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likely to have elevated nitrate concentrations than deeper ground water. This indicates that shallow ground water is more susceptible to contamination from surface sources.

Suspended-sediment concentrations were evaluated for this report, but the coverage throughout the basin was sparse. Although suspended solids concentrations were available for many more sites, the data were incompatible with suspended-sediment concentrations. That is because samples for suspended solids concentration often were collected and analyzed using methods that would miss larger particles, and often would underestimate material suspended in the water. Suspended-sediment concentrations generally were highest on the Red River. Median concentrations at most sites were much less than 100 mg/L. The Red River at Emerson, Manitoba and three sites on the Pembina River were the only sites that had median sediment concentrations greater than 100 mg/L. About 10 percent of the sediment concentrations at each of three sites on the Pembina River were higher than 2,000 mg/L.

Pesticide data that are available within large national data bases (STORET and NWIS) are mainly limited to the period from the mid 1960s to the early 1980s. More recent data were available from several sources such as small, county-level studies and statewide surveys of drinking water wells, and Environment Canada's ENVIRODAT data base.

Most of the pesticide analyses summarized show no quantities of pesticides above reporting limits. When detected, reported concentrations nearly always met water quality standards.

The only pesticides detected in a relatively large fraction of surface water samples are 2,4-D (present in 43 percent of USGS samples and 38 percent of Environment Canada samples), α–HCH (present in 80 percent of Environment Canada samples), γ-HCH (present in 39 percent of Environment Canada samples), and atrazine (present in 42 percent of Environment Canada samples). These pesticides were measured over fairly long time spans (approximately 15 years for some pesticides), and are from sites having large drainage areas. Concentrations of these pesticides generally were low, rarely approaching water-quality or drinking-water standards. A few county-level studies have measured pesticide concentrations at sites in smaller watersheds, but during relatively short periods of time (a few months to one or two years). The highest concentrations (sometimes exceeding drinking water standards), and the only detections for some pesticides out of all data sources, were sometimes observed in these studies. One study showed higher concentrations of 2,4-D at upstream sites in a river basin, and no detectable levels of 2,4-D at the outlet from that basin. This observation may indicate that reliance solely on downstream sites (those that drain large areas) may fail to show impaired water-quality conditions, if they should exist, and may fail to account for the environmental fate of pesticides used within a drainage basin.

Analyses of pesticides in ground water are quite limited in number and geographic distribution, especially in the North Dakota part of the basin. Available data show that very few wells are contaminated with pesticides. Wells in which pesticides were detected are mainly limited to aquifers in sandy glacial deposits that underlie agricultural lands in the extreme southern and southeastern parts of the basin. The low-permeability soils of the Red River Valley are not conducive to downward movement of pesticides into aquifers. Atrazine is the most commonly detected pesticide in ground water in the Red River Basin and throughout Minnesota. Atrazine use is greater in the southern part of the Red River Basin, where corn is grown in significant amounts.

Selected organochlorine pesticides in fish tissue have been periodically analyzed in samples from the Red River at Noyes, Minn. since 1967. Following the 1972 ban on DDT, concentrations of DDT in fish quickly decreased to near or below the reporting limits. Concentrations of the principal metabolites of DDT (DDE and DDD) in fish decreased more slowly. Low levels of these compounds continued to be detected in fish fourteen years after DDT was banned in the United States. While these compounds may have persisted in the Red River Basin from past DDT use, atmospheric transport from countries that continue to use DDT is also a likely source of these compounds.

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River Basin are supported by long-range atmospheric transport from countries that continue to use DDT. Supporting this hypothesis are recent measurements of DDT and its metabolites in air, water, and (or) biota from very remote locations such as the Canadian Arctic (Bidleman and others, 1990) and the South Atlantic and Antarctic Oceans (Weber and Montone, 1990).

Other pesticides detected by the NPMP in Red River fish in the late 1960s and early 1970s include dieldrin, HCH, and infrequent, low-level detections of endrin. In one laboratory cross-check sample, heptachlor and chlordane were also detected. Similarly, low concentrations (hundredths of µg/g) were occasionally detected for these compounds from the mid 1970s to mid 1980s. Toxaphene, noticeably absent in the early 1970s, began to appear in detectable quantities in the mid 1970s in the tenths of µg/g range, and also appeared in the mid 1980s samples. Nonachlor residues have been detected at the 0.01 µg/g detection limit in some samples from 1984 and 1986. Mirex was analyzed since 1980, and DCPA was analyzed since 1976, but neither was detected in any tissue samples from the Red River.

Agricultural statistics for North Dakota (McMullen and others, 1990) indicate that mirex and DCPA were not used in the State when surveys were made in 1978, 1984, and 1989. Minnesota statistics show very minor usage of DCPA in a 1990 survey.

Summary

This report is part of a series planned as part of the National Water Quality Assessment Program (NAWQA). Focusing on the Red River Basin. This report is a review of data collected during 1970-90. Plant nutrients (phosphorus and nitrogen), suspended sediment, and pesticides are the topics covered in this review of existing information.

Water quality data have been collected by several agencies for many different purposes throughout the Red River Basin. Although the coverage of the data varies considerably across the basin, especially across state lines, it does provide some insight into the distribution of agriculture-related chemicals, and analysis of existing data suggests where additional data collection is needed. Subsequent sampling could be conducted in several areas because available data are inadequate, or additional sampling and analysis could document the cause of high concentrations of specific constituents and compounds.

Agriculture is the primary land use in this basin. Although nutrient concentrations may be high in agricultural areas, they generally do not exceed water quality standards. The 10 mg/L drinking water standard for nitrate rarely was exceeded at any of the surface water sites or in water wells, except in localized areas. The highest nitrogen concentrations usually were found in the Red River. The composition of that nitrogen often was difficult to determine from the data, but appeared to be mostly organic nitrogen with some nitrate and rarely any nitrite nitrogen. Concentrations of ammonia nitrogen were negligible except during mid-winter (usually January), when concentrations could exceed 1.0 mg/L. Stream nutrient concentrations generally were highest at sites on the Red River downstream from the urban areas of Fargo, N. Dak. and Moorhead, Minn.

Certain tributary streams can carry high concentrations of nitrogen that occasionally exceeded concentrations in the Red River. Some streams draining the corn and soybean areas in the southern part of the basin had high nitrogen and nitrate concentrations. The Pembina River, which drains the northwestern part of the basin, had a large range in nitrogen concentrations and often exceeded those in the Red River.

Phosphorus concentrations were distributed throughout the basin in a pattern similar to that of nitrogen. The highest concentrations tended to occur in the Red River. Tributary streams, especially the Pembina River, occasionally had peak concentrations of phosphorus that exceeded those in the Red River. The phosphorus data indicate effects of point sources, including discharges from the Fargo-Moorhead area into the Red River and from Hallock into Two Rivers.

Nutrient loading typically was more a function of streamflow than of concentration. The largest nutrient loads were carried by the Red River, with substantial additions from the Red Lake and Sheyenne Rivers. Increased nutrient loading downstream from the Fargo-Moorhead area appeared to come from urban and industrial sources.

Discussion of nutrient concentrations in ground water generally was restricted to nitrate, because fewer other data were available and coverage of the basin was inadequate for phosphorus and other forms of nitrogen. Median nitrate (as nitrogen) concentrations were less than 1.0 mg/L for all counties in the basin except Otter Tail County in Minnesota. Nitrate concentrations also were elevated in wells in Becker County. Of 31 wells sampled in Otter Tail County by the U.S. Geological Survey, half had more than 3.0 mg/L nitrate in the water. This could result from sampling in Otter Tail and Becker Counties that focused on contaminated aquifers, but probably is caused by irrigation water leaching nitrogen fertilizers from porous soils into aquifers susceptible to contamination. Nitrate concentrations in some counties occasionally exceeded the MCL of 10 mg/L. Shallow ground water was much more

toxaphene, α-HCH and β-HCH, hexachlorobenzene, methoxychlor, mirex, DCPA, and pentachloroanisole. Not all of these chemicals were analyzed throughout this program. Also, fish species sampled varied among collection periods within sites, and among sites. Results of the NPMP/NCBP have been presented by Henderson and others (1969), Henderson and others (1971), Schmitt and others (1981), Schmitt and others (1983), Schmitt and others (1985), and Schmitt and others (1990). Data from this program's 1986 samplings are not published, but were made available by the U.S. Fish & Wildlife Service (S.L. Smith, written commun., 1992).

Analytical methods for trace organochlorine chemicals have improved remarkably over the period of the program. In this report, semi-quantitative descriptions of chemicals that were detected are given. The original references contain information on quality assurance procedures, statistical tests used to analyze national and local trends, as well as the raw analytical data for composited fish samples.

Although analytical methods improved with time, it appears that a clear trend in the DDT data exists. In the early years of the NPMP, the parent compound DDT was frequently detected at roughly the same concentrations to those of the principal metabolites, DDE and DDD (DDE was usually the predominant metabolite). After the 1972 ban on DDT, concentrations in fish decreased rapidly. From the early 1970s to the mid 1980s, DDE and DDD concentrations in fish from the Red River slowly decreased from the tenths of μg/g (micrograms per gram) range to the hundredths of μg/g range, while the parent DDT quickly decreased from tenths of μg/g to less than, or occasionally equal to the 0.01 μg/g detection limit (fig. 28).

In 1986 (the last year for which data are available), low levels of DDE and DDD were detected in fish from the Red River even fourteen years after the ban on DDT use in the United States. It is possible that these metabolites persist in soils and stream sediments, and are eroded into streams, or cycled into the food chain by benthic organisms. It is also possible that the levels of DDT metabolites in the Red

Table 16.--Pesticides and reporting limits for ground water pesticide surveys in Minnesota by (A) Minnesota Department of Health (Klauseus and Hines, 1989), (B) Minnesota Department of Agriculture (Klaseus, Buzicky, and Schneider, 1988), and (C) Minnesota Department of Health (Klaseus, Buzicky, and Schneider, 1988).

[µg/L, micrograms per liter; --, not analyzed; *, pesticide degradation product; numbers in parentheses denote number of wells having at least one sample above the respective reporting limit for the analyte. Total number of wells for each study are (A) 200, (B) 100, (C) 400]

Chemical	Reporting limit (A) (µg/L)	Reporting limit (B) (µg/L)	Reporting limit (C) (µg/L)
Alachlor	0.05 (15)	0.16 (8)	0.05 (8)
Aldicarb	.5	.5 (2)	.5
Aldicarb sulfone *	--	.5	--
Aldicarb sulfoxide *	--	.5	--
Atrazine	.02 (85)	.05 (47)	.01 (107)
Butylate	.01	.79	.01
Carbaryl	.05	.5	.05
Carbofuran	.05	.5	.05
3-hydroxy-carbofuran *	--	.5	--
Chloramben	.05	1.6	.05
Chlorpyrifos	.05	.24	.05
Cyanazine	.5 (1)	.12 (3)	.5 (1)
2,4-D	.04 (1)	.21	.04 (7)
Diallate	.12	--	.12
Dicamba	.04 (2)	.18 (1)	.04 (3)
Dimethoate	.2	--	.2
Disulfoton	.45	.82	.45
EPTC	.01	.24	.01 (1)
Fonofos	.03	.16	.03
Linuron	.4	.17	.4
MCPA	.05	.27	.05 (2)
Methyl parathion	.02	.10	.02
Metolachlor	.13 (4)	.56	.13 (2)
Metribuzin	.02 (1)	.17 (4)	.02 (2)
PCNB	.02	--	.02
Pentachlorophenol	--	.28 (3)	--
Phorate	.1	.49	.1
Phosphamidon	--	.70	--
Picloram	.04 (3)	1.80	.04 (3)
Propachlor	.2	(2)	.08
Simazine	.3	.08 (1)	.3
2,4,5-T	.04	--	.04 (1)
2,4,5-TP	.05	--	.05
Terbufos	.2	--	.2
Trifluralin	.03	.21	.03

the Red River Basin, which is probably due to the lower rate of atrazine use and the less permeable soils in the Red River Valley Lake Plain.

An important factor in determining susceptibility of aquifers to contamination by pesticides is the permeability of the overlying soil. The low-permeability soils at the surface of most of the Red River Valley ecoregion are not conducive to downward movement of pesticides. It is possible that these chemicals are flushed through surface waters, or they degrade in the soil before reaching buried aquifers in appreciable concentrations. While the Red River Valley ecoregion is an area of extensive agricultural chemical use, the available data, although limited, indicate that aquifers in the region are not highly susceptible to contamination.

The sandy, glacial deposits in upland areas nearer the drainage basin boundary contain aquifers that appear to be more susceptible to pesticide contamination, although the pesticide concentrations are quite low compared to some aquifers in other parts of Minnesota.

Fish Tissues

The U.S. Fish and Wildlife Service has operated the National Pesticide Monitoring Program (NPMP; renamed the National Contaminant Biomonitoring Program (NCBP)) since 1967. Numerous freshwater fish species from stream sites around the Nation, including the Red River at Noyes, Minn., have been sampled periodically and analyzed for organochlorine chemicals. Analytes include DDT and its metabolites DDE and DDD, dieldrin, endrin, heptachlor, chlordane and oxychlordane, nonachlor,

Table 13.--Summary of U.S. Geological Survey pesticide data for ground-water samples in the Red River of the North Basin, 1979-90.

[µg/L, micrograms per liter; <, less than; ND, detection limit not reported in data base, concentration reported as 0 µg/L]

Chemical	Minimum reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
Alachlor	<0.1	<0.1	10	0
Aldrin	ND	ND	2	0
Ametryne	ND	<.1	15	0
Atrazine	ND	2.9	15	4
Chlordane	ND	ND	2	0
DDD	ND	ND	2	0
DDE	ND	ND	2	0
DDT	ND	ND	2	0
1,2-dibromoethane	<3.0	<3.0	2	0
1,2-dichloropropane	<3.0	<3.0	2	0
1,3-dichloropropene	<3.0	<3.0	2	0
cis-1,3-dichloropropene	<3.0	<3.0	2	0
trans-1,3-dichloropropene	<3.0	<3.0	2	0
Dieldrin	ND	ND	2	0
Endosulfan	ND	ND	2	0
Endrin	ND	ND	2	0
Heptachlor	ND	ND	2	0
Heptachlor epoxide	ND	ND	2	0
Lindane	ND	ND	2	0
Methoxychlor	ND	ND	2	0
Mirex	ND	ND	2	0
Prometone	ND	<.1	15	0
Propazine	ND	<.1	15	0
Simazine	ND	<.1	15	0
Trifluralin	<.1	<.1	10	0
Toxaphene	ND	ND	2	0

Table 14.--Minnesota Pollution Control Agency pesticide concentration data for ground-water samples collected in and near the Red River of the North Basin

[µg/L, micrograms per liter; <, less than]

Chemical	Reported concentration (µg/L)	Number of observations
Alachlor	<0.16	26
2,4-D	<.1	4
DDT	<.01	4
1,2-dibromoethane	<.5	31
1,2-dichlorobenzene	<1.0	31
1,3-dichloropropane	<3.0	24
cis-1,3-dichloropropene	<.2	31
trans-1,3-dichloropropene	<.2	31
1,1-dichloropropene	<.2	31
EPN	<.24	26
Metribuzin	<.17	26
Metolachlor	<.56	26
Silvex	<.02	4
Simazine	<.49	26
2,4,5-T	<.1	4
1,1,1,2-tetrachloroethane	<.2	31
1,1,2,2-tetrachloroethane	<2.0	31
1,2,3-trichloropropane	<2.0	24
Toxaphene	<.1	4

Table 15.--Pesticides and their reporting limits for Minnesota Department of Health community well water system survey, 1986-91 (T. Klaseus, Minn. Department of Health, written commun., 1992, and J. Walsh, Minnesota Department of Health, oral commun., 1993)

[µg/L, micrograms per liter]

Pesticide	Reporting limit (µg/L)
Alachlor	0.02
Atrazine	.02
Butylate	.02
Chlorpyrifos	.01
Cyanazine	.1
Diallate	.05
EPTC	.01
Fonofos	.01
Linuron	.5
Methyl parathion	.01
Metolachlor	.1
Metribuzin	.05
Phorate	.05
Propachlor	.01
Simazine	.05
Trifluralin	.05

percentage of wells within the Red River Basin, especially within the Red River Valley Lake Plain. In central and eastern Otter Tail County, several wells yielded reportable levels of pesticides. Similarly, the MDA data showed no wells with pesticide detections in the Red River Valley Lake Plain, and a few wells with pesticide detections near the southeastern margin of the drainage basin.

Atrazine was the most frequently detected pesticide in these statewide surveys. Statewide, atrazine was detected in 85 of 200 private wells (Klaseus and Hines, 1989) and in 154 of 500 selected wells (Klaseus, Buzicky and Schneider, 1988). Alachlor was the second most frequently detected pesticide in Minnesota wells in both of these studies. Fifteen of 200 wells (Klaseus and Hines, 1989) and 16 of 500 wells (Klaseus, Buzicky, and Schneider, 1988) had detectable levels of alachlor. Other pesticides were detected with much less frequency (table 16). These surveys were generally targeted toward agricultural lands, and toward areas where ground water was thought to be susceptible to contamination because of permeable soils. Pesticides were detected relatively infrequently in wells in

runoff sample from a farm field at a concentration of 10 µg/L, which exceeds the USEPA lifetime health advisory limit of 1 µg/L (no MCL has been established for cyanazine).

The majority of pesticide analyses of stream samples in the Red River Basin showed no detectable levels of analytes. Where detected, nearly all of the reported concentrations were below the USEPA MCL or lifetime health advisory limit standards. The exceptions have been noted. It is noteworthy that the highest concentrations of 2,4-D, simazine, and cyanazine were reported at smaller, upstream tributaries and farm-field runoff. The effects of chemical degradation, dilution by other tributaries, and sorption to sediments that are deposited in stream beds may decrease pesticide concentrations at downstream sites on larger streams. This may be an important consideration when studying movement and fate of pesticides in hydrologic systems. By relying solely on measurements at sites that drain large areas, a study may fail to detect the highest pesticide concentrations that may exist in a hydrologic system.

Ground Water

Pesticide data for ground water in NWIS are sparse for the Red River Basin (fig. 27). Three ground-water samples in the North Dakota part of the basin have been analyzed for pesticides (two from the surficial Warwick aquifer and one from the confined Spiritwood aquifer). The sites were sampled in May 1986, and are within 10 km of each other. A total of 14 samples from 9 sites within or very near the Minnesota part of the basin have been analyzed for pesticides during 1980-91. Two sites are from a surficial sand aquifer near the Otter Tail River; the remaining sites are from the Des Moines drift aquifer near the headwaters of the Clearwater River. Of these analyses, only atrazine was detected. Three samples from one well and one sample from another well had detectable atrazine concentrations. These wells are shallow (less than 10 feet deep and less than 6 feet to water) and are in the surficial Des Moines drift aquifer in Clearwater County, Minn. The analytes are shown in table 13.

The MPCA (STORET data base) has analyzed water samples from wells within and very near the Red River Basin (fig. 27). A total of 30 samples from 16 wells in surficial outwash aquifers (well depths 15.5-160 feet) and a total of 30 samples from 26 wells in buried outwash aquifers (well depths 43-364 feet) were sampled from 1978-88. Fifteen of the wells were clustered in a small area in Big Stone County, Minn., south of the basin boundary near the headwaters of the Minnesota River. These wells were sampled in 1987-88 for four triazine herbicides and one thiophosphate insecticide. Four wells near the Otter Tail River headwaters were sampled in 1978 for chlorinated hydrocarbon insecticides and chlorophenoxy acid herbicides. The remaining wells were sampled mainly for chlorinated propenes, chlorinated propanes, tetrachloroethane, dibromoethane, and dichlorobenzene. These compounds are variously used as soil fumigants, herbicides, and solvents in pesticide formulations and other products. None of the samples from the STORET data base yielded reportable quantities of any of the pesticides or fumigants analyzed. Analytes and their reporting limits are shown in table 14.

The MDH (Minnesota Department of Health) conducted a statewide survey of community well-water systems from 1986-91 that focused on pesticide contamination (T. Klaseus, Minnesota Department of Health, written commun., 1992). Atrazine was the most widely detected of those pesticides analyzed throughout Minnesota. Very few of the samples from within the Red River Basin yielded detectable quantities of atrazine. Atrazine detections were generally limited to the extreme southern and southeastern portions of the drainage basin, in an area characterized by morainal topography with sandy, permeable surficial aquifers where corn, a crop on which atrazine commonly is applied, is grown. Where detected in the basin, atrazine concentrations ranged from 0.01to 0.23 µg/L, and were lower than the range of concentrations reported in other regions of the state (some sites in other regions of the state yielded concentrations of several µg/L). Table 15 shows the analytes and their reporting limits for this survey.

Another MDH survey (Klaseus and Hines, 1989) showed similar results. A total of 21 private wells within or very near the basin boundary (in Polk, Norman, Clay, and Otter Tail Counties) were analyzed for pesticides. The authors did not report pesticide results for individual wells; however, pesticide detections were summarized for wells in a five county area. Fifteen wells, four of which were within or near the Red River Basin in eastern Otter Tail County, had pesticide detections. All 15 of these wells had detections of atrazine (0.02-0.48 µg/L); one well had a detection of alachlor (0.16 µg/L); and one well had a detection of picloram (0.03 µg/L). Sites in the Red River Valley Lake Plain showed no detectable levels of any of the pesticides analyzed. Table 16 lists the pesticides analyzed for this study.

The MDH and the MDA (Minnesota Department of Agriculture) jointly prepared a report describing surveys of selected pesticides in Minnesota wells, conducted from July 1985 to June 1987 (Klaseus, Buzicky, and Schneider, 1988); the analytes, reporting limits, and number of detections are shown in table 16. Data from the MDH survey show reportable levels of pesticides at a very low

Figure 26

compound. The MCL for γ-HCH is 0.2 μg/L (U.S. Environmental Protection Agency, 1991; U.S. Environmental Protection Agency, 1993). The U.S. EPA has classified this compound as a possible human carcinogen, and calculated that lifetime exposure to a concentration of 0.2 μg/L is not expected to result in adverse human health effects. However, the assessment for potential human carcinogenicity of γ-HCH is currently under review (U.S. Environmental Protection Agency, 1993). An ambient stream water quality criterion for the protection of human health (based on ingestion of water and aquatic organisms and a 10^{-6} risk level) was set at 0.0186 μg/L (U.S. Environmental Protection Agency, 1980). This value is based on carcinogenic potency and it consists of the γ-HCH concentration estimated to result in an excess cancer risk of 1 in 10^6 over a lifetime exposure. Only one of 309 samples exceeded this criterion. Ambient stream water quality criteria for the protection of aquatic life were set at 2 μg/L for acute toxicity and 0.08 μg/L for chronic toxicity (U.S. Environmental Protection Agency, 1980). None of the samples exceeded either of these criteria.

Since 1985, atrazine has been analyzed in 64 samples from the Red River at Emerson, Manitoba and 19 samples from the Roseau River at Gardenton, Manitoba. The reporting limit for atrazine was lowered from 0.10 to 0.05 μg/L in 1988. The Red River at Emerson, Manitoba has significantly higher atrazine concentrations (fig. 26A). Higher atrazine concentrations generally occur at the Red River at Emerson, Manitoba during the growing season, June through August (fig 26B). Data are not sufficient to detect seasonal peaks in concentration for the Roseau River at Gardenton, Manitoba (fig. 26C). Atrazine, used almost exclusively for corn, is used in modest amounts in the Red River Basin, particularly in the southern part of the basin. Atrazine is used only sparingly in counties of the Roseau River drainage basin (J.W. Hines, Minnesota Department of Agriculture, written commun., 1992).

Where significant differences in concentrations of any pesticide exist between the Red and Roseau River, concentrations tend to be higher at the Red River at Emerson, Manitoba. This could be expected, given the larger proportion of agricultural land use in the Red River Basin than in the Roseau River drainage basin.

Investigators of two recent county-level studies in Minnesota, coordinated with the Minnesota Board of Water and Soil Resources, have collected stream samples for pesticide analyses. These studies were similar in scale, used similar methods for sample collection, and used the same commercial laboratory for pesticide analyses.

The Kittson County Water Plan Coordinator's office has conducted a two-year (1991-93) study of the Joe River and Two Rivers. Data from the first part of this study are available in an interim report (Money, 1992). Three samplings for base-neutral pesticides (June 24, July 3, and October 21, 1991) showed evidence of a seasonal peak in concentrations of some pesticides, probably related to the timing of application. Linuron was detected at concentrations ranging from 2 to 18 μg/L on the earliest sampling date, but was below the reporting limit at subsequent samplings. Simazine was detected at one site at a concentration of 10 μg/L on June 24, 1991, which exceeds the MCL of 4 μg/L (U.S. Environmental Protection Agency, 1992), but was below its reporting limit at all other sites and sampling dates. Several other herbicides were occasionally detected at sub-microgram per liter concentrations. Cyanazine was detected at two sites on the earliest sampling date. Chlorpyrifos and pendimethalin were detected only later in the season. Acid pesticides were analyzed once (June 24, 1991), and only 2,4-D and picloram were detected.

The Red Lake Watershed District sponsored a cooperative project assessing water quality of the Clearwater River watershed (Holder, 1991). This watershed supports about 14,500 acres of man-made wild-rice paddies, which may have substantial effects on water quality and streamflow in the river basin. Stream and agricultural-runoff sites were sampled with varying frequency, depending on the site, throughout the 1990 growing season. Sites were sampled up to eight times from early May to late October. Of the pesticides sampled, 2,4-D was detected with greatest frequency and at the greatest number of sites. The highest concentrations and frequencies of detection for 2,4-D in stream water samples were measured in early May and during a major runoff event in early June 1990. Concentrations of 2,4-D, when detected, ranged from about 0.5 to 17 μg/L in early May, and from about 2 to 4 μg/L in early June. None of the pesticides were present in the stream at detectable levels during the late October sampling. The higher 2,4-D concentrations detected in this study are considerably greater than concentrations other agencies have detected on larger streams in the Red River Basin. Concentrations of 2,4-D did not approach its MCL of 70 μg/L (U.S. Environmental Protection Agency, 1991). The USEPA has not established an ambient stream-water quality criterion for 2,4-D. However, the National Academy of Sciences' water-quality criterion of 3 μg/L (National Academy of Sciences, 1972) was exceeded frequently in the May and June sampling. Bottom materials were sampled in early May and late October. In early May, 2,4-D was present at five of seven sites and was the only pesticide detected in the sediments. The late October sediment sampling indicated detectable concentrations of 2,4-D, dicamba, MCPA, and bromoxynil. Cyanazine was detected in a

Figure 25

Figure 24

Figure 23

Table 12.--Summary of Environment Canada pesticide data for the Roseau River at Gardenton, Manitoba
[µg/L, micrograms per liter; <, less than]

Chemical	Minimum reported concentration (µg/L)	Median reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
2,4-D	<0.03	<0.03	0.4	132	32
2,4-DB	<.05	<.05	<.05	133	0
2,3,6-TBA	<0.03	<0.03	<0.03	40	0
2,4,5-T	<.05	<.05	.06	133	1
Aldrin	<.001	<.001	<.001	127	0
Atrazine	<.05	<.1	.13	19	10
Barban	<.1	<.1	<.1	18	0
α-HCH	<.001	.003	.06	135	113
γ-HCH	<.001	<.001	.004	138	38
Benzoylprop-ethyl	<.025	<.025	<.025	18	0
α-chlordane	<.003	<.003	<.003	127	0
γ-chlordane	<.002	<.002	<.002	127	0
o,p'-DDT	<.001	<.001	<.003	125	0
p,p'-DDT	<.004	<.004	<.004	127	0
p,p'-DDD	<.002	<.002	<.002	126	0
p,p'-DDE	<.001	<.001	<.001	127	0
Diallate	<.1	<.1	<.1	18	0
Dicamba	<.03	<.03	.27	41	3
Dichlorprop	<.03	<.03	.05	168	2
Dieldrin	<.002	<.002	<.002	127	0
α-endosulfan	<.001	<.001	<.001	127	0
β-endosulfan	<.005	<.005	<.005	127	0
Endrin	<.002	<.002	.006	127	1
Fenoprop	<.03	<.03	<.03	118	4
Heptachlor	<.001	<.001	<.001	127	0
Heptachlor epoxide	<.001	<.002	<.002	127	0
Hexachlorobenzene	<.001	<.001	<.001	125	0
Hoegrass	<.05	<.05	<.05	18	0
MCPA	<.2	<.2	<.2	133	0
MCPB	<.05	<.05	<.05	40	0
Methoxychlor	<.01	<.01	<.01	126	0
Mirex	<.001	<.001	<.001	125	0
Picloram	<.2	<.2	.2	99	2
Triallate	<.01	<.01	<.01	18	0
Trifluralin	<.005	<.005	<.005	18	0

these guidelines is warranted. In calculating the RSD for water, it is assumed that human exposure occurs by ingestion of water (2 L/day) by a 70 kg adult for 70 years. For calculation of the EPA water quality criterion for the protection of human health, it is assumed that human exposure occurs by both ingestion of water and ingestion of aquatic organisms (fish and (or) shellfish) that live in the water and bioconcentrate the contaminant. Thus, in addition to the exposure assumptions used for the RSD, it is also assumed that an average of 6.5 g of fish or shellfish that live in the contaminated water are consumed daily. In this report, the criteria are used for comparative purposes only. Both of these guidelines are based solely on carcinogenicity, and do not consider other health effects that may result from chronic, low-level exposure, other routes of exposure, and additive or synergistic adverse effects that may result from exposure to other contaminants. Also, contaminants may be removed from drinking water by various treatment processes. Thus, ambient stream-water concentrations may not necessarily reflect concentrations of the contaminant in drinking water.

The maximum observed γ-HCH concentration was 0.02 µg/L; this value is lower than most water quality standards and guidelines for protection of human health for this

Table 11.--Summary of Environment Canada pesticide data for the Red River of the North at Emerson, Manitoba

[µg/L, micrograms per liter; <, less than]

Chemical	Minimum reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
Aldrin	<0.001	<0.001	159	0
Atrazine	<.05	.65	64	25
Barban	<.01	<.1	63	0
Benzoylprop-ethyl	<.025	<.025	63	0
α-chlordane	<.003	<.003	154	0
γ-chlordane	<.002	<.002	154	0
2,4-D	<.004	.82	179	87
2,4-DB	<.05	.2	178	1
p,p'-DDT	<.004	<.004	159	0
o,p'-DDT	<.001	<.004	152	0
p,p'-DDD	<.002	.002	159	1
p,p'-DDE	<.001	<.001	159	0
Diallate	<.01	.104	63	1
Dicamba	<.03	.04	75	1
Dichlorprop	<.03	.23	178	10
Dieldrin	<.002	<.002	159	0
α-endosulfan	<.001	<.001	159	0
β-endosulfan	<.003	<.003	159	0
Endrin	<.002	<.002	154	0
Fenoprop	<.03	<.03	154	0
γ-HCH	<.001	.02	171	83
α-HCH	<.001	.094	163	128
Heptachlor	<.001	<.002	159	0
Heptachlor epoxide	<.001	<.002	159	0
Hexachlorobenzene	<.001	<.001	151	0
Hoegrass	<.05	<.05	63	0
MCPA	<.2	.32	178	2
MCPB	<.05	<.05	75	0
Methoxychlor	<.01	<.012	159	0
Mirex	<.001	.001	152	1
Picloram	<.2	.20	158	4
2,4,5-T	<.05	.06	179	1
2,3,6-TBA	<.03	<.03	75	0
Triallate	<.01	.08	63	5
Trifluralin	<.005	.006	63	1

samples exceeded this criterion. A recalculated value for this criterion, based on more recent health data, was established at 0.0039 µg/L (U.S. Environmental Protection Agency, 1992c, 1993). This recalculated criterion was exceeded in 119 of 298 samples (40 percent). In the period from 1986-90, however, this criterion was exceeded in only 7 of 108 samples (6 percent). Ambient stream water quality criteria for protection of aquatic life are generally established for both acute toxicity and chronic toxicity. There are no aquatic life criteria for α-HCH specifically. For technical HCH (of which α-HCH is one component) the USEPA reported a lowest-observed-adverse-effect level (LOAEL) of 100 µg/L, in lieu of an aquatic-life criterion (data were not sufficient to establish an aquatic-life criterion) (U.S. Environmental Protection Agency, 1993). This LOAEL value is much higher than the measured concentrations in this data set. No chronic-toxicity criteria have been established for either α-HCH or technical HCH.

Because a larger number of samples had α-HCH concentrations above the RSD and the ambient water-quality criteria for protection of human health, a brief explanation of exposure assumptions used in calculating

River); this report reviews data collected through early 1990. Chacko and Ronmark (Environment Canada, written commun., 1990) have summarized the data from these sites in a draft report.

Several organochlorine insecticides and chlorophenoxy acid herbicides were analyzed in over 150 samples from the Red River at Emerson, Manitoba and over 120 samples from the Roseau River at Gardenton, Manitoba. Nitrogen-containing herbicides, including selected carbamates, thiocarbamates, triazines, and others, were analyzed in over 60 samples from the Red River at Emerson, Manitoba and in 18 samples from the Roseau River. Very few samples had concentrations above reporting limits for most of these pesticides. Twenty mono- and polychlorophenol compounds (several of which are used as fungicides, insecticides, and bactericides; pentachlorophenol is also a general herbicide and wood preservative) were analyzed in five monthly samples in 1990 at the Red River at Emerson, Manitoba; none were detected at concentrations at or above their reporting limits. The pesticide data are summarized in tables 11 and 12. Only four pesticide compounds were detected in a substantial fraction of samples. The herbicide 2,4-D was reported at concentrations at or greater than its higher reporting limit in 119 of 311 samples (38 percent). Alpha-hexachloro-cyclohexane (α-HCH) was present in 241 of 298 samples (80 percent). Gamma-hexachlorocyclohexane (γ-HCH) was present in 121 of 309 samples (39 percent), (α-HCH and γ-HCH are components of technical lindane). Atrazine, an herbicide used for corn crops, was present above reporting limits in 35 of 83 samples (42 percent).

The analytical method for 2,4-D changed in 1985, with a concomitant increase in reporting limit from 0.004 to 0.03 µg/L. The fraction of samples with concentrations above reporting limits decreased substantially at each site after this change was implemented. For this report, all data were censored at the 0.03 µg/L reporting limit. Figures 23A and 23B show the presence of seasonal peaks in 2,4-D concentrations for the Red River at Emerson, Manitoba and the Roseau River at Gardenton, Manitoba. For the period of record, median 2,4-D concentration exceeded 0.03 µg/L only in the months of June-August for the Red River at Emerson, Manitoba, and in March and July for the Roseau River at Gardenton, Manitoba. Concentrations of 2,4-D were significantly higher at the Red River at Emerson, Manitoba than at the Roseau River at Gardenton, Manitoba (fig. 23C). Concentrations of 2,4-D at both sites were well below water-quality criteria.

Chacko and Gummer (1980) reported 2,4-D concentrations in the Red River at Emerson, Manitoba and downstream sites for 1972-77. Data from routine water-quality monitoring and from a special investigation of 2,4-D in water, suspended sediments, and bottom sediments showed that 2,4-D was frequently detected in water samples from the Red River. Occasionally, 2,4-D was detected in suspended sediments, but at low levels relative to water concentrations. None of the bottom sediment samples from this study had detectable levels of 2,4-D.

Two HCH isomers (α-HCH and γ-HCH) were analyzed in over 160 samples from the Red River at Emerson, Manitoba and over 130 samples from the Roseau River at Gardenton, Manitoba. γ-HCH was detected in nearly half the samples from the Red River at Emerson, Manitoba and in about 27 percent of the samples from the Roseau River at Gardenton, Manitoba. Concentrations of γ-HCH were significantly higher at the Red River at Emerson, Manitoba than at the Roseau River at Gardenton, Manitoba (fig. 24A). The alpha isomer was detected in many more samples from both sites: nearly 80 percent at the Red River at Emerson, Manitoba and 84 percent at the Roseau River at Gardenton, Manitoba. There was no significant difference in the concentrations of α-HCH between these two sites (fig. 24B). During the period of record, the monthly patterns of concentrations show an early-summer peak in γ-HCH concentration at the Red River at Emerson, Manitoba. During other seasons, nearly all concentrations were at or below the reporting limit. For the Roseau River at Gardenton, Manitoba median γ-HCH concentrations were below the reporting limit for all months. Conversely, median α-HCH concentrations were above the reporting limit for nearly all months for both sites (fig. 24C and 24D). HCH concentrations (α and γ isomers) have decreased since 1985 (fig. 25). The period from the mid-1970s to the mid-1980s has significantly higher concentrations than the mid-1980s to 1991. In the United States, nearly every lindane-containing agricultural product was either banned or subject to use restrictions in the mid-1980s. Therefore, decreased concentrations would be expected.

Several water-quality criteria and health guidelines exist for α-HCH and γ-HCH. An MCL has not been established for α-HCH. However, a quantitative carcinogenicity assessment has been made. The USEPA has classified α-HCH as a probable human carcinogen, and calculated a risk-specific dose (RSD) of 0.006 µg/L (10^{-6} risk level) for this compound (U.S. Environmental Protection Agency, 1993). This means that the excess cancer risk due to lifetime consumption of drinking water containing α-HCH at this concentration (0.006 µg/L) is estimated to be 1 in 10^6. Fifty-six of 298 samples (from both the Red River and Roseau River sites) had concentrations equal to or exceeding this value. An ambient stream water quality criterion for protection of human health (based on ingestion of water and aquatic organisms and a 10^{-6} risk level) was set at 0.0092 µg/L (U.S. Environmental Protection Agency, 1980). Fifteen of 298

Data from a drinking-water survey at four water treatment plants conducted in February 1975 are also in the STORET data base. Stream water was sampled before and after treatment at drinking-water treatment plants on the Otter Tail River, Red Lake River, and Red River. Analytes included several organochlorine insecticides, thiophosphates, and chlorophenoxy acids (tab. 10). The analytes included pesticides that are widely used in the region, and some that were no longer in use (such as DDT). Small amounts (0.01 µg/L) of the fungicide hexachlorobenzene were detected at two sites on the Red Lake River; otherwise all pesticide analytes were below reporting limits. This February sampling was at least one-half year after the peak period of pesticide application.

Data from the Red River at Emerson, Manitoba and the Roseau River at Gardenton, Manitoba were retrieved from Environment Canada's ENVIRODAT data base, which includes data from Environment Canada's NAQUADAT (National Water Quality Database). These are the most complete single-station records examined for pesticide data in this report. No significant tributaries contribute to either of these streams between the U.S.-Canada border and the sampling sites (fig. 5). For most of the time, monthly samples analyzed for pesticides have been collected from these sites since 1972 (Red River) and 1974 (Roseau

Table 10.--Summary of pesticide data for treated and untreated stream water from four drinking-water treatment plants in the Red River of the North Basin; data from U.S. Environmental Protection Agency Drinking Water Survey, February 1975

[µg/L, micrograms per liter; <, less than]

Chemical	Minimum reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
Aldrin, total	<0.002	<0.002	8	0
Atrazine, total	<1	<1	8	0
Chlordane, total	<.002	<.002	8	0
Chlorobenzilate, total	<.01	<.01	8	0
Cyanazine, total	<1	<1	8	0
2,4-D, total	<.02	<.02	8	0
Dacthal (DCPA), total	<.003	<.003	8	0
o,p'-DDD, total	<.003	<.003	8	0
o,p'-DDE, total	<.003	<.003	8	0
o,p'-DDT, total	<.003	<.003	8	0
p,p'-DDD, total	<.003	<.003	8	0
p,p'-DDE, total	<.003	<.003	8	0
p,p'-DDT, total	<.003	<.003	8	0
Dieldrin, total	<.003	<.003	8	0
Dyfonate	<1	<1	8	0
α-endosulfan, total	<.005	<.005	8	0
β-endosulfan, total	<.005	<.005	8	0
Endrin, total	<.003	<.003	8	0
EPN, whole water, total	<1	<1	8	0
β-HCH, total	<.002	<.002	8	0
Heptachlor epoxide, total	<.002	<.002	8	0
Hexachlorobenzene, total	<.002	.006	8	3
Isodrin, total	<.003	<.003	8	0
Lindane, total	<.002	<.002	8	0
Methoxychlor, total	<.01	<.01	8	0
Methyl parathion, total	<1	<1	8	0
Mirex, total	<.005	<.005	8	0
2,4,5-T, total	<.01	<.01	8	0
Terbufos	<5	<5	8	0
Trifluralin, total recoverable	<.002	<.002	8	0
Trithion, total	<.02	<.02	8	0

advisory level of 200 µg/L (U.S. Environmental Protection Agency, 1993). However, the USEPA ambient stream-water criterion for the protection of aquatic organisms of 0.1 µg/L (chronic exposure level; U.S. Environmental Protection Agency, 1976) was exceeded frequently in samples from this study. North Dakota agricultural statistics show that reported malathion applications increased by over 15-fold from 1978 to 1984. Usage in 1989 was about the same as in 1984. Therefore, it may be of interest to assess malathion concentrations in the near future, to see if increases in usage result in high concentrations in streams of the Red River Basin. Bottom material samples from this survey showed that virtually none of the analytes were present. One sample (Red River at Moorhead) had DDT, DDD, and DDE concentrations that were lower than the highest reporting limit for the period, and thus may not be confirmed.

Table 9.--Summary of Minnesota Pollution Control Agency pesticide data from all surface-water sites in the Red River of the North Basin (from STORET data base), 1967-79.

[ND, not detected (reported concentration=0; detection limit not specified); µg/L, micrograms per liter; µg/kg, micrograms per kilogram dry solids; NA, not applicable]

Chemical	Minimum reported concentration (µg/L)	Median reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
		Water-column concentrations			
2,4-D, total	--	0.01	--	1	1
Aldrin, total	<0.01	<.01	0.2	33	3
α-HCH, total	<.02	<.02	<.02	26	0
Chlordane, total	<.1	<.1	<.1	26	0
cis-chlordane, total	<.02	<.02	<.02	26	0
trans-chlordane, total	<.03	<.03	<.03	26	0
Chlordane-nonachlor, *trans*, total	<.02	<.02	<.02	26	0
γ-chlordane, total	<.02	<.02	<.02	6	0
Chlorpyrifos, total	--	.21	--	1	1
DDE, total	<.01	<.01	.05	19	8
DDT, total	<.01	<.01	.1	44	1
o,p' -DDD, total	<.05	<.05	<.05	26	0
p,p' -DDD, total	<.05	<.05	<.05	26	0
o,p' -DDE, total	<.05	<.05	<.05	26	0
p,p' -DDE total	<.05	<.05	<.05	26	0
o,p' -DDT, total	<.1	<.10	<.1	30	0
p,p'- DDT, total	<.1	<.1	.9	146	7
Dieldrin, total	<.05	<.05	.19	35	5
Endrin, total	<.07	<.07	<.07	26	0
Heptachlor, total	.08	.09	.09	2	2
Heptachlor epoxide, total	--	.03	--	1	1
Hexachlorobenzene, total	<.05	<.05	<.05	30	0
Lindane, total[1]	<.01	<.01	<.01	20	0
Lindane, total[1]	<.05	<.05	<.05	4	0
Malathion, total	<.1	.19	.97	26	21
Methoxychlor, total	<.8	<.8	<.8	30	0
Mirex, total	--	<.5	--	1	0
Parathion, total	<50	<50	<50	12	0
Toxaphene, total	--	ND	--	1	1

Chemical	Minimum reported concentration (µg/kg)	Median reported concentration (µg/kg)	Maximum reported concentration (µg/kg)	Number of observations	Number of observations greater than reporting limit
		Bottom material concentrations			
Aldrin	<3	<3	<3	12	0
α-HCH	<3	<3	<3	9	0
Chlordane	<5	<5	<5	9	0
o,p' DDD	<30	<30	<30	9	0
p,p'-DDD	<30	<30	30	9	1
o,p'-DDE	<30	<30	30	9	1
p,p'-DDE	<30	<30	<30	9	0
o,p'-DDT	<60	<60	<60	12	0
p,p'-DDT	<20	<20	60	12	1
Dieldrin	<5	<5	<5	12	0
Endrin	<9	<9	<9	9	0
Hexachlorobenzene	<3	<3	<3	16	0
Lindane	<3	<3	<3	9	0
Methoxychlor	<50	<50	<50	12	0
Mirex, total	<1	<1	<1	7	0

[1] Data for total lindane in water were stored in the data base under two separate parameter codes, reflecting different methods of analysis.

Table 8.--Summary of U.S. Geological Survey pesticide data from all surface-water sites in the Red River of the North Basin, 1968-82

[ND, not detected (reported concentration=0; detection limit not specified); µg/L, micrograms per liter; µg/kg, micrograms per kilogram dry solids; <, less than]

Chemical	Minimum reported concentration (µg/L)	Median reported concentration (µg/L)	Maximum reported concentration (µg/L)	Number of observations	Number of observations greater than reporting limit
		Water-column concentrations			
2,4,5-T, total	ND	ND	0.13	175	9
2,4-D, total	ND	ND	.40	174	75
Aldrin, total	ND	ND	<.01	196	0
Atrazine, total	ND	ND	ND	23	0
Chlordane, total	ND	ND	.10	174	4
DDD, total	ND	ND	.04	196	4
DDE, total	ND	ND	.02	195	4
DDT, total	ND	ND	.08	196	9
Diazinon, total	ND	ND	.26	149	6
Dieldrin, total	ND	ND	.03	196	8
Endosulfan, total	ND	ND	<.01	65	0
Endrin, total	ND	ND	<.01	196	0
Ethion, total	ND	ND	<.01	128	0
Heptachlor epoxide, total	ND	ND	.01	190	2
Heptachlor, total	ND	ND	.24	196	2
Lindane, total	ND	ND	.02	195	5
Malathion, total	ND	ND	<.01	145	0
Methoxychlor, total	ND	ND	.01	62	1
Methyl parathion, total	ND	ND	<.01	149	0
Methyl trithion, total	ND	ND	<.01	127	0
Mirex, total	ND	ND	<.01	40	0
Parathion, total	ND	ND	<.01	149	0
Silvex, total	ND	ND	.01	173	2
Simazine, total	ND	ND	ND	17	0
Toxaphene, total	ND	ND	<1.00	130	0
Trithion, total	ND	ND	<.01	127	0

Chemical	Minimum reported concentration (µg/kg)	Median reported concentration (µg/kg)	Maximum reported concentration (µg/kg)	Number of observations	Number of observations greater than reporting limit
		Bottom material concentrations			
2,4,5-T	ND	ND	ND	26	0
2,4-D	ND	ND	1.00	25	2
Aldrin	ND	ND	<.20	47	0
Atrazine	ND	ND	ND	6	0
Chlordane	ND	ND	1.00	47	1
DDD	ND	ND	.60	45	10
p,p'-DDD	.49	1.07	1.65	2	2
DDE	ND	ND	.57	47	9
DDT	ND	ND	2.15	46	4
Diazinon	ND	ND	ND	32	0
Dieldrin	ND	ND	.20	47	3
Endosulfan	ND	<.10	<.10	8	0
Endrin	ND	ND	<.20	47	0
Ethion	ND	ND	ND	30	0
Heptachlor	ND	ND	1.20	47	1
Heptachlor epoxide	ND	ND	<.20	47	0
Lindane	ND	ND	.20	47	2
Malathion	ND	ND	<.20	33	0
Methoxychlor	ND	ND	.20	28	2
Methyl parathion	ND	ND	<.20	33	0
Methyl trithion	ND	ND	ND	30	0
Mirex, total	ND	<.10	<.10	8	0
Parathion	ND	ND	<.20	34	0
Silvex	ND	ND	ND	27	0
Simazine	ND	ND	ND	6	0
Toxaphene	ND	ND	<10.00	42	0
Trithion	ND	ND	ND	30	0

Figure 21

resources than a single measurement of a pesticide. Additionally, there are a number of commonly used pesticides, such as carbofuran and ethyl parathion (tables 2 and 3), which have been infrequently analyzed in water of the Red River Basin.

Where sufficient data exist, Wilkoxon rank-sum tests were performed to test for statistically significant differences between data sets. All differences herein described as "significant" are significant at the $\alpha = 0.01$ level (99 percent confidence level) using the rank-sum test.

Surface Water

The NWIS data base was searched for 350 constituents that include pesticides and pesticide-degradation products in water and bed sediments for surface-water sites sampled during 1960-91 in the Red River Basin. Pesticide data were found for 16 sites and 53 constituents (26 constituents in water samples and 27 in bottom-sediment samples) relating to 23 pesticides during 1968-82. DDE and DDD (metabolites of DDT) and heptachlor epoxide (a metabolite of heptachlor) were analyzed for some samples. These data are summarized in table 8. Many individual stations have data for only a few years and most data are from the early 1970s or late 1970s. Valid reporting limits were not used until later in the period of record; early data reported less-than-detectable concentrations as 0 micrograms per liter (µg/L). Data were censored at the higher reporting limit for the discussion in this report.

All samples for 13 pesticides had concentrations below their respective reporting limits. Nine of the remaining 10 pesticides had more than 90 percent of their data censored at the highest reporting limit. The herbicide 2,4-D in water was measured at concentrations at or above the reporting limit for 43 percent of 174 samples. These concentrations ranged from <0.01 (the highest reporting limit) to 0.40 µg/L. Figure 21A shows the distributions of 2,4-D concentration for each site.

The herbicide 2,4-D was detected over the entire period of record (1968-82); however, periods of record for individual stations are often less than 5 years. Two sites (Roseau River near Caribou, Minn. and Red River at Oslo, Minn.) had no samples that showed reportable levels of 2,4-D. Other sites on these rivers sampled by Environment Canada (discussed below), and the Red River at Hickson, sampled by the USGS, showed concentrations of 2,4-D greater than 0.01 µg/L during similar seasons and periods of record. Red River sites and Sheyenne River sites tended to have higher 2,4-D concentrations than the sites on other tributaries in the Red River Basin (fig. 21B).

Data from all sites were combined to yield a large enough statistical sample to examine seasonality in 2,4-D concentrations. March and June tended to have the highest concentrations; median concentrations exceeded the 0.01 µg/L reporting limit (fig. 21C).

The MPCA has pesticide data from 1967-79 (tab. 9) that are maintained in STORET. Most of the samples were analyzed for DDT only, or for DDT and its metabolites (DDD and DDE), and other chlorinated hydrocarbons. There are few analyses of other pesticides, with the exception of a survey that included malathion, a thiophosphate insecticide.

The MPCA has measured DDT (total, or individual isomers) and, less frequently, its degradation products DDD and DDE, in a total of 171 surface-water samples in the Red River Basin from April 1967 to September 1979. The analytical schedule was not consistent over this period. Several sites have had DDT, and sometimes its metabolites DDD and DDE, measured one or a few times during the period of record; some sites have DDT data for as many as thirteen dates. Thirteen Red River sites and twelve tributary sites are included in this data set. Of these samples, the *p,p'*-DDT isomer was detected at or above 0.10 µg/L (highest reporting limit) in 7 of 146 samples. Total DDT was detected at or above 0.05 µg/L (highest reporting limit) in only one of 43 samples. These data indicate that DDT contamination is not widespread in the region. In 1972, DDT was banned in the United States because it has deleterious effects on organisms. The highest concentrations of *p,p'*-DDT in this data base (>0.90 µg/L in three samples) were detected only before 1972.

The STORET data base also contains data from several MPCA surveys that focused on several more pesticides in stream bottom material and water samples. These surveys were conducted from 1977 to 1979, with most samples collected in October. A total of 12 stream-bottom material samples from 9 sites, and 26 water samples from 22 sites were collected from Red River Basin streams over this period (fig. 22). Samples from this survey were analyzed for DDT, DDD, DDE, chlordane, aldrin, HCH, lindane, dieldrin, endrin, methoxychlor, hexachlorobenzene, and malathion. Reporting limits for several of the analytes increased over this period. Some of these pesticides were in limited use at the time of the survey, and DDT had been banned in the United States. The October timing of this survey may not have detected the presence of pesticides that are applied earlier in the growing season. Malathion was detected in 21 of 26 surface-water samples at or above its lower reporting limit of 0.1 µg/L. For the 1979 samples, however, a reporting limit of 0.25 µg/L was established. Censoring all data at this higher limit, only 7 of 26 samples showed reportable concentrations of malathion, with a maximum concentration of 0.97 µg/L. These concentrations are well below the USEPA lifetime health

other inputs such as atmospheric deposition. Loading also can be affected by aqueous solubility and adsorption to soils; loss mechanisms such as biological or chemical degradation and volatilization; and environmental factors such as runoff events and topography that affect transport of chemicals to aquatic systems. Occurrence of detectable levels of pesticides in water, aquatic sediments, or aquatic biological tissues thus depends on many factors, including loading rates, time since application, chemical half-life with respect to biological and chemical degradation, and physical and chemical properties of a chemical that influence its distribution among various media.

Because sampling programs vary greatly in analytes determined, time periods in which samples were collected, and sites or areas sampled, pesticide data are discussed separately for each sampling program (where sufficient data exist). Analytical capabilities can commonly allow chemicals to be measured at extremely low concentrations—levels that are well below established water-quality standards, guidelines, and criteria. The purpose of this report is to summarize available data whether or not criteria are exceeded. Measured concentrations are compared to established water-quality criteria, where appropriate. Analyses in which pesticides were not detected (below reporting limits) also are important in assessing contamination of water resources.

Relatively few sites in the Red River Basin have enough pesticide data to warrant statistical analyses and tests for trends in concentrations. Most of the data described in this section are from programs or surveys in which several sites over a large area are sampled infrequently, sometimes only once or several times over several decades. These data are insufficient to assess seasonal variations or long-term trends in pesticide concentrations, but are useful in providing an indication of which pesticides have been detected in surface and ground waters. However, seasonal and long-term patterns in concentrations are far more important in assessing potential contamination of water

the Roseau River. The mean annual yield in tons per square mile for each of these streams was 35.5 for the Pembina River, 23.5 for the Red River, and 6.12 for the Roseau River. A report by Hydrocon Engineering (Continental), Ltd. (1987) provides a detailed discussion of the sediment transport characteristics of the Pembina River at Windygates, Manitoba based on data collected by the Water Survey of Canada during 1962-84. A report by Glavic and others (1988) discusses sediment transport characteristics for the Red River at Emerson, Manitoba during 1978-86 and compares data collected by the USGS with data collected by the Water Survey of Canada.

Pesticides

This report is limited to a description of the presence of synthetic organic pesticides. Although inorganic compounds, such as copper sulfate (an algicide) and various arsenic compounds, have been used as pesticides, these chemicals will not be considered in this report. The term pesticides encompasses hundreds of commonly-used chemicals (herbicides, insecticides, fungicides, and other types) that have a large range in physical and chemical properties. Key factors that affect the movement and fate of pesticides in the environment are aqueous solubility, vapor pressure, lipophilicity (the tendency of a chemical to dissolve in lipids), and biological and chemical degradation processes. Extensive reviews of the properties and environmental behavior of pesticides have been published elsewhere (see, for example, Howard, 1991; Worthing and Hance, 1991).

Loading of pesticides to aquatic systems is related to usage or accidental release in contributing watersheds, and

Two common measurements of the suspended-material content in streams are suspended sediment (Guy, 1969) and suspended solids (Fishman and Friedman, 1989). Historically, the USGS has collected much more suspended-sediment data than suspended-solids data. Suspended sediment is collected as a depth-integrated sample from several verticals across the stream and the entire sample, often several liters, is analyzed without subsampling. Conversely, the suspended-solids method used by the U.S. Geological Survey subsamples from a composited depth- and width-integrated sample and the most dense particles (such as sand) may not be evenly dispersed in the composite sample, even with vigorous agitation. Laboratory analysts pipette a second subsample from the field sample, purposefully avoiding large particles that might clog the pipettes. Each subsampling may exclude the largest and most dense particles, biasing suspended-solids data relative to suspended-sediment data.

Figure 19 shows the relation between concentrations of suspended sediment and suspended solids in samples collected by the USGS in Minnesota and North Dakota. Suspended-solids data underestimates suspended-sediment content by more than a factor of two. There also is substantial scatter in the data. Because of the substantial difference between suspended-sediment and suspended-solids data and the difficulty trying to reliably relate the two values, this report focuses only on suspended-sediment data. The USGS and Environment Canada are the two agencies that have collected the suspended-sediment data included in this report.

Figure 20 shows the distribution of suspended-sediment concentrations for those sites in the basin where values meet the same criteria that were applied to nutrient data. Data were available for only a few sites, with limited spatial coverage of the basin. Median concentrations of suspended sediment in the Red River ranged from 46 mg/L below Fargo, N. Dak. to 108 mg/L at Emerson, Manitoba. Median sediment concentrations were lowest in Beaver Creek, N. Dak. and the Red Lake and Roseau Rivers, Minn. The highest suspended-sediment concentrations generally were found in the Pembina River, especially at Walhalla, N. Dak. Suspended-sediment concentrations in the Pembina River ranged from 3 mg/L to nearly 7,000 mg/L. The steep topography in the watershed of the Pembina River leaves the soils more susceptible to erosion. Also, the stream-bed gradient increases the sediment-carrying capacity of the stream. Other streams in the Red River Basin have the capacity to carry large quantities of suspended sediment, but data to quantify this were not available.

Data have been collected at only a few sampling sites to determine the amount of coarse material (sand and gravel) in proportion to the amount of finer material (clay and silt). The Red River at Emerson, Manitoba tended to carry the finest suspended sediment; in more than half the samples, 98 percent of the material was finer than sand. The site on the Red River at Halstad, Minn. also carried a high percentage of fine material. The Red River at sites below Fargo, N. Dak. and at Oslo, Minn. had median percentages finer than sand of 84 and 89, respectively, indicating that coarser material is transported at these sites. The Pembina River typically had about 85 percent of the suspended-sediment load as material finer than sand.

Additional data on suspended sediment, including daily sediment samples for several years, have been collected by the Water Survey of Canada for Environment Canada. Sites sampled on streams discussed in this report include the Pembina River at Windygates, the Red River at Emerson, and the Roseau River at Gardenton, all in Manitoba. Suspended-sediment data from these sites and from many other sites throughout Manitoba through 1985 are summarized in a report by Penner and others (1987). During the period of data analyzed by Penner and others (1987) the mean daily suspended-sediment concentration was 393 mg/L in the Pembina River, 223 mg/L in the Red River, and 35 mg/L in the Roseau River. The mean annual load in tons for each of these streams was 104,000 for the Pembina River, 952,000 for the Red River, and 10,700 for