1996

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Environ. Sci. Technol. **1996**, *30,* 908−916

Pesticides in Streams Draining Agricultural and Urban Areas in Colorado

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A study was conducted from April 1993 through April 1994 to describe and compare the occurrence and distribution of pesticides in streams in a small agricultural and a small urban area in Colorado. Twenty-five water samples collected at least monthly at the mouths of two tributary streams of the South Platte River were analyzed for 47 pesticides. The results indicate that both agricultural and urban areas are probable sources for pesticides in streams. In the agricultural area, 30 pesticides were detected, and in the urban area, 22 pesticides were detected in one or more samples. Most often, the more frequently detected pesticides in both areas also were some of the more commonly used pesticides. In both areas, pesticide concentrations were higher during the summer (application period) with maximum concentrations generally occurring in storm runoff. The year-round detection of some pesticides in both areas at consistently low concentrations, regardless of season or streamflow volume, could indicate that these compounds persist in the shallow alluvial aquifer year-round.

Introduction

In 1991, the U.S. Geological Survey (USGS) began full-scale implementation of the National Water-Quality Assessment (NAWQA) program. The goals of the NAWQA program are to describe the status and trends in the quality of a large, representative part of the nation's surface-water and groundwater resources and to provide a sound, scientific understanding of the primary natural and anthropogenic factors affecting the quality of these resources (*1*). A specific objective of the NAWQA program is to examine land-use effects on the occurrence and distribution of pesticides in streams (*2*).

The principal building blocks of the NAWQA program are the study-unit investigations on which national-level assessments are based. The South Platte River Basin, located in parts of Colorado, Wyoming, and Nebraska, is one of 35 current (1995) study units. The South Platte River originates in the central Rocky mountains of Colorado and flows northeastward for about 725 km to its confluence with the North Platte River in Nebraska. Within the South Platte River Basin, land use is 41% rangeland, 37% agriculture, 16% forest, 3% urban, and 3% other land-use classes (*3*). Urbanization and agriculture are some of the primary activities that affect water quality in the basin (*4*).

Although pesticide occurrence in streams has been documented separately for agricultural (*5*−*7*) and urban areas (*8*−*10*) around the nation, less work has focused on comparing the two environments in a single basin using a common sampling and laboratory protocol. The purpose of this paper is to describe and compare the occurrence and distribution of pesticides in an agricultural and urban land-use setting within the South Platte River Basin by using analyses of water samples collected at the mouths of two tributary streams from April 1993 through April 1994.

Description of Study Areas

Agricultural Area. A portion of the Lonetree Creek Basin was selected to represent the agricultural land-use area for the study (Figure 1). Lonetree Creek originates in Wyoming and flows southward through Weld County, CO, to its confluence with the South Platte River, about 10 km east of Greeley, CO. A general land-use classification for Lonetree Creek includes rangeland in the upper part, dryland farming in the middle part, and irrigated agriculture in the lower part of the basin. Irrigation practices in the lower part of the basin include canal/ditch networks, which import water into Lonetree Creek Basin from the west, and alluvial groundwater-fed center-pivot irrigation systems. Water samples in the agricultural study area were collected at the USGS streamflow-gaging station, Lonetree Creek near Greeley, located near the mouth of Lonetree Creek (Figure 1).

Although the Lonetree Creek Basin is 1476 km^2 in size, the contributing drainage area for the study was considered to be the 202-km^2 area of predominantly irrigated land located in the lower part of the basin. This decision was based on observations that most of the water in the lower part of the basin originates from irrigation within the study area. As an example, a detailed water balance for Lonetree Creek in August 1993 during the irrigation season indicated that Lonetree Creek was dry in the upper reaches of the study area, yet streamflow increased by 0.05 $m^3\ s^{-1}\ km^{-1}$ in an 8-km reach further downstream. The total increase in streamflow was attributed to surface-water and groundwater irrigation return flows.

Comparison of hydrographs for two stations on Lonetree Creek also illustrates the contribution of irrigation return flows to the agricultural monitoring site (Figure 2). Mean daily streamflow at the Lonetree Creek near Greeley site for the period of study was 0.37 m^3/s, while mean daily streamflow at the USGS streamflow-gaging station, Lonetree Creek near Carr, located about 65 km upstream in the rangeland land-use setting (Figure 1)was 0.02 m^3/s. Except for a large peak in streamflow in late May caused by a localized rainfall runoff event, the variability in the hydrograph at the Lonetree Creek monitoring site is primarily due to irrigation practices. For example, the peak in early May was caused by preirrigation season flushing of one of the canal systems; weekly flow patterns during July−

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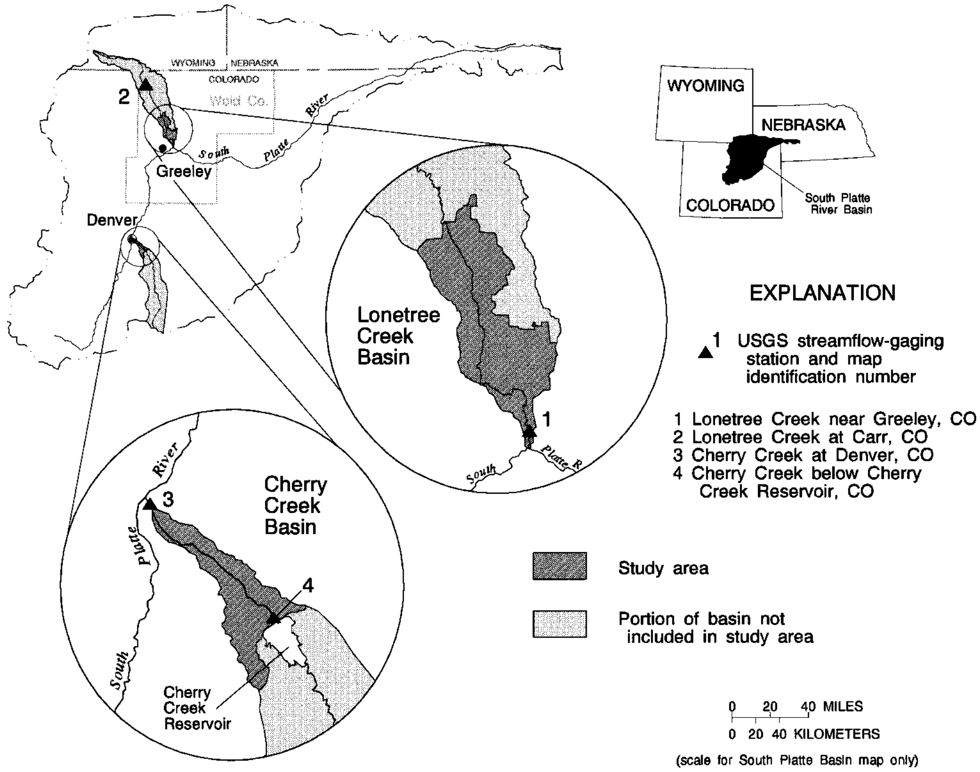

FIGURE 1. Location of study areas in the South Platte River Basin.

September were caused by a weekday–weekend pattern in irrigation water use prescribed by many of the growers in the basin; and diminishing baseflow during October–April 1994 was due to the gradual depletion of accumulated groundwater return flows in the alluvial aquifer.

Land use within the 202-km^2 agricultural study area is 66% irrigated crop land, 10% field and road borders, 9% water and perennial wetlands, 8% nonagricultural grass and bare ground, 2% rangeland, 2% dryland wheat, and 3% other land use, as determined from Landsat imagery by using classification techniques described by Wagner (*11*). Corn (53% of irrigated crop acreage), alfalfa (26%), sugar beets (8%), pinto beans (6%), onions (3%), and carrots (1%) were the major crops in 1993 (*11*).

The population density in the agricultural study area is about 6 people/km^2 (*12*). Elevations range from 1540 to 1400 m, and the average stream slope is about 0.3%. Although precipitation records are not available for areas within the lower Lonetree Creek Basin, total precipitation for the period of study at a location in Greeley (10 km from the monitoring site) was 38.90 cm and was 0.48 cm less than the long-term (1961–1990) average (*13, 14*).

Urban Area. A portion of the Cherry Creek Basin was selected to represent the urban land-use area for the study (Figure 1). Cherry Creek originates on the southern border of the South Platte River Basin and flows northward through rangeland and some nonirrigated farmland before entering Cherry Creek Reservoir, located on the southern edge of the Denver metropolitan area. Downstream from the reservoir, Cherry Creek flows through predominantly urbanized land before joining the South Platte River in downtown Denver. Streamflow in Cherry Creek was monitored at two USGS streamflow-gaging stations; one located below the reservoir (Cherry Creek below Cherry Creek Reservoir), and one located near the mouth (Cherry Creek at Denver) (Figure 1). Water samples in the urban area were only collected at the streamflow-gaging station located near the mouth.

Although the Cherry Creek Basin is about 1060 km^2 in size, only the 65-km^2 area located downstream from Cherry Creek Reservoir was considered to be the effective drainage area for the study. The rationale for this decision was based on streamflow volume in Cherry Creek. During the study, mean daily streamflow at the mouth (equal to 0.62 m^3/s) was about 3.5 times greater than mean daily streamflow at the outflow from the reservoir (0.17 m^3/s). Sources of additional water in the lower Cherry Creek Basin are alluvial groundwater inflows and surface-water inflows from tributaries, urban storm runoff, and treated effluent from a small wastewater-treatment plant. A water balance computed for Cherry Creek through the urban study area during one nonstorm day in August 1993 when the reservoir outflow was shut off indicated that as much as 74% of the increase in streamflow was from groundwater inflow. Eighteen percent of the increase was attributed to tributary inflows, and 8% was from the small wastewater-treatment plant. A water balance computed for the same reach 5 months later (January 1994) when the reservoir outflow was still shut off indicated that the percentage of flow from groundwater was about the same at 77%.

With the exception of large releases from Cherry Creek Reservoir in May and February to check gate operations, all the streamflow peaks recorded at the Cherry Creek at Denver gage are the result of storm runoff originating in the study area (Figure 2). The slight decline in baseflow from late August through January may result from the decline in return flows from residential and commercial lawn watering, which are curtailed during these months.

Current (1995) land use in the lower Cherry Creek Basin is 57% residential, 26% commercial and industrial, and 17% undeveloped and open space. The population density in the lower Cherry Creek Basin is about 1740 people/km^2

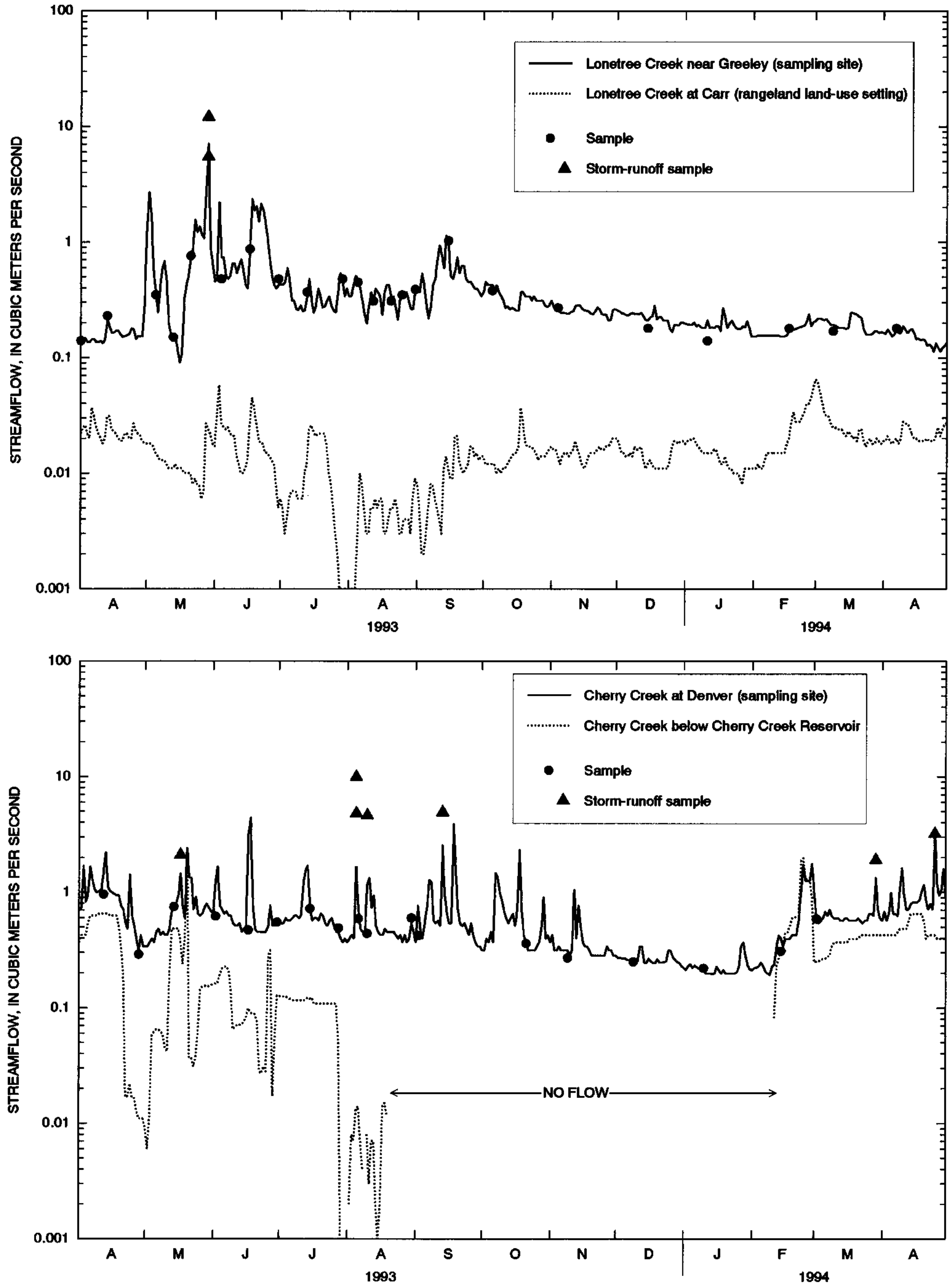

FIGURE 2. Selected streamflow data, Lonetree Creek and Cherry Creek, April 1993−April 1994.

(*12*). Elevations range from 1770 to 1580 m, and the average stream slope is about 0.5%. Total rainfall at the Cherry Creek Reservoir dam was 44.91 cm during the study and was 7.54 cm less than the long-term average (*13, 14*).

Methods

Sample Collection, Preparation, and Analysis. Water samples were collected from each area at least monthly from April 1993 through April 1994 (Figure 2). A total of 25 samples was collected from each sampling site. Samples were collected more frequently in the spring and summer in anticipation of increased pesticide concentrations related to application timing. Other studies have concluded that concentrations of pesticides are greater during spring and summer, following spring application (*5, 6*). Previous studies (*6, 7, 9*) have documented higher pesticide concentrations in storm runoff; therefore, two samples were collected during the single storm runoff event in the agricultural area and seven samples were collected during six events in the urban area (the early August event in the urban area was sampled twice) (Figure 2).

Field collection and processing equipment were made from Teflon, glass, or stainless steel to prevent sample contamination from plasticizers and to minimize analyte losses through adsorption. All sampling equipment was cleaned prior to use with a nonphosphate laboratory detergent and then rinsed with organic-free water followed by high-purity methanol. The equipment was rinsed with copious amounts of native water at the sampling sites before sample collection. Glass sample bottles and glass fiber filters were cleaned by baking at 450 °C for 8 h and were not field rinsed.

Depth-integrated water samples were collected across each stream by using the equal-width-increment method

TABLE 1

Selected Data for the 47 Pesticides Analyzed during the Study

Compound	MDL[a]	Use rank in ag. area[b]	Agricultural Area: Percent Detections (0 50 100)	Agricultural Area: Concentration, microgram per liter Median	Agricultural Area: Concentration, microgram per liter Maximu	Urban Area: Percent Detections (0 50 100)	Urban Area: Concentration, microgram per liter Median	Urban Area: Concentration, microgram per liter Maximum
Herbicides								
Alachlor	0.009	2		0.012	5.4		<0.009	0.009
Atrazine	0.017	3		0.12	2.7		<0.017	1.1
Atrazine, Deethyl	0.02			0.03	0.10		<0.02	0.053
Benfluralin	0.009			--[c]	--		--	--
Butylate	0.008	4		<0.008	1.1		--	--
Cyanazine	0.013	7		0.058	5.9		<0.013	0.045
DCPA	0.005	8		0.033	100.		<0.005	0.029
2,6-Diethylaniline	0.006			--	--		<0.006	0.006
EPTC	0.01	1		0.029	7.3		<0.01	0.019
Ethalfluralin	0.013			<0.013	0.073		--	--
Linuron	0.039			<0.039	0.57		--	--
Metolachlor	0.009	9		0.06	8.4		<0.009	0.051
Metribuzin	0.012			<0.012	0.012		<0.012	0.017
Molinate	0.007			--	--		<0.007	0.01
Napropamide	0.01			<0.01	0.012		--	--
Pebulate	0.009			--	--		--	--
Pendimethalin	0.018			<0.018	0.18		--	--
Prometon	0.008			0.066	0.11		0.063	0.17
Pronamide	0.009			--	--		--	--
Propachlor	0.015			--	--		--	--
Propanil	0.016			--	--		<0.016	0.022
Simazine	0.01			<0.01	0.033		0.022	0.17
Tebuthiuron	0.015			<0.015	0.047		<0.015	0.061
Terbacil	0.03			--	--		<0.03	0.035
Thiobencarb	0.008			--	--		--	--
Triallate	0.008			--	--		<0.008	0.036
Trifluralin	0.012			<0.012	0.11		--	--
Insecticides								
Azinphos-Methyl	0.08			--	--		--	--
Carbaryl	0.046	6		<0.046	1.5		0.15	2.5
Carbofuran	0.013	5		<0.013	1.2		--	--
Chlorpyrifos	0.008	2		<0.008	0.22		<0.008	0.30
DDE	0.02			--	--		--	--
Diazinon	0.008	10		<0.008	0.66		0.033	0.45
Dieldrin	0.02			<0.02	0.027		--	--
Dimethoate	0.024	9		<0.024	0.05		--	--
Disulfoton	0.02	4		--	--		--	--
Ethoprop	0.012			<0.012	0.022		--	--
Fonofos	0.008			<0.008	0.046		--	--
HCH, alpha-	0.007			<0.007	0.011		--	--
HCH, gamma-	0.011			--	--		<0.011	0.11
Malathion	0.014			--	--		<0.014	0.16
Methyl Parathion	0.035			<0.035	0.097		--	--
Parathion	0.022	7		--	--		--	--
Permithrin, *cis*	0.016			--	--		--	--
Phorate	0.02	8		<0.02	0.60		--	--
Propargite	0.01	3		<0.01	0.32		<0.01	0.015
Terbufos	0.012	1		<0.012	0.56		--	--

[a] Method detection limit, in microgram per liter. [b] Use ranking data for agricultural area. Data for herbicides is for Weld County, 1987–1989, from Gianessi and Puffer (*22*). Data for insecticides is for northeast Colorado (includes Weld County) for 1989, from Bohmont (*21*) (samples not analyzed for herbicides ranked 5, 6, and 10). [c] Pesticide not detected during the study.

(*15*) and processed on-site using methods described by Shelton (*16*). Samples were filtered on-site using glass fiber filters with a nominal pore diameter of 0.7 μm. Filtered samples were immediately chilled to 4 °C before delivery to the USGS National-Water Quality Laboratory (NWQL) in Denver for analysis. Pesticides were extracted and analyzed from 1-L water samples at the NWQL using methods described by Zaugg et al. (*17*). Pesticide concentrations were determined by capillary column gas chromatograph/mass spectrometry operated in the selective ion monitoring mode. Pesticides analyzed for the study had individual method detection limits (MDLs) varying from 0.005 to 0.08 μg/L with a median of 0.012 μg/L (Table 1).

Quality Assurance. About 14% of the samples were analyzed for quality-assurance purposes. Two equipment blanks processed with organic-free water, one prior to sample collection and one after 40% of the samples had been collected, contained no evidence of pesticides. To address analytical precision and accuracy of analyte recovery in the sample matrix, three replicates and three field-spiked replicates were obtained at the Cherry Creek site after 40% of the samples had been collected. Analytes were spiked into 1-L environmental samples at a concentration of 0.1 μg/L. The relative standard deviation for compounds detected in triplicate in Cherry Creek water ranged from 1.2 to 12%. Average recoveries in the three field-spiked replicates ranged from 39 to 141% with a median of 96%. Reported concentrations have not been adjusted on the basis of percent recoveries.

Statistical Comparisons. The Mann-Whitney nonparametric rank-sum test (*18*) is used to determine if significant statistical differences exist between two data sets. Attained significance levels, or p values, are reported to determine the strength of each test. For example, a value of $p > 0.05$ indicates no statistical difference between two data sets at a 95% confidence level, whereas $p < 0.05$ indicates a statistical difference at a 95% confidence level.

Concentrations Related to Drinking Water Standards. Peak pesticide concentrations in discrete samples are compared to the U.S. Environmental Protection Agency's maximum contaminant levels (MCLs) and health advisory levels (HALs) for finished drinking water. Pesticide MCLs and HALs are based on annual average concentrations; therefore, pesticide concentrations in individual samples that exceed these criteria may not necessarily indicate a violation of a standard. Water originating in the study areas is not directly used as drinking water; however, conventional treatment plants do not always remove all the pesticides that are dissolved in water (*19*). Comparisons between peak pesticide concentrations and drinking water standards are offered only as a point of reference for the pesticide concentrations measured in the study areas.

Results and Discussion

Individual samples were analyzed for 47 pesticides (27 herbicides and 20 insecticides). In the agricultural area, 30 compounds (17 herbicides and 13 insecticides) were detected at or above the MDLs in at least one sample, and 22 compounds (16 herbicides and 6 insecticides) were detected at or above the MDLs in the urban area (Table 1). Out of a total of 1,175 individual analyses for each area (25 samples, each analyzed for 47 compounds), the agricultural area had 271 detections, or about 23% of the total possible. The urban area had 139 pesticide detections, or about 12% of the total possible.

Urban Detections Related to Reservoir Outflows. Urban water samples were considered to be representative of water originating in the lower Cherry Creek Basin; however, there was the possibility of detecting pesticides that had passed through the reservoir from the upper part of the basin. The potential for detecting pesticides from the upper Cherry Creek Basin increased as the contribution of flow from the reservoir increased. Three water samples in particular were composed of more than 50% of reservoir outflow, including samples collected on April 12, 1993 (outflows from reservoir represented about 70% of the flow), May 14 (65%), and February 14 (92%) (Figure 2).

Nonirrigated wheat and hay are the principle crops grown in the upper Cherry Creek Basin (*20*). Most of the pesticides that were analyzed for in water samples are not applied to wheat and hay in the upper basin; thus, the possibility of contamination from the upper basin for many analytes was limited. Exceptions are the herbicides EPTC and pronamide, which account for about 8% of the total herbicide use in the upper basin (*20*), and the insecticides disulfoton and chlorpyrifos, which account for 87% of the total insecticide use on nonirrigated wheat in eastern Colorado (*21*).

In the urban area, pronamide and disulfoton were not detected in any sample whereas EPTC was detected in one storm runoff sample in May at a concentration of 0.019 μg/L. The May storm sample consisted of about 62% surface runoff and 20% reservoir outflow. Chlorpyrifos was detected in eight urban samples. The percentage of reservoir outflow in samples containing chlorpyrifos ranged from 0 to 65% with a median of 17.5%; however, chlorpyrifos was detected in only one of three urban samples identified as being composed of more than 50% reservoir outflow (May 14, 65%).

Herbicide Detections. The number of different herbicides detected at least once was about equal for each area, although the frequent detection of several agricultural herbicides resulted in a greater number of detections in the agricultural area by a ratio of more than 2:1 (Table 1). Of the eight herbicides that were detected in at least 50% of the samples from the agricultural area, six are included in a list of the 10 most frequently used herbicides for agriculture in Weld County (*22*), including alachlor, atrazine, cyanazine, DCPA, EPTC, and metolachlor (Table 1). A seventh compound (deethylatrazine) is a metabolite of atrazine.

The herbicide prometon, detected in all of the samples from the agricultural area (Table 1), is not applied to the types of crops grown in the Lonetree Creek Basin but mainly is used as a soil sterilant. Prometon also was the most commonly detected herbicide in the urban area (in 92% of the samples). Although prometon became unavailable to Colorado homeowners in 1991 (*23*), it still is used infrequently as a long-term, nonselective herbicide in rural and urban areas by licensed applicators. Prometon concentrations were not significantly different ($p > 0.05$) between the two areas. Median concentrations of prometon equaled 0.066 μg/L for the agricultural area and 0.063 μg/L for the urban area.

The compound DCPA, typically used for weed control in onion fields, was detected in highest concentration of any herbicide in the agricultural area. Used for crabgrass control on lawns, DCPA was one of the more frequently detected herbicides in the urban area, although the urban DCPA concentrations were significantly less ($p < 0.05$) than agricultural concentrations. Atrazine was detected in highest concentration of any herbicide in the urban area. Nonagricultural use of atrazine in Colorado is limited to roadside application by licensed applicators and on turf by nonlicensed users; however, turf application is not recommended because of Colorado's semi-arid climate (*24*).

Simazine and tebuthiuron were the only herbicides found in significantly higher ($p < 0.05$) concentrations in the urban area as compared to the agricultural area. Prior to 1991, a mixture of simazine and prometon was available to the general public under the trade name Pramitol 5PS for total vegetation control, but because of the prometon content, Pramitol 5PS became a restricted-use product in Colorado in 1991. Used alone, simazine was available to the general public in 1993 as an algicide for ponds and swimming pools. Tebuthiuron is mainly used for total vegetation control in industrial areas.

For the period of study, the average concentration of individual herbicides was well below any established MCL or HAL in both areas. However, herbicide concentrations were greater than drinking water standards in several individual samples. The MCL for alachlor (two samples) and the HAL for cyanazine (four samples) were exceeded in the agricultural area. No herbicides exceeded MCLs or HALs in individual urban-area samples.

Insecticide Detections. The number of insecticides detected at least once was greater in the agricultural area by a ratio of 2:1; however, the frequent detection of four insecticides in the urban area resulted in the total number of insecticide detections being more evenly distributed between the two areas (Table 1). The four compounds that predominated insecticide detections in the urban area (carbaryl, chlorpyrifos, diazinon, and malathion) commonly are used by homeowners and certified applicators to control insects in residential areas. In a survey of 2447 homeowners across the nation (including Denver) in 1990 (*25*), carbaryl, chlorpyrifos, diazinon, and malathion were in the top 10% of the most frequently used active ingredients in pesticides out of 312 identified compounds. The distributions of carbaryl, diazinon, and malathion concentrations were significantly higher ($p < 0.05$) in the urban area, whereas no significant difference ($p > 0.05$) was determined for chlorpyrifos concentrations.

Many of the insecticides detected in the agricultural area are some of the more common insecticides used for agriculture in northeastern Colorado, which includes Weld County (*21*), including carbaryl, carbofuran, chlorpyrifos, diazinon, and propargite. Because carbofuran and propargite are used exclusively for agriculture, the concentrations of these compounds were significantly higher ($p < 0.05$) in the agricultural area compared to the urban area.

Carbaryl, typically used for insect control on corn and pinto beans and around residences in the study area, was detected in highest concentration of any insecticide in each area. For the period of study, the average concentration of individual insecticides was well below any established MCL or HAL in both areas. However, the diazinon HAL of 0.6 μg/L was exceeded in one nonstorm agricultural sample at a concentration of 0.66 μg/L. Diazinon is typically used on onions in agriculture and for urban ant control. No insecticides exceeded MCLs or HALs in individual urban-area samples.

Seasonal Pattern of Pesticide Detections. In the agricultural area, pesticide concentrations generally were higher during the growing season (April–September) as compared to the nongrowing season (Figure 3). Within the growing season, the highest concentrations occurred soon after the application period. This pattern was observed for pesticides applied before or early in the growing season (March–May) and for pesticides applied mid-growing season (June–July). As an example, the insecticide carbofuran, commonly applied to corn early in the growing season, and the herbicide pendimethalin, typically applied to corn and pinto beans at planting, were detected only in Lonetree Creek from April through August (Figure 3). The insecticide carbaryl, applied to beans in June and July for beetle control, and the insecticide propargite, applied to corn in July, were detected only in the agricultural area in July and August (Figure 3).

Although fewer data have been compiled on the timing of pesticide application in urban areas, pesticides were detected more frequently and at generally higher concentrations during the summer (growing season) when pesticide applications are most likely to occur (Figure 4). As an example, concentration plots for the more frequently detected compounds in the urban area indicate that atrazine, chlorpyrifos, malathion, diazinon, DCPA, and carbaryl primarily were detected only during the growing season (Figure 4).

Application practices employed by users in the two land-use areas may be inferred from pesticide detection patterns. As mentioned above, carbaryl is applied to crops in the agricultural area in June and July and was only detected during July and August. The short duration of carbaryl detections in the agricultural area may be caused by its relatively short soil half-life of 4–29 days (*26*). The numerous detections of carbaryl in the urban area probably result from repeated applications for residential and commercial insect control.

Pesticide Detections Related to Storm Runoff and Irrigation Return Flows. Storm runoff (both areas) and irrigation return flows (agricultural area) are two processes other than application timing that might have resulted in higher pesticide concentrations during the growing season. In both processes, pesticides can be flushed from fields and lawns and transported to receiving waters either in the dissolved phase after being leached from the soil or in the suspended phase while adsorbed to soil particles.

The single storm runoff event that was sampled in the agricultural area occurred in late May. Peak flows in Lonetree Creek resulted from large amounts of surface runoff (mainly from fields) generated from an intense, localized precipitation event. Most of the pesticides applied to fields early in the growing season occurred in peak concentrations in this post-application event (Figure 3); in fact, 19 of the 30 pesticides that were detected at least once in the agricultural area were determined in highest concentration in one of the two samples collected during the event. Both alachlor concentrations that exceeded the MCL of 2 μg/L were in the two storm samples. Alachlor concentrations were 5.4 μg/L at the peak of the storm runoff event (flow equal to 12.1 m^3/s) and 2.6 μg/L on the recession (flow equal to 5.5 m^3/s). The cyanazine HAL of 1 μg/L also was exceeded in both storm samples. Cyanazine concentrations were 5.9 μg/L at the peak of the runoff event and 3.3 μg/L on the recession. The two other cyanazine concentrations (equal to 1.4 and 2.2 μg/L) that exceeded the HAL occurred in two nonstorm samples during the first half of the growing season.

Higher pesticide concentrations in storm runoff in the urban area also contributed to higher pesticide concentrations during the growing season. Detections of atrazine, malathion, diazinon, DCPA, and carbaryl were significantly higher ($p < 0.05$) in concentration in storm samples as compared to detections in nonstorm samples (Figure 4). This could indicate that these compounds were present on surfaces in the urban area and transported to the stream in overland flow.

Nonstorm streamflows in the agricultural area at the time of sample collection were significantly higher ($p < 0.05$) during the irrigation season (May–September) as compared to the nonirrigation season. The additional water primarily is irrigation surface-water and groundwater return flows that drain to Lonetree Creek after application to the fields. The return flows might contain elevated concentrations of pesticides.

Pesticide Persistence. The detection of some pesticides in both areas at consistently low concentrations after the growing season could indicate that these compounds persist in the shallow alluvial groundwater system. As previously mentioned, streamflow after the growing season in the agricultural area is predominantly groundwater return flows. In the urban area, groundwater was the major source of base flow from late August through January as a result of the Cherry Creek Reservoir outflow being shut off.

In the agricultural area, the concentrations of four herbicides (metolachlor, EPTC, alachlor, and cyanazine) declined from maximum concentrations, which occurred shortly after pre/early-growing season application, to

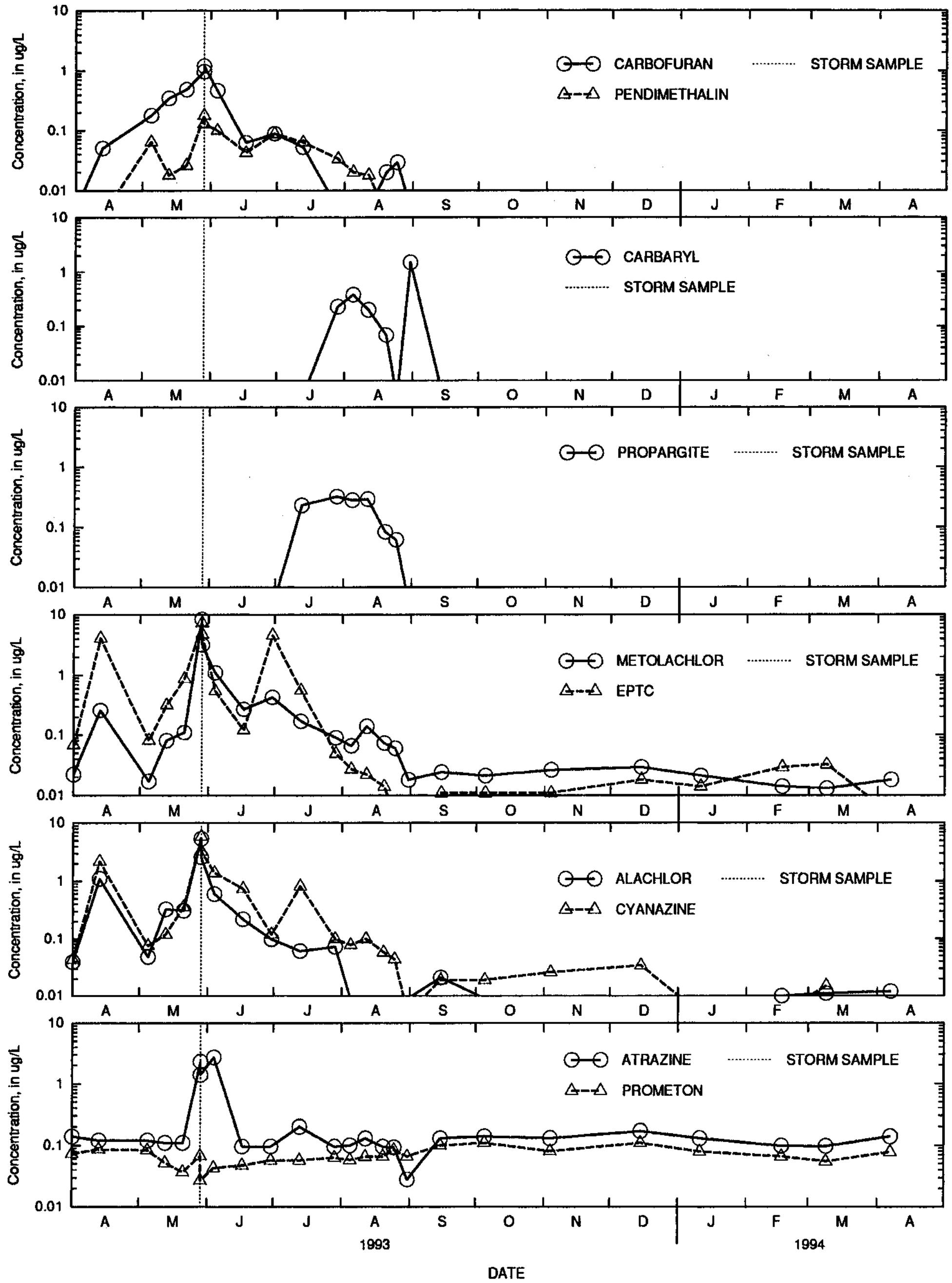

FIGURE 3. Selected pesticide data for Lonetree Creek near Greeley, April 1993–April 1994. Concentrations below the *x*-axis are less than the method detection limit.

consistently low concentrations from September through April (Figure 3). Of the four herbicides, metolachlor and cyanazine appear to persist longer in the agricultural area. Metolachlor and EPTC were detected in at least six of the seven remaining samples collected after the growing/irrigation season, whereas alachlor and cyanazine were detected in at least three of the remaining samples.

The consistency of atrazine and prometon concentrations in the agricultural area throughout the study could indicate that these two herbicides persist in the alluvial aquifer system year-round (Figure 3). Other than an increase in atrazine during and following the late May storm event, the concentrations of atrazine and prometon during the growing season were similar to the concentrations found in groundwater-dominated baseflow from September through April. Additionally, concentrations of atrazine and prometon in Lonetree Creek were similar to concentrations measured in alluvial groundwater in agricultural areas near the South Platte River in 1994 (*27*).

Simazine and prometon are pesticides suspected of persisting in the urban alluvial groundwater system. The concentrations of simazine and prometon in Cherry Creek when baseflow consisted primarily of groundwater return flows (late August–January) are similar to concentrations throughout the study (Figure 4). The absence of higher concentrations during the growing season might indicate that simazine and prometon are not applied seasonally in the urban environment but persist in the urban alluvial groundwater system year-round. In 1993, prometon and simazine were the two most frequently detected pesticides in alluvial groundwater in the lower Cherry Creek basin (*28*).

Simazine and prometon concentrations in Cherry Creek generally did not increase in storm runoff events but tended

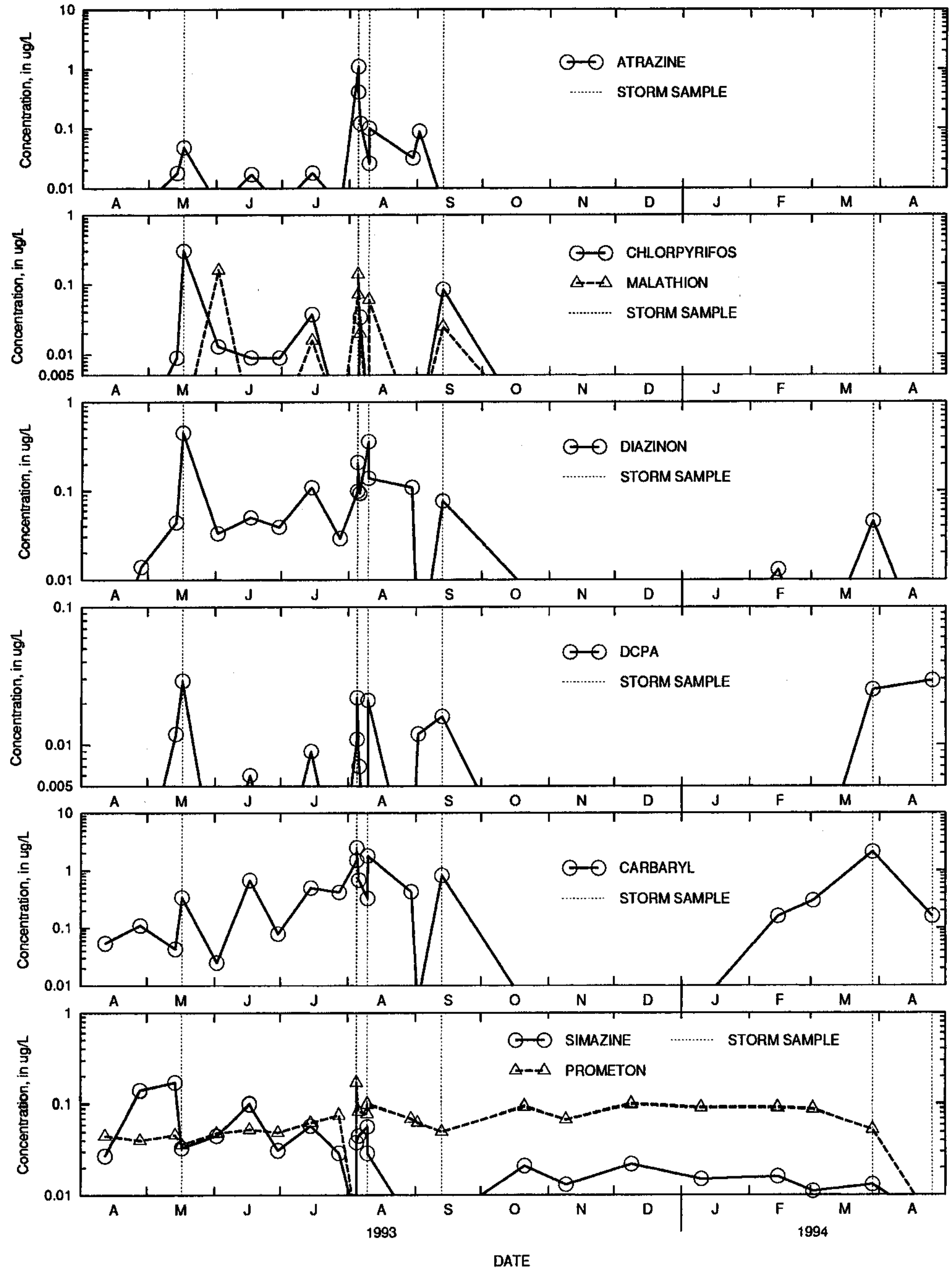

FIGURE 4. Selected pesticide data for Cherry Creek at Denver, April 1993—April 1994. Concentrations below the *x*-axis are less than the method detection limit.

to decrease. In fact, the only two samples in which prometon was not detected and three out of five samples in which simazine was not detected were storm runoff events. The decreases in concentration during storms could result from the dilution of background levels by the large percentage of surface runoff sampled during storm events.

Summary

Two tributary streams of the South Platte River in Colorado were each sampled 25 times for 47 pesticides from April 1993 through April 1994. The results indicate that both agricultural and urban areas are sources for pesticides in streams. Thirty pesticides were detected at least once in the agricultural area, and 22 pesticides were detected at least once in the urban area.

The frequent detection of herbicides commonly used for agriculture resulted in more herbicide detections in the agricultural area as compared to the urban area. Simazine and tebuthiuron were the only herbicides detected in significantly higher concentration in the urban area as compared to the agricultural area. Prometon was the only herbicide that was detected in at least 90% of the samples in each area and at similar concentrations. Herbicides detected in highest concentration in a single sample were DCPA in the agricultural area and atrazine in the urban area.

The number of different insecticides detected was greater in the agricultural area, although the frequent detection of four insecticides in the urban area resulted in the total number of insecticide detections being more evenly distributed between the areas. Carbaryl, chlorpyrifos, diazinon, and malathion predominated the urban insecticide detections, and, except for chlorpyrifos, the concentrations of these compounds were significantly higher in the urban area. The most frequently detected insecticides in the agricultural area also are some of the more commonly used insecticides in the area. Carbaryl was detected in highest concentration of any insecticide in each area.

In both areas, the average concentration of individual pesticides were well below any established MCL or HAL, although alachlor (two samples), cyanazine (four samples), and diazinon (one sample) exceeded drinking water standards in individual samples in the agricultural area. No pesticides exceeded MCLs or HALs in individual urban-area samples.

In the agricultural area, pesticide concentrations generally were higher during the growing season with the highest concentrations occurring soon after the application period. Although fewer data have been compiled on the timing of pesticide application in urban areas, pesticide concentrations were also generally higher during the growing season when pesticide applications are the most likely to occur. Two processes other than application timing that contribute to higher detections during the growing season are storm runoff (both areas) and irrigation return flows (agricultural area).

In both areas, certain pesticides were only detected during the growing season following application. As an example, pendimethalin and carbaryl detections in the agricultural area were limited to March−August. In the urban area, atrazine, chlorpyrifos, and malathion were detected only between March and September.

The year-round detection of some pesticides in both areas at consistently low concentrations, regardless of season or streamflow volume, could indicate that these compounds persist in the local alluvial groundwater system. Examples of some of the more persistent pesticides are atrazine (in the agricultural area), simazine (in the urban area), and prometon (both areas).

Acknowledgments

The authors thank Monfort, Inc., for permitting the installation of a streamflow-gaging station on their property and Urban Drainage and Flood Control District for allowing access to their on-line streamflow-monitoring system. Special thanks are given to Dennis Smits, USGS, who assisted in all of the sample collection. The use of brand names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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Received for review May 25, 1995. Revised manuscript received October 13, 1995. Accepted October 17, 1995.[⊗]

ES950353B

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1996.