

GB
707
C338
no. 115E

Cover photograph

Red River at North Perimeter road bridge



Environment
Canada

Environnement
Canada

Content and Distribution Pattern of 2,4-D in the Red River

V. T. Chacko and Wm. D. Gummer

TECHNICAL BULLETIN NO. 115

**INLAND WATERS DIRECTORATE
WESTERN AND NORTHERN REGION
WATER QUALITY BRANCH
REGINA, SASKATCHEWAN, 1980**

© Minister of Supply and Services Canada 1980

Cat. No. En 36-503/116

ISBN 0-662-10905-8

Contents

| | Page |
|---|------|
| ABSTRACT | v |
| RÉSUMÉ | v |
| INTRODUCTION | 1 |
| STUDY AREA | 1 |
| METHODS | 1 |
| CHARACTERISTICS OF 2,4-D | 3 |
| RESULTS AND DISCUSSION | 4 |
| Historical perspective | 4 |
| Spatial distribution of 2,4-D in the Red River | 6 |
| Accumulation of 2,4-D in suspended sediment | 8 |
| Sampling reproducibility, cross-sectional heterogeneity and sample preservation | 9 |
| Reproducibility of the sampling technique | 9 |
| Cross-sectional heterogeneity | 10 |
| Sample preservation | 10 |
| CONCLUSIONS | 11 |
| ACKNOWLEDGMENTS | 11 |
| REFERENCES | 11 |

Tables

| | |
|---|---|
| 1. The 2,4-D analytical method precision for water and sediments | 3 |
| 2. Historical 2,4-D concentrations for the period July 1972 to August 1977 | 4 |
| 3. Results of the 2,4-D study in 1977 | 6 |
| 4. Bottom sediment and benthos sampling sites and sampling dates | 8 |
| 5. Concentration of 2,4-D in Red River water and partitioned suspended sediments. . . | 9 |

Tables (Cont.)

| | Page |
|--|------|
| 6. Results of replicate sampling | 10 |
| 7. Results of cross-sectional sampling | 10 |
| 8. Evaluation of sample preservation technique for 2,4-D | 10 |
| 9. Evaluation of sample preservation technique for 2,4,5-T | 11 |

Illustrations

| | |
|--|---|
| Figure 1. Study area and sampling locations | 2 |
| Figure 2. Historical variation of 2,4-D at selected sampling sites on the Red and Assiniboine Rivers | 5 |
| Figure 3. Spatial comparison of 2,4-D concentrations in the Red and Assiniboine Rivers during the 1977 study | 7 |

Abstract

The distribution of 2,4-D in the Red River between Emerson and Netley Lake was studied. The herbicide was found primarily in the water, less on the suspended sediment and not detectable in the bottom sediments and benthos. The recorded high concentration of 2,4-D in February 1977 that prompted this study is believed to be derived in part from the effluent of the City of Winnipeg's North End Pollution Control Center, which was found to contain 30 500 ng/L 2,4-D. There is no measurable accumulation of 2,4-D in the deposited river sediment.

This report also addresses (1) the variability of 2,4-D concentrations attributed to the sampling technique, (2) the river cross-sectional heterogeneity and (3) the sample preservation technique.

Résumé

Il a été déterminé que, dans la rivière Rouge entre Emerson et le lac Netley, l'herbicide 2,4-D se trouvait surtout dans l'eau, un peu moins sur les matières en suspension, et que dans les sédiments et le benthos sa concentration était inférieure au seuil de détection. Il semble que les fortes concentrations, relevées en février 1977 et qui ont motivé l'étude, soient dues à l'effluent de l'usine d'épuration du nord de Winnipeg, qui en contenait 30 500 ng/L. Il n'y a aucune accumulation mesurable de 2,4-D dans les dépôts de sédiments.

Il est également question dans ce rapport (1) des fluctuations de concentrations de 2,4-D attribuables à la technique d'échantillonnage, (2) de l'hétérogénéité dans la section transversale de la rivière et (3) de la méthode de préservation des échantillons.

Content and Distribution Pattern of 2,4-D in the Red River

V. T. Chacko and Wm. D. Gummer

INTRODUCTION

Residual concentrations of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) have been detected in many surface waters of western Canada (Gummer, 1978). The largest user, and therefore the largest potential source, of this contaminant is agriculture. However, as reported by Gummer (1978), urban activities and industry contribute 2,4-D to the aquatic environment as well.

Routine water sampling during early 1977 revealed anomalously high winter concentrations of 2,4-D in the Red River near Selkirk, Manitoba. In February the level of 2,4-D recorded was 3400 ng/L, and in March two samples recorded 2400 and 610 ng/L.

The Red River Basin (which covers more than 170 000 km²) drains almost exclusively agricultural land, therefore, it is not surprising that 2,4-D residuals are detected in the surface waters within the basin. Nevertheless, the levels described above were unprecedented.

On account of these anomalously high levels of 2,4-D in the Red River, officials from Environment Canada; the Manitoba Department of Mines, Resources and Environmental Management; and the City of Winnipeg met and agreed that follow-up surveys were necessary. The Water Quality Branch designed a pollutant-specific study for the period April to August 1977 with the following objectives: (1) to investigate the distribution of 2,4-D in the Red River, (2) to investigate the reproducibility of a depth-integrating sampler, (3) to investigate cross-sectional heterogeneity and (4) to compare the 2,4-D recovery with different preservation techniques.

Other herbicides (2,4-DB, 2,4-DP and 2,4,5-T) were analyzed simultaneously with 2,4-D, but except for occasional comments regarding one or more of these herbicides, the discussion is restricted to 2,4-D.

STUDY AREA

The study area extended from Emerson, Manitoba, where the Red River crosses the international border, to the mouth of the river at Lake Winnipeg. The river distance

from Emerson to Lake Winnipeg is approximately 240 km (Fig. 1).

The drainage basin of the Red River lies almost entirely within the agricultural districts of Manitoba, North Dakota and Minnesota. The major tributaries within the Canadian portion of the basin are the Roseau, Morris, La Salle, Seine and Assiniboine Rivers. The major urban centres and industries of Manitoba are located within the Red River Basin.

METHODS

Bottom sediment samples (400 g) were obtained using a mini-Shipek dredge. A 6-in. Ekman dredge was used to collect the benthos, which was immediately sieved with a 250- μ m net. Samples were frozen in aluminum foil and shipped air express to the Branch laboratory in Calgary, Alberta, for analysis.

Depth-integrated water samples were collected using a well-rinsed 2-L polyethylene bottle affixed to a metal holder and allowing the bottle to fill as it sank at a constant rate. Data generated when using this sampling technique reflect 2,4-D concentrations in the water and suspended sediment phases. The water was immediately transferred to a clean and rinsed 1.1-L glass bottle with a teflon-lined cap. The sample was acidified to a pH of 1 to 2 with five millilitres (5 mL) of concentrated sulphuric acid (36.0 N) dispensed from a glass and teflon dispenser.

Within 12 h, and usually within 3 h, the water sample was transferred from the glass bottle to a 2-L separatory funnel, and extracted with 100 mL of dichloromethane. The sample was shaken thoroughly for at least 1 min before the extract was drawn off into a 500-mL separatory funnel. Any emulsions present were usually eliminated with gentle swirling of the 500-mL funnel, but on occasion it was necessary to add 0.3 mL of acetone to break up the emulsion. The extraction was repeated, and the combined extract (200 mL) was transferred to a clean 250-mL glass bottle with a teflon-lined cap. Aluminum foil, treated with acetone and hexane, was inserted between the cap and the bottle. The bottled extracts were shipped via bus to the Calgary laboratory for analysis. The extract

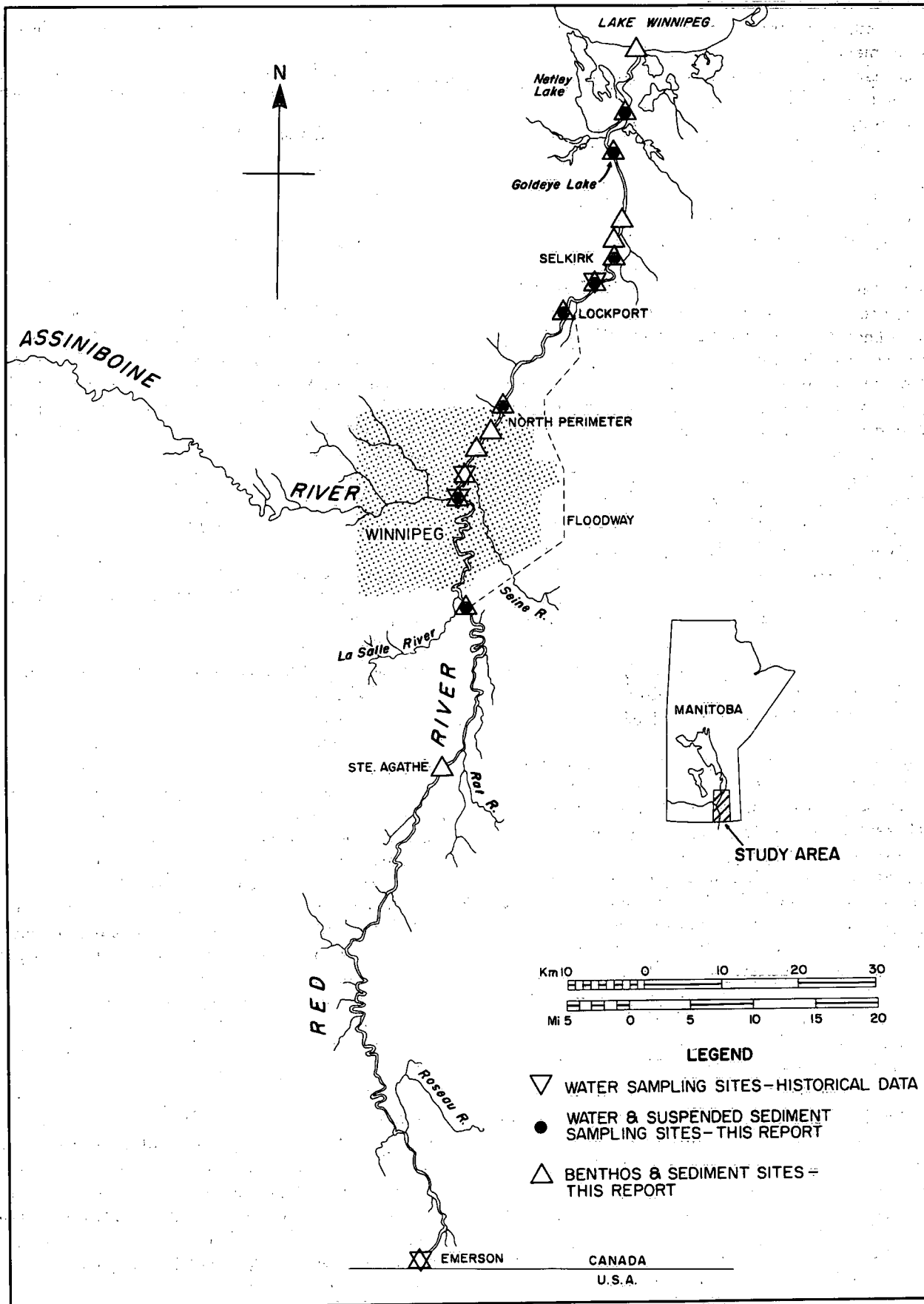


Figure 1. Study area and sampling locations.

was then dried, concentrated and replaced with a small amount of methanol. The herbicide residues were converted to their methyl esters using BF_3 -methanol. The methyl esters were extracted into benzene, cleaned up, and analyzed by gas-liquid chromatography using standard analytical procedures (Environment Canada, 1974).

The number of water samples collected varied with each sampling trip. During the first trip, all eight stations were sampled in triplicate, and all samples were preserved with 5 mL sulphuric acid and extracted. On the second trip, three of the eight stations (Red River at North Perimeter, Lockport, and Selkirk) were sampled in triplicate, and only one sample was taken from each of the remaining five stations. Each of the triplicate samples collected during the second sampling trip was treated differently. Five millilitres of sulphuric acid was added to one sample, and the sample was extracted in Winnipeg. The second sample was acidified with 5 mL of sulphuric acid and the third sample was left non-acidified.

To determine the lateral heterogeneity of the river, depth-integrated samples were collected from five evenly spaced verticals within the cross section at two stations. Each sample was acidified and extracted in the field laboratory.

Samples for suspended sediment analysis were collected in 12.5-L glass jugs, which were capped with rubber stoppers wrapped in aluminum foil. The sediments were partitioned by first centrifuging the water sample at 600 rpm and removing the compacted material. The supernatant was then re-centrifuged at 18 000 rpm and the deposited suspended matter was removed, wrapped in aluminum foil separately and then frozen. The final supernatant was extracted in the field laboratory. For those samples in which sediments were not partitioned but for which the concentration of total suspended sediments was required, the total sediment was removed by centrifuge at 18 000 rpm.

The centrifuge used was a continuous flow-through system, the Sorval Superspeed RC2-B automatic centrifuge. The running temperature of the centrifuge was set at 4°C. The water was transferred from the glass jugs to the centrifuge rotor by gravitational flow through glass and teflon tubing. The suspended matter was collected in teflon-lined stainless steel centrifuge tubes. A magnetic stirrer with a teflon-coated magnet was used to ensure that all sediment was in suspension. When centrifugation was complete, the deposited suspended matter was removed from the centrifuge tubes and placed in aluminum foil which had been treated with acetone and hexane. The samples were then frozen. All suspended matter samples

were centrifuged and frozen within 24 h of collection (usually within 3-4 h).

Bottom sediment samples were weighed (wet), acidified and extracted with dichloromethane in an ultrasonic bath. The extract was then treated as described above for the analysis of water samples. Benthos samples were treated in a similar manner but extracted with dichloromethane in a blender.

The precision of the analytical methods used for determining 2,4-D in water and sediment is shown in Table 1.

Table 1. The 2,4-D Analytical Method Precision for Water and Sediments

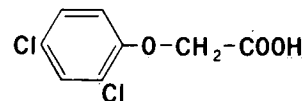
| Sample Type | ng/L | No. of Tests | % Recovery | Coefficient of Variation (%) |
|--------------------|---------|--------------|------------|------------------------------|
| Organic free water | 100 | 28 | 83 | 23.4 |
| Natural water | 100 | 7 | 81 | 17.7 |
| Sediment | 40 000* | 12 | 70 | 18.9 |

*ng/kg

Sulphuric acid and dichloromethane blanks were also submitted for analysis. All glassware used in the study was washed with tap water and soap, rinsed with distilled water and then rinsed with acetone and hexane. Heat treatment was carried out at 250°C on all glassware except volumetric flasks and pipets. All solvents used in the study were of pesticide quality.

CHARACTERISTICS OF 2,4-D

The chemical 2,4-dichlorophenoxyacetic acid is a white crystalline substance, slightly soluble in water and very soluble in ethyl alcohol and similar organic solvents (Weed Science Society of America, 1967).



The molecular weight is 221 g/mol and the vapour pressure at 160°C is 0.4 mm Hg. Water, diesel oil or oil-water emulsions are common carriers. Solubility in water ranges from 6% to 7% over a temperature range of 20-23°C. The sodium, potassium and amine salts are quite soluble in water and esters of 2,4-D are oil-like substances, which

form an emulsion when mixed with water. The herbicide 2,4-D behaves as an organic anion in aqueous solution and is readily adsorbed to clay and organic matter (Mansell and Hammond, 1971).

Toxicity of the basic herbicide (2,4-D) and its amine salts is low to organisms other than higher plants, but ester formulations are more toxic and may result in fish kills (Morre, 1974). In Manitoba, the most commonly used form is the amine salt of 2,4-D (personal communication, Manitoba Dept. of Agriculture).

Other chlorophenoxy aliphatic herbicides such as MCPA, 2,4-DB, 2,4,5-T and silvex have since been developed as effective hormone-like growth regulators and are also widely used (Borey, 1971).

The disappearance of 2,4-D from a river system may be through any or all of the following processes: biodegradation, photolysis (decomposition by light), volatilization and hydrolysis.

Biodegradation appears to be the dominant process of degradation in soil and bottom sediment, whereas photolysis and hydrolysis seem to be more important pathways in water (Aly and Faust, 1964). DeMarco *et al.* (1967) found that 2,4-D was degradable in 6 days in warm aerobic water, but persisted as long as 80 days in cold deoxygenated water. Hemmett and Faust (1968) report that 2,4-D is degraded quite rapidly (1-4 weeks) in the terrestrial environment, whereas conditions in the aquatic environment may not be as favourable for rapid degradation. Volatilization is not considered important for salts of 2,4-D, however, it is an important pathway of loss for 2,4-D esters (Zepp *et al.*, 1975). In any case, the difference in amine versus ester volatility is not thought to be important in the disappearance of 2,4-D from water, since both formulations are readily hydrolyzed to the free acid.

Work done by Aly and Faust (1964) has shown that 2,4-D is biodegradable in the bottom sediment and that the rate of biodegradation is higher when 2,4-D has been present in the medium over a long period. This is achieved by microbial adaptation as the responsive organisms grow and divide. DeRose and Newman (1947) suggest that the biodegradation process is achieved by microorganisms modifying the enzyme in the progeny to allow the foreign molecule to be used as a source of energy.

RESULTS AND DISCUSSION

Historical Perspective

Herbicide data (Table 2) reported by the Water Quality Branch (Fisheries and Environment Canada, 1978a) during

the period 1972 to 1977 show that 65% of the tests for 2,4-D in the Red River near Emerson were greater than the analytical detection limit of 4 nanograms per litre (ng/L).

Table 2. Historical 2,4-D Concentrations (ng/L) for the Period July 1972 to August 1977

| Sample Collection Date | Sampling Location | | |
|------------------------|----------------------|----------------------|----------------------------------|
| | Red River at Emerson | Red River at Selkirk | Assiniboine River at Highway 100 |
| <u>1972</u> | | | |
| July | 56 | - | - |
| October | 33 | 41 | - |
| <u>1973</u> | | | |
| January | <4 | - | - |
| February | - | 34 | - |
| May | 8 | 705 | - |
| July | 50 | <4 | - |
| October | 15 | 32 | - |
| <u>1974</u> | | | |
| January | - | 47 | - |
| April | 20 | <4 | - |
| August | <4 | - | <4 |
| October | <4 | - | - |
| <u>1975</u> | | | |
| February | <4 | <4 | <4 |
| May | <4 | <4 | <4 |
| June | 9 | - | - |
| July | - | 200 | 10 |
| August | 200 | - | - |
| September | 10 | 20 | 7 |
| <u>1976</u> | | | |
| January | - | 7 | 10 |
| February | <4 | - | - |
| April | 90 | - | - |
| August | 10 | 4 | 6 |
| October | 10 | 80 | 20 |
| <u>1977</u> | | | |
| January | <4 | - | - |
| February | - | 3400 | - |
| March 1 | - | 610 | - |
| March 14 | - | 2400 | - |
| April | - | 360 | - |
| May | 100 | - | - |
| July 6 | - | 110 | - |
| July 25 | - | 9 | - |
| August | - | 24 | - |

- No value.

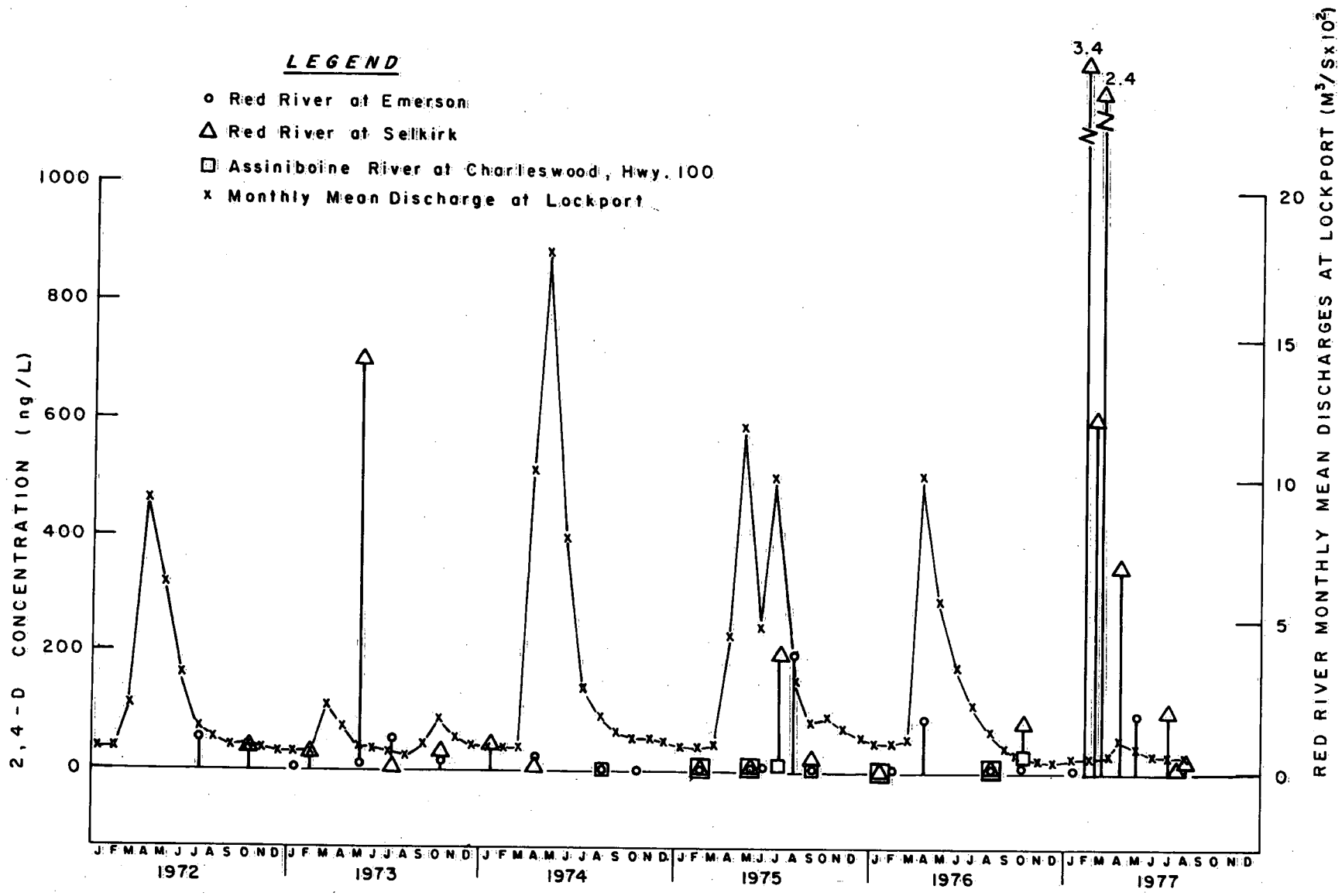


Figure 2. Historical variation of 2,4-D at selected sampling sites on the Red and Assiniboine Rivers.

During the same period the Red River at Selkirk and the Assiniboine River at Highway 100 had positive detections (above the detection limit) 81% and 62% of the time, respectively.

The maximum herbicide concentrations in surface waters have occurred most frequently during the months of May to June. Figure 2 shows how 2,4-D concentrations have varied at some of the monitoring sites since 1972. The unprecedented 2,4-D concentration of 3400 ng/L at Selkirk, and the time of year (winter) that this maximum was recorded, suggest an unusual event. Local runoff is dis-

counted as the cause, since winter conditions prevailed at the time of sample collection. Further speculation about the cause of the high herbicide concentration is discussed later.

Spatial Distribution of 2,4-D in the Red River

To ascertain whether there is a concentration gradient in the Red River, a total of seven sites (Table 3 and Fig. 1) were sampled. The results of the sample collections are shown in Table 3. All tests conducted at river sites during

Table 3. Results of the 2,4-D Study in 1977 (ng/L)

| Location | Sample Collection Date* | | | |
|---|--------------------------|-----------------------|------------------------|----------------------|
| | April | June | July | August |
| <i>Red River</i> | | | | |
| Floodway | 90 (27) | 200 [†] (23) | 9 (13) | — |
| | — | — | 10 (29) | — |
| North Perimeter | 490 (27) | 760 [†] (23) | 12 (18) | 99 [§] (3) |
| Lockport | — | — | 180 [†] (4) | 64 [§] (11) |
| | — | — | 120 (19) | — |
| Lower Fort Garry | — | — | 53 [†] (6) | 67 (4) |
| | — | — | 16 (21) | — |
| Selkirk | 360 [‡] (27) | — | 110 [†] (6) | 24 (4) |
| | — | — | 9 (25) | — |
| Goldeye Lake | — | — | 69 [†] (11) | 38 (8) |
| | — | — | 36 (27) | — |
| Netley Lake | — | — | 28 [†] (11) | 36 (8) |
| | — | — | 7 (27) | — |
| <i>Assiniboine River</i> | | | | |
| Main Street | — | 15 [†] (23) | 8 (14) | 99 (2) |
| Winnipeg North End Pollution Control Center | 30 500 [§] (27) | — | 1100 [‡] (22) | — |
| Winnipeg South End Pollution Control Center | <4 (27) | — | 300 [‡] (22) | — |

*The sampling day is shown in parentheses.

[†]The median from triplicate samples.

[‡]The mean of two results.

[§]The median of five samples collected at different points in the river cross-section.

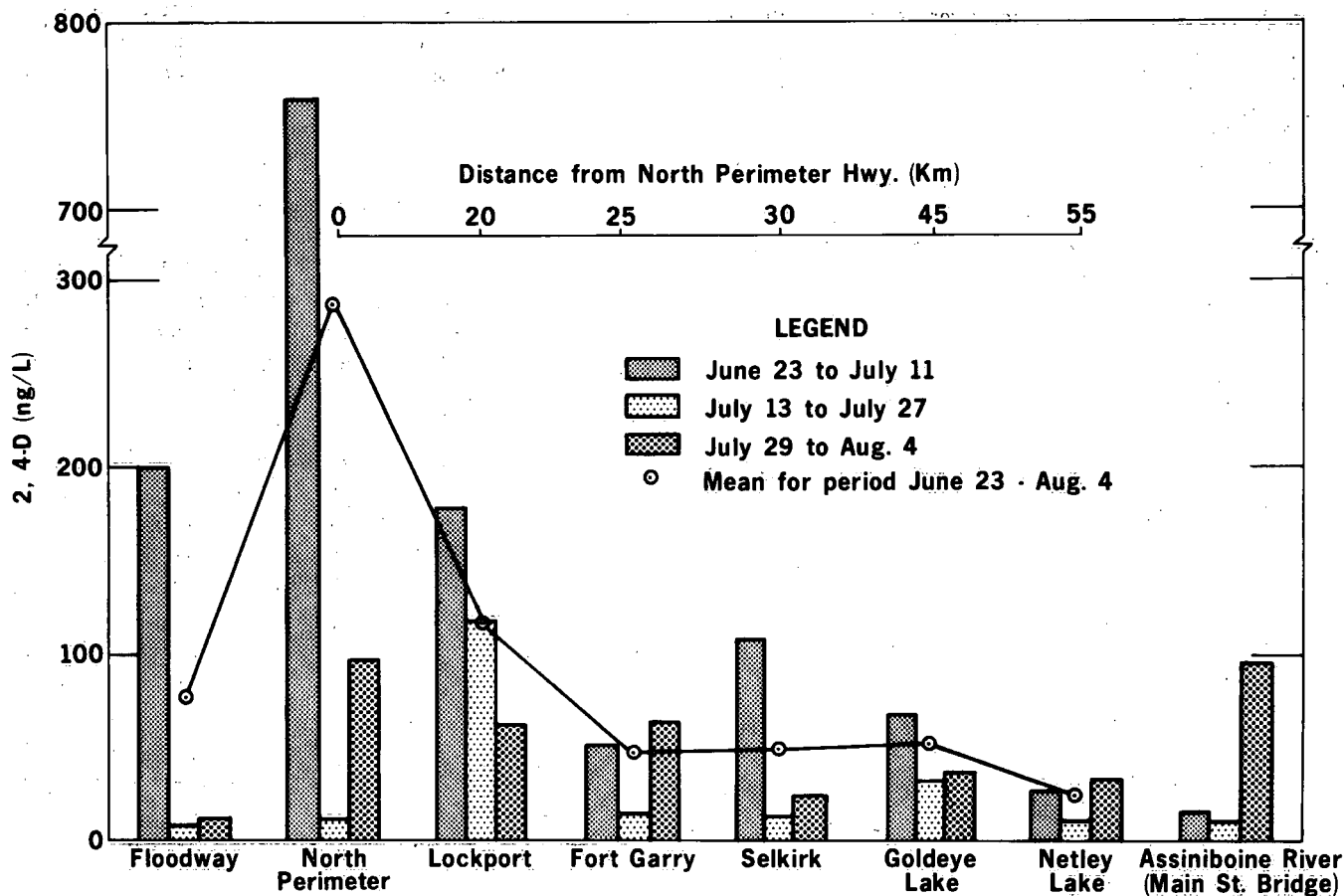


Figure 3. Spatial comparison of 2,4-D concentrations in the Red and Assiniboine Rivers during the 1977 study.

the study were positive for 2,4-D. Since time of travel was not taken into consideration when samples were collected, concentrations at downstream sites were not necessarily related to concentrations at upstream sites.

The sample collections conducted in April suggested that a major 2,4-D source was located within the City of Winnipeg. In fact, a 24-h composite sample of the effluent from the City of Winnipeg North End Pollution Center collected during April 27th and 28th revealed a 2,4-D concentration of 30 500 ng/L. It is highly probable that the above-mentioned effluent was responsible for the high 2,4-D levels observed at Selkirk during February and March of 1977 (Table 2).

The average daily effluent discharge from the North End Pollution Control Center during April was about 2.8 m³/s (City of Winnipeg Technical Laboratory, personal communication). With this figure and the mean daily discharge of 97 m³/s for the Red River near Lockport (Fisheries and Environment Canada, 1978b), the dilution factor is approximately 35. Applying this factor to the

mean effluent 2,4-D concentration of 30 500 ng/L yields a 2,4-D concentration after complete mixing of 870 ng/L. The measured value was 490 ng/L. The difference between the actual and calculated values may be attributed to a combination of analytical variability, degradation, volatilization and sorption to sediment that may have deposited between the sampling site and the effluent point source.

It is evident from the June data as well (Table 3) that there is a source of the chlorophenoxy acid herbicide within the City of Winnipeg. The 2,4-D level north of the city on June 23, 1977, was a factor four higher than that recorded the same day at the floodway, the southern extremity. The mean concentrations found during the study period (see Fig. 3) also suggest a source of 2,4-D within the city.

The source of the high 2,4-D level in the effluent of the North End Pollution Control Center has not been determined. If the local runoff directed to the storm sewers contributed the contaminant, it should have been detected at the South End Pollution Control Center as well. No 2,4-D was detected at the South End Pollution Control Center on April 27th when the concentration at the North End

Pollution Control Center was 30 500 ng/L. There are two herbicide packing plants in the City of Winnipeg that are located within the collector system of the North End Pollution Control Center. Contribution of 2,4-D to the municipal sewage system by these plants, if any, has not been established. Although it may merely be a coincidence, it is worth noting that the February and March 2,4-D maximums at Selkirk correspond with the peak herbicide packaging activities in Winnipeg (D. Rabb, Environmental Protection Service, personal communication).

Bottom benthos samples were collected at 16 sites (Table 4) for herbicide analysis. Figure 1 shows the geographic location of these sampling locations. There were no detections of any of the herbicides analyzed (2,4-D; 2,4,5-T; 2,4-DP and 2,4-DB) in the benthos and sediment samples.

Table 4. Bottom Sediment and Benthos Sampling Sites and Sampling Dates

| | | |
|-----|---|----------|
| 1. | Red River at Emerson | 27/05/77 |
| 2. | Red River 1.6 km downstream from Ste. Agathe | 09/06/77 |
| 3. | Red River 90 m south of South Floodway gates | 27/05/77 |
| 4. | Red River at Winnipeg, approximately 1.6 km downstream from Assiniboine River | 27/05/77 |
| 5. | Red River at Kildonan Golf Course | 20/05/77 |
| 6. | Red River 45 m downstream from North-End Waste Treatment Plant effluent discharge | 20/05/77 |
| 7. | Red River at North Perimeter Highway | 20/05/77 |
| 8. | Red River at Lockport Bridge | 20/05/77 |
| 9. | Red River 1.6 km downstream from lower Fort Garry | 10/06/77 |
| 10. | Red River at Selkirk | 10/06/77 |
| 11. | Red River 3 km downstream from Selkirk | 13/06/77 |
| 12. | Red River 6 km downstream from Selkirk | 13/06/77 |
| 13. | Red River 14 km downstream from Selkirk (at Goldeye Lake) | 13/06/77 |
| 14. | Red River at Netley Lake | 13/06/77 |
| 15. | Red River mouth at Lake Winnipeg | 13/06/77 |
| 16. | Assiniboine River 0.5 km upstream from Red River (in Winnipeg) | 27/05/77 |

It is therefore apparent that even though these herbicides have been detected in water samples for a number of years (Table 2), they have not accumulated on the river bed.

Accumulation of 2,4-D in Suspended Sediment

The herbicide 2,4-D was detected in all of the water samples, but it was not detected in the majority of the suspended sediment samples (Table 5). Whenever it was detected in the suspended sediment, the concentration was higher than that of the water samples. Since the amount of suspended sediment per litre of water is small, however, the amount of 2,4-D contributed by sediment to a 1-L water sample is also small. The concentration of 2,4-D in Red River suspended sediment on July 19, 1977, at Lockport was 5 µg/kg (wet weight). The concentration of 2,4-D in the unfiltered river sample was 120 ng/L. The total suspended sediment collected by centrifuge was 26.6 mg/L, therefore, the sediment contributed only 0.13 ng/L of 2,4-D to the water sample. If the 1961-1976 median dry weight suspended sediment of 37 mg/L is used in this calculation, the amount of 2,4-D contributed is 0.19 ng/L. Based on this information, it would appear that virtually all of the 2,4-D observed in the Red River at Lockport on this date was in solution.

Suspended sediment samples were partitioned at four river sites (Table 5). In every case, the calculated total 2,4-D (suspended sediment plus supernatant) was less than the 2,4-D concentration in the unfiltered water sample (water plus suspended sediment). Since the 2,4-D level in the suspended sediment was near the detection limit (Table 5) and the recovery of the spiked sediment was 70%, with a coefficient of variation of 19%, a quantitative comparison may not be valid. Nevertheless, it would appear that part of the 2,4-D was lost during centrifugation and/or during the lag time between sample collection and analysis.

Partitioning of the suspended sediment showed that 2,4-D was detected in both the smaller particles (centrifugation at 18 000 rpm) and the larger particles (centrifugation at 6000 rpm). Considerably more 2,4-D was removed along with the larger particles. This is attributed primarily to the greater quantity of the larger particles than to higher concentrations of 2,4-D.

At two sites, the Red River at the floodway and the Assiniboine River at Main Street, 2,4-DB was detected in the suspended sediment. None of the water samples collected had detectable levels of 2,4-DB.

Table 5. Concentration of 2,4-D in Red River Water and Partitioned Suspended Sediments

| Location | Date (1977) | Partitioned Water Sample | | | | | Unfiltered Water Sample [‡] ng/L | |
|--------------------------|-------------|--------------------------|--------|---------------------|--------|---------------------|--|------------------------------------|
| | | 6000 rpm µg/kg | ng/L* | 18 000 rpm µg/kg | ng/L | Supernatant ng/L | | Total (Calc.) [†] ng/L |
| <i>Red River</i> | | | | | | | | |
| Floodway | 13.7 | 4 (52) [§] | 0.21 | 4 (20) | 0.08 | <4 | <4 | 9 |
| | 29.7 | | | <4 | | | | 10 |
| North Perimeter | 18.7 | 3.8 | | trace | | | | 12 |
| | 3.8 | | | <4 | | | | 99 |
| Lockport | 4.7 | 5 (20) | 0.1 | <4 | | <4 | <4 | 180 |
| | 19.7 | | | trace (6.6) | | | | 120 |
| | 11.8 | | | <4 | | | | 64 |
| Lower Fort Garry | 6.7 | <4 (22) | <0.088 | trace | <0.039 | <4 | <4 | 53 |
| | 21.7 | | | <4 (9.9) | | | | 16 |
| | 4.8 | | | <4 | | | | 67 |
| Selkirk | 4.7 | <4 (38) | <0.16 | <4 | <0.088 | 6 | 6 | 110 |
| | 25.7 | | | <4 (22) | | | | 9 |
| | 4.8 | | | <4 | | | | 24 |
| Goldeye Lake | 11.7 | | | <4 | | | | 69 |
| | 27.7 | | | <4 | | | | 36 |
| | 8.8 | | | <4 | | | | 38 |
| Netley Lake | 11.7 | | | trace | | | | 28 |
| | 27.7 | | | <4 | | | | 7 |
| | 8.8 | | | <4 | | | | 36 |
| <i>Assiniboine River</i> | | | | | | | | |
| Main St. bridge | 14.7 | | | <4 | | | | 8 |
| | 2.8 | | | <4 | | | | 99 |

* Contribution of 2,4-D to one litre river water from the sediment partitioned at the given rpm.

† A summation of 2,4-D found in the sediment fractions plus concentration in the supernatant.

‡ The 2,4-D found by analyzing an unfiltered water sample.

§ Concentration of suspended sediment in water sample is shown in parentheses and is expressed as mg/L, wet weight.

Trace = not in measurable quantity.

Sampling Reproducibility, Cross-Sectional Heterogeneity and Sample Preservation

Reproducibility of the Sampling Technique

Multiple samples were collected at eight sampling sites to determine whether the results obtained using the present sampling technique were reproducible or not. The results of the replicate samples are shown in Table 6.

The precision for the analytical method is 47% (or twice the coefficient of variation in percent). The variability

in replicates for five of the eight test cases shown in Table 6 can therefore be fully accounted for by the analytical variability. Two test cases are borderline. The other test case, Red River at Selkirk, showed a significant difference in concentration between samples. Although the poor precision in this case may in part be attributed to the sampling technique, incomplete extraction or poor identification could also be the cause.

It is concluded that the sampling technique does not result in poorer precision than that accounted for by the analytical methodology.

Table 6. Results of Replicate Sampling for 2,4-D (ng/L)

| Location | Date | Samples | | | Statistics | | | |
|--------------------------|----------|----------------|----------------|----------------|------------|-----------|----------------|--------------------|
| | | X ₁ | X ₂ | X ₃ | Range | \bar{X} | S _x | L _x (%) |
| <i>Red River</i> | | | | | | | | |
| Floodway | 23/06/77 | 200 | 210 | 150 | 60 | 187 | 32 | 34 |
| North Perimeter | 23/06/77 | 600 | 760 | 850 | 250 | 737 | 127 | 34 |
| Lockport | 04/07/77 | 180 | 240 | 160 | 80 | 193 | 42 | 44 |
| Lower Fort Garry | 04/07/77 | 53 | 73 | 49 | 24 | 58 | 13 | 45 |
| Selkirk | 04/07/77 | 110 | 29 | 140 | 111 | 93 | 57 | 123 |
| Goldeye Lake | 11/07/77 | 95 | 48 | 69 | 75 | 71 | 24 | 68 |
| Netley Lake | 11/07/77 | 23 | 44 | 28 | 21 | 32 | 11 | 69 |
| <i>Assiniboine River</i> | | | | | | | | |
| Main Street | 23/06/77 | 11 | 15 | 14 | 4 | 13 | 2 | 31 |

The analytical detection limit is 4 ng/L. Analytical precision (L_α) is 47%.

S_x = standard deviation of X.

L_x = precision = two times the coefficient of variation in percent.

Cross-Sectional Heterogeneity

Cross-sectional sampling was done at two stations, the Red River at the North Perimeter Highway and at Lockport. There were five sampling sites placed about 30 m apart starting at 30 m from the west bank. Depth-integrated samples were collected from each site. The results are shown in Table 7.

Table 7. Results of Cross-Sectional Sampling for 2,4-D (ng/L)

| Sampling Site (metres from left bank) | North Perimeter 03/08/77 | Lockport 11/08/77 |
|--|-----------------------------|----------------------|
| 30 | 99 | 51 |
| 60 | 99 | 68 |
| 90 | 113 | 64 |
| 120 | 77 | 62 |
| 150 | 83 | 89 |
| Mean | 94.2 | 66.8 |
| Standard deviation | 14 | 14 |
| Precision (%) | 30 | 42 |

In both cases the precision (L_x) is less than the analytical precision (L_α) of 47%, therefore, the Red River at

these sites was homogeneous within analytical variability at time of sample collection.

Sample Preservation

Two of the three test cases sampled in triplicate showed higher 2,4-D recovery for samples acidified and extracted at the field laboratory than for samples acidified and extracted later in Calgary (Table 8). In fact, the recovery was about 100% greater. In the third case, there was essentially no difference between these two preservation techniques. One sample receiving no pre-treatment in the field gave greater recovery than either acid preservation technique.

Table 8. Evaluation of Sample Preservation Technique for 2,4-D (ng/L)

| Location | Date | Acid/ Extraction | Acid Only* | No Treatment |
|------------------|----------|---------------------|---------------|-----------------|
| <i>Red River</i> | | | | |
| North Perimeter | 18/07/77 | 25 | 12 | 66 |
| Lockport | 19/07/77 | 260 | 120 | NR |
| Selkirk | 25/07/77 | 9 | 11 | 8 |

*This method of preservation is presently used by the Water Quality Branch.

NR = no result.

Although 2,4,5-T was not the focal point of this report, comments regarding sample preservation for this test must be made. The same procedure used for evaluating the preservation of 2,4-D samples was used for 2,4,5-T. Table 9 shows the results. In one of three test cases, acidification followed by field extraction resulted in greater recovery than acidification alone and one out of three samples without any preservation yielded greater recovery than either acid preservation technique.

Table 9. Evaluation of Sample Preservation Technique for 2,4,5-T (ng/L)

| Location | Date | Acid/ Extraction | Acid Only | No Treatment |
|------------------|----------|---------------------|--------------|-----------------|
| <i>Red River</i> | | | | |
| North Perimeter | 18/07/77 | 15 | NR | 14 |
| Lockport | 19/07/77 | 77 | 44 | <2 |
| Selkirk | 25/07/77 | 22 | 26 | 68 |

NR = no result.

CONCLUSIONS

The herbicide 2,4-D was found to be ubiquitous in the Red River between the City of Winnipeg and Netley Lake, located in the Red River delta. It is speculated that the February and March concentrations of 3400 ng/L, and 2400 and 610 ng/L, respectively, are linked to the herbicide packaging activities within the City of Winnipeg.

The study revealed that 2,4-D was not present in measurable amounts in deposited sediment or benthos of the Red River, whereas it was detected in all water and several of the suspended sediment samples collected. On a weight per weight basis the 2,4-D concentration in the suspended sediment was higher than the concentration in the surrounding water. Because of the low concentration of suspended sediment, the suspended sediment did not contribute significantly to the 2,4-D concentration of an unfiltered water sample. In this regard, 2,4-D was found to be primarily in the water phase.

Comparison of 2,4-D concentrations in replicate samples suggests that the sampling technique does not result in poorer precision than that accounted for by the analytical methodology. The variance in measurements attributable to the homogeneity of the Red River and to the sampling technique appears to be within the analytical variability.

The test results suggest that field acidification followed immediately by sample extraction is superior to acidification without field extraction. In one of three test cases, however, the sample with no pre-treatment recovered higher 2,4-D and 2,4,5-T than by both of the acidified techniques.

The data derived from the investigation of sample preservation for 2,4-D and 2,4,5-T are equivocal and are at best only indicative of the uncertainty concerning present sample preservation techniques.

ACKNOWLEDGMENTS

The authors wish to thank Messrs. B. Chu and G. Wurtak for the collection and field preparation of samples. The contributions of R.J. Allan and staff of NWRI in collecting the bottom sediment, and the staff of Analytical Services Division of the Water Quality Branch for expeditiously analyzing the entire sample, are gratefully acknowledged. The editorial comments of Water Quality Branch Headquarters' personnel are appreciated. Thanks are also extended to L. Babcock, who typed the manuscript.

REFERENCES

- Aly, O.M., and S.D. Faust. 1964. Study on the fate of 2,4-D and ester derivatives in natural surface waters. *J. Agric. Food Chem.* 12:541.
- Borey, R.W. 1971. Hormone like herbicide in weed control. *Econ. Bot.* 25:385-400.
- DeMarco, J.J., J.M. Symons and G.G. Robeck. 1967. Behaviour of synthetic organics in stratified impoundments. *J. Am. Water Works Assoc.* 59:965.
- DeRose, H.R., and A.S. Newman. 1947. The comparison of the persistence of certain plant growth regulations when applied to soil. *Proc. Soil Sci. Soc. Am.* 12:222.
- Environment Canada. 1974. Analytical Methods Manual. Water Quality Branch, Inland Waters Directorate, Ottawa, Canada.
- Fisheries and Environment Canada. 1978a. Water Quality Data, Manitoba (1961-1976). Water Quality Branch, Inland Waters Directorate.
- Fisheries and Environment Canada. 1978b. Surface Water Data, Manitoba 1977. Water Survey of Canada, Inland Waters Directorate.
- Gummer, Wm. D. 1978. Pesticide Monitoring in the Prairies of Western Canada. Inland Waters Directorate, Fisheries and Environment Canada.
- Hemmett, Roland B. Jr., and Samuel D. Faust. 1968. Biodegradation kinetics of 2,4-dichlorophenoxy acetic acid by aquatic microorganisms. Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers, the State University of New Jersey, New Brunswick, N.J.
- Mansell, R.S., and L.C. Hammond. 1971. Movement and adsorption of pesticides in sterilized soil columns. Publication No. 16, Water Resources Center, University of Florida.

Morre, D.J. 1974. Brush Control along Agricultural Drainage Ditches, Environmental Safety and Efficiency of Herbicide Formulations. University of Indiana.
Weed Science Society of America. 1967. Herbicide Handbook of the

Weed Science Society of America. Champaign, Illinois.
Zepp, Richard G., N. Lee Wolfe, John A. Gordon and George L. Baughman. 1975. Dynamics of 2,4-D esters in surface waters. Environ. Sci. Technol. 9:1144.

