Occurrence and flux of selected pesticides in surface water of the upper Snake River Basin, Idaho and western Wyoming

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ABSTRACT: During May and June 1994, 37 water samples were collected at 31 sites in the upper Snake River Basin and analyzed for 83 pesticides and pesticide metabolites. EPTC, atrazine, and the atrazine metabolite deethylated atrazine were the most frequently detected and were found in 30, 20, and 13 of the samples, respectively. Fifteen additional pesticides were detected at least once. All the compounds detected were at concentrations of less than 1 microgram per liter. Total annual applications of EPTC and atrazine within subbasins and their instantaneous instream fluxes have a logarithmic relation with coefficients of determination (R^2 values) of 0.55 and 0.62, respectively. At the time of sampling, the median daily flux of EPTC was about 0.0001% of the annual amount applied in a subbasin, whereas the median daily flux of atrazine was between 0.001 and 0.01%. The difference in fluxes between EPTC and atrazine probably results from differences in their physical properties and in the method and timing of application.

Intensive use of pesticides in many parts of the United States poses a potential for serious non-point source contamination of receiving water. More than 1,400 compounds are found in various pesticide products used to control crop pests in agriculture and silviculture (Rao et al. 1988). Additionally, new pesticides are continually being formulated and introduced to improve safety and minimize adverse environmental impacts. The evolving nature of agrochemicals necessitate ongoing sampling efforts to provide a better understanding of pesticide behavior in the environment. However, in many watersheds in the nation, data on pesticide concentrations in water are lacking. The U.S. Geological Survey (USGS), through its National Water quality Assessment (NAWQA) Program, began a series of investigations in 1991 to provide a nationally consistent description of water quality conditions for a large part of the nation's water resources. The upper Snake River Basin (USNK) in Idaho and western Wyoming was selected as one of 20 study units to begin activities in 1991. As part of the NAWQA Program, ground- and surface-water resources were sampled to determine the occurrence and distribution of commonly used pesticides throughout the nation.

Although pesticide use on agricultural crops in the USNK is extensive (Gianessi and Puffer, 1991, 1992), information on their concentrations in surface water is lacking. Collection of most pesticide data in the USNK since 1975 has been directed primarily toward detecting compounds in fish tissue and bed sediments (Clark, 1994a). Fish tissue and bed sediment data are good indicators for the historical use of recalcitrant and water-insoluble pesticides, such as organochlorine insecticides, many of which have been banned from use in the United States. Pesticides in current use are generally more water soluble and degrade more rapidly than many of the pesticides used in the past, thus increasing the likelihood of transport to surface water and decreasing the likelihood of accumulation in tissue and sediments (Smith et al. 1988).

As part of the USNK NAWQA study, water samples were collected at 31 sites during May and June 1994. The objectives of the sampling were to assess the occurrence and distribution of selected pesticides in surface water and to relate total annual pesticide applications to daily pesticide fluxes at subbasin outlets. This article describes the results of the sampling effort.

Description of study area

The USNK drains an area of approximately 93,000 km^2 (229,799,847.3 acres) from its headwaters near the southern border of Yellowstone National Park in Wyoming to the basin outlet at King Hill in south-central Idaho (Figure 1). The USNK includes parts of four states and 24 major subbasins tributary to the Snake River. The environmental setting of the USNK is discussed comprehensively in a report by Maupin (1995).

Approximately 20% of the USNK, or more than 18,500 km^2 (45,712,872.85 acres), is used for agriculture. Principal crops grown in the basin in 1993 were potatoes, barley, wheat, dry beans, alfalfa, and sugar beets (Idaho Agricultural Statistics Service 1994). The agricultural land in the basin is concentrated along the Snake River in Idaho, and near the mouths of tributary drainage basins to the Snake River. Because of the semiarid climate, crops grown in the basin are irrigated primarily through a network of canals and lateral ditches and from pumping of ground water. In 1990, approximately 9.4x10^9 cubic meters (m^3) of surface water and 8.1x10^9 m^3 of ground water were used for irrigation in the USNK (Maupin 1995).

Numerous pesticides are applied to a variety of crops in the USNK (Table 1). The herbicide EPTC, which is used primarily for weed control in dry beans, potatoes, and sugar beets, is the pesticide applied in the largest quantity in the basin. The herbicides triallate and 2,4-D, which are used primarily on barley and wheat, are also applied extensively. Most of the herbicides are applied from late April to mid-June, depending on the crop

Interpretive summary

In the spring of 1994, water samples were collected and analyzed for pesticides in the upper Snake River Basin. The pesticides EPTC (used on beans, potatoes, and sugar beets) and atrazine (used primarily on corn) were the most commonly detected pesticides. Fifteen other pesticides were detected at least once. All of the pesticides found were at very low concentrations and for those with established water quality criteria, all concentrations were well below criteria. A relation between the amount of pesticide used in a watershed and the amount found in streams was determined for EPTC and atrazine.

Key words: Atrazine, desethlyatrazine, EPTC, GIS, Idaho, pesticides, Snake River, surface water.

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J. Soil and Water Cons. 52(5) 381-388

Reprinted from the *Journal of Soil and Water Conservation*
September-October 1997, Volume 52 Number 5

and the targeted pest. For instance, EPTC and triallate are incorporated into the soil prior to planting. Other herbicides and most insecticides are applied later in the growing season to control weeds and insects during and after crop emergence. A study done during one growing season on Rock Creek in southern Idaho showed that the number of pesticides detected in surface water was greatest between mid-May and mid-June (Clark 1994b). However, the study also indicated that the period of maximum concentration for individual pesticides varied depending on the physical properties of the pesticide and how they were applied.

Methods

Thirty-one sites were selected for pesticide sampling during May and June 1994 (Figure 1). Sites were selected to represent drainage from subbasins both affected and unaffected by irrigated agriculture. Subbasin characteristics for each of the sites are listed in Table 2.

The geographic information system (GIS) computer software package ARC INFO was used to develop maps of the drainage boundaries for the 31 subbasins and combine them with land- and pesticide-use information to determine subbasin characteristics. Boundaries and total area for each of the 31 subbasins were digitized from a 1:500,000-scale hydrographic map. The amount of agricultural land in each subbasin was determined by overlaying the boundaries for each of the 31 subbasins on a map of land use derived from remotely sensed data (U.S. Geological Survey 1986).

Pesticide applications. Annual pesticide applications in each of the 31 subbasins were estimated using county-level pesticide-use data (Gianessi and Puffer 1991, 1992) in combination with GIS maps of county boundaries, land use, and subbasin boundaries. County-level use estimates are based primarily on a survey by U.S. Department of Agriculture Extension Service weed scientists, and on other published surveys by State and Federal agencies. The estimates reflect pesticide use during 1989-91. Because the pesticide use data are tabulated by county, ARC INFO was used to determine pesticide usage in each subbasin. First, the land-use map was overlaid onto the county boundary map to create a county-level land-use map. The amount of agricultural land in each county in the USNK then was determined from the county-level land-use map. Next, the percentage of agricultural land in each county that was part of a subbasin was determined by overlaying the county-level land-use map onto each of the subbasin boundary maps. The percentages then were multiplied by the amount of pesticide applied for each county in a subbasin and summed to compute the total quantity of pesticide applied in each of the 31 subbasins.

Table 1. Estimated total annual applications of pesticides used in the largest quantity in the upper Snake River Basin

[Estimates are from Gianessi and Puffer (1991, 1992) and are based on average application rates (metric tons of active ingredient) by crop cover in each county in the upper Snake River Basin during 1989-91. The first 16 pesticides are those used in the largest quantity in the upper Snake River Basin. Atrazine is the 31st most applied. t/yr, metric tons per year]

Pesticide	Quantity applied (t/yr)	Type of pesticide	Primary crop
EPTC	370	Herbicide	Dry beans, potatoes, sugar beets
Triallate	300	Herbicide	Barley, wheat
2,4-D	260	Herbicide	Pasture, barley, wheat
Phorate	240	Insecticide	Dry beans, potatoes
Ethoprop	120	Insecticide	Potatoes
Disulfoton	120	Insecticide	Barley, dry beans, potatoes
Terbutryn*	100	Herbicide	Sorghum
Dicamba	100	Herbicide	Wheat
Cycloate*	86	Herbicide	Sugar beets
Chlorpyrifos	86	Insecticide	Alfalfa, sugar beets
Metribuzin	83	Herbicide	Alfalfa, potatoes
Alachlor	81	Herbicide	Dry beans, corn
MCPA	81	Herbicide	Barley, wheat
Bromoxynil	63	Herbicide	Barley, alfalfa, wheat
Fonofos	46	Insecticide	Dry beans, sugar beets
Metolachlor	39	Herbicide	Corn, dry beans, potatoes
Atrazine	10	Herbicide	Corn

*Not analyzed

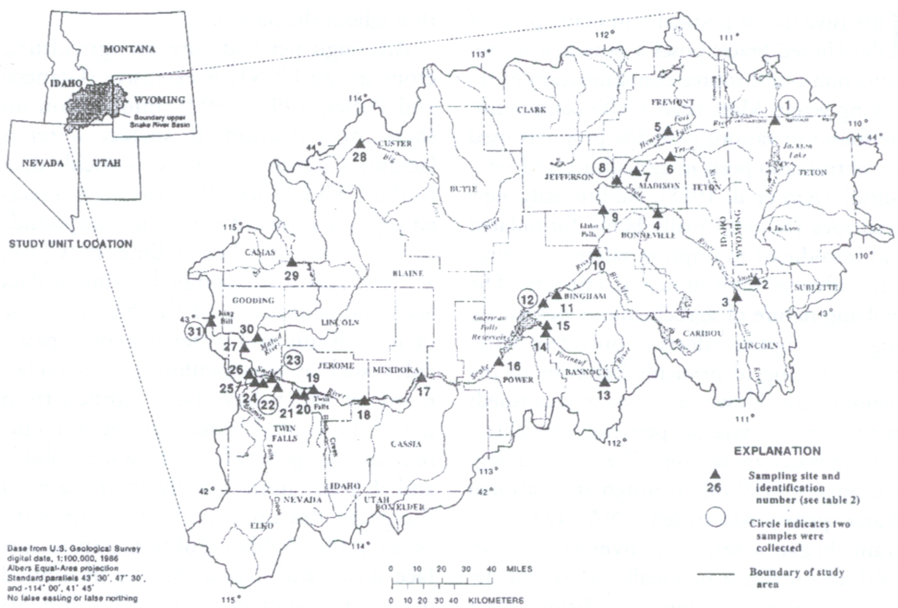

Figure 1. The upper Snake River Basin and locations of sampling sites

Sample collection and analytical techniques. Thirty-seven water samples were collected at the 31 sampling sites during two 1-week periods to span the period of maximum pesticide use. Water samples from sites upstream from American Falls Reservoir (upper basin) (Figure 1) were collected during May 23 to 26, 1994, and water samples from sites downstream from the reservoir (lower basin) were collected during June 13 to 17, 1994. Water samples from six sites (three upstream and three downstream from the reservoir) were collected during both weeks to assess the variability between the collection periods.

Standardized equipment and procedures employed by the USGS were used

Table 2. Physical and agricultural characteristics of subbasins in the upper Snake River Basin where pesticide samples were collected

[Sampling site number refers to Figure 1; crop and pesticide-use information is based on data from Gianessi and Puffer (1991, 1992); km2, square kilometers; sites are in Idaho unless otherwise indicated; Wyo., Wyoming; <, less than; ---, crops not grown in subbasin; brly, barley; alf, alfalfa, pots, potatoes; wht, wheat; bns, dry beans; Dic, Dicamba; Pic, Picloram; Trial, Triallate; Phor, Phorate; Terb, Terbutryn; Brom, Bromacil; Alac, Alachlor; Chlor, Chlorpyrifos]

Sampling site number and name	Subbasin area (km2)	Percent of - sub basin classified as agriculture	Primary crops produced in subbasin	Pesticides used in the largest quantity
1 Snake River at Flagg Ranch, Wyo.	1,320	< 1	----	----
2 Snake River near Alpine, Wyo.	8,500	2	brly, alf	2,4-D, Dic, Pic
3 Salt River near Etna, Wyo.	2,210	18	brly, alf	2,4-D, Dic, Pic
4 Snake River near Heise	14,400	6	brly, alf	2,4-D, Dic, Pic
5 Henrys Fork near Ashton	2,930	7	pots, brly, wht	Trial, EPTC, Phor
6 Teton River near St. Anthony	2,300	42	brly, pots, wht	Trial, EPTC, Phor
7 South Fk. Teton River at Rexburg	2,750	47	brly, pots, wht	Trial, EPTC, Phor
8 Henrys Fork near Rexburg	8,340	27	brly, pots, wht	Trial, EPTC, Phor
9 Snake River near Idaho Falls	24,700	16	brly, pots, wht	Trial, EPTC, Phor
10 Snake River near Shelley	27,500	19	brly, pots, wht	Trial, EPTC, Phor
11 Blackfoot River near Blackfoot	2,850	13	brly, wht, pots	Trial, 2,4-D, Terb
12 Snake River near Blackfoot	31,100	20	brly, pots, wht	Trial, EPTC, Phor
13 Portneuf River at Topaz	1,520	35	brly, wht, pots	Trial, 2,4-D, Brom
14 Portneuf River near Tyhee	3,440	37	brly, wht, pots	Trial, 2,4-D, Terb
15 Ross Fork near Fort Hall	585	42	brly, pots, wht	Trial, Phor, EPTC
16 Snake River at Neeley	41,200	23	brly, pots, wht	Trial, EPTC, Phor
17 Snake River near Minidoka	48,400	23	brly, pots, wht	Trial, EPTC, Phor
18 Snake River at Milner	57,500	23	brly, pots, wht	Trial, EPTC, Phor
19 Snake River near Kimberly	58,500	24	brly, pots, wht	Trial, EPTC, Phor
20 Perrine Coulee near Twin Falls	40.1	90	bns, alf, pots	EPTC, Alac, 2,4-D
21 Rock Creek near Twin Falls	624	24	bns, alf, pots	EPTC, Alac, Trial
22 Cedar Draw near Filer	218	76	bns, alf, pots	EPTC, Alac, Trial
23 Snake River near Buhl	75,600	22	brly, pots, wht	EPTC, Trial, Phor
24 Mud Creek near Buhl	90.1	97	bns, alf, pots	EPTC, Alac, Trial
25 Deep Creek near Buhl	316	53	bns, alf, pots	EPTC, Alac, Trial
26 Salmon Falls Creek near Hagerman	5,410	5	bns, alf, pots	EPTC, Alac, Trial
27 Snake River near Hagerman	82,400	21	brly, pots, wht	EPTC, Trial, Phor
28 Big Lost River near Chilly	1,100	< 1	----	----
29 Camas Creek near Blaine	1,610	26	brly, alf, wht	Trial, Chlor, 2,4-D
30 Malad River near Gooding	8,600	15	brly, pots, alf	Trial, Chlor, EPTC
31 Snake River at King Hill	92,700	21	brly, pots, wht	EPTC, Trial, 2,4-D

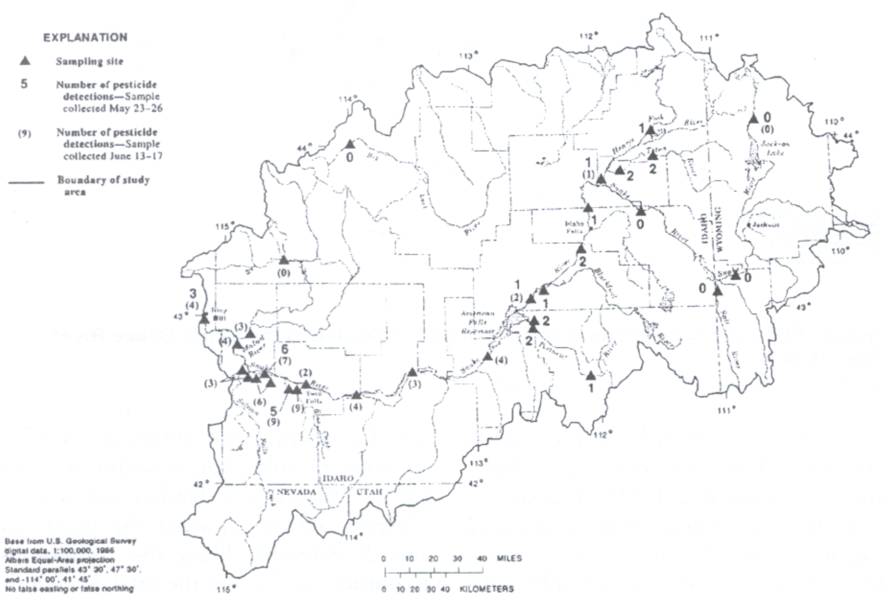

Figure 2. Number of pesticide detections in water samples collected in the upper Snake River Basin, 1994

for sample collection (Shelton 1994). Water samples were collected in three 3-liter Teflon bottles using an equal-width-increment sampling method to ensure collection of a width- and depth-integrated water sample. After collection, sample water in the Teflon bottles was poured sequentially through a Teflon cone splitter into glass sample bottles to produce equal subsamples. Field measurements at each site included discharge, specific conductance, pH, and water temperature.

From the subsamples, approximately 3 to 4 liters were processed for pesticide analysis. Water was filtered through a 0.7-micrometer (1-micron) pore size, baked glass-fiber filter to remove suspended particulates. Known quantities of surrogate compounds then were added to the filtrate, which was pumped through a solid-phase extraction (SPE) cartridge. Because two analytical techniques were used to determine pesticide concentrations, two sets of SPE cartridges were required for retention of pesticides. Both sets were composed of disposable polypropylene; one was packed with 0.5 grams of porous silica coated with a carbon-18 organic phase, and the other was packed with 0.5 grams of a graphitized carbon solid sorbent.

Following extraction, the SPE cartridges were chilled on ice and sent to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado for analysis of 83 pesticides and pesticide metabolites. In the laboratory, pesticides and metabolites retained on the porous silica cartridges were eluted with a small amount of a hexane-isopropanol mixture and analyzed by capillary-column gas chromatography/mass spectrometry (GC/MS) with selected-ion monitoring (Zaugg et al. 1995). The GC/MS analytical method determined concentrations for 47 pesticides and pesticide metabolites from a variety of pesticide classes. The compounds retained on the graphitized carbon cartridges were eluted in a two-step process to separate a base/neutral pesticide fraction from an acidic pesticide fraction. The pesticide concentrations in both fractions were determined using high-performance liquid chromatography (HPLC) with ultraviolet spectroscopy for detection, identification, and quantification (NWQL, written comm. 1995). The HPLC analytical method determined concentrations for 36 pesticides and pesticide metabolites. Concentrations of all but 2 (terbutryn and cycloate) of the 10 most commonly used pesticides were determined by either the GC/MS or HPLC analytical method.

Quality-control (QC) samples were collected to evaluate the quality of the data. Quality-control samples included four field-equipment blanks to document possible contamination during sampling, processing, and analysis; three sets of duplicate or split samples to evaluate the variability in the analytical technique; and two sample-matrix spikes to evaluate potential bias and the ability of the analytical technique to recover analytes from the water-sample matrix.

Table 3. Pesticides detected in water samples collected in May and June 1994 in subbasins of the upper Snake River Basin

[The number of detections are based on 37 samples; method detection limits are from Sandstrom and others (1995) and USGS water-quality lab (written commun.), and are calculated based on procedures from U.S. Environmental Protection Agency (1992a); EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant levels; criteria for human health are based on report by EPA (1992b); criteria for aquatic organisms are based on report by EPA (1991); ng/L, nanograms per liter or parts per trillion; --, criteria not established]

Pesticide	Number of detections	Maximum concentration detected (ng/L)	Method detection limit (ng/L)	EPA water-quality criteria (ng/L): Human health MCL	Aquatic organisms freshwater Acute	Chronic
EPTC	30	310	2	--	--	--
Atrazine	20	38	1	3,000	--	--
Atrazine, deethylated	13	10	2	--	--	--
Metolachlor	7	17	2	--	--	--
Alachlor	6	40	2	2,000	--	--
2,4-D	5	160	35	70,000	--	--
Diazinon	3	3	2	--	--	--
Ethoprop	3	4	3	--	--	--
Metribuzin	2	8	4	--	--	--
Triallate	2	3	1	--	--	--
Trifluralin	2	4	2	--	--	--
Carbofuran	1	55	3	40,000	--	--
Chlorpyrifos	1	10	4	--	83	41
p,p-DDE	1	2	6	--	--	--
Ethalfluralin	1	9	4	--	--	--
Fonofos	1	1	3	--	--	--
Simazine	1	10	5	4,000	--	--
Tebuthiuron	1	55	10	--	--	--

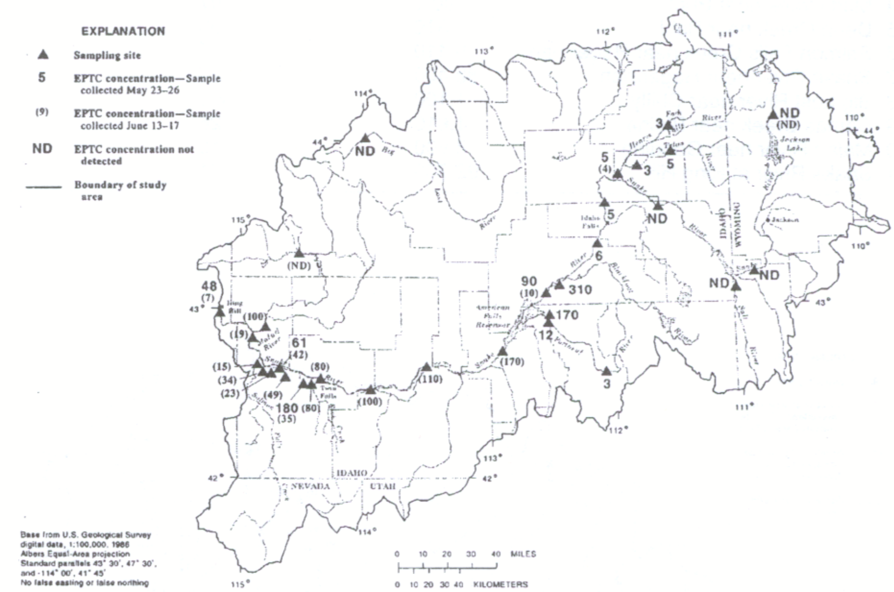

Figure 3. EPTC concentrations in water samples collected in the upper Snake River Basin, 1994.

Note:(All concentrations are in nanograms per liter)

Results and discussion

Pesticide occurrence. Nine of the 16 pesticides most commonly applied in the USNK (Table 1) were detected at least once (Table 3). Thirty of the 37 samples contained at least one detectable pesticide, and 16 of the samples contained three or more (Figure 2). However, all pesticide detections were at concentrations of less than 1 microgram per liter [1,000 nanograms per liter (ng/L)]. For pesticides with established water quality criteria, all concentrations were well below criteria.

Most of the pesticides detected were in samples collected in the lower basin (Figure 2), where 17 pesticides or metabolites were detected at least once. Upper basin detections included EPTC (13 detections), atrazine (3 detections), triallate (2 detections), and diazinon (1 detection). The herbicide triallate was the only pesticide detected in the upper basin and not in the lower basin. No pesticides were detected upstream from site 4, where agriculture constitutes only 6% of the land use. Basinwide, the herbicides EPTC, atrazine, metolachlor, alachlor, and the atrazine metabolite deethylated atrazine (desethylatrazine), were the most frequently detected. These five compounds accounted for 76% of the total detections.

On the basis of estimated total annual application (Table 1), the presence of EPTC throughout a large part of the basin would be expected. EPTC was not

Table 4. Results from quality-control samples collected in the upper Snake River Basin, 1994

[All concentrations are reported in nanograms per liter; relative percent difference calculated as the absolute value of; [(S-D) / ((S+D) / 2)] x 100, where S is the sample concentration and D is the duplicate concentration; lab spike recoveries are based on data from the U.S. Geological Survey National Water Quality Laboratory (written comm. 1995) and represent recoveries from 29 to 31 laboratory spikes in pesticide-free water; nd, not detected; ---, not calculated]

Field-equipment blanks

Date collected	Pesticides detected
May 24	None
May 25	None
June 15	None
June 16	None

Duplicate samples

Date collected	Pesticide detected	Sample concentration	Duplicate concentration	Relative percent difference
May 26	EPTC	310	380	20
June 15	Alachlor	4	nd	---
	Atrazine	13	12	8
	2,4-D	110	100	10
	Desethylatrazine	10	11	10
	EPTC	49	42	15
	Metolachlor	17	16	6
June 15	Atrazine	38	38	0
	Desethylatrazine	22	23	4
	EPTC	34	30	12

Field spikes

Date collected	Pesticide spiked	Actual field spike concentration	Measured field spike concentration	Percent field spike recovery	Percent lab spike recovery and standard deviation
May 24	Atrazine	104	91	88	104 (17)
	Alachlor	104	110	106	122 (16)
	2,4-D	1,033	680	66	64 (20)
	Desethylatrazine	104	32	31	30 (06)
	EPTC	104	105	101	107 (14)
	Metolachlor	104	120	115	133 (19)
June 13	Atrazine	107	107	100	104 (17)
	Alachlor	107	120	112	122 (16)
	2,4-D	1,096	620	57	64 (20)
	Desethylatrazine	107	22	21	30 (06)
	EPTC	107	80	75	107 (14)
	Metolachlor	107	120	112	133 (19)

detected in water samples collected from sites 1 through 4 in the headwater streams of the USNK (Figure 3). Barley and alfalfa are the primary crops produced upstream from site 4, and EPTC normally is not used on these crops. However, in water samples from Henry's Fork and Teton River Basins (sites 5 through 8), where potatoes are a primary crop, EPTC was present in small concentrations. The largest concentration of EPTC in the Snake River was 170 ng/L sampled in June just downstream from American Falls Reservoir at site 16. Concentrations of EPTC in the Snake River decreased from 170 ng/L to 7 ng/L between site 16 and site 31 at the outlet of the USNK.

Atrazine and desethylatrazine were the second and third most frequently detected compounds, respectively. Although atrazine is applied extensively in the midwestern United States on corn, it is not extensively applied in the USNK. Estimated application rates indicate that only about 10 metric tons (11 t) of atrazine are applied annually in the basin, primarily in the lower basin. However, atrazine is highly water soluble 34 parts per million (ppm) at 22°C (71.6 F) (Mills and Thurman 1994), has a low vapor pressure—0.04 millipascales (mpa) at 20°C (68°C) (Taylor and Glotfelty 1988), and can persist in soil and ground water for over 10 months after application (Verschueren 1983). Because of these characteristics, atrazine has a large potential for transport to and subsequently within streams (Larson et al. 1995). Additionally, atrazine is normally applied as a pre-emergent spray to the soil surface and is more easily washed into streams than are soil-incorporated pesticides. Desethylatrazine, which is formed by microbial dealkylation of atrazine, has a water solubility that is two orders of magnitude larger than that of atrazine—3,200 ppm at 22°C (Mills and Thurman 1994)—and is as persistent as the parent compound (Thurman et al. 1991). Clark (1994b) reported that atrazine detected in samples collected from Rock Creek in southern Idaho was derived primarily from ground water and that small concentrations of atrazine and desethylatrazine persisted in Rock Creek well past the end of the irrigation season. Ground water discharge as a source of atrazine and desethylatrazine in streams is supported by ground water data collected in the USNK. Basinwide, 27% of 195 wells sampled during 1994-95 had detectable concentrations of atrazine and desethylatrazine (M.G. Rupert, unpub. data 1996). A more concentrated sampling effort of domestic wells in agricultural lands along the margins of the Snake River found that over 60% of 105 samples contained both compounds (M.G. Rupert, unpub. data 1996). These numbers are similar to those found in the Central Columbia Plateau of eastern Washington where 34 and 31% of 138 public supply wells were found to contain detectable concentrations of atrazine and desethylatrazine, respectively (Ryker and Williamson 1996). Thus, even low-level use of atrazine may result in transport to streams either as direct surface runoff or in ground water discharge.

The relatively small number of detections of triallate (2 detections) and 2,4-D (5 detections) in the stream samples (Table 3) is probably attributable to their chemical characteristics, use patterns, and current cropping patterns. Both compounds are water soluble—triallate, 4 ppm at 25°C (77°F)(Taylor and Glotfelty 1988), and 2,4-D, 890 ppm at 25°C (77°F) (Verschueren 1983); however, use of both compounds in the USNK is limited primarily to grain crops such as barley and wheat. Barley and wheat are primarily dryland crops and, because heavy rainfall is infrequent in the USNK, runoff from dryland crops would not contribute a significant quantity of pesticides to streams. In addition, the annual application rates for triallate and 2,4-D (Table 1) during 1989-91 may overestimate actual 1994 applications. The use of triallate, which is applied primarily to control wild oats, has been reduced in recent years in favor of post-emergent herbicides. Heavy applications of triallate currently occur only in isolated areas of the USNK. One of these areas is the Teton River Basin, where samples from sites 6 and 7 contained the only triallate detected during the study. Hypothetical pasture applications account for almost 60% of the total annual 2,4-D applications shown in Table 1. Although still used on numerous crops in the USNK, 2,4-D is not applied extensively to irrigated pasture. In addition, 2,4-D generally biodegrades rapidly and its half-life typically ranges from less than 1 day to several weeks (Howard 1991).

Of the three most extensively applied insecticides (phorate, ethoprop, and disulfoton), only ethoprop was detected in any of the water samples. Ethoprop was detected at sites 16, 17, and 18, which are on the main stem of the Snake River. However, concentrations of ethoprop did not exceed 4 ng/L. The insecticide diazinon was also detected in three of the water samples, although only about 6 metric tons are used annually.

At four of the six sites sampled during both May and June, greater numbers of pesticides were detected in June (Figure 2). The other two sites had the same number of pesticides detected during both sampling periods. Although the number of pesticides detected in samples was generally greater in June than in May, concentrations of EPTC were larger in the May samples. Of the six sites sampled during both May and June, five had larger EPTC concentrations in May (Figure 3). Used as a pre-emergent herbicide in the USNK, EPTC is applied to most fields in May prior to planting. EPTC concentrations in surface water probably are largest soon after application when early season irrigation transports sediment and chemicals from farmlands to streams. Although EPTC is very water soluble—370 ppm at 25°C (77°F) Taylor and Glotfelty 1988)—compared with most other pesticides, it is also one of the most volatile pesticides—2,800 mPa at 25°C (77°F) (Taylor and Glotfelty 1988)—is rapidly degraded by microbes, and can dissipate entirely from soils and water within 4 weeks of application (Verschueren 1983). Cliath et al (1980) found that 74% of the EPTC applied to alfalfa in irrigation water dissipated within 52 hours of application. Because of its timing of application, physical characteristics, and relative ease of degradation EPTC probably is found in streams only during a short period of time following application.

Quality control. QC samples were used to detect any possible contamination which may have occurred during collection, processing, and analysis; and evaluate the variability and bias of the data generated. No pesticides were detected in the four field-equipment blanks (Table 4). The lack of pesticides in the blanks suggests that there was no significant contamination from sampling, processing, or laboratory procedures.

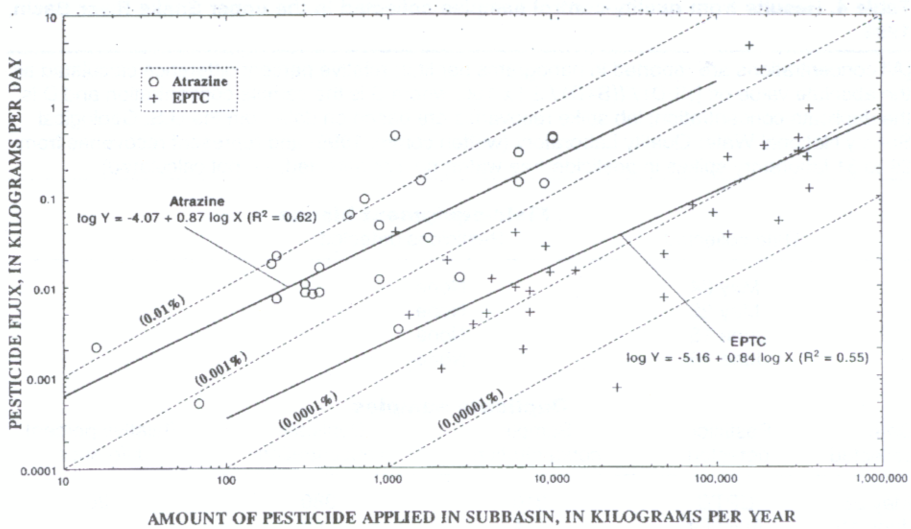

Figure 4. Relations of EPTC and atrazine applications of daily fluxes of EPTC and atrazine in subbasins of the upper Snake River Basin

Note: (Percentage lines represent daily flux as a percentage of the total annual application; regression lines reflect values for censored data as one-half the method detection limit)

Six herbicides were detected in the three duplicate samples (Table 4). In only one of the samples and for only one herbicide (alachlor in the June 15 duplicate) was a compound detected in one of the duplicates and not the other. However, the concentration of alachlor in the duplicate was only 4 ng/L, only slightly larger than the 2 ng/L detection limit for alachlor. The relative difference for the other herbicides detected in both duplicates ranged from 0 to 15%, indicating low analytical variability even at the small concentrations in which the herbicides were found.

Analytical recoveries from field-spiked pesticide samples are useful in determining the bias of analytical results for the actual sample matrices encountered in the study. Recoveries exceeding 100% suggests reported concentrations in water samples could be larger than the actual concentrations. In contrast, recoveries of less than 100% suggests that reported concentrations may underestimate actual concentrations. Pesticide recoveries from field-spiked samples for the six most commonly detected pesticides, in general, are slightly smaller than recoveries from laboratory-spiked samples (Table 4). This is probably because laboratory spikes are prepared in pesticide-free water, whereas field spikes are prepared using an environmental sample matrix. Desethylatrazine recoveries are low for both laboratory and field spikes. Because desethylatrazine is a very polar molecule and very soluble in water, its retention on the SPE cartridge is not complete. Although laboratory-spike

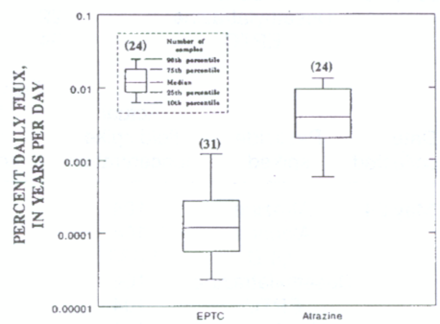

Figure 5. Daily fluxes of EPTC and atrazine as a percentage of total annual applications in subbasins of the upper Snake River Basin

recoveries for desethylatrazine are only 30%, the standard deviation for 31 samples is only 6%, indicating small analytical variability even though recoveries are low.

Application-flux relations. The relations between estimated total annual applications and the daily EPTC and atrazine flux at the time of sampling were assessed for a subset of the 31 subbasins. Other compounds were detected too infrequently for quantitative assessment. A subbasin was excluded from assessment when EPTC or atrazine was not applied in the subbasin and was not detected in the water sample at the subbasin outlet. On this basis, 13 subbasin samples were excluded for atrazine and 6 were excluded for EPTC. Neither EPTC nor atrazine was detected in subbasin samples when the pesticide was not applied in the subbasin. In subbasins where the pesticide was applied but not detected in the water sample (censored data value), a range of

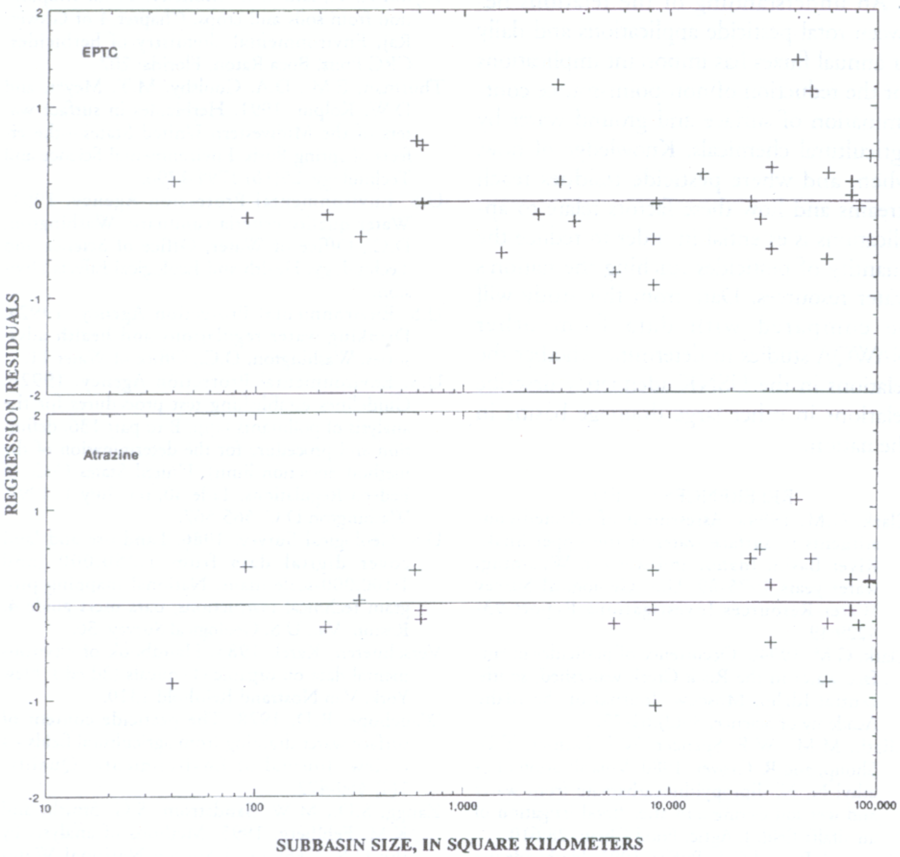

Figure 6. Residuals from regression of daily fluxes and total annual applications for EPTC and atrazine in subbasins of the upper Snake River Basin

values was used to determine how substituting different values less than the method detection limit (mdl) would affect the application-flux relations. Values substituted for censored data included the mdl (Table 3), one-half the mdl, one-tenth the mdl, and random values between the mdl and one-tenth the mdl.

To calculate daily EPTC and atrazine subbasin fluxes, concentrations of EPTC, atrazine, and desethylatrazine in the subbasin samples were assumed to remain constant during the day in which the samples were collected. Concentrations then were corrected on the basis of laboratory-spike recoveries (Table 4). Corrected atrazine and desethylatrazine concentrations were summed to calculate a total corrected atrazine concentration. Because laboratory-spike recoveries are, in general, larger than field-spike recoveries, correcting sample data by laboratory recoveries may slightly underestimate true sample concentrations and, thus, lead to conservative estimates for subbasin fluxes.

Log-log plots of the total annual amounts of EPTC and atrazine applications in relation to the daily flux at the subbasin outlet show a linear correlation for both compounds (Figure 4). Coefficients of determination, which represent the fraction of the variance explained by the regression between annual applications and daily flux, ranged from 0.54 to 0.56 for EPTC and 0.57 to 0.62 for atrazine, depending on which values were used for the censored data. The slope estimates ranged from 0.83 to 0.85 for EPTC and 0.83 to 0.95 for atrazine. The regression slopes of less than 1.0 indicate that daily fluxes of EPTC and atrazine from a subbasin become a smaller percentage of the total applied as application quantities increase. The regression for EPTC also indicates that on the date of sampling, a median daily flux of 0.0001% of the EPTC applied annually in a subbasin was being transported from the subbasin (Figure 5). For atrazine, the median daily flux from a subbasin was between 0.001 and 0.01% of the annual total applied. Because samples were collected only on one day, it is impossible to calculate total seasonal fluxes on the basis of these data. However, because the samples were collected during the maximum-use period for both EPTC and atrazine, these fluxes probably represent near-maximum daily values for the entire year.

The relative differences in the subbasin fluxes between EPTC and atrazine, in general, support findings by Wauchope (1978), who noted that edge-of-field losses were about 10 times less for EPTC than for atrazine in a number of different agricultural settings. Wauchope (1978) estimated that mean seasonal edge-of-field losses for EPTC were less than 0.3% of the annual total applied, whereas for atrazine, the mean losses were 2 to 3%. These values are larger than those found in this study, even if daily fluxes determined during application periods were assumed to remain constant over a 4-month growing season. In large, complex watersheds such as those in this study, seasonal fluxes probably would be a smaller percentage of the total applications than would fluxes measured at the edges of individual fields. This is because of the increased distance that a pesticide is transported in a large watershed, which allows for a longer period of degradation and storage. Larson et al (1995) found that in large (about 30,000 to 3,000,000 km^2; 74,128,983 to 7,412,898,300 acres) subbasins of the Mississippi River, 0.62 to 1.9% of the annually applied atrazine (a relatively stable herbicide) was transported, and that once atrazine reached streams, it was transported with relatively little loss. The investigation also estimated that annual fluxes of EPTC ranged from nondetectable to 0.05% of the annual amount applied, indicating that EPTC had degraded or volatilized prior to reaching the sampling point. However, for the range of subbasin sizes sampled in the USNK (about 40 to 93,000 km^2; 98,838.644 to 229,799,847.3 acres), subbasin size did not appear to be an important factor in the relations between total annual applications and daily fluxes. When plotted against subbasin size, residuals from the regressions for both EPTC and atrazine show a uniform scatter around the zero residual line (Figure 6), indicating that the relations between total annual applications of EPTC and atrazine and daily subbasin fluxes are fairly constant regardless of subbasin size. However, the residual plots in Figure 6 show a wider range of scatter at larger subbasin sizes, suggesting that the relations between total annual applications and daily fluxes may not be as accurate as subbasin size increases.

Because variations in pesticide applications during the year and year-to-year differences in climate, water use, and the types of crops grown can affect pesticide occurrence in surface water, data throughout the growing season and for more than one growing season are necessary to determine whether the results from this study truly represent annual pesticide fluxes.

Several more detailed subbasin studies are needed to determine what percentage of the annual applications of certain pesticides is transported to streams and how basin characteristics such as size, soil type, irrigation patterns, and application techniques affect pesticide transport.

Summary and conclusions

Data from this study indicate that total use, timing of application, and physical characteristics may be important factors in whether, and at what concentration, a pesticide is detected in surface water. Although concentrations of pesticides in surface water of the USNK are low, a number of pesticides are reaching streams in the basin. A total of 18 pesticides were detected during the study, primarily in samples collected downstream of American Falls Reservoir. EPTC, the pesticide applied in the largest quantity in the basin, was detected in 30 samples. EPTC is detected the most frequently because of widespread and heavy application, primarily in May. Although water soluble, EPTC tends to volatilize and break down rapidly in the environment once it is applied to fields. Diminishing concentrations and fluxes of EPTC in subbasins between late May and mid-June support this. Atrazine and its breakdown product, desethylatrazine, were the second and third most frequently detected compounds, respectively. In contrast to EPTC, atrazine is not applied extensively in the basin and its presence is likely to be a result of its high water solubility and slower breakdown rates. Because of these physical characteristics, atrazine and desethylatrazine can be transported to streams in direct surface runoff or in ground water discharge throughout the year.

Use of GIS in conjunction with pesticide application rates and land-use information made it possible to evaluate relations between the quantity of pesticide used in a subbasin and the pesticide flux at the subbasin outlet. Correlations were found between the total annual applications of EPTC and atrazine in the subbasins and their daily fluxes at the subbasin outlets. The 1 to 1.5 order of magnitude difference between the application and flux relations of EPTC and atrazine appears to agree with findings from other studies. Although watershed size may be an important factor in assessing pesticide fluxes from watersheds, subbasin size in this study did not appear to reduce the percentage of the total annual applications of EPTC and atrazine transported from subbasins.

An understanding of the relations between total pesticide applications and daily or annual fluxes has important implications for the reduction of non-point-source contamination of surface and ground water by agricultural chemicals. Knowledge of how, when, and where pesticide residues reach streams and how these factors relate to applications is essential in order to reduce the quantity of pesticides reaching the nation's water resources. Data from this study will be compared with data from other NAWQA studies to determine whether the relations in the USNK adequately describe relations in other large drainage basins in the nation.

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