Brigham, M.E., 1994, Pesticides Detected in Surface Waters and Fish of the Red River of the North Drainage Basin: North Dakota Water Quality Symposium Proceedings, March 30-31, 1994, Fargo, North Dakota, North Dakota State University Extension Service, pp.256-269.

PESTICIDES DETECTED IN SURFACE WATERS AND FISH OF THE RED RIVER OF THE NORTH DRAINAGE BASIN

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INTRODUCTION

The Red River of the North drainage basin (herein referred to as Red River Basin) within the United States is a study unit under the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program. The overall goals of this program, initiated to better define the status and trends of the Nation's water quality, are to address regional and national water-quality issues in a nationally consistent manner. Pesticide contamination of surface water and fish is one focus of this program.

The Red River Basin is about 90,600 square kilometers (km^2) in area and is composed of rolling prairie with a high density of prairie-pothole wetlands to the west; a very flat glacial lake bed with drainage ditches and meandering streams in the center (Red River Valley Lake Plain); morainal hills with a mosaic of agriculture, lakes, and forest in the southeast; and a flat lake-washed till plain with extensive peatlands in the northeast (fig. 1). Stoner and others (1993) have given a more complete description of the environmental setting of the Red River Basin.

Agriculture is a major component of the region's economy, and is greatest in the Red River Valley Lake Plain. Principal crops are wheat, barley, oats, sunflowers, corn, soybeans, dry beans, potatoes, sugarbeets, alfalfa hay, and other hay. Herbicide, insecticide, and fungicide use depends on crop type and environmental stresses such as crop disease, drought, and periodic insect-pest infestation. This paper focuses on the occurrence, movement, and fate of agricultural pesticides that are applied to crops, but improper disposal, and use of pesticides for household pests, lawn care, golf courses, and home gardening can also result in contamination of the aquatic environment. Furthermore, atmospheric transport is known to transport pesticides to regions far from their source (Kurtz, 1990).

Pesticide data have been collected in the Red River Basin by various Federal, State, and local agencies. Tornes and Brigham (1994) recently summarized many of these historical data. This paper summarizes selected data collected as part of the NAWQA program during 1992-93, and briefly compares these data to historical data and to pesticide usage.

MATERIALS AND METHODS

Site selection. Stream water-quality sampling sites were chosen to represent either (1) relatively homogeneous settings that have a characteristic mixture of land uses and landscape features, or (2) larger areas that integrate several smaller, relatively homogeneous settings. Fish were sampled in the summer of 1992 at sites distributed throughout the study area on streams draining single physiographic areas, and on the Red River. Figure 1 shows physiographic areas of the Red River Basin and site locations for this study. Table 1 lists sampling sites and, for surface-water sites, lists important crops. A large amount of water quality data, especially historical data from Environment Canada and the U.S. Fish and Wildlife Service (USFWS) are available for a reach of the Red River near the United States-Canada border, including sites at Emerson, Manitoba, and Noyes, Minnesota. This river reach serves as an integrator of net water and chemical loadings from most of the U.S. portion of the Red River Basin, with the exception of the Roseau River. This reach also includes the Pembina River drainage basin, which begins in Canada.

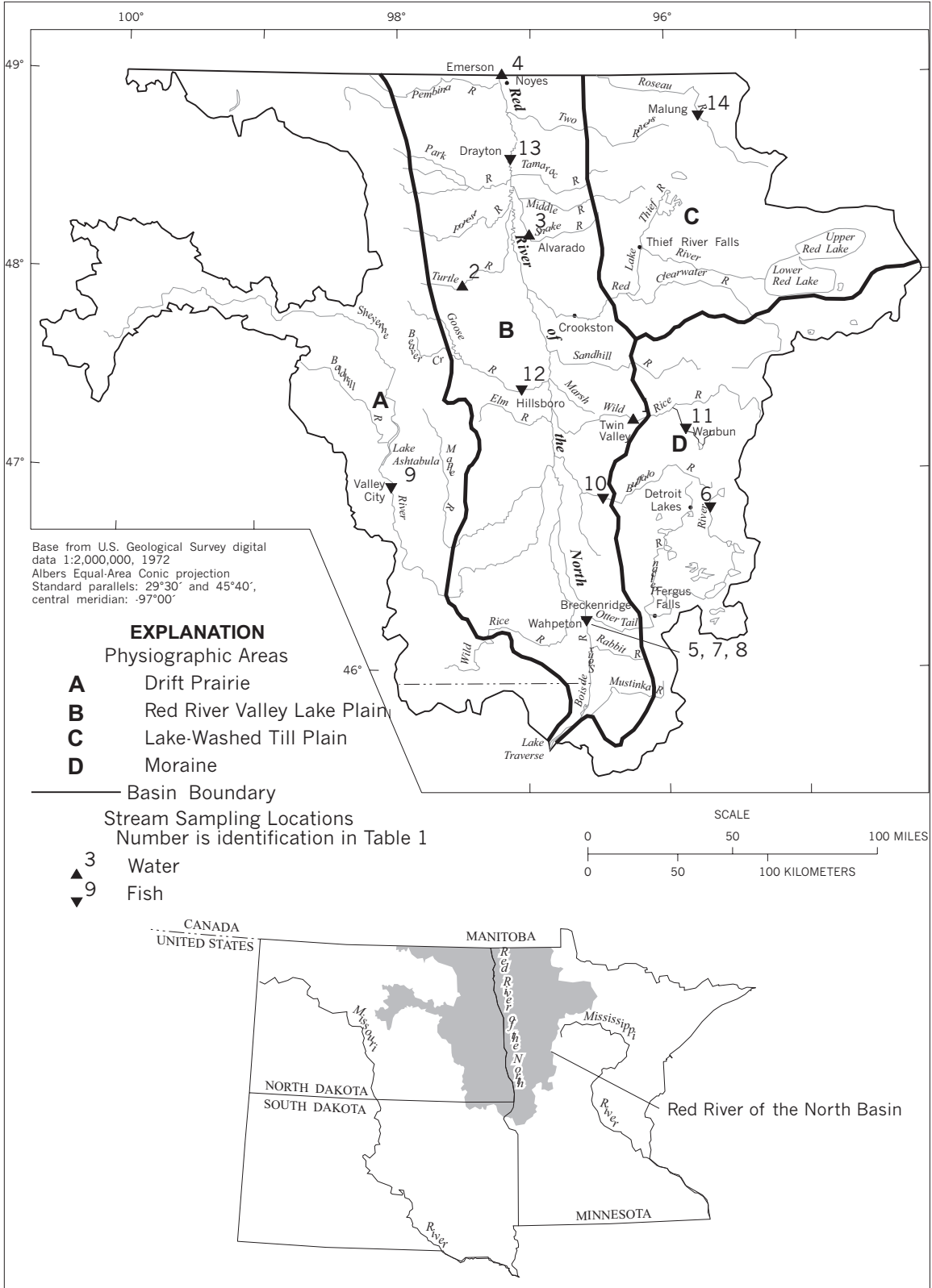


Figure 1.--Physiographic areas (modified from Maclay and others, 1972, and Winter and others, 1984) and location of sampling sites.

Sampling methods. Water samples were collected by lowering into the stream an enamel-painted, brass D-77 (or DH-81) sampler fitted with a 3 liter (L) Teflon[1] FEP (fluorinated ethylene propylene) bottle and nylon nozzle for isokinetic sampling of flow (Ward and Harr, 1990). Several vertical samples, collected from stream surface to stream bed, were collected at a stream cross section from a highway bridge. The composited vertical samples were poured from the Teflon bottle through a Teflon PTFE (polytetrafluoroethylene) decaport cone splitter (Geotech Environmental Equipment) fitted with Teflon FEP tubing, and into sample containers. For pesticide samples, 1 L amber glass bottles with Teflon-lined lids were used. At each pesticide sampling, samples also were collected for analysis of nitrogen and phosphorus nutrients, major ions, suspended sediment, and dissolved and suspended organic carbon. Stream temperature, pH, dissolved oxygen, specific conductance, and alkalinity were determined in the field.

Table 1. Stream sites sampled for pesticides, listed in downstream order.

Map site identifier (figure 1)	Site name	Percent of drainage basin that is cropland[a]	Major crops
Water sampling sites			
1	Wild Rice River near Twin Valley, Minn.	50	wheat, barley, sunflower, edible bean, soybean
2	Turtle River at Turtle River State Park, N. Dak.	79	wheat, sunflower, edible bean, soy bean, barley
3	Snake River near Alvarado, Minn.	85	wheat, barley, sunflower, sugar beet, edible bean
4	Red River at Emerson, Manitoba	80	wheat, barley, hay, soybean, sunflower, corn
Fish sampling sites			
5	Bois de Sioux River near Wahpeton, N. Dak.		
6	Otter Tail River at County Rd. 29, Minn.		
7	Otter Tail River at Breckenridge, Minn.		
8	Red River at Wahpeton, N. Dak.		
9	Sheyenne River at Valley City, N. Dak.		
10	Buffalo River at Buffalo River State Park, Minn.		
11	White Earth River near Waubun, Minn.		
12	Goose River at Hillsboro, N. Dak.		
13	Red River at Drayton, N. Dak.		
14	South Branch Roseau River near Malung, Minn.		

[a] Percent cropland based on 1:250,000-scale land use and land cover map. Data available from the U.S. Geological Survey.

Carp (*Cyprinus carpio*), creek chub (*Somotilis atromaculatus*), and white sucker (*Catostomus commersoni*) were collected with the use of a fish shocker and dip nets. For organic chemical analyses, 6 to 10 fish of the same species and similar size class were composited as one sample, and processed according to methods described in Crawford and Luoma (1993).

During all phases of pesticide sampling, sample contamination was minimized by cleaning equipment that contacts the sample (before initial use and between samples) with dilute detergent (Liquinox) in tap water followed by a tap water rinse, deionized water rinse, and methanol rinse (EM Science, HPLC (high performance liquid chromatography) grade). The 1 L amber glass bottles (for water samples) were obtained from the USGS National Water Quality Laboratory (herein referred to as the laboratory) in Arvada, Colo., and were baked at 450°C prior to use. These were often reused, and were cleaned as described above prior to reuse. Field personnel

[1] Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

wore clean, disposable, latex gloves while handling sampling equipment, and care was taken to avoid touching surfaces that contact the sample. Quality-control samples were collected to provide data to assess sample contamination, method reproducibility, accuracy, matrix effects, and recovery.

Analytical methods. The method for water analyses is summarized as follows: Water samples are filtered through baked 0.45 micrometer glass-fiber filters into two-1 L glass bottles and are analyzed by two separate methods. The first method involves addition of 100 µL (microliters) of a chemical surrogate solution (terbuthylazine; α-hexachlorocyclohexane (α-HCH), d6 (hexadeuterated); and diazinon, d10 (decadeuterated)); each at a concentration of 100 µg/L (micrograms per liter) in methanol. Surrogates are used to assess method performance (analyte recovery) for each analysis. Next, methanol (one percent v/v) is added, and the sample is pumped through a methanol-and-water conditioned solid-phase extraction (SPE) cartridge that contains octadecyl (C-18) bonded silica. Analytes are eluted from the solid phase with 3 mL hexane:isopropanol (3:1) solution. The solvent is evaporated with nitrogen to a final volume of 100 µL, and the extracts are analyzed by capillary-column gas chromatography with mass-spectrometric detection in the selected-ion monitoring mode (Hewlett-Packard 5971). The filtration, SPE cartridge conditioning, surrogate addition, and extraction procedure can be performed either in the field or in the laboratory. For this study, about half of the extractions for this method (referred to herein as the C-18 SPE method) were performed in the field, and the rest in the laboratory. Spiked quality-control samples were fortified with 100 µL of a solution containing 0.1 micrograms of each analyte per 100 µL.

The second analytical method, which uses an activated-carbon (AC) SPE cartridge, is used to extract pesticides that are poorly quantified by the C-18 SPE method. Pesticides analyzed using this method include chlorophenoxy acid herbicides, carbamates, and other compounds. Data from this method are not presented herein.

A brief description of the analytical strategy for fish tissues has been reported by Crawford and Luoma (1993). Each sample was spiked in the laboratory with a chemical surrogate (3,5-dichlorobiphenyl) to assess method performance. Also, within each set of sample analyses, one subsample is spiked with all compounds on the analytical schedule.

Data analysis. Historical water-quality data were obtained from Environment Canada's ENVIRODAT/ NAQUADAT data base. Historical fish-tissue data were obtained from the USFWS National Contaminant Biomonitoring Program (NCBP) (Schmitt and others, 1983; Schmitt and others, 1990; and S.L. Smith, U.S. Fish and Wildlife Service, written commun., 1992). The historical data and the USGS data (this study) were transferred to SAS (SAS Institute) data sets for statistical and graphical analysis. All groups of data described as having significantly different concentrations were analyzed with the Wilcoxon rank-sum test, and have a significance level of 0.01 or less ($p \leq 0.01$). For these tests, the value of the method detection limit was used for values reported as less than the method detection limit.

RESULTS AND DISCUSSION

Pesticides in surface water. A total of 114 surface-water (82 from stream sites discussed herein) and quality-control samples were analyzed by the C-18 SPE method. Performance of the C-18 SPE method was assessed by examining data for chemical surrogates and spiked samples. Mean recoveries of each analyte, including surrogates, should ideally be 100 percent; mean recoveries substantially different from 100 percent may indicate inaccurate spike (or surrogate) solution concentrations, degradation, extraction efficiencies less than 100 percent, sample contamination, or analytical interference. The surrogate recovery data (table 2) show that mean recoveries for each compound are fairly close to 100 percent, and standard deviations are equal to about 10 percent of the mean.

Table 2. Surrogate recovery data for dissolved pesticide analyses.

Surrogate compound	Number of samples	Mean percent recovery	Standard deviation
Diazinon, d10[a]	112	96	10
Terbuthylazine	114	110	13
α-HCH, d6[b]	114	91	8.7

[a] d10 Diazinon is the decadeuterated synthetic analog of diazonon.
[b] d6 α-HCH is the hexadeuterated synthetic analog of α-hexachlorocyclohexane.

Table 3 lists analytes, method detection limits, summary data for 82 stream samples, and recovery data for three spiked samples. Analyte recoveries for spiked solutions were computed by adjusting for ambient concentrations in paired, unspiked samples. Spike-recovery data indicate that the method performs well for most analytes. For unknown reasons, azinphos-methyl, carbaryl, and terbacil had mean recoveries greatly exceeding 100 percent, and *cis*-permethrin had a low mean recovery of 13 percent. Desethyl atrazine had a low (mean=27 percent), but fairly reproducible recovery. This compound is more hydrophilic than its parent compound (atrazine), and should, therefore, sorb less efficiently to the C-18 phase.

Atrazine was the most frequently detected pesticide during the period of study (table 3). It was detected in all 18 samples from the Red River at Emerson. This site had significantly higher atrazine concentrations than the other surface-water monitoring sites in this study (fig. 2A). The maximum measured atrazine concentration, 0.37 µg/L, was measured in a sample from the Wild Rice River at Twin Valley, and is less than the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) of 3.0 µg/L. The Wild Rice River and Snake River sites each had significantly higher concentrations than the Turtle River site. Since atrazine is used primarily on corn crops, areas of greater corn production could be expected to have higher atrazine concentrations in streams. The Red River at Emerson, which drains the entire study area, drains an area of greater corn-production density than any of the other sites. All sites except the Turtle River site had maximum atrazine concentrations in July. The highest concentration at the Turtle River site was 0.08 µg/L, and was measured in late March during spring runoff.

Metolachlor also was detected in all 18 samples from the Red River at Emerson, but in only 54 percent of samples from the other three sites. The Red River at Emerson had significantly higher metolachlor concentrations than the other sites (fig. 2B). The maximum metolachlor concentration was measured in a July 15 sample from the Red River at Emerson.

Triallate was the third most frequently detected pesticide for all study sites. The Red River at Emerson, Wild Rice River, and Snake River sites each had significantly higher concentrations than the Turtle River site (fig. 2C).

Cyanazine was detected in 17 of 18 (94 percent) samples from the Red River at Emerson, with a peak concentration of 0.15 µg/L measured on July 15, the same date as the maximum atrazine and metolachlor concentrations for that site. Cyanazine was detected in only 25 percent of the samples from the other three sites, and cyanazine concentrations were significantly higher at the Red River at Emerson than the other sites (fig. 2D). Trifluralin was detected in 11 of 20 samples from the Wild Rice River; prometon and alachlor also were detected relatively frequently (in 14 and 12 of 18 samples, respectively) at the Red River at Emerson. The other pesticides (table 3) were detected in fewer than 50 percent of samples from any given site.

Pesticide concentrations in surface waters are affected by seasonal application and seasonal hydrologic events. The maximum atrazine concentration at the Red River at Emerson was measured in mid-July during a period of runoff (fig. 3A). Following heavy rains and flooding in many parts of the drainage basin, high flows (more than 500 cubic meters per second) ensued at the Red River at Emerson site in late July and continued through most of August. Atrazine concentrations decreased during this high-flow period. A similar pattern was observed for metolachlor (fig. 3B), as well as cyanazine and prometon concentrations (not shown).

Table 3. Pesticides analyzed in stream-water samples for this study.

Stream-sample data				Spiked-sample data	
	Concentration, in µg/L		Percent greater than method detection limit	Mean percent recovery	Standard deviation
Pesticide	Minimum[a]	Maximum			
Atrazine	[c]< 0.004	0.37	91	99	4.0
Metolachlor	< 0.002	0.17	67	134	10
Triallate	< 0.003	0.28	67	96	1.0
Cyanazine	< 0.01	0.15	43	111	18
Trifluralin	< 0.005	0.018	38	64	1.6
EPTC	< 0.002	0.047	35	77	5.9
Prometon	< 0.004	0.037	33	92	6.5
Alachlor	< 0.003	0.11	26	123	1.3
Carbofuran	< 0.005	0.21	18	120	18
Dacthal (DCPA)	< 0.002	0.005	9.8	117	5.4
Metribuzin	< 0.004	0.017	9.8	91	9.0
Simazine	< 0.01	0.015	9.8	83	1.9
p,p'-DDE	< 0.002	0.020	7.3	56	7.0
Propanil	< 0.003	0.016	4.9	89	5.5
Tebuthiuron	< 0.005	0.056	4.9	75	18
Desethyl atrazine	< 0.02	0.025	3.7	27	4.1
Chlorpyrifos	< 0.002	0.031	2.4	93	5.5
Malathion	< 0.003	0.014	2.4	99	10
Propachlor	< 0.001	0.015	2.4	91	7.4
Diazinon	< 0.004	0.008	1.2	96	1.0
Ethalfluralin	< 0.005	0.015	1.2	82	2.3
γ-HCH[b]	< 0.008	0.011	1.2	85	1.5
Molinate	< 0.005	0.019	1.2	73	11
Terbacil	< 0.005	0.030	1.2	143	13
Azinphos-methyl	< 0.01	--[d]	0	225	35
Benfluralin	< 0.007	--	0	60	1.6
Butylate	< 0.002	--	0	85	10
Carbaryl	< 0.008	--	0	169	3.4
Dieldrin	< 0.02	--	0	93	5.0
Diethylanaline	< 0.002	--	0	77	3.6
Dimethoate	< 0.02	--	0	--	--
Disulfoton	< 0.02	--	0	61	24
Ethoprop	< 0.005	--	0	87	7.7
Fonofos	< 0.005	--	0	96	8.1
α-HCH[b]	< 0.007	--	0	79	2.4
Linuron	< 0.01	--	0	93	5.0
Methyl parathion	< 0.01	--	0	96	8.1
Napropamide	< 0.002	--	0	105	8.0
Parathion	< 0.008	--	0	131	7.9
Pebulate	< 0.009	--	0	80	6.8
Pendimethalin	< 0.01	--	0	62	2.2
cis-permethrin	< 0.01	--	0	13	2.8
Phorate	< 0.02	--	0	62	23
Pronamide	< 0.009	--	0	86	0.71
Propargite	< 0.01	--	0	123	15
Terbufos	< 0.01	--	0	93	26
Thiobencarb	< 0.008	--	0	93	5.0

[a] Minimum concentration in all cases were less than method detection limit, which is the value listed in this column.
[b] HCH = hexachlorocyclohexane. α-HCH and γ-HCH are components of technical lindane.
[c] < = less than. [d] -- = no data above method deteciton limit.

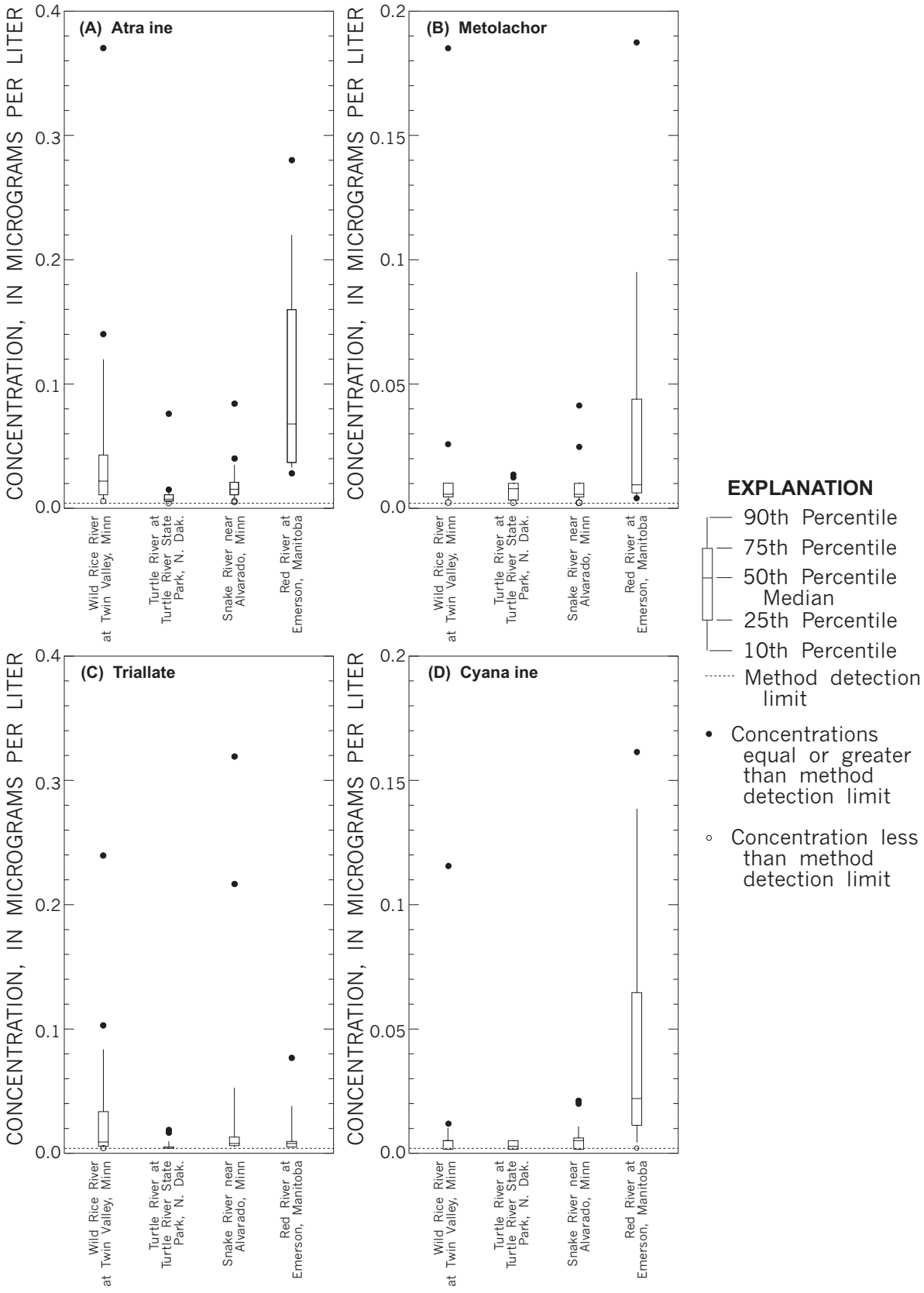


Figure 2.--Comparison of stream ater concentrations of (A) atra ine, (B) metolachor, (C) triallate, and (D) cyana ine.

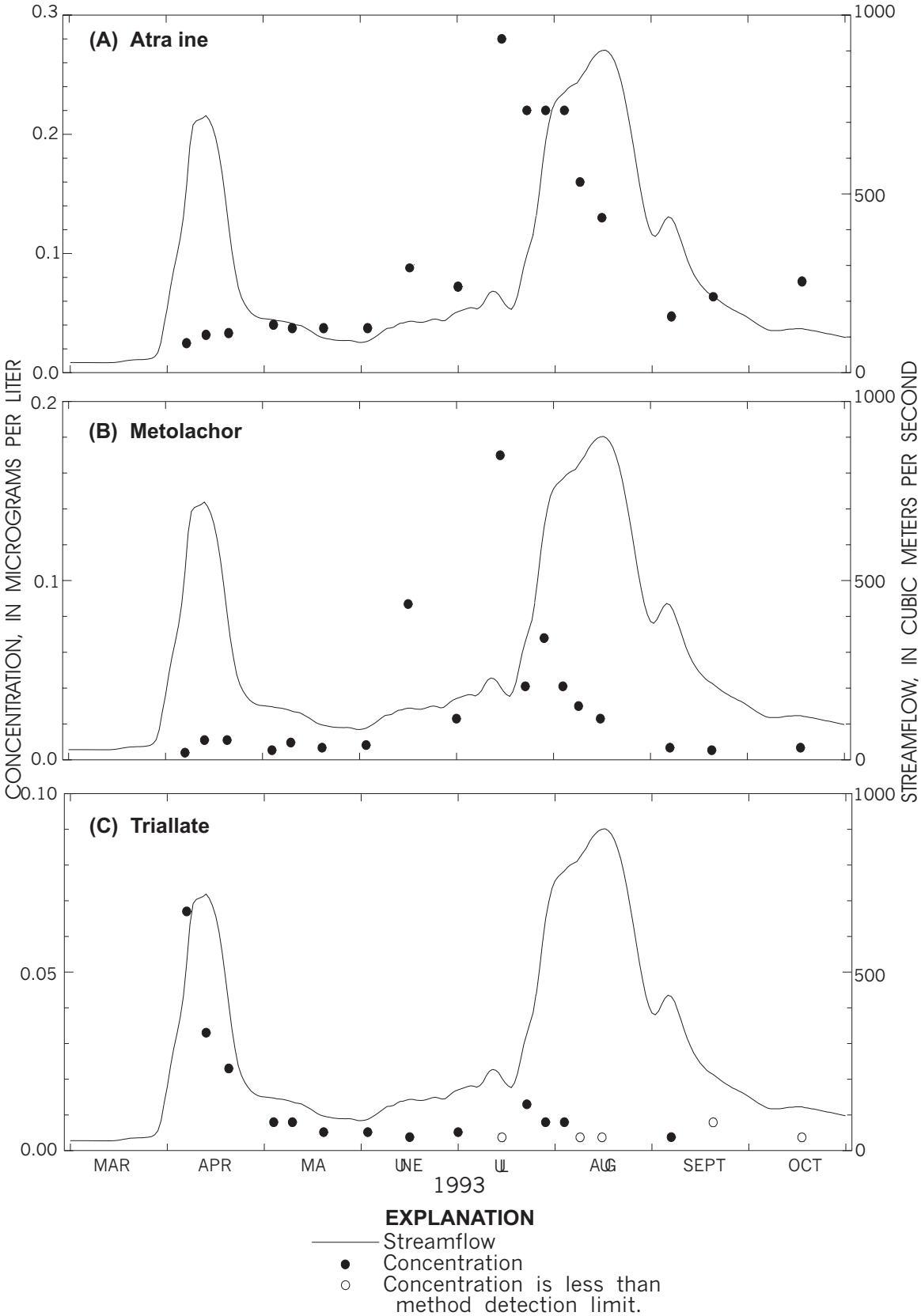


Figure .--Concentration and mean daily streamflo ersus sample date, ed i er at Emerson, Manito a for (A) atra ine, (B) metolachlor, and (C) triallate.

This pattern of peaks in midsummer atrazine concentrations concomitant with periods of runoff was also present at the Wild Rice River site (not shown). Here also, decreasing atrazine concentrations accompanied heavy rains and high water later in the summer (late July through early August).

Triallate exhibits a different relation to season and stream flow. At the Red River at Emerson site (fig. 3C), as well as the Wild Rice River and Snake River sites (not shown), the highest measured triallate concentrations were in the first samples collected in the spring (late March or early April), and are coincident with high stream flows associated with spring runoff. Following this peak, triallate concentrations remain low through the summer and into autumn. The differences in the timing of peak concentrations are most likely related to timing of pesticide application. Atrazine, metolachlor, and cyanazine are applied during the summer, whereas triallate (a pre-emergent herbicide) is applied in late fall and early spring.

At the Red River at Emerson, Manitoba, maximum atrazine and metolachlor loads were associated with the high streamflows of late July-early August. Atrazine load reached a maximum of 1.5 kilograms per day (kg/d) on August 4, and exceeded 1.0 kg/d for samples collected from July 29 to August 16. Metolachlor load reached a maximum of 0.38 kg/d on July 29, and decreased throughout the remainder of the high-flow period.

To estimate annual atrazine and metolachlor loads at the Red River at Emerson, Manitoba, I interpolated concentrations between sample dates and extrapolated (using the lowest measured concentration of each pesticide) concentrations for the remainder of [2]1993. Summing the product of concentration and mean daily streamflow yields annual (1993) loads of 0.60 megagrams (Mg, or metric tons) for atrazine and 0.16 Mg for metolachlor. In July and August, 45 percent of the annual streamflow was transported, while 77 percent of the annual atrazine and metolachlor loads were carried past this site.

From available agricultural statistics (McMullen and others, 1990; J.W. Hines, Minnesota Department of Agriculture, written commun.; Gianessi and Puffer, 1988; Gianessi and Puffer, 1990), I estimated annual atrazine usage in the Red River Basin to be 35 to 70 Mg. Based on the annual load estimate for the Red River at Emerson, approximately 0.8 to 1.7 percent of the applied atrazine was transported from the basin. This range is similar to reports by others for drainage basins in the midwestern United States (Squillace and Thurman, 1992; Schottler and others, 1991).

Environment Canada has collected a large amount of water-quality (including pesticide) data from the Red River at Emerson, Manitoba (V.T. Chacko, and T.H. Ronmark, written commun., 1990, Environment Canada's ENVIRODAT/NAQUADAT data base; summarized in Tornes and Brigham, 1994). Comparisons between the Environment Canada data and data from this study are somewhat confounded by use of different methods and detection limits. The pesticide α-HCH, the most frequently detected pesticide by Environment Canada at the Red River at Emerson (128 of 163 samples had concentrations at or above the 0.001 µg/L reporting limit), was not detected in any samples from this study (detection limit 0.007 to 0.010 µg/L). Since 1985, α-HCH concentrations have been below 0.005 µg/L in all Environment Canada samples from the Red River at Emerson; thus it is unlikely that the method used in this study, with a higher detection limit, would have detected α-HCH residues. The pesticide γ-HCH was detected in 83 of 171 Environment Canada samples from the Red River at Emerson, but was not detected in the Red River at Emerson, and was detected in only one of 82 stream samples during this study. The herbicide 2,4-D was detected frequently by Environment Canada at the Red River at Emerson, but was not quantified by the C-18 SPE method[3]. Atrazine was detected frequently by Environment Canada. Twenty-five of 64 samples (39 percent) had concentrations greater than the reporting limit, which was lowered from 0.10 to 0.05 in 1988. In this study, atrazine was detected even more frequently: all Red River at Emerson samples had detectable levels, and 90 percent of samples

[2] Substituting zero for the extrapolated values results in annual loads that are about five percent smaller.

[3] 2,4-D was measured by the activated carbon SPE method; a complete set of these data were not available for analysis at the time of this writing.

from the other stream sites had detectable levels. The lower detection limit in this study (0.004 µg/L) was likely the main reason for the higher incidence of atrazine detection.

Pesticides in fish tissue. Six carp, six white sucker, and one creek chub composite fish samples were analyzed for organochlorines, mainly chlorinated pesticides. Results of the fish tissue analyses are given in table 4. The mean surrogate (3,5-dichlorobiphenyl) recovery was 66 percent (standard deviation = 18 percent). Mean percent recoveries for most compounds were between 46 and 83 percent. Dacthal had a consistently low recovery, averaging 18 percent. Recoveries for *o,p'*-DDE were fairly consistent in three spiked samples (mean = 83 percent), but was 260 percent in one spiked sample. The spike-recovery data indicate that the method was performing fairly well for most analytes.

Table 4. Pesticides analyzed in fish-tissue samples for this study.

	Fish-sample data			Spiked-sample data[a]	
	Reported concentration, in micrograms per kilogram		Percentage greater than method detection limit[b]	Mean percent recovery	Standard deviation
Pesticide	Minimum[c]	Maximum			
p,p'-DDE	[d]< 5.0	71	75	69	26
p,p'-DDD	< 5.0	25	25	46	30
cis-chlordane	< 5.0	36	8.3	58	20
trans-chlordane	< 5.0	23	8.3	53	20
o,p'-DDD	< 5.0	5.0	8.3	64	25
trans-nonachlor	< 5.0	27	8.3	62	25
Aldrin	< 5.0	--[e]	0	64	23
Dacthal (DCPA)	< 5.0	--	0	18	6
o,p'-DDE	< 5.0	--	0	127	89
o,p'-DDT	< 5.0	--	0	65	29
p,p'-DDT	< 5.0	--	0	54	23
Dieldrin	< 5.0	--	0	46	20
Endrin	< 5.0	--	0	65	28
α-HCH	< 5.0	--	0	78	60
β-HCH	< 5.0	--	0	63	31
δ-HCH	< 5.0	--	0	52	22
γ-HCH	< 5.0	--	0	71	28
Heptachlor	< 5.0	--	0	64	22
Heptachlor epoxide	< 5.0	--	0	63	35
Hexachlorobenzene	< 5.0	--	0	54	20
o,p'-methoxychlor	< 5.0	--	0	49	20
p,p'-methoxychlor	< 5.0	--	0	58	23
Mirex	< 5.0	--	0	64	23
cis-nonachlor	< 5.0	--	0	83	34
Oxychlordane	< 5.0	--	0	50	34
Pentachloroanisole	< 5.0	--	0	68	32
Toxaphene	< 100	--	0	--	--

[a] Mean and standard deviation based on four samples.
[b] Includes carp and white sucker data only, all analytes for creek chub were less than method detection limit.
[c] Minimum concentration in all cases were less than method detection limit, which is the value listed in this column.
[d] < = less than. [e] -- = no data above method detection limit.

All six carp samples had detectable amounts of *p,p'*-DDE; three carp samples had detectable levels of *p,p'*-DDD. One carp sample also had detectable levels of *cis*- and *trans*-chlordane, and *trans*-nonachlor. One carp sample had *o,p'*-DDD at a concentration of 5.0 micrograms per

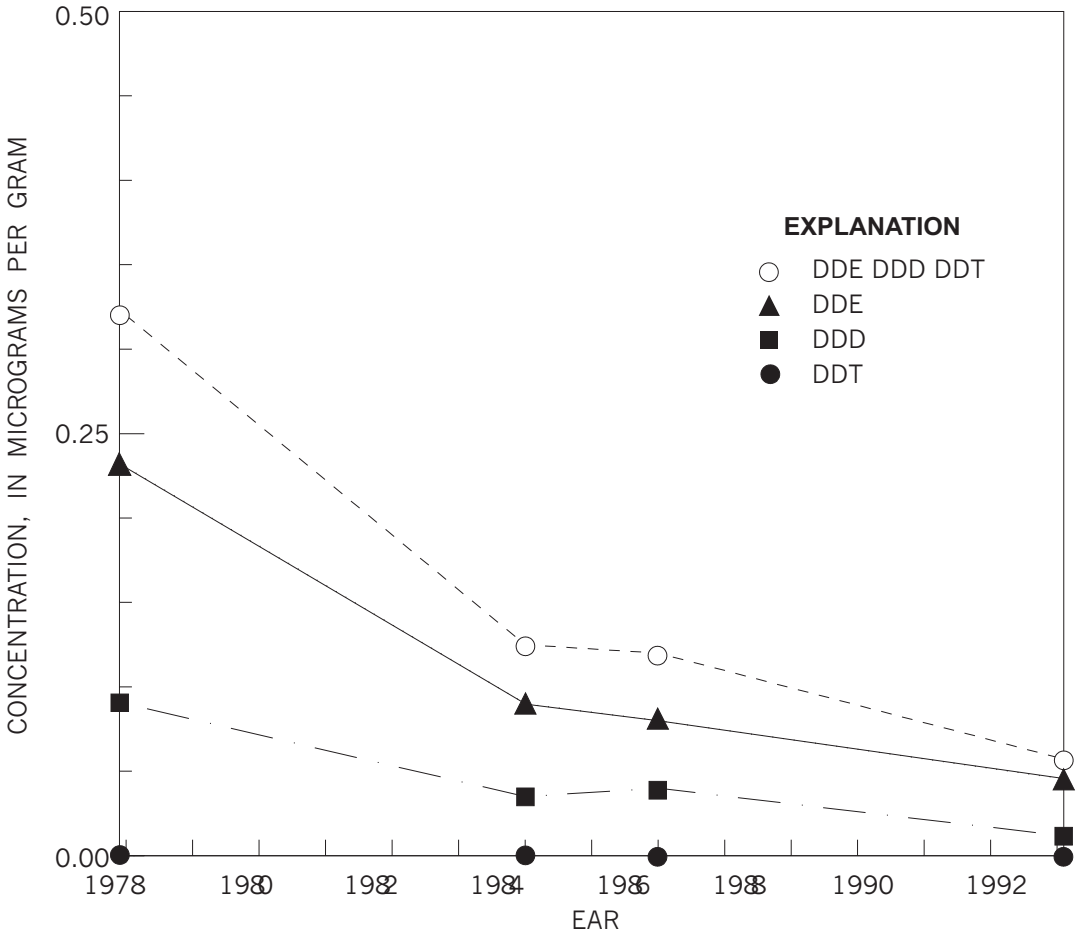
kilogram (µg/kg), the method detection limit. The metabolite *p,p*'-DDE was detected in three white sucker samples; this was the only pesticide detected in white suckers. No organochlorines were detected in the creek chub sample. Organochlorine pesticides were detected more frequently in carp samples than in white sucker samples. This difference could result from differences in assimilation of organochlorines between species, a difference in ages (sizes) of fish sampled, or an artifact of the sampling locations. Carp samples averaged about twice the length (400 millimeters, mm) and age (4-5 years) of the white sucker samples (200 mm; 2-3 years) (R.M. Goldstein, U.S. Geological Survey, oral commun., 1994). Because organochlorines bioaccumulate, older fish may be expected to have higher concentrations. Also, white suckers generally were collected from smaller streams or upstream reaches of streams, whereas carp were collected from downstream reaches of streams or from larger streams.

The *p,p*' isomers of DDE and DDD (metabolites of DDT) were the most frequently detected compounds in fish samples. These compounds were detected in sauger (*Stizostedion canadense*) and carp from the Red River at Noyes, Minn. from 1969 to 1986 (Henderson and others, 1971; Schmitt and others, 1981; Schmitt and others, 1983; Schmitt and others, 1990; S.L. Smith, U.S. Fish and Wildlife Service, written commun., 1992). Tornes and Brigham (1994) summarized these data for sauger, noting that DDE and DDD concentrations have decreased since the mid 1970s. Data from analyses of carp, which the USFWS sampled less frequently than sauger, also show decreasing DDE and DDD concentrations with time. While sampling and analytical methods used in this study differ slightly from those used by the USFWS, DDE and DDD in carp from the Red River at Drayton, N. Dak. (this study) appear to follow the trend of decreasing concentration over time when compared with the USFWS carp data from the Red River at Noyes, Minn. (fig. 4). Total DDT concentrations (DDT+DDE+DDD) decreased from 0.32 µg/g (micrograms per gram) in 1978 (USFWS data) to 0.058 µg/g in 1992. These concentrations are well below the Food and Drug Administration's action level of 5 µg/g (U.S. Food and Drug Administration, 1990), but exceed the 0.0316 µg/g concentration established by USEPA for protection of human health (U.S. Environmental Protection Agency, 1992). (This level, based on carcinogenicity, assumes that exposure occurs for a 70 kg person consuming 6.5 g of fish daily over a 70 year lifetime, and a 10^{-6} risk level; for a 10^{-5} risk level, the concentration is 0.316 µg/g. Persons consuming larger amounts of contaminated fish may have a higher cancer risk).

DDT was banned in the United States in 1972, yet residues of its metabolites continue to be detected in fish throughout the Red River Basin and in other areas of the United States. A large amount of research has established that DDT and its metabolites, and many other organochlorines, are atmospherically transported to regions far from where these chemicals are used; furthermore, atmospheric deposition is often the main source of these chemicals in regions where they are not used (Kurtz, 1990; Iwata and others, 1993; Kucklick and others, 1994). This is a likely mechanism for continued loading of these compounds to the Red River Basin. It is also possible that residual DDT (and metabolites) contamination from past use in the basin is augmenting the cycling of these compounds. The DDT metabolite concentrations in fish are similar to recent fish analyses from other North American rivers (Schmitt and others, 1990; Puri and others, 1990) and, correcting for lipid content, from Lake Baikal, Siberia (Kucklick and others, 1994).

Comparison to pesticide use. Data from a 1989 survey (McMullen and others, 1990) show that 2,4-D (including ester and amine derivatives of this compound), MCPA (including ester and amine derivatives), trifluralin, dicamba, diclofop, metsulfuron, and triallate were the most widely used pesticides in North Dakota. Each of these pesticides was applied to more than 4,000 km^2 statewide. MCPA (including ester and amine derivatives), terbufos, bromoxynil, trifluralin, and 2,4-D (including ester and amine derivatives) were the most widely used pesticides in counties that lie within the Minnesota portion of the Red River Basin, according to data from a 1989 survey (J.W. Hines, Minnesota Department of Agriculture, written commun.). Of these compounds, trifluralin and triallate were detected relatively frequently, but most of the other high-use compounds were not (some were not analyzed). Two of the highest-use compounds, 2,4-D and MCPA, were detected in only four and five of 44 samples, respectively, using the AC SPE method.

Figure 4.--Tissue concentrations of p,p -DDT and its degradation products p,p -DDE and p,p -DDD in carp *(Cyprinus carpio)* from the ed i er at Noyes, Minnesota (. . Fish and Wildlife er ice data, 197 -198) and the ed i er at Drayton, North Da ota (this study, 1992).



The higher reporting limit (0.05 µg/L) and possibly lower extraction efficiency associated with this method may account for this apparent discrepancy. In contrast, some of the most frequently detected compounds in this study, atrazine, metolachlor, cyanazine, EPTC, and prometon, account for a small percentage of pesticide usage in the Red River Basin.

Historical data from Environment Canada also show some frequently detected pesticides that have low usage rates. Components of technical lindane, α- and γ-HCH, were two of the most frequently detected pesticides by Environment Canada. Lindane was banned in the mid 1980s, but continued to be detected at low concentrations. Atrazine, a relatively low-usage herbicide in the Red River Basin, was detected in 39 percent of samples. The only high-usage pesticide that was detected frequently (in 48 percent of samples) was 2,4-D. Chacko and Gummer (1980) have reported on further studies of 2, 4-D in the Red River. MCPA, triallate, trifluralin, and dicamba—all high-usage pesticides—were detected in fewer than 10 percent of samples from the Red River at Emerson.

SUMMARY

Atrazine, metolachlor, triallate, and cyanazine were the pesticides most frequently detected in the Red River and tributaries in this study. Prometon and alachlor also were detected frequently at the Red River at Emerson, Manitoba, and trifluralin was detected frequently at the Wild Rice River near Twin Valley, Minn. Atrazine, metolachlor, and cyanazine concentrations were significantly higher in water samples from the Red River at Emerson than from the other study sites. None of the pesticides detected in water samples collected for this study exceeded their respective USEPA MCL values.

Degradation products of *p,p*'-DDT (*p,p*'-DDE and *p,p*'-DDD) were the most frequently detected compounds in fish tissues. All six carp, and three of six white sucker samples from this study had detectable residues of *p,p*'-DDE; *p,p*'-DDD was detected in three carp samples. While concentrations were well below the Food and Drug Administration's action level of 5 µg/g, the USEPA level of 0.0316 µg/g for DDT and metabolites in fish tissue for protection of human health (10^{-6} risk level) was exceeded in several carp samples. Since DDT was banned in the United States in 1972, its degradation products have continued to be detected in fish from the Red River Basin; however, concentrations in fish appear to have decreased since the 1970s. Atmospheric transport from sources outside the basin may account for continued presence of these compounds.

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