027**	<.035
BC-aCC	<.005	<.021	<.002	<.009	<.005	<.003	**0.031**	<.035
BC-aSV	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BC-aSV	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
Inflows								
CC	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
CC	<.005	<.021	<.002	<.009	<.005	<.003	<.004	<.035
NED-EFF	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
NED-EFF	<.005	<.021	<.002	<.009	<.005	<.003	<.02	<.035
BLD-EFF	<.001	<.017	<.002	<.004	<.003	<.003	<.004	<.002
BLD-EFF	<.005	<.021	<.006	<.009	<.005	<.003	<.004	<.035

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

Site	Malathion 121-75-5 39532E	Metolachlor 51218-45-2 39415E	Metribuzin 21087-64-9 82630E	Molinate 2212-67-1 82671E	Napropamide 15299-99-7 82684E	p,p'-DDE 72-55-9 34653E	Parathion 56-38-2 39542E	Methyl parathion 298-00-0 82667E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.005	<0.002	<0.004	<0.004	<0.003	<0.006	<0.004	<0.006
MBC-ELD	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
BC-CAN	<.005	<.002	<.004	<.004	<.003	<.006	<.004	<.006
BC-CAN	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
BC-30	<.005	<.002	<.004	<.004	<.003	<.006	<.004	<.006
BC-30	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
BC-aWWTP	<.005	<.002	<.004	<.004	<.003	<.006	<.004	<.006
BC-aWWTP	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
BC-75	<.005	<.002	<.004	<.004	<.003	<.006	<.004	<.006
BC-75	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
BC-aCC	<.005	<.002	<.004	<.004	<.003	<.006	<.004	**0.126**
BC-aCC	<.005	<.002	<.004	<.004	<.003	<.006	<.004	**0.126**
BC-aCC	<.027	**E.005**	<.006	<.002	<.007	<.003	<.007	<.006
BC-aCC	<.027	**E.005**	<.006	<.002	<.007	<.003	<.007	<.006
BC-aSV	<.005	**0.008**	<.004	<.004	<.003	<.006	<.004	**0.05**
BC-aSV	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
Inflows								
CC	<.005	<.002	<.004	<.004	<.003	<.006	<.004	**0.055**
CC	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
NED-EFF	**0.02**	<.002	<.004	<.004	<.003	<.006	<.004	<.006
NED-EFF	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006
BLD-EFF	<.005	<.01	<.004	<.004	<.003	<.006	<.004	<.006
BLD-EFF	<.027	<.013	<.006	<.002	<.007	<.003	<.007	<.006

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

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

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

Site	Tebuthiuron 34014-18-1 82670E	Terbacil 5902-51-2 82665E	Terbufos 13071-79-9 82675E	Thio-bencarb 28249-77-6 82681E	Tri-allate 2303-17-5 82678E	Trifluralin 1582-09-8 82661E	Diazinon-D10, surrogate* 100155-47-3 91063E	alpha-HCH-D6, surrogate* 319-84-6-d6 91065E
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.01	<0.007	<0.013	<0.002	<0.001	<0.002	102	85
MBC-ELD	<.016	<.034	<.017	<.005	<.002	<.009	104	103
BC-CAN	<.01	<.007	<.013	<.002	<.001	<.002	114	96
BC-CAN	<.016	<.034	<.017	<.005	<.002	<.009	101	94
BC-30	<.01	<.007	<.013	<.002	<.001	<.002	111	81
BC-30	<.016	<.034	<.017	<.005	<.002	<.009	109	106
BC-aWWTP	<.01	<.007	<.013	<.002	<.001	<.002	111	87
BC-aWWTP	<.016	<.034	<.017	<.005	<.002	<.009	104	100
BC-75	<.01	<.007	<.013	<.002	<.001	<.002	107	88
BC-75	<.016	<.034	<.017	<.005	<.002	<.009	80	88
BC-aCC	<.01	<.007	<.013	<.002	<.001	<.002	116	87
BC-aCC	<.01	<.007	<.013	<.002	<.001	<.002	104	94
BC-aCC	<.016	<.034	<.017	<.005	<.002	<.009	113	86
BC-aCC	<.016	<.034	<.017	<.005	<.002	<.009	137	106
BC-aSV	<.01	<.007	<.013	<.002	<.001	<.002	105	84
BC-aSV	<.016	<.034	<.017	<.005	<.002	<.009	101	99
Inflows								
CC	<.01	<.007	<.013	<.002	<.001	<.002	94	90
CC	<.016	<.034	<.017	<.005	<.002	<.009	106	103
NED-EFF	<.01	<.1	<.013	<.002	<.001	<.002	97	83
NED-EFF	<.016	<.075	<.017	<.005	<.002	<.009	99	80
BLD-EFF	<.01	<.007	<.013	<.002	<.001	<.002	89	80
BLD-EFF	<.016	<.034	<.017	<.005	<.002	<.009	95	85

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

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

Site	Date	Time	Medium	2,4,5-T 93-76-5 39742B	2,4-D 94-75-7 39732B	2,4-DB 94-82-6 38746A	2-(2,4,5-Trichloro-phenoxy) propionic acid 93-72-1 39762B	3-Hydroxy-carbofuran 16655-82-6 49308A	4,6-Dinitro-2-methylphenol 534-52-1 49299A	Acifluorfen 62476-59-9 49315A	Aldicarb 116-06-3 49312A
Middle Boulder Creek/Boulder Creek											
MBC-ELD	6/12/00	0820	9	<0.04	<0.11	<0.1	<0.06	<0.11	<0.42	<0.09	<0.21
MBC-ELD	10/9/00	0830	9	<.04	<.11	<.1	<.025	<.011	<.25	<.05	<.21
BC-30	6/12/00	1430	9	<.04	<.11	<.1	<.06	<.11	<.42	<.09	<.21
BC-30	10/10/00	1345	9	<.04	<.11	<.1	<.025	<.011	<.25	<.05	<.21
BC-CAN	6/13/00	1330	9	<.04	<.11	<.1	<.06	<.11	<.42	<.09	<.21
BC-CAN	10/10/00	1236	9	<.04	<.11	<.1	<.025	<.011	<.25	<.05	<.21
BC-aWWTP	6/13/00	1910	9	<.04	<.11	<.1	<.06	<.11	<.42	<.09	<.21
BC-aWWTP	10/11/00	0815	9	<.04	<.11	<.1	<.025	<.011	<.25	<.05	<.46
BC-75	6/13/00	2000	9	<.15	<.82	<1	<.06	<.43	<.42	<.16	<.22
BC-75	10/11/00	0900	9	<.29	<.23	<.7	<.39	<1.51	<.65	<.66	<8.6
BC-aCC	6/13/00	1720	9	<.04	<.11	<.1	<.06	<.11	<.42	<.09	<.21
BC-aCC	6/13/00	1725	R	<.04	<.2	<.1	<.06	<.11	<.42	<.09	<1.1
BC-aCC	10/10/00	1630	9	<.04	<.14	<.7	<.025	<.22	<.53	<.05	<.37
BC-aCC	10/10/00	1635	R	<.19	<.56	<.3	<.26	<.33	<.25	<.63	<8.8
BC-aSV	6/12/00	1700	9	<.04	<.31	<.1	<.06	<.11	<.42	<.09	<1.3
BC-aSV	10/9/00	1545	9	<.38	<.66	<.8	<.19	<.30	<.25	<.05	<3.7
Inflows											
CC	6/13/00	1615	9	<0.04	<0.29	<0.5	<0.06	<0.86	<0.42	<0.09	<2.5
CC	10/10/00	1600	9	<.55	<.51	<.7	<.38	<.91	<.25	<.26	<7.2
NED-EFF	6/12/00	1330	9	<.75	<.11	<3	<1.11	<19	<.67	<1.3	<19
NED-EFF	10/17/00	1345	9	<.04	<.259	<.4	<.135	<.011	<.25	<.43	<1.7
BLD-EFF	6/13/00	2030	9	<.23	<.11	<1.8	<.5	<.57	<.42	<.09	<4.8
BLD-EFF	10/17/00	1600	9	<.13	<.75	<.7	<.025	<.72	<.25	<.13	<3.3

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

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

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

Site	Chloro-thalonil 1897-45-6 49306A	Clopyralid 1702-17-6 49305A	Dacthal monoacid 887-54-7 49304A	Dicamba 1918-00-9 38442A	Dichlobenil 1194-65-6 49303A	Dichlorprop 120-36-5 49302A	Dinoseb 88-85-7 49301A	Diuron 330-54-1 49300A
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.48	<0.23	<0.039	<0.043	<0.07	<0.032	<0.06	<0.06
MBC-ELD	<.28	<.42	<.07	<.043	**E.015**	<.05	<.09	<.049
BC-30	<.48	<.23	<.039	<.043	<.07	<.032	<.06	<.06
BC-30	<.28	<.42	<.07	<.043	<.049	<.05	<.09	<.049
BC-CAN	<.48	<.23	<.039	<.043	<.07	<.032	<.06	<.06
BC-CAN	<.28	<.42	<.07	<.043	<.049	<.05	<.09	<.049
BC-aWWTP	<.48	<.23	<.039	<.043	<.07	<.032	<.12	<.06
BC-aWWTP	<.28	<.42	<.07	<.043	**E.039**	<.05	<.09	<.049
BC-75	<.48	<.40	<.039	<.17	<.27	<.032	<.06	<.88
BC-75	<.13	<.54	<.28	<.54	**E2.49**	<.57	<.23	<.29
BC-aCC	<.48	<.23	<.039	<.043	**E.102**	<.032	<.06	<.06
BC-aCC	<.48	<.23	<.12	<.043	**E.104**	<.032	<.06	<.06
BC-aCC	<.28	<.66	<.18	<.24	**2.16**	<.05	<.09	<.26
BC-aCC	<.13	<.57	<.12	<.15	**E8.97**	<.29	<.09	<.34
BC-aSV	<.48	<.23	<.039	<.043	<.07	<.032	<.06	<.06
BC-aSV	<.28	<.42	<.165	<.102	<.049	<.158	<.09	<.232
Inflows								
CC	<0.48	<0.23	<0.14	<0.11	<0.1	<0.032	<0.06	<0.99
CC	<.28	<.42	<.27	<.043	<.049	<.05	<.09	<.22
NED-EFF	<.48	<.44	<1.78	<.59	<4.4	<.032	<2.54	<.77
NED-EFF	<.28	<.623	<.202	<.043	<1.5	<.129	<.213	<.418
BLD-EFF	<.48	<.82	<.13	<.27	<1.2	<.18	<.12	<.54
BLD-EFF	<.28	<.728	<.09	<2.4	<.42	<.413	<.117	<.247

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

Site	Fenuron 101-42-8 49297A	Fluometuron 2164-17-2 38811A	Linuron 330-55-2 38478A	MCPA 94-74-6 38482A	MCPB 94-81-5 38487A	Methiocarb 2032-65-7 38501A	Methomyl 16752-77-5 49296A	Neburon 555-37-3 49294A
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.07	<0.06	<0.09	<0.17	<0.13	<0.026	<0.017	<0.07
MBC-ELD	<.07	<.06	<.021	<.08	<.13	<.07	<.017	<.017
BC-30	<.07	<.06	<.09	<.17	<.13	<.026	<.017	<.07
BC-30	<.07	<.06	<.021	<.08	<.13	<.07	<.017	<.017
BC-CAN	<.07	<.06	<.09	<.17	<.13	<.026	<.017	<.07
BC-CAN	<.07	<.06	<.021	<.08	<.13	<.07	<.017	<.017
BC-aWWTP	<.07	<.06	<.09	<.17	<.13	<.026	<.017	<.07
BC-aWWTP	<.07	<.06	<.021	<.08	<.13	<.07	<.017	<.017
BC-75	<.17	<.23	<.49	<.17	<.96	<.58	<.74	<.07
BC-75	<.18	<1.2	<.29	<.7	<1.7	<.22	<4.044	<.017
BC-aCC	<.07	<.06	<.09	<.17	<.13	<.026	<.017	<.07
BC-aCC	<.07	<.06	<.09	<.17	<.13	<.15	<.15	<.07
BC-aCC	<.34	<.2	<1.4	<.23	<.13	<.13	<1.04	<.28
BC-aCC	<.56	<.06	<.24	<.15	<.92	<.19	<2.43	<.13
BC-aSV	<.18	<.06	<.09	<.17	<.23	<.22	<.85	<.07
BC-aSV	<.22	<.06	<.02	<.13	<.85	<.346	<.114	<.017
Inflows								
CC	<0.12	<0.06	<0.09	<0.17	<1.3	<1.4	<0.97	<0.19
CC	<.29	<.21	<.43	<.13	<1.5	<.78	<.47	<.017
NED-EFF	<.15	<.68	<.09	<7.1	<7.2	<.22	<.75	<.65
NED-EFF	<.77	<.66	<.36	<.08	<1.4	<.47	<1.0	<.14
BLD-EFF	<.4	<1.36	<1.4	<.17	<.13	<3.02	<.82	<.07
BLD-EFF	<.85	<.83	<1.0	<.92	<1.7	<1.2	<2.5	<.017

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

Site	Norflurazon 27314-13-2 49293A	Oryzalin 19044-88-3 49292A	Oxamyl 23135-22-0 38866A	Picloram 2/1/18 49291A	Propham 122-42-9 49236A	Propoxur 114-26-1 38538A	Triclopyr 55335-06-3 49235A	BMDC, surrogate* 99835A
Middle Boulder Creek/Boulder Creek								
MBC-ELD	<0.042	<0.31	<0.018	<0.05	<0.035	<0.08	<0.25	93
MBC-ELD	<.042	<.28	<.018	<.09	<.09	<.12	<.07	81
BC-30	<.042	<.34	<.018	<.05	<.035	<.08	<.25	93
BC-30	<.042	<.28	<.17	<.09	<.09	<.12	<.104	80
BC-CAN	<.042	<.36	<.018	<.05	<.035	<.08	<.25	93
BC-CAN	<.042	<.28	<.527	<.09	<.09	<.12	<.07	82
BC-aWWTP	<.042	<.31	<.018	<.05	<.035	<.08	<.25	86
BC-aWWTP	<.042	<.28	<.202	<.09	<.09	<.12	<.07	81
BC-75	<.042	<.43	<.018	<.05	<1.01	<.85	<.25	81
BC-75	<.042	<.59	<.018	<.12	<.09	<.44	<6.0	52
BC-aCC	<.042	<.31	<.018	**E.042**	<.035	<.08	<.25	90
BC-aCC	<.042	<.36	<.21	<.05	<.19	<.25	<.25	62
BC-aCC	<.042	<.28	<.65	<.17	<.52	<.88	<4.22	25
BC-aCC	<.042	<.296	<1.34	<.09	<.09	<.12	<6.2	74
BC-aSV	<.042	<.44	<.22	<.05	<.2	<.4	<.34	90
BC-aSV	<.042	<.28	<.966	<.106	<.137	<.752	<1.7	73
Inflows								
CC	<0.042	<0.31	<0.018	<0.05	<0.035	<0.65	<0.91	53
CC	<.042	<.28	<.14	<.29	<.12	<.67	<.98	24
NED-EFF	<.13	<6.1	<1.92	<.2	<.8	<5.9	<.77	62
NED-EFF	<.191	<.28	<.018	<.22	<.39	<.35	<1.4	41
BLD-EFF	<.042	<.31	<.74	<.35	<2.24	<1.8	<7.4	51
BLD-EFF	<.042	<.41	<.159	<.19	<.09	<.96	<32	45

Table 6.5. Concentrations of glyphosate, June 2000

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

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

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

Spatial Variations

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

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

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

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

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

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

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

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

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

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

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

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

Seasonal Variations

There were seasonal differences in the detection frequency and distribution of pesticides in Boulder Creek samples. During high-flow conditions in June, three herbicides and four insecticides were found (tables 6.3 and 6.4). During low-flow conditions in October, four herbicides and three insecticides were found. In June, pesticides were only detected at concentrations greater than 0.01 µg/L in BC-aCC and Boulder Creek upstream of Saint Vrain Creek (BC-aSV) and in inflows. The herbicide picloram (table 6.4) and insecticides parathion-methyl and malathion (fig. 6.4)were only found in June. In October, the herbicide dichlobenil was found in samples from MBC-ELD, BC-aWWTP, BC-75 and BC-aCC (fig. 6.5). It was not found in any of the inflows. Other herbicides used in agriculture, including atrazine and its degradate desethylatrazine, and metolachlor, were found only in October (fig. 6.2 and 6.3). These herbicides are probably transported to surface water through infiltration of ground water, because higher concentrations of the herbicides are typically found in spring storm runoff (Larson and others, 1999). The presence of desethylatrazine at concentrations comparable to atrazine (fig. 6.2) also suggests ground water rather than overland flow transport (Kimbrough and Litke, 1998). Dichlobenil, carbaryl, and prometon were found at some sites during both sampling times.

Pesticide Concentrations

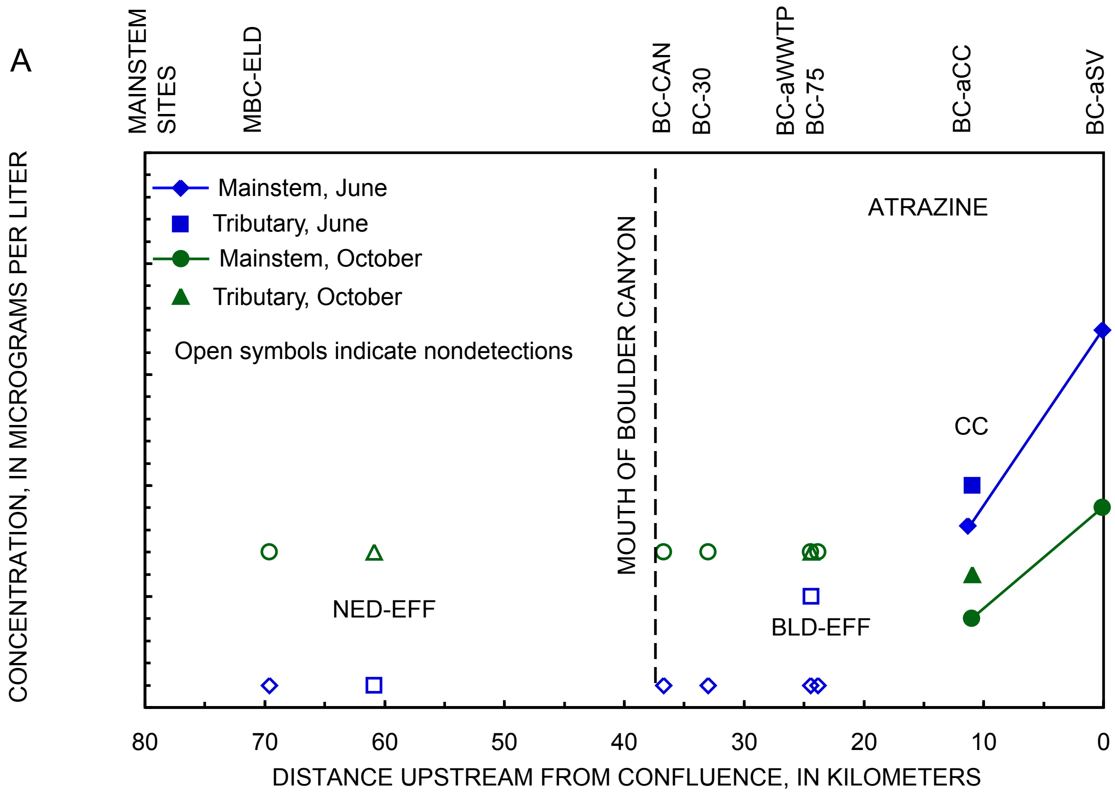
Concentrations of herbicides generally were less than 0.02 µg/L, while the insecticides diazinon and methyl parathion were found in concentrations ranging from 0.05 to 0.126 µg/L (tables 6.3 and 6.4). With the exception of dichlobenil, concentrations of herbicides were less than 0.01 µg/L, whereas diazinon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

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

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

Inflow Concentrations

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



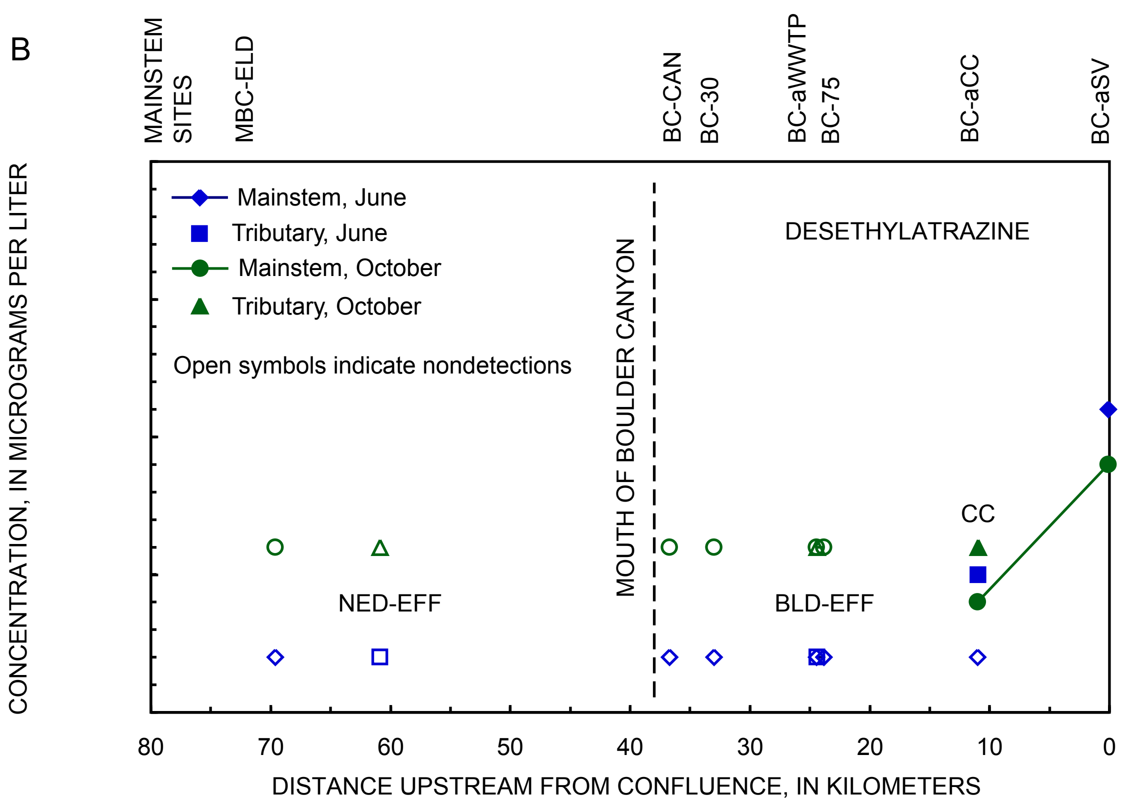


Figure 6.2. Graph showing downstream variation in concentrations of (A) atrazine and (B) desethylatrazine for Boulder Creek and its inflows.

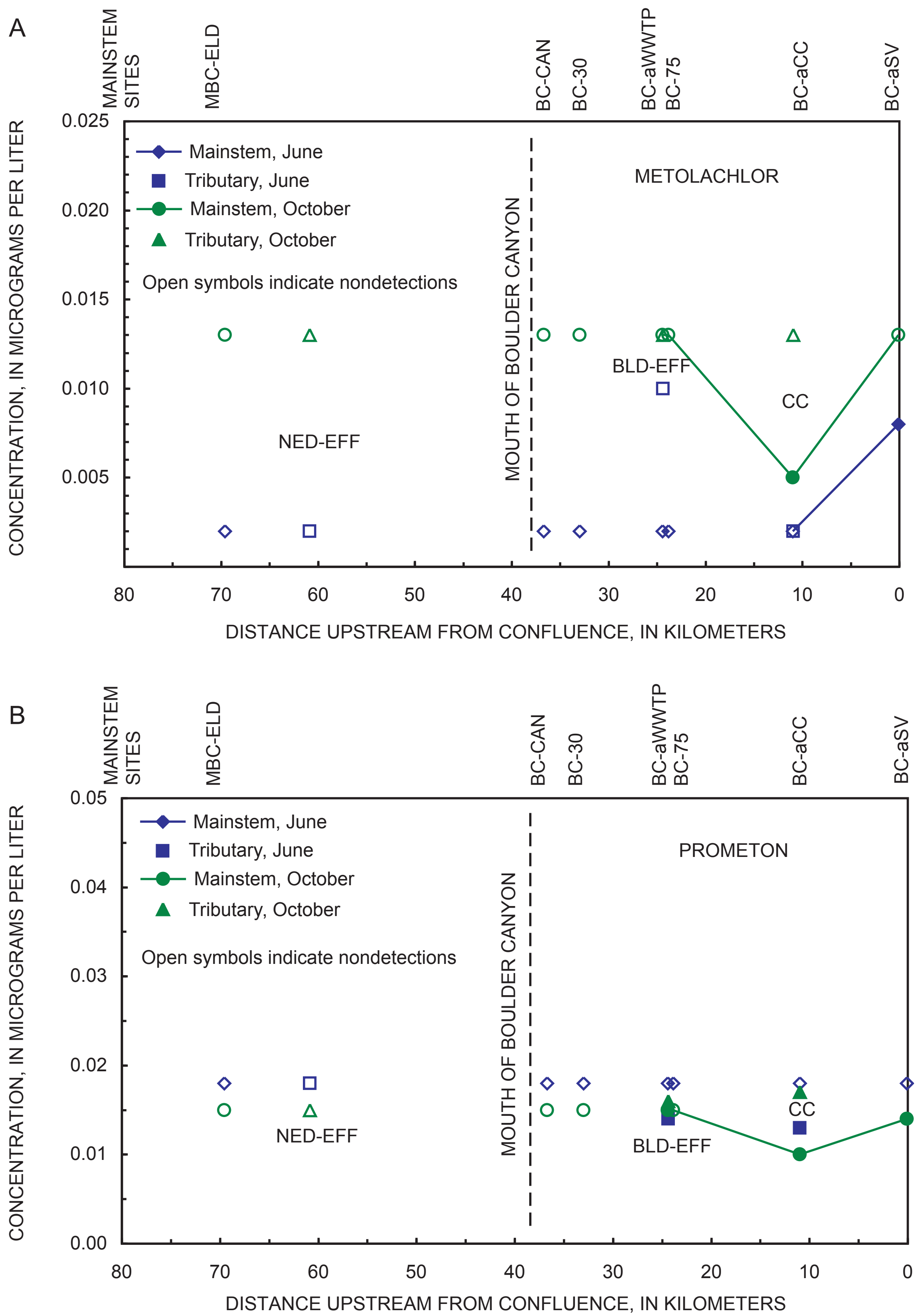


Figure 6.3. Graph showing downstream variation in concentrations of (A) metolachlor and (B) prometon for Boulder Creek and its inflows.

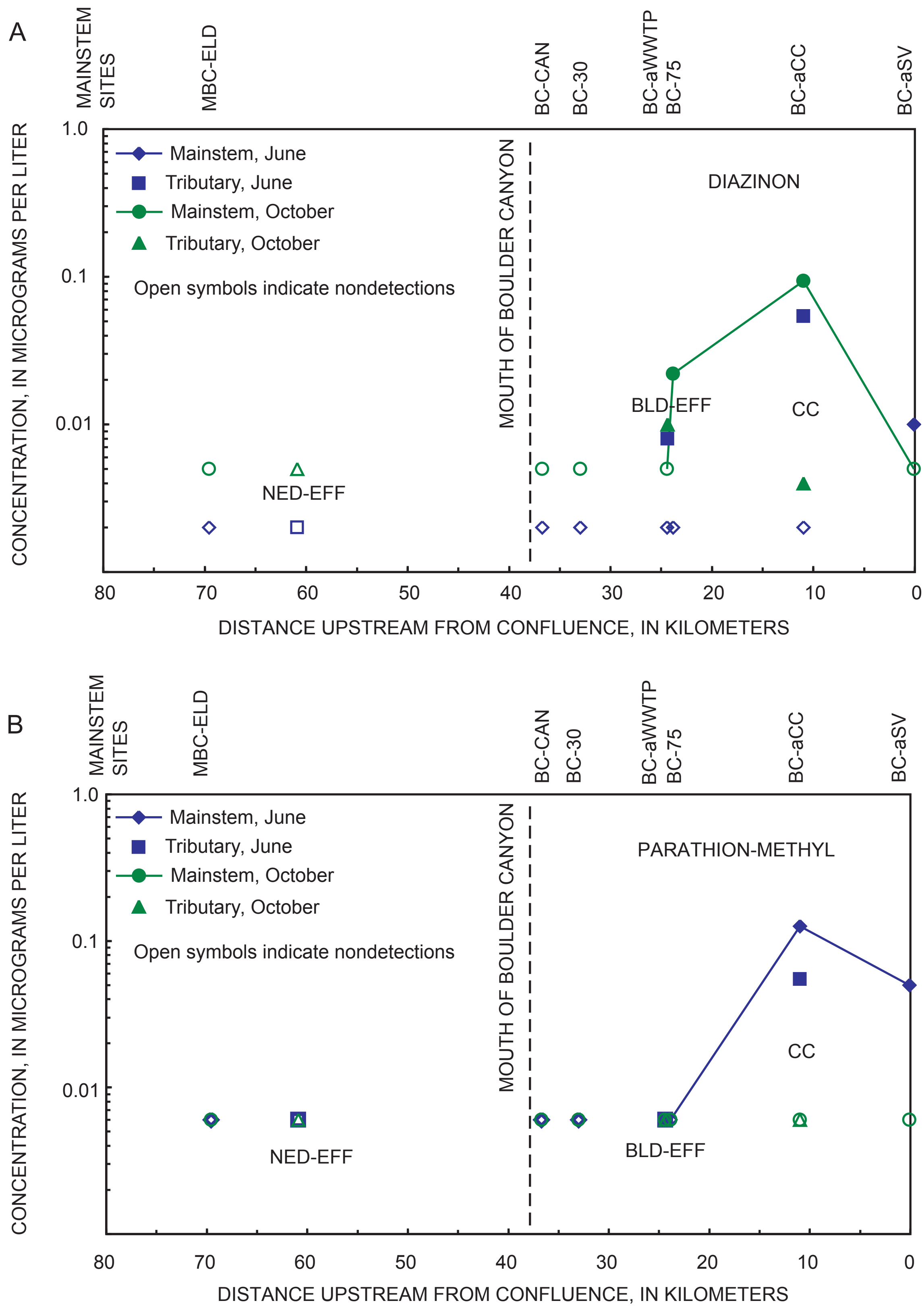


Figure 6.4. Graph showing downstream variation in concentrations of (A) diazinon and (B) parathion-methyl for Boulder Creek and its inflows.

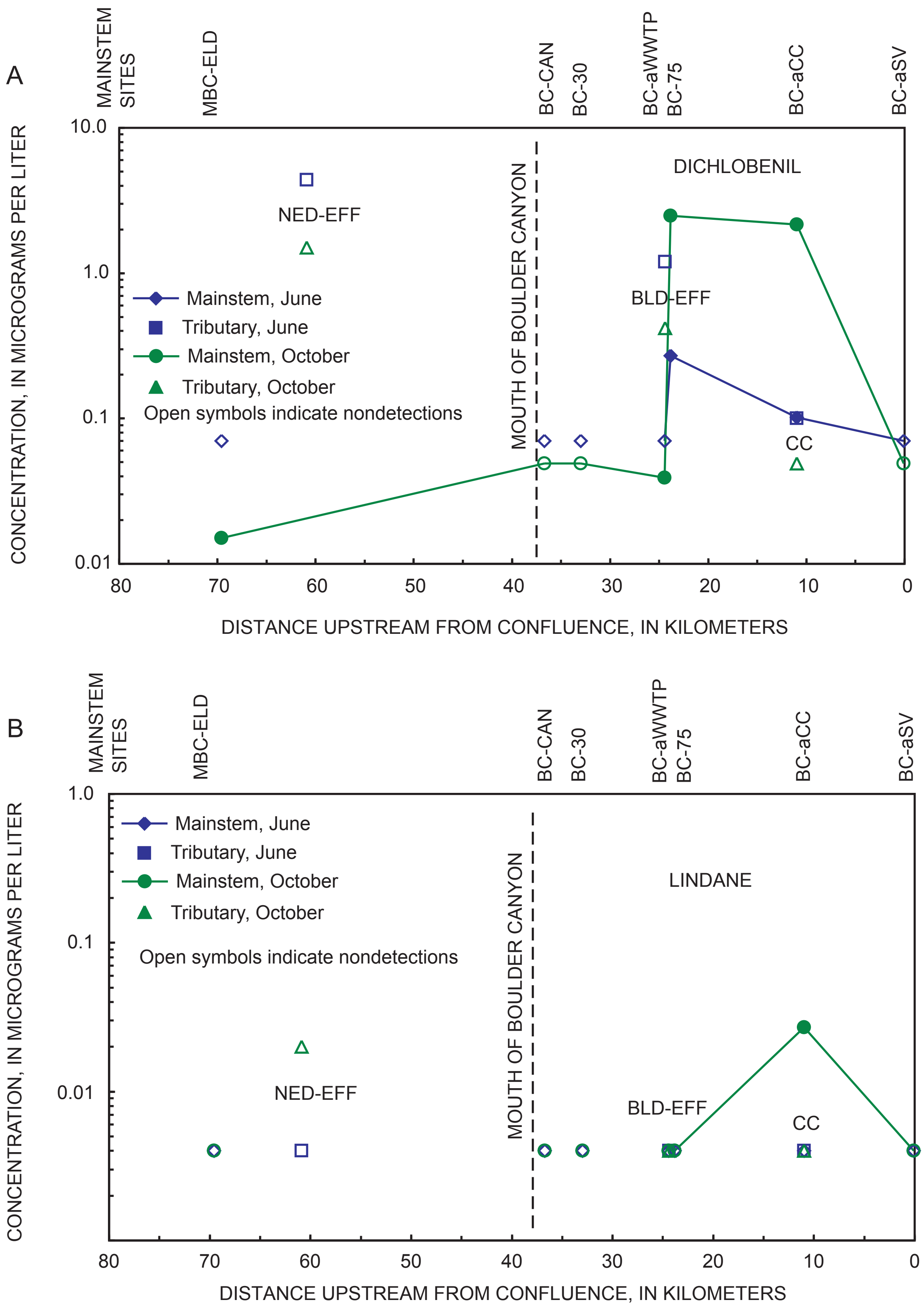


Figure 6.5. Graph showing downstream variation in concentrations of (A) dichlobenil and (B) lindane for Boulder Creek and its inflows.

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

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

Pesticide Presence in Relation to Estimated Application

Estimates of pesticides used on crops in Boulder County in 1997 are listed in table 6.1. Although the Boulder Creek Watershed only contains about half of the agricultural land use in Boulder County, the pesticide-use data provides an estimate of the relative amounts of the different pesticides used in agriculture in the basin. About 7890 kilograms of pesticides (active ingredient) are applied annually to agricultural land in Boulder County. The most commonly used pesticides are the herbicides atrazine, 2,4-D, dicamba, metolachlor, and glyphosate, and the insecticides terbufos, carbofuran, and chlorpyrifos. There was little correlation between pesticides found in Boulder Creek and estimated agricultural pesticide use. Atrazine, metolachlor, and parathion-methyl are among the top ten most abundantly used pesticides in the region and were detected in Boulder Creek, but not as frequently as other pesticides. None of the other commonly used pesticides were detected. This might be explained by differences in actual pesticide use in the Boulder Creek Watershed and County-wide estimates, as well as differences in time of application, persistence, and mobility of the pesticides.

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

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

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

[Population from U.S. Census Bureau, 2001; Land use in Boulder Creek Watershed based on aerial photographs from 1989-1994 (Kinner, 2003); person/km^2, persons per square kilometer; kilometer; km^2, square kilometer; %, percent; Agr., agricultural; number of analyses, number of individual pesticides in each method multiplied by number of sites multiplied by number of events sampled; H, number of herbicides found; I, number of insecticides found; MDL, method detection level; >, greater than; <, less than]

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

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

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

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

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

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

SUMMARY

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

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

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

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

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