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EFFECTS OF HERBICIDE USAGE ON WATER QUALITY OF SELECTED STREAMS IN WYOMING

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GLOSSARY

Amine--An organic compound formed by the replacement of one or more hydrogen atoms of ammonia with a hydrocarbon or other organic molecular group. Amines are basic and react with acids to form salts.

Ester--An organic compound produced by reaction of an organic acid and an alcohol or organic base. One group of herbicides, containing such compounds as 2,4-D and silvex, are organic acids but are often formulated as esters.

Herbicide--A chemical used for killing weeds, grass, or brush or for disturbing their growth pattern. Selective herbicides will kill only certain plants while not harming other plants around them. Nonselective herbicides are designed for killing most or all vegetation.

LC50--The lethal concentration of some toxicant that is fatal to 50 percent of a test organism. It is the measure of a chemical's toxicity in water or air and is expressed in units of concentration such as milligrams per liter or micrograms per liter.

LD50--The lethal dose or amount of a toxicant that is fatal to 50 percent of a test organism. It is the weight of chemical per unit body weight expressed in milligrams per kilogram.

Leafy spurge--Considered a noxious or undesirable weed on all agricultural lands. Leafy spurge is a perennial weed that reproduces by seeds and creeping roots. It is difficult to control, usually requiring an initial treatment with picloram and re-treatment with dicamba, 2,4-D, or a mixture of both.

Microgram per liter (µg/L)--A unit of concentration with 1 microgram (µg) or 10^{-6} gram of solute per a volume of 1 liter (L).

Milligram per kilogram (mg/kg)--A unit of concentration with 1 milligram (mg) or 10^{3} gram in a mass of 1 kilogram (kg) or 1,000 grams.

Milligram per liter (mg/L)--A unit of concentration with 1 milligram (mg) or 10^{-3} gram of solute per a volume of 1 liter (L).

Solubility--The maximum amount of a chemical that will dissolve in a specified amount of solvent. It is often expressed as a concentration at 25°C.

Station-numbering system--Eight-digit numbers are assigned to surface-water stations in downstream order. The first two digits correspond to a main drainage basin (06, Missouri River; 09, Green River), and the last six digits designate the individual station. For sites that do not have an eight-digit number established, a 15-digit latitude-longitude number is used. The first six digits are degrees, minutes, and seconds of latitude; the next seven digits are degrees, minutes, and seconds of longitude; and the last two digits are a sequence number used to distinguish stations with the same latitude and longitude.

TLm--The median tolerance limit expressed as a concentration of a toxicant at which 50 percent of the test organisms survive for a particular period of exposure (usually 24, 48, or 96 hours).

METRIC CONVERSION TABLE AND TRADE NAMES

Multiply	By	To obtain
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
foot (ft)	0.3048	meter (m)
gallon (gal)	3.785	liter (L)
	3.785×10^{-3}	milliliter (ml)
mile (mi)	1.609	kilometer (km)
pound (lb)	0.4536	kilogram (kg)
	4.536×10^{-2}	milligram (mg)
	4.536×10^{-5}	microgram (μg)

The use of trade names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

EFFECTS OF HERBICIDE USAGE ON WATER QUALITY OF SELECTED STREAMS IN WYOMING

By David L. Butler

ABSTRACT

During 1977 and 1978 the Wyoming Department of Agriculture, in conjunction with county weed and pest control districts, conducted a noxious-weed-control program in Wyoming. The herbicides primarily used were picloram, 2,4-D, and dicamba. The U.S. Geological Survey, in cooperation with the Wyoming Department of Agriculture, sampled and analyzed water from selected streams for these herbicides plus silvex; 2,4,5-T; and 2,4-DP.

This report contains data for samples collected during 1977 and 1978. The most commonly detected herbicides in water samples were 2,4-D with 41-percent nonzero values and picloram with 34.5-percent nonzero values. Herbicide occurrence in bottom-matterial samples was uncommon; dicamba was found with 9-percent nonzero values. The maximum herbicide concentration in water was 1.1 micrograms per liter of 2,4-D, and the maximum herbicide concentration in bottom material was 8.0 micrograms per kilogram of 2,4-D. Based on available toxicity data and water-quality criteria, these herbicide concentrations do not constitute dangerous or harmful concentrations to humans or to the environment.

INTRODUCTION

During 1977 the Wyoming Department of Agriculture, in conjunction with the Carbon County Weed and Pest Control District, initiated a herbicide application program for controlling leafy spurge and other undesirable weeds that were spreading into rangeland and fields. The program was expanded during 1978 to include 15 of the 23 weed and pest control districts in Wyoming.

The primary herbicides used in this program were Tordon (active ingredient, picloram), Banvel (active ingredient, dicamba), and 2,4-D. A list of the amounts of chemicals used during 1978 based on data collected from 15 of the 23 weed and pest control districts follows (Hittle, 1979):

Herbicide	Formulation	Amount used
Tordon 22K	2 lb picloram per gallon of water	3,468 gal
Tordon 212	1 lb picloram + 2 lb 2,4-D per gallon of water	3,601 gal
Tordon 2K beads	2 percent picloram as picolinic acid	530,852 lb
Banvel	4 or 8 lb equivalent dicamba per gallon of water	2,647 gal
Banvel granular	5 percent dicamba	15,700 lb
2,4-D amine	--------	26,739 gal

Treatments were applied in scattered areas of leafy spurge infestations. These were commonly small patches of weeds growing on just a few acres. Many of the affected areas were near or along streambanks. Some small islands in the North Platte River in Carbon County were also treated. Much of the herbicide application was done on the ground; however, 2,500 acres were treated with Tordon beads applied from an airplane (G.F. Hittle, Wyoming Department of Agriculture, oral commun., 1980). The chemicals were usually applied only once, but some areas were re-treated if 2,4-D was used.

The U.S. Geological Survey, in cooperation with the Wyoming Department of Agriculture, began a sampling program to determine herbicide residues in water and bottom material from streams in areas of intense chemical use. The purpose of the sampling program was to determine the effects of herbicide application on the water quality of streams in the treatment areas. The Wyoming Department of Agriculture wanted to insure that State and Federal water-quality standards were not being exceeded and that herbicide concentrations were not adversely affecting drinking-water supplies, fish, and wildlife.

During 1977, only the Carbon County Weed and Pest Control District was involved in the sampling program. Sampling was done at four sites on the North Platte River from the State line to near Saratoga and at two sites on the Encampment River (fig.1). When other weed and pest control districts came into the program during 1978, other areas in the State needed to be monitored.

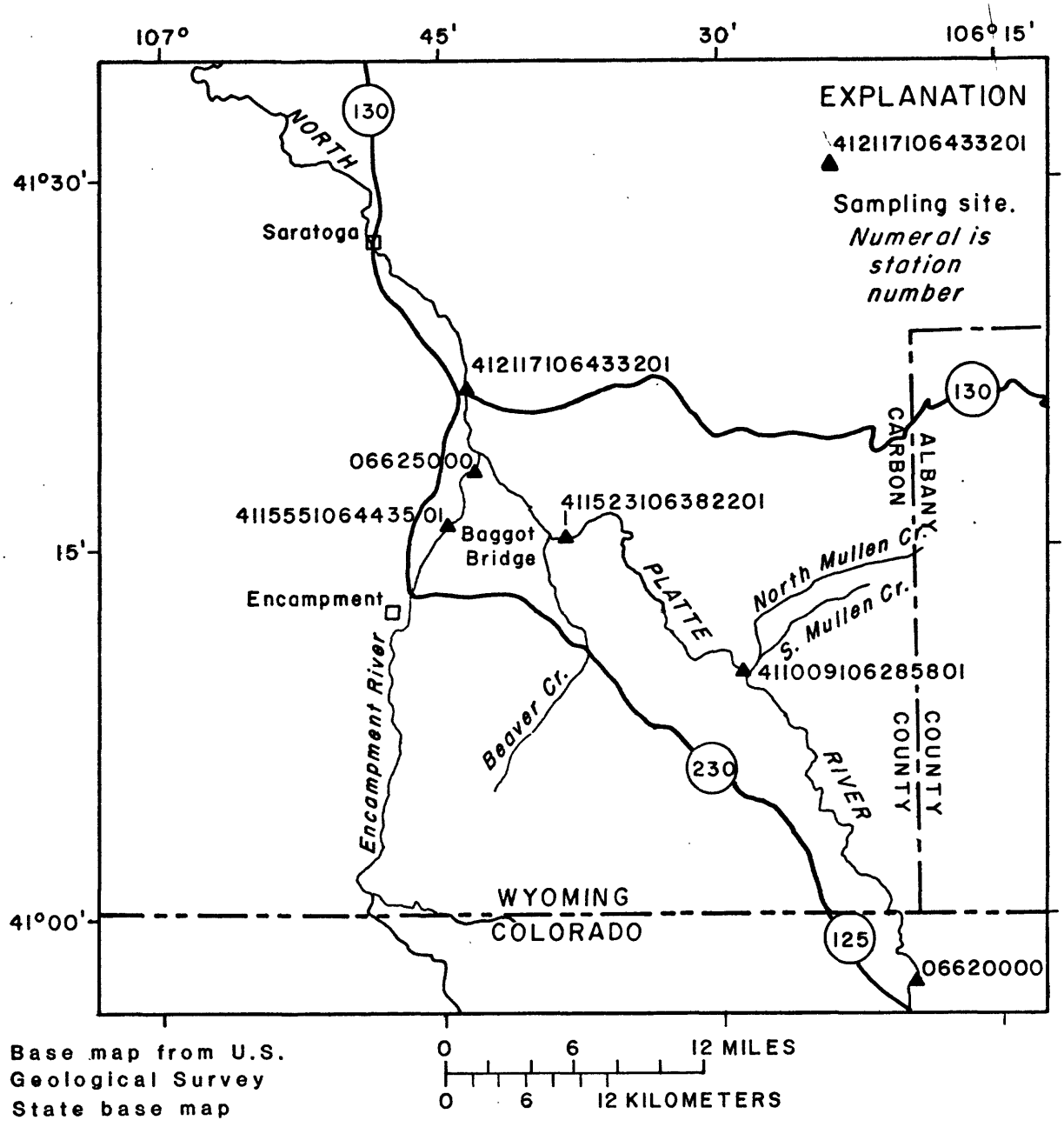

Figure 1.--Location of sampling sites in the upper North Platte River basin.

Consequently, 3 of the North Platte River sites and 1 of the Encampment River sites were discontinued while 10 new sites were added. The new sampling sites were in the Little Snake River, Wind River, Clear Creek, Belle Fourche River, and Beaver Creek basins (fig. 2). A list of station-identification names is presented in table 1. Sampling was done to detect possible gross pollution resulting from herbicide use and to detect a possible increase in herbicide concentrations with time. No allowances were made in the sampling schedule for storms or for sampling streams near spraying areas at the time of application. Sampling was done during May through October, and samples usually were collected only when U.S. Geological Survey personnel made a regular visit to the station.

Site Selection

The U.S. Geological Survey and the Wyoming Department of Agriculture cooperated in the site selection process. Environmental concerns such as the importance of a stream as a fishery were considered. High priority was given to streams in areas of intense herbicide use. Due to manpower and time considerations, site selection was limited to existing U.S. Geological Survey stream-gaging or water-quality stations with the exception of the four miscellaneous stations in Carbon County, which were selected in specific areas of herbicide use. North Platte River at Northgate, station 06620000, is upstream from all herbicide-treatment areas in Wyoming and was selected as the control site.

Sample Collection and Methods of Analysis

Water samples were collected with a DH48TM sampler using suspended-sediment sampling techniques. Prior to sample collection at the site, the glass sampler bottles and the sampler nozzle were rinsed with pesticide-grade acetone followed by rinsing with native water. Water samples were transferred to 1-liter narrow-mouth glass bottles and kept chilled until shipment to the laboratory. In addition to each water sample, bottom-material samples were collected from areas of the stream bottom with plentiful deposits. These samples were collected in wide-mouth glass bottles and kept chilled until shipment. All water and bottom samples were acidified with redistilled sulfuric acid to pH 2 or less upon receipt by the laboratory to keep the herbicides in their acid form until extraction.

All sample containers were provided by the U.S. Geological Survey water-quality laboratory in Denver, Colo. Sample containers were washed with Alconox, rinsed with distilled water, and heat treated at 300°C overnight at the laboratory. Bottles were provided with lids lined by Teflon or aluminum foil.

All samples were analyzed by the U.S. Geological Survey water-quality laboratory in Denver. The laboratory does routine herbicide analysis for 2,4-D, 2,4,5-T, silvex, and 2,4-DP in water and bottom material using methods described by Goerlitz and Brown (1972). In the methods two procedures can be used: (1) Boron trifluoride methanol esterfication and (2) diazomethane esterfication. Boron trifluoride methanol is used when only the four common herbicides are being determined. For this study, analysis for dicamba and

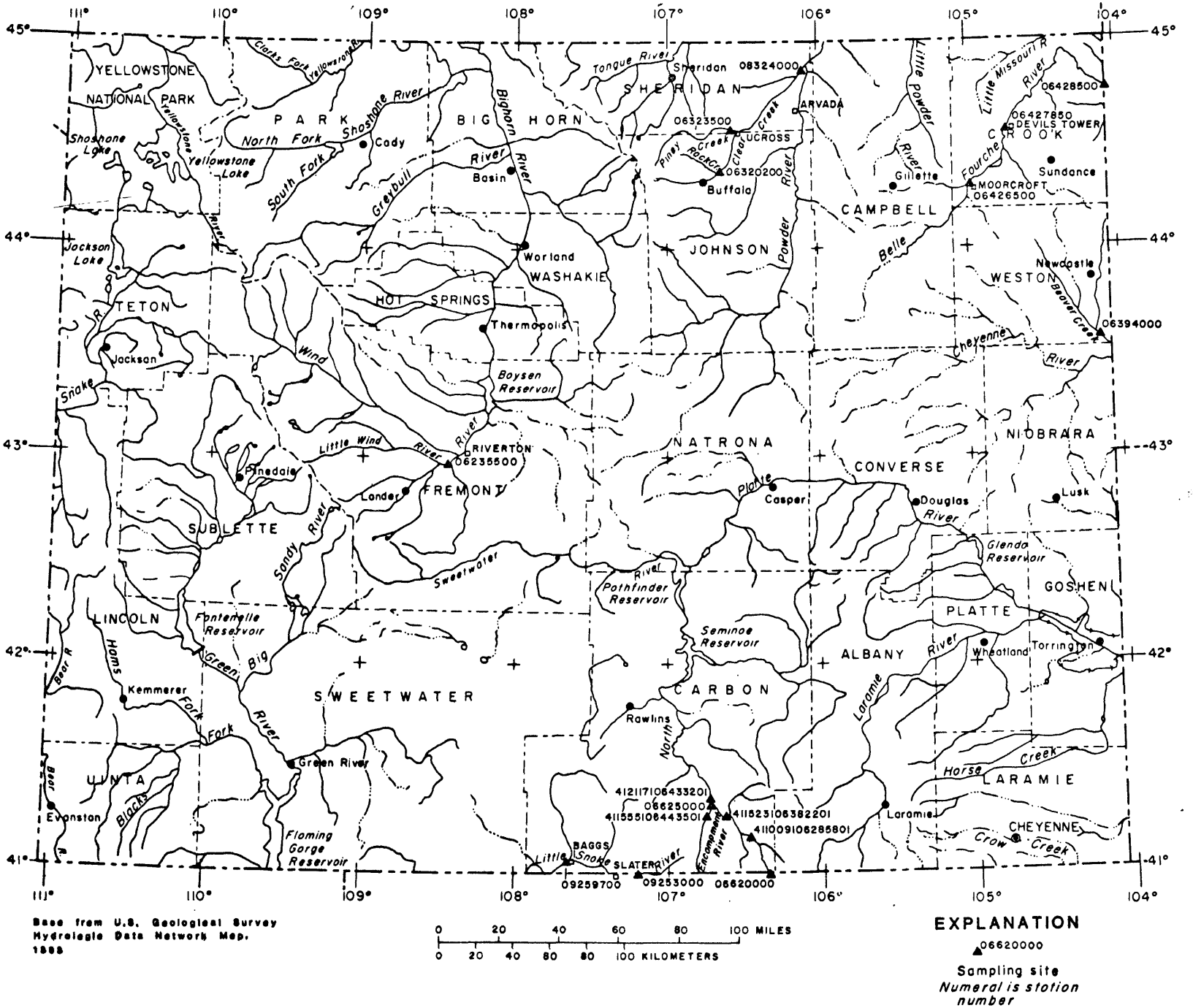

Figure 2.--Location of sampling sites.

Table 1.--Station numbers and names of sampling sites

Station number	Station name
06235500	Little Wind River near Riverton, Wyo.
06320200	Clear Creek below Rock Creek, near Buffalo, Wyo.
06323500	Piney Creek at Ucross, Wyo.
06324000	Clear Creek near Arvada, Wyo.
06394000	Beaver Creek near Newcastle, Wyo.
06426500	Belle Fourche River below Moorcroft, Wyo.
06427850	Belle Fourche River at Devils Tower, Wyo.
06428500	Belle Fourche River at Wyoming-South Dakota State line
06620000	North Platte River near Northgate, Colo. (Northgate is about 4 mi southeast of the station)
06625000	Encampment River at mouth, near Encampment, Wyo.
09253000	Little Snake River near Slater, Colo.
09259700	Little Snake River near Baggs, Wyo.
411009106285801	North Platte River below Mullen Creek, near Encampment, Wyo.
411523106382201	North Platte River above Beaver Creek, near Encampment, Wyo.
411555106443501	Encampment River at Baggot Bridge, near Encampment, Wyo.
412117106433201	North Platte River at Highway 130, near Saratoga, Wyo.

picloram were also needed. Because dicamba is not methylated by boron trifluoride methanol, the diazomethane esterfication was used. After satisfactory recovery studies had been done using diazomethane, that method was used to analyze all samples collected for this study.

The analytical method requires that a 2.0-ml benzene elution fraction be collected during the microcolumn cleanup step. That fraction will recover the 2,4-D; 2,4,5-T; silvex; 2,4-DP; and dicamba methyl esters. In a modification of the method, a second fraction, using 20-percent ethyl ether in benzene, is collected to recover the picloram methyl ester. Both fractions are analyzed on the same gas chromatographic system.

The detection limits reported for the analytical methods were 0.01 µg/L for water samples and 0.1 µg/kg for bottom samples. A nonzero value is any concentration equal to or greater than the detection limits. Values less than the detection limits are reported as zero, but a reported concentration of zero does not preclude the existence of herbicide residues in minute concentrations.

RESULTS AND DISCUSSION

The tables in this report present the data collected during 1977-78 for the herbicide program. The date of sample collection, water temperature, streamflow, and the herbicide results for each sample are summarized in table 2. Summaries by station for each herbicide in water samples are given in table 3 and for bottom-material samples in table 4. A summary of all samples by herbicide is give in table 5.

2,4-D

The herbicide 2,4-D is a selective herbicide used on a large variety of broad-leafed weeds. Its uses range from domestic lawns and gardens to large-scale agriculture uses. The herbicide is a chlorinated organic acid with a water solubility of 620 mg/L. It is usually formulated in various esters and amine salts, which are much more water soluble. The U.S. Environmental Protection Agency has set 100 µg/L as the criteria for 2,4-D in public-water supplies (U.S. Environmental Protection Agency, 1977a, p. 137). The LD50 for rats is 370 mg/kg for the acid, 500-1,200 mg/kg for the esters, and 300-1,200 mg/kg for the amines (Berg, 1977, p. D77). The herbicide 2,4-D is not highly toxic to fish. The 48-hour TLm's include 2,200 µg/L for trout fingerlings (McKee and Wolfe, 1963, p. 366) and 800-2,100 µg/L for several ester forms for bluegills (Lawless and others, 1975, p. 47). Some crop-injury values include greater than 10 mg/L for corn and greater than 0.2 mg/L for sugar beets (National Academy of Sciences, National Academy of Engineering, 1973, p. 347). Values of LD50 for cattle are reported to be 300-1,000 mg/kg (National Academy of Sciences, National Academy of Engineering, 1973, p. 320).

Table 2.--Herbicide concentrations at sampling sites

Date	Time (h)	Stream-flow, instan-taneous (ft^3/s)	Temper-ature (°C)	2,4-D, total in water (µg/L)	2,4-D, total in bottom material (µg/kg)	2,4,5-T total in water (µg/L)	2,4,5-T, total in bottom material (µg/kg)	Silvex, total in water (µg/L)	Silvex, total in bottom material (µg/kg)	2,4-DP, total in water (µg/L)	2,4-DP, total in bottom material (µg/kg)	Dicamba, total in water (µg/L)	Dicamba, total in bottom material (µg/kg)	Picloram, total in water (µg/L)	Picloram, total in bottom material (µg/kg)
06235500 Little Wind River near Riverton, Wyo. (lat 42°59'51", long 108°22'29")															
1978															
June 1	1300	1610	10.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.01	0.0
Nov. 2	0800	273	3.5	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.01	.0
06320200 Clear Creek below Rock Creek near Buffalo, Wyo. (lat 44°21'44", long 106°39'13")															
1978															
May 15	1630	497	13.0	0.11	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
July 24	1730	136	20.5	.05	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Aug. 21	1710	65	20.0	.00	.0	.00	.0	.00	.0	.00	.0	.01	1.8	.01	.0
Sept.18	1630	100	13.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
06323500 Piney Creek at Ucross, Wyo. (lat 44°33'45", long 106°32'25")															
1978															
May 15	1430	372	13.0	0.08	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.12	0.0
July 24	1620	144	22.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.03	.0
Aug. 21	1500	158	20.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	1.5	.00	.0
Sept.18	1500	44	14.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
06324000 Clear Creek near Arvada, Wyo. (lat 44°52'18", long 106°04'56")															
1978															
May 12	1330	573	9.0	0.15	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.06	0.0
July 21	1330	207	16.5	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.14	.0
Aug. 18	1320	210	17.0	.05	.0	.00	.0	.00	.0	.00	.0	.01	.0	.06	.0
Sept.15	1230	122	15.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
06394000 Beaver Creek near Newcastle, Wyo. (lat 43°32'07", long 104°07'02")															
1978															
May 10	1700	683	10.5	0.17	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Sept.13	1610	8.0	16.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
06426500 Belle Fourche River below Moorcroft, Wyo. (lat 44°17'45", long 104°58'35")															
1978															
May 11	1400	825	12.0	0.59	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.01	0.0
July 20	1450	15	21.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Aug. 17	1330	28	18.0	.02	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Sept.14	1510	8.7	15.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0

Table 2.--Herbicide concentrations at sampling sites--Continued

Date	Time (h)	Stream-flow, instan-taneous (ft^3/s)	Temper-ature (°C)	2,4-D, total in water (µg/L)	2,4-D, total in bottom material (µg/kg)	2,4,5-T total in water (µg/L)	2,4,5-T, total in bottom material (µg/kg)	Silvex, total in water (µg/L)	Silvex, total in bottom material (µg/kg)	2,4-DP, total in water (µg/L)	2,4-DP, total in bottom material (µg/kg)	Dicamba, total in water (µg/L)	Dicamba, total in bottom material (µg/kg)	Picloram, total in water (µg/L)	Picloram, total in bottom material (µg/kg)
06427850 Belle Fourche River at Devils Tower, Wyo. (lat 44°35'22", long 104°42'12")															
1978															
May 11	1200	E570	11.0	0.10	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.18	0.0
July 20	1210	19	19.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Aug. 17	1130	90	18.5	.05	.0	.00	.0	.00	.0	.00	.0	.00	.0	.02	.0
Sept.14	1315	44	15.0	.00	--	.00	--	.00	--	.00	--	.00	--	.00	--
06428500 Belle Fourche River at Wyoming-South Dakota State line (lat 44°44'59", long 104°02'49")															
1978															
May 11	0915	1500	12.0	0.32	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.13	0.0
Sept.14	0930	60	12.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
06620000 North Platte River near Northgate, Colo. (lat 40°56'10", long 106°20'21")															
1977															
June 11	1600	545	--	0.00	--	0.00	--	0.00	--	0.00	--	--	--	--	--
20	0930	153	15.5	.00	0.0	.00	0.0	.00	0.0	.00	0.0	0.00	0.0	0.00	0.0
Oct. 10	0930	112	2.0	.00	--	.00	--	.00	--	.00	--	--	--	--	--
Nov. 7	1430	110	6.0	.09	.0	.00	.0	.00	.0	.00	3.0	.00	.0	.00	.0
1978															
May 22	0820	1480	7.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
July 31	0830	795	14.5	.04	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Aug. 29	0830	162	9.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Sept.26	0830	130	7.0	.00	4.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.7
06625000 Encampment River at mouth, near Encampment, Wyo. (lat 41°18'12", long 106°42'53")															
1977															
June 20	1245	207	15.0	0.02	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Nov. 7	1145	68	5.0	.10	.0	.01	.0	.00	.0	.00	.0	.00	.0	.06	.0
1978															
May 22	1000	844	4.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
July 31	1030	159	14.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Aug. 29	1030	39	11.5	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Sept.26	1015	63	8.0	.00	8.0	.00	.0	.00	4.0	.00	.0	.00	2.6	.00	.0

Table 2.--Herbicide concentrations at sampling sites--Continued

Date	Time (h)	Stream-flow, instan-taneous (ft^3/s)	Temper-ature (°C)	2,4-D, total in water (µg/L)	2,4-D, total in bottom material (µg/kg)	2,4,5-T total in water (µg/L)	2,4,5-T, total in bottom material (µg/kg)	Silvex, total in water (µg/L)	Silvex, total in bottom material (µg/kg)	2,4-DP, total in water (µg/L)	2,4-DP, total in bottom material (µg/kg)	Dicamba, total in water (µg/L)	Dicamba, total in bottom material (µg/kg)	Picloram, total in water (µg/L)	Picloram, total in bottom material (µg/kg)
		0925300 Little Snake River near Slater, Colo. (lat 40°59'58", long 107°08'34")													
1978															
June 9	1230	1950	--	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
July 20	1330	157	18.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Aug. 22	1530	25	17.5	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Sept.28	1330	20	13.0	.00	1.0	.00	.0	.00	1.0	.00	.0	.00	.0	.00	.0
		09250700 Little Snake River near Baggs, Wyo. (lat 41°00'11", long 107°55'11")													
1978															
June 9	1415	3400	--	0.03	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	00
July 20	0930	95	18.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Aug. 22	1330	22	18.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.1	.01	.0
Sept.28	1010	45	12.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
		411009106285801 North Platte River below Mullen Creek, near Encampment, Wyo. (lat 41°10'09", long 106°28'58")													
1977															
July 21	1100	50	18.0	1.1	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.8	0.18	0.0
		411523106382201 North Platte River above Beaver Creek, near Encampment, Wyo. (lat 41°15'23", long 106°38'22")													
1977															
Aug. 1	1100	110	17.0	--	0.0	--	0.0	--	0.0	--	0.0	--	0.0	--	0.0
1	1230	220	19.5	0.07	--	0.00	--	0.00	--	0.00	--	0.00	--	0.00	--
		411555106443501 Encampment River at Baggott Bridge, near Encampment, Wyo. (lat 41°15'55", long 106°44'35")													
1977															
June 20	1130	190	14.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Nov. 7	1245	65	6.5	.08	.0	.01	.0	.00	.0	.00	.0	.00	.0	.11	.0
		412117106433201 North Platte River at Wyoming Highway 130, near Saratoga, Wyo. (lat 41°21'17", long 106°43'32")													
1977															
June 20	1345	E600	18.5	0.01	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
July 21	1430	E150	21.5	.32	.0	.00	.0	.00	.0	.00	.0	.00	.0	.15	.0
27	1330	E500	21.0	.10	.0	.00	.0	.00	.0	.00	1.0	.00	.0	.01	.0
Aug. 1	1230	E220	19.5	.07	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0
Sept.29	0900	E130	10.0	.00	.0	.00	.0	.00	.0	.00	.0	--	.0	--	.0
Nov. 7	1045	160	6.0	.18	.0	.02	.0	.00	.0	.00	.0	.00	.0	.02	.0

E = Estimated

Table 3.--Summary of results by station for herbicides in water samples.

N= number of samples

NZ= number of nonzero values

MAX= maximum concentration (µg/L)

Station number	2,4-D			2,4,5-T			Silvex			2,4-DP			Dicamba			Picloram		
	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX
06235500	2	0	0.00	2	0	0.00	2	0	0.00	2	0	0.00	2	0	0.00	2	2	0.01
60320200	4	2	.11	4	0	.00	4	0	.00	4	0	.00	4	1	.01	4	1	.01
06323500	4	1	.08	4	0	.00	4	0	.00	4	0	.00	4	0	.00	4	2	.12
06324000	4	2	.15	4	0	.00	4	0	.00	4	0	.00	4	1	.01	4	3	.14
06394000	2	1	.17	2	0	.00	2	0	.00	2	0	.00	2	0	.00	2	0	.00
06426500	4	2	.59	4	0	.00	4	0	.00	4	0	.00	4	0	.00	4	1	.01
06427850	4	2	.10	4	0	.00	4	0	.00	4	0	.00	4	0	.00	4	2	.18
06428500	2	1	.32	2	0	.00	2	0	.00	2	0	.00	2	0	.00	2	1	.13
06620000	8	2	.09	8	0	.00	8	0	.00	8	0	.00	6	0	.00	6	0	.00
06625000	6	2	.10	6	1	.01	6	0	.00	6	0	.00	6	0	.00	6	1	.06
09253000	4	0	.00	4	0	.00	4	0	.00	4	0	.00	4	0	.00	4	0	.00
09259700	4	1	.03	4	0	.00	4	0	.00	4	0	.00	4	0	.00	4	1	.01
411009106285801	1	1	1.1	1	0	.00	1	0	.00	1	0	.00	1	0	.00	1	1	.18
411523106382201	1	1	.07	1	0	.00	1	0	.00	1	0	.00	1	0	.00	1	0	.00
411555106443501	2	1	.08	2	1	.01	2	0	.00	2	0	.00	2	0	.00	2	1	.11
412117106433201	6	5	.32	6	1	.02	6	0	.00	6	0	.00	5	0	.00	5	3	.15

Table 4.--Summary of results by station for herbicides in bottom-material samples.

N= number of samples

NZ= number of nonzero values

MAX= maximum concentration (µg/kg)

Station number	2,4-D			2,4,5-T			Silvex			2,4-DP			Dicamba			Picloram		
	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX	N	NZ	MAX
06235500	2	0	0.0	2	0	0.0	2	0	0.0	2	0	0.0	2	0	0.0	2	0	0.0
60320200	4	0	.0	4	0	.0	4	0	.0	4	0	.0	4	1	1.8	4	0	.0
06323500	4	0	.0	4	0	.0	4	0	.0	4	0	.0	4	1	1.5	4	0	.0
06324000	4	0	.0	4	0	.0	4	0	.0	4	0	.0	4	0	.0	4	0	.0
06394000	2	0	.0	2	0	.0	2	0	.0	2	0	.0	2	0	.0	2	0	.0
06426500	4	0	.0	4	0	.0	4	0	.0	4	0	.0	4	0	.0	4	0	.0
06427850	3	0	.0	3	0	.0	3	0	.0	3	0	.0	3	0	.0	3	0	.0
06428500	2	0	.0	2	0	.0	2	0	.0	2	0	.0	2	0	.0	2	0	.0
06620000	6	1	4.0	6	0	.0	6	0	.0	6	1	3.0	6	0	.0	6	1	.7
06625000	6	1	8.0	6	0	.0	6	1	4.0	6	0	.0	6	1	2.6	6	0	.0
09253000	4	1	1.0	4	0	.0	4	1	1.0	4	0	.0	4	0	.0	4	0	.0
09259700	4	0	.0	4	0	.0	4	0	.0	4	0	.0	4	1	.1	4	0	.0
411009106285801	1	0	.0	1	0	.0	1	0	.0	1	0	.0	1	1	.8	1	0	.0
411523106382201	1	0	.0	1	0	.0	1	0	.0	1	0	.0	1	0	.0	1	0	.0
411555106443501	2	0	.0	2	0	.0	2	0	.0	2	0	.0	2	0	.0	2	0	.0
412117106433201	6	0	.0	6	0	.0	6	0	.0	6	1	1.0	6	0	.0	6	0	.0

Table 5.--Summary of results for all samples by herbicide.

N= number of samples

NZ= number of nonzero values

PCT = percentage of samples that are nonzero

MAX= maximum concentration

Herbicide	Water samples				Bottom-material samples			
	N	NZ	PCT	MAX (µg/L)	N	NZ	PCT	MAX (µg/kg)
2,4-D	58	24	41.4	1.1	55	3	5.5	8.0
2,4,5-T	58	3	5.2	.02	55	0	.0	.0
Silvex	58	0	.0	.00	55	2	3.6	4.0
2,4-DP	58	0	.0	.00	55	2	3.6	3.0
Dicamba	55	2	3.6	.01	55	5	9.1	2.6
Picloram	55	19	34.5	.18	55	1	1.8	.7

Using the classifications described in Lawless and others (1975, p. 51-52), 2,4-D is nonpersistent in nature. These classes, defined in terms of the time required for 75 to 100 percent of a pesticide to disappear or degrade to harmless substances in the environment, are: Less than 3 months, nonpersistent; 3-18 months, moderately persistent; greater than 18 months, persistent; indefinite or infinite is called permanent. Mobility is defined as the ability of a compound to move through the soil; 2,4-D is classed as mobile in soil when compared with other pesticides (Lawless and others, 1975, p. 51).

Some 2,4-D was detected in at least one water sample at all but two of the sampling stations. Forty-one percent of all water samples had detectable concentrations of 2,4-D. The maximum concentration of 1.1 µg/L detected is much less than concentrations harmful to wildlife, fish, or crops. In contrast to the water samples, 2,4-D was found in only 3 of 55 bottom-material samples, and concentrations did not exceed 8.0 µg/kg. These three samples were from different stations.

2,4,5-T

The herbicide 2,4,5-T also is a chlorinated organic acid and was used for brush control in rangeland and on road and other rights-of-way. Commonly, 2,4,5-T was mixed with 2,4-D in commercial weed killers. The acid form of 2,4,5-T is not very water soluble (238 mg/L), but the salts are soluble. An LD50 for rats of 500 mg/kg is listed in Berg (1977, p.D252), while an LD50 of 300 mg/kg is stated in McKee and Wolf (1963, p. 388) and in Lawless and others (1975, p. 37). A 48-hour TLm range of 560-16,700 µg/L for bluegills for three ester forms is reported (Lawless and others, 1975, p. 47). The toxicity of 2,4,5-T to cattle is similar to that of 2,4-D and silvex, with an LD50 of 300-1,000 mg/kg (National Academy of Sciences, National Academy of Engineering, 1973, p. 320). This herbicide is mobile in soil and moderately persistent (Lawless and others, 1975, p. 51-52).

During the 1970's, controversy surrounded the production procedures and use of 2,4,5-T. A very poisonous byproduct called TCDD (popularly but incorrectly referred to as dioxin) appeared in excessive amounts; at present (1979), production of 2,4,5-T has been suspended by the U.S. Environmental Protection Agency.

Small amounts of 2,4,5-T were detected in only three water samples at concentrations of 0.01 µg/L and 0.02 µg/L, which are near the detection limit of the analytical method. These samples were all from the upper North Platte River basin. No bottom-material samples had detectable concentrations of 2,4,5-T.

Silvex

Silvex, also known as 2,4,5-TP, was used on woody plants, weeds, and some aquatic plants in or along ditches, along roads, and in some cropland and pastures. It also is a chlorinated organic acid and is slightly soluble in water (180 mg/L). Silvex commonly is formulated in ester and amine forms,

which are more water soluble. The U.S. Environmental Protection Agency has set a domestic water-supply criteria of 10 µg/L for silvex (U.S. Environmental Protection Agency, 1977a, p. 250). The smallest LD50 found for rats was 650 mg/kg (Berg, 1977, p. D237). Fish toxicities ranged from a 48-hour TLm of 650 µg/L for rainbow trout (Lawless and others, 1975, p. 49) to a LC50 of 83,000 µg/L on bluegills for the potassium salt (National Academy of Sciences, National Academy of Engineering, 1972, p. 432). The LD50 for cattle was listed at 300-1,000 mg/kg, (National Academy of Sciences, National Academy of Engineering, 1973, p. 320) and some crop-injury values include greater than 5.0 mg/L for corn and greater than 0.02 mg/L for sugar beets (National Academy of Sciences, National Academy of Engineering, 1973, p. 347). Because silvex is chemically and structurally similar to 2,4,5-T, it is likely to be moderately persistent in soil. During 1979, the U.S. Environmental Protection Agency issued a stop order on production of silvex.

Silvex was not detected in any water samples and in only two bottom-material samples, one from station 06625000 on the Encampment River and one from station 09253000 on the Little Snake River. The herbicide 2,4-D also was detected in the bottom material from the same two samples.

2,4-DP

Dichloroprop, or 2,4-DP, is used for control of brush and some aquatic weeds. It is a more selective herbicide than 2,4-D and has a water solubility of 350 mg/L and an LD50 for rats of 800 mg/kg (Lawless and others, 1975, p. 35). The 48-hour TLm for bluegills is 1,100 µg/L as reported by Lawless and others (1975, p. 47). Because 2,4-DP is structurally and chemically similar to 2,4-D, it is expected to be nonpersistent in soil by the classification described in Lawless and others (1975).

No 2,4-DP was detected in any water sample and some was detected in only two bottom-material samples. Detectable concentrations were found in the North Platte River near Northgate, Colo., station 06620000, during November 1977 and the North Platte River at State Highway 130, near Saratoga, Wyo., station 412117106433201, during July 1977.

Dicamba

Dicamba, commonly known as Banvel or Banvel D, is a chlorinated derivative of benzoic acid. It is used for brush and weed control on rangeland, road and other rights-of-way, and some crops. Dicamba commonly is formulated with 2,4-D or 2,4,5-T amines and esters. The LD50 for rats is listed at 800-2,900 mg/kg (Berg, 1977, p. D27), whereas Lawless and others (1975, p. 35) give a value of 1,100 mg/kg. The U.S. Environmental Protection Agency (1977b, sec. 5, table 24) lists dicamba as nontoxic to fish. The chemical is very mobile in soil and is classed as nonpersistent (Lawless and others, 1975, p. 51-52).

Dicamba was detected in two water samples at concentrations of 0.01 µg/L. Both samples were collected within 3 days of each other from the two Clear Creek stations. Five bottom-material samples from five stations in three river basins had dicamba present. Two of the nonzero values for bottom-material samples were from the Clear Creek basin, two were from the upper North Platte River basin, and one was from the Little Snake River. The maximum concentration was 2.6 µg/kg in bottom material from the Encampment River.

Picloram

Picloram, more commonly known as Tordon, is a chlorinated organic acid derivative. It differs from the other herbicides studied because it contains nitrogen in its acid form, and the other herbicides do not. The most common use of picloram is for weeds and brush on rangeland and pastures. Picloram is slightly water soluble (430 mg/L) but the picloram salts are very water soluble. The potassium or amine salt commonly is mixed with 2,4-D or 2,4,5-T to extend the range of use (Berg, 1977, p. D265). The LD50 for rats is 8,200 mg/kg, and the 48-hour TLm for rainbow trout is 2,500 µg/L (Lawless and others, 1975, p. 49). Crop-injury values are greater than 10 mg/L for corn and greater than 1.0 mg/L for sugar beets (National Academy of Sciences, National Academy of Engineering, 1973, p. 347). Picloram is persistent in soil and is very mobile (Lawless and others, 1975, p. 51-52).

Picloram was detected in one-third of all water samples collected and occurred in at least one sample from every basin except the Beaver Creek basin. The concentrations reported were all very small, with a maximum of 0.18 µg/L. The only bottom-material sample that had picloram (0.7 µg/kg) was collected at station 06620000, North Platte River near Northgate, Colo. This analysis seems anomalous because picloram salts are very soluble in water and the sampling site is upstream from all areas treated with picloram.

FUTURE WORK

The Wyoming Department of Agriculture has continued the noxious-weed-control program since 1978. The application areas have been expanded and the amounts of herbicide used have increased. The U.S. Geological Survey, in cooperation with the Wyoming Department of Agriculture, has continued the monitoring program through 1980 and plans to continue sampling in areas of intense herbicide use.

SUMMARY

Some 2,4-D was detected in 41 percent and some picloram in 34.5 percent of all water samples. These frequencies of occurrence are to be expected because 2,4-D is one of the most available and widely used herbicides, and the sampling sites were chosen in areas of intense 2,4-D and picloram use. Dicamba occurred in two samples and 2,4,5-T in three samples, at very small concentrations. Silvex and 2,4-DP were not detected in any of the water samples. The greatest herbicide concentration reported for any water sample was 1.1 µg/L of 2,4-D in the North Platte River. That concentration is less than any harmful concentrations for fish, wildlife, or crops, and also is less than the drinking-water standard set by the U.S. Environmental Protection Agency. Herbicides do not accumulate in animal or fish tissue in any significant amount, so there is little chance of herbicide concentrations in water increasing in fish or animals.

Fifty-five bottom-material samples were analyzed for six herbicides for a total of 330 analyses. Only 13 of these analyses had herbicides in detectable concentrations. Because the herbicides analyzed for are used in the ester or amine salt form, which are water soluble, the frequency of occurrence of these herbicides should be much greater in the water phase than in the bottom-material sediments. All herbicides except 2,4,5-T were detected at least once, and detectable concentrations ranged from 0.7 µg/kg of picloram to 8.0 µg/kg of 2,4-D.

Based on available toxicity data and water-quality criteria, the herbicide concentrations in Wyoming streams in areas of intense herbicide use do not seem to be significant. However, the Wyoming Department of Agriculture plans to continue and to expand the noxious-weed-control program with an expected increase in herbicide use. The U.S. Geological Survey in cooperation with the Wyoming Department of Agriculture plans to continue monitoring Wyoming streams for herbicides in areas of intense use.

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