

NOTE TO USERS

The original manuscript received by UMI contains pages with slanted print. Pages were microfilmed as received.

This reproduction is the best copy available

UMI

**THE TRANSPORT AND DEPOSITION OF CURRENT USE PESTICIDES AND
PCBs TO SURFACE WATERS IN THE RED RIVER DRAINAGE BASIN**

BY

DOROTHEA FLORENCE KENNY RAWN

**A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of**

Doctor of Philosophy

**Department of Soil Science
University of Manitoba
Winnipeg, Manitoba**

© October, 1998



National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-32019-7

**THE UNIVERSITY OF MANITOBA
FACULTY OF GRADUATE STUDIES

COPYRIGHT PERMISSION PAGE**

**THE TRANSPORT AND DEPOSITION OF CURRENT USE PESTICIDES AND
PCBs TO SURFACE WATERS IN THE RED RIVER DRAINAGE BASIN**

BY

DOROTHEA FLORENCE KENNY RAWN

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University
of Manitoba in partial fulfillment of the requirements of the degree
of
DOCTOR OF PHILOSOPHY**

**Dorothea Florence Kenny ©1998
Rawn**

**Permission has been granted to the Library of The University of Manitoba to lend or sell
copies of this thesis/practicum, to the National Library of Canada to microfilm this thesis
and to lend or sell copies of the film, and to Dissertations Abstracts International to publish
an abstract of this thesis/practicum.**

**The author reserves other publication rights, and neither this thesis/practicum nor
extensive extracts from it may be printed or otherwise reproduced without the author's
written permission.**

ABSTRACT

Rawns, Dorothea Florence Kenny. Ph.D. The University of Manitoba, August, 1998. The transport and deposition of current use pesticides and PCBs to surface waters in the Red River drainage basin. Major Professor; Derek C.G. Muir.

Pesticide concentrations were determined in surface water, precipitation and air over a four-year period in the South Tobacco Creek Watershed, a small (70 km²) agricultural watershed in southern Manitoba, Canada. The objectives of this project were to determine pesticide temporal trends in rivers and streams in southern Manitoba and to relate concentrations to pesticide use patterns. Samples were collected on a weekly basis between 1993 and 1995. During 1996, sample collection frequency was increased to a two-day schedule. PCBs also were measured in atmospheric and water compartments in the watershed. As part of a larger spectrum examination of pesticide levels in Manitoba surface waters, the Red River and its tributaries were sampled. Sample collection in 1993 was performed once every three weeks and sampling frequency between 1994 and 1995 was biweekly.

Temporal trends of pesticides in the South Tobacco Creek Watershed generally reflected regional uses of each chemical, with maximum concentrations occurring during and extending beyond regional application periods. Creek water concentrations of pesticides were consistently at maximum levels when both precipitation and air concentrations were elevated. During the period of high pesticide concentrations in the precipitation and air,

water flow was low in South Tobacco Creek and no overland flow events were observed, indicating that atmospheric compartments were significant contributors to pesticide loadings.

Results in the Red River and its tributaries were similar to observations in the South Tobacco Creek Watershed, with maximum pesticide concentrations occurring during regional application times. The widely used phenoxyacid herbicides were detected in river water at highest concentrations, however, minor use products were observed. A notable exception observed between the small watershed and the Red River was the detection of alachlor in the Red River, although it is not used in Canada. It is, however, applied in the Red River drainage basin within the US which indicates that pesticide usage in the neighbouring states can impact Canadian water quality.

No temporal trends of PCBs were observed in South Tobacco Creek water, however, seasonal differences in air concentrations were observed. Air concentrations were correlated with temperature, indicating PCB sources were volatilization from soil and plant surfaces. PCB concentrations in the water column were higher than anticipated, based on levels observed in large lakes. These elevated concentrations may reflect PCB inputs to the watershed via surface runoff, in addition to direct atmospheric deposition of these chemicals to the water surface.

ACKNOWLEDGMENTS

I thank Derek Muir for giving me the opportunity to study environmental chemistry under his direction. I have had exposure to a broad spectrum of ideas and have grown in many ways under his guidance. His imagination and persistence secured the funding that carried this project to its completion.

I thank each member of my advisory committee, who encouraged me and still found the ways and means to challenge me at every turn. Geza Racz has been supportive of me throughout my tenure as a graduate student and has always had an open door for discussions. Lyle Lockhart has not only served as an advisor in my program, but he has encouraged me when I was finding myself overwhelmed and helped me look at things from new perspectives. Brian Amiro has consistently been helpful and made himself available to answer questions and to provide comments and support throughout my program of study. I thank Don Mackay for sitting as the External Examiner of my thesis.

The Deerwood Soil and Water Management Association and landowners provided me with the land use data needed for the interpretation of the results. Bill Turner (Deerwood Soil and Water Management Association), Bob Woychuk (Environment Canada) and Dale Stepler (landowner, Deerwood Soil and Water Management Association) consistently provided sampling assistance and advice whenever it was needed. Air mass back trajectories and interpretation were provided by Bevan Lawson (Atmospheric Environment Service).

Jim Yarotski (Prairie Farm Rehabilitation Agency), Claire Bowden and Carol Walker (Water Survey of Canada) provided detailed hydrology information for the South Tobacco Creek and the rivers in southern Manitoba. Pesticide use data for southern Manitoba were provided by Doug Wilcox (Manitoba Crop Insurance Corporation).

I have had great pleasure in working with Thor Halldorson, who was my assistant throughout my program of study. I also received a great deal of assistance from three helpful summer students, Jeff Billeck, Alex Muir and Debbie Armstrong. I received additional assistance from Steven Kotowich in the air sample preparation. Each of these people played a key role in sample collection and processing.

Funding for this project was provided by the Systems and Monitoring Branch and the Environmental Conservation Branch of Environment Canada. Additional funding was provided by the Canada-Manitoba Agreement on Agricultural Sustainability (CMAAS). I thank the University of Manitoba for a Graduate Fellowship.

Although I am a graduate student of the Department of Soil Science, I conducted my research at the Freshwater Institute where I received assistance and support from many people including Brian Billeck, Bob Danell and Gary Stern. During my time at the Freshwater Institute, however, I found constant support and help from my very dear friend Bert Grift who is not only a gifted chemist, but also someone who helped to keep me going.

I thank my family for their caring and support throughout this marathon program. My husband has given me more patience and understanding throughout the duration of this exercise than I can express and for that I am eternally grateful.

FOREWORD

This thesis has been formatted to the manuscript style and contains five individual manuscripts. Two of the manuscripts, presented in this document as Chapter Three (A multi-year study of four herbicides in surface water of a small prairie watershed, authored by: D.F.K. Rawn, T.H.J. Halldorson, W.N. Turner, R.N. Woychuk, J-G. Zakrevsky and D.C.G. Muir) and Chapter Four (A multi-year study of four herbicides in air and precipitation from a small prairie watershed, authored by D.F.K. Rawn, T.H.J. Halldorson, B.D. Lawson and D.C.G. Muir) have been submitted to the Journal of Environmental Quality for publication as a paired set. Chapter Five (Atmospheric transport and deposition, an additional input pathway for atrazine to surface waters, authored by D.F.K. Rawn, T.H.J. Halldorson and D.C.G. Muir) is published in the American Chemical Society Symposium series Book 683 entitled "Triazine Herbicides: Risk Assessment". The fourth manuscript, presented as Chapter Six (Pesticides in the Red River and its tributaries in southern Manitoba, 1993-1995, authored by D.F.K. Rawn, T.H.J. Halldorson, R.N. Woychuk and D.C.G. Muir), has been submitted to the Water Quality Research Journal of Canada. The final manuscript, Chapter Seven (Polychlorinated biphenyls in a rural watershed in the southern prairie region of Canada, authored by D.F.K. Rawn, T.H.J. Halldorson, B.D. Lawson and D.C.G. Muir) has been accepted for publication in Environmental Pollution.

Each manuscript presented in this thesis was written using the results of my graduate

research under the direction of Dr. Derek C.G. Muir. Although I am the senior author of each manuscript, I have included Thor Halldorson as a second author because he has worked with me consistently in the field and in the laboratory on this project as a summer student, contractor and technician. Derek Muir, who has supervised this research, also is present on each manuscript in the thesis.

Other coauthors have been included when special assistance was received. Where help in the interpretation of air movements was needed, Bevan Lawson, from the Atmospheric Environment Service in Winnipeg, provided assistance and has been included as an author on the original papers. Additionally, technical assistance and support in the field was provided by R.N. Woychuk and W.N. Turner, who have been recognized by coauthorships on the appropriate papers. Funding and data crucial to the interpretation of herbicide movement in surface waters were provided by Jean-Guy Zakrevsky, who is also included as a coauthor.

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ACKNOWLEDGMENTS	iv
FOREWORD	vi
LIST OF TABLES	xii
LIST OF FIGURES	xv
LIST OF ABBREVIATIONS	xviii
1. INTRODUCTION	1
2. LITERATURE REVIEW	4
2.1 Pathways of Pesticides and PCBs to Surface Waters	4
2.1.1 Surface Runoff	4
2.1.2 Leaching	8
2.1.3 Atmospheric Pathways	10
2.1.3.1 Washout via Precipitation	12
2.1.3.2 Dry Deposition	15
2.1.3.3 Gas Exchange	19
2.2 Pesticides	25
2.2.1 Pesticide Contamination of Surface Waters	25
2.2.2 Pesticides in the Atmosphere	41
2.2.2.1 Air	41
2.2.2.2 Precipitation	46
2.3 Polychlorinated Biphenyls	50
2.3.1 PCB Contamination of Surface Waters	51
2.3.2 PCBs in the Atmosphere	56
2.3.2.1 Air	56
2.3.2.2 Precipitation	61

3. A MULTI-YEAR STUDY OF FOUR HERBICIDES IN SURFACE WATER OF A SMALL PRAIRIE WATERSHED	63
3.1 Abstract	63
3.2 Introduction	64
3.3 Materials and Methods	68
3.3.1 Sample Collection	68
3.3.2 Sample Analysis	70
3.4. Results	72
3.4.1 Temporal Patterns	72
3.4.2 Herbicides in Runoff from the Twin Watershed	78
3.4.3 Herbicides in Spring Runoff	78
3.4.4 Application and Post-Application Period	81
3.5 Discussion	83
3.6 Conclusions	91
4. A MULTI-YEAR STUDY OF FOUR HERBICIDES IN AIR AND PRECIPITATION FROM A SMALL PRAIRIE WATERSHED	93
4.1 Abstract	93
4.2 Introduction	94
4.3 Materials and Methods	96
4.3.1 Sample Collection	96
4.3.2 Sample Analysis	97
4.4. Results	99
4.4.1 Air	99
4.4.2 Precipitation	105
4.5 Discussion	108
4.6 Conclusions	116
5. ATMOSPHERIC TRANSPORT AND DEPOSITION, AN ADDITIONAL INPUT PATHWAY FOR ATRAZINE TO SURFACE WATERS	118
5.1 Abstract	118
5.2 Introduction	118
5.3 Materials and Methods	127
5.3.1 Watershed Description	127
5.3.2 Sample Collection	129
5.3.3 Sample Analysis	130
5.3.4 Quality Assurance	131
5.4 Results and Discussion	131
5.4.1 Air	131
5.4.2 Water	133

5.4.3 Precipitation	135
5.4.4 Sources	136
5.4.5 Flux	140
5.5 Conclusions	147
6. PESTICIDES IN THE RED RIVER AND ITS TRIBUTARIES IN SOUTHERN MANITOBA: 1993-1995	149
6.1 Abstract	149
6.2 Introduction	150
6.3 Materials and Methods	154
6.3.1 Sample Collection	154
6.3.2 Sample Extraction and Cleanup	155
6.3.3 Sample Analysis	155
6.3.4 Pesticide Use Estimates	157
6.3.5 Discharge Estimates	157
6.4 Results	158
6.4.1 Pesticide and Nutrient Concentrations	158
6.4.2 Pesticide Use	181
6.4.3 Temporal Trends	183
6.5 Discussion	191
6.5.1 Pesticide Loadings	195
6.5.2 Mass Balance	203
6.5.3 Water Quality	205
6.6 Conclusions	206
7. POLYCHLORINATED BIPHENYLS IN A RURAL WATERSHED IN THE SOUTHERN PRAIRIE REGION OF CANADA	208
7.1 Abstract	208
7.2 Introduction	209
7.3 Materials and Methods	211
7.3.1 Sample Collection	211
7.3.2 Sample Analysis	214
7.3.3 Data Analysis	215
7.3.4 Quality Assurance/Quality Control	215
7.4. Results and Discussion	216
7.4.1 Air-Temperature Relationships	225
7.4.2 Sources	227
7.4.3 Air-water Gas Exchange	227
7.4.4 Mass Balance	235
7.5 Conclusions	242

8. GENERAL DISCUSSION	243
8.1 Surface Water	243
8.1.1 Temporal Trends	243
8.1.2 Riverine Inputs from Other Regions	246
8.1.3 Water Quality Guidelines	247
8.2 Atmospheric Compartments	248
8.2.1 Temporal Trends	248
8.2.2 Long Range Transport	249
8.2.3 Correlations	250
8.2.4 Flux	251
9. CONCLUSIONS	254
10. CONTRIBUTION TO KNOWLEDGE	257
11. REFERENCES	259
12. APPENDICES	278
I. Pesticide Method Detection Limits	279
II. Pesticide Concentrations in South Tobacco Creek Water	280
III. Pesticide Concentrations in Precipitation in the South Tobacco Creek Watershed	290
IV. Pesticide Concentrations in Air in the South Tobacco Creek Watershed	294
V. Pesticide Concentrations in the Red River and Tributaries	302
VI. PCB Concentrations in South Tobacco Creek Water	342
VII. PCB Concentrations in Precipitation in the South Tobacco Creek Watershed	360
VIII. PCB Concentrations in Air in the South Tobacco Creek Watershed	369

LIST OF TABLES

Table	Page
2.1 Canadian water quality guidelines for the protection of freshwater aquatic life for the 16 pesticides in this review	27
2.2 Physical properties of the pesticides under investigation	32
3.1 Comparison of the chemical properties of the well-studied neutral compound atrazine with three phenoxyacid and one phenolic herbicide used in this study	65
3.2 Herbicide concentrations observed in field runoff events at the Twin Watershed site	79
3.3 Comparison of Canadian and German guideline values for protection of freshwater aquatic life with maximum concentrations (ng/L) measured in South Tobacco Creek	84
3.4 Seasonal discharge via South Tobacco Creek compared with amounts of each chemical applied within the South Tobacco Creek Watershed	90
4.1 Maximum concentrations (pg/m ³) of each herbicide observed in ambient air	102
4.2 Seasonal precipitation fluxes (g) to the South Tobacco Creek water surface and land surface of the watershed	114
4.3 The contribution of herbicide inputs via precipitation to total discharge from the South Tobacco Creek	114
5.1 Physical/chemical properties related to atmospheric behaviour of triazines	121
5.2 Recent observations of atrazine in precipitation	122
5.3 Atrazine in ambient air	126
5.4 Precipitation weighted atrazine concentrations	136

5.5	Average monthly conditions during sample times in the South Tobacco Creek Watershed (STCW) and the Experimental Lakes Area (ELA)	144
5.6	Seasonal flux estimates for the South Tobacco Creek Watershed (STCW) 1994-1995 with Experimental Lakes Area (ELA) results	145
5.7	Comparison with other predicted or observed fluxes for atrazine	146
6.1	Effective drainage area of the tributaries on the Canadian side of the Red River	152
6.2	Pesticide recovery from spiked water samples and method detection limits for individual pesticides	156
6.3	Pesticide concentrations (ng/L) in the Red River and tributaries	159
6.4	Correlation coefficients between pesticides, nutrients and water flow in six watersheds	179
6.5	Water quality parameters for the Red River and tributaries during 1993-1995 ..	180
6.6	Estimates of the amount (kg) of pesticide used in six watersheds of southern Manitoba	182
6.7	Seasonal discharge (m ³) of water and estimates of discharge (g) of six pesticides in the tributaries of the Red River	197
6.8	Seasonal discharge (m ³) of water and estimates of discharge (kg) of nine pesticides at each sampling station in the Red River	198
6.9	Discharge losses in the six small rivers as a percentage of applied levels in each watershed during 1994-1995	202
7.1	Average PCB concentration in air (pg/m ³), creek water (pg/L) and precipitation (pg/L) in the South Tobacco Creek Watershed during the 1994 and 1995 seasons	217
7.2	Correlation parameters for PCBs (of the form $\log C(\text{pg/m}^3) = b + m/T$)	226
7.3	Average monthly conditions during paired air-water sample collections in the South Tobbaco Creek Watershed (1994-1995)	229

7.4	Average PCB air-water gas exchange ($\text{ng}/\text{m}^2\cdot\text{d}$) across the South Tobacco Creek (\pm S.D. of the six monthly averages)	232
7.5	Comparison of Σ PCB gas exchange with other studies	233
7.6	Seasonal flux estimates (mg) of representative PCBs to the South Tobacco Creek water	239
8.1	Uncertainty in predicting atmospheric inputs into surface waters for PCBs and atrazine	253

LIST OF FIGURES

Figure	Page
2.1 Pathways of chemical movement into rivers or stream systems	11
2.2 Removal of atmospheric species in the gas phase and associated with particles via wet deposition	13
2.3 Removal of atmospheric species via dry deposition	17
2.4 The two-film model for gas exchange of organic contaminants	21
2.5 The surface renewal model for gas exchange of organic contaminants	22
3.1 Location of the South Tobacco Creek Watershed	66
3.2 Map of the South Tobacco Creek Watershed	69
3.3 Nutrient loading in the South Tobacco Creek 1993-1996	73
3.4 2,4-D concentrations in the dissolved phase of the South Tobacco Creek	74
3.5 MCPA concentrations in the dissolved phase of the South Tobacco Creek	75
3.6 Dichlorprop concentrations in the dissolved phase of the South Tobacco Creek . .	76
3.7 Bromoxynil concentrations in the dissolved phase of the South Tobacco Creek . .	77
3.8 2,4-D and dichlorprop concentrations in 1994 in the South Tobacco Creek Watershed	86
3.9 MCPA and bromoxynil concentrations in 1995 in the South Tobacco Creek Watershed	87
3.10 MCPA and 2,4-D concentrations in 1996 in the South Tobacco Creek Watershed	88

4.1	MCPA concentrations in air (Σvapour and particulate phases) in the South Tobacco Creek Watershed	100
4.2	Dichlorprop concentrations in air (Σvapour and particulate phases) in the South Tobacco Creek Watershed	101
4.3	2,4-D concentrations in air (Σvapour and particulate phases) in the South Tobacco Creek Watershed	103
4.4	Bromoxynil concentrations in air (Σvapour and particulate phases) in the South Tobacco Creek Watershed	104
4.5	2,4-D and bromoxynil concentrations in precipitation in the South Tobacco Creek Watershed 1993-1996	106
4.6	Dichlorprop and MCPA concentrations in precipitation in the South Tobacco Creek Watershed 1993-1996	107
4.7	24 hour air mass trajectories prior to sampling events on June 13, 1994 and June 19, 1994	110
5.1	Atmospheric inputs and loss pathways of atrazine in agricultural watersheds ...	120
5.2	South Tobacco Creek Watershed and Experimental Lakes Area locations	128
5.3	Atrazine concentrations - 1995 in South Tobacco Creek water, ambient air in the South Tobacco Creek watershed and Experimental Lakes Area	132
5.4	Atrazine concentrations (ng/L) in precipitation samples collected in the South Tobacco Creek Watershed and Experimental Lakes Area	134
5.5	Air mass back trajectories to the South Tobacco Creek Watershed and the Experimental Lakes Area	138
5.6	Atrazine temperature relationships	139
6.1	Red River drainage basin indicating sampling locations along the Red River and tributaries	151
6.2	MCPA, bromoxynil and 2,4-D concentrations in the Assiniboine River, LaSalle River, Morris River and Pembina River during 1994 and 1995	184

6.3	MCPA, bromoxynil and 2,4-D concentrations in the Rat River, Roseau River and Seine River during 1994 and 1995	185
6.4	MCPA, bromoxynil and 2,4-D concentrations in the Red River at Emerson, Ste. Agathe and Selkirk during 1994 and 1995	186
6.5	Atrazine, chlorpyrifos and trifluralin concentrations in the Assiniboine River, LaSalle River, Morris River and Pembina River during 1994 and 1995	187
6.6	Atrazine, chlorpyrifos and trifluralin concentrations in the Rat River, Roseau River and Seine River during 1994 and 1995	188
6.7	Atrazine, chlorpyrifos and trifluralin concentrations in the Red River at Emerson, Ste. Agathe and Selkirk during 1994 and 1995	189
7.1	The South Tobacco Creek Watershed	212
7.2	Relative contributions to total PCBs in the South Tobacco Creek Watershed ..	221
7.3	CB 8,18 and 28 concentrations in air and water in the South Tobacco Creek Watershed in 1994 and 1995	222
7.4	CB 64, 99 and 138 concentrations in air and water in the South Tobacco Creek Watershed in 1994 and 1995	223
7.5	Air mass back-trajectories to the South Tobacco Creek Watershed	228

LIST OF ABBREVIATIONS

cm	centimetre
cm ²	square centimetre
cm ³	cubic centimetre
d	day
g	gram
h	hour
ha	hectare
K	Kelvin
kg	kilogram
L	litre
m	metre
m ²	square metre
m ³	cubic metre
μg	microgram
mL	millilitre
ng	nanogram
pg	picogram
s	second
Σ	sum of (total)

1. INTRODUCTION

Traditionally, surface runoff has been considered the major route of entry of pesticides into river systems. The highest concentrations of pesticides measured in runoff generally occur during the first major runoff event following application (Wauchope, 1978). Many studies, particularly in the US midwest, have been performed to determine pesticide losses via this pathway and reviews of this research are available (Wauchope, 1978; Leonard, 1988). In Manitoba, Muir and Grift (1987) found that pesticides were lost from agricultural land resulting in contamination of rivers following rainfall events which produced overland flow. Beck et al. (1992) observed pesticide residues in the Stephenfield reservoir following major runoff events. These studies established that surface runoff from agricultural use of pesticides contributed to pesticide loads in Manitoba surface waters. However, they did not continue over a period of years sufficient to define and confirm temporal trends.

Major rivers and some of their tributaries in Manitoba have been monitored routinely for pesticide levels by various provincial and federal monitoring programs (Currie and Williamson, 1995). Although these programs have reported pesticide residues in surface waters, sampling frequency has been restricted to monthly, seasonal or even annual collection. Defining temporal trends and identifying factors which influence levels of pesticides in Manitoba river systems is difficult with the limited sampling schedules used for these routine monitoring studies.

Recent studies have shown that atmospheric pathways also are significant routes of deposition of persistent organic pollutants, such as the older organochlorine insecticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) to soil, plant and water surfaces (Jeremiason et al., 1997; Hornbuckle et al., 1995; McLachlan et al., 1995; Franz and Eisenreich, 1993; McConnell et al., 1993; Bacci et al., 1990; Swackhamer et al., 1988). Research in the Great Lakes region and Chesapeake Bay has repeatedly shown the significance of atmospheric deposition of persistent organic contaminants to large lakes (Achman et al., 1993; Eisenreich and Strachan, 1992; Baker and Eisenreich, 1990). There is less information on direct atmospheric inputs to rivers.

Although current use pesticides have been detected in atmospheric compartments (precipitation, vapour and associated with particles) (Chevreuil and Garmouma, 1993; Nations and Hallberg, 1992; Richards et al., 1987), their deposition to aquatic environments via these pathways have been studied only to a limited extent (Goolsby et al., 1994; Glotfelty et al., 1990). Atmospheric levels of persistent, current use herbicides have been shown to contribute to pesticide loads in river systems in Maryland during application periods (Glotfelty et al., 1990). Precipitation samples collected in regions of high pesticide usage have been shown to contain higher concentrations than locations remote from use (Goolsby et al., 1995). Atmospheric transport and deposition of pesticides has been shown to occur in Switzerland and Germany (Bester et al., 1995; Buser, 1990). Buser (1990) concluded that atmospheric deposition was a major pathway of atrazine to alpine lakes. Similarly, Muir and Grift (1995) found that atmospheric deposition was important for pesticide entry into lakes from a remote area of northwestern Ontario.

The objectives of this study were to establish the temporal trends of pesticides in streams and rivers of southern Manitoba and to relate pesticide concentrations in these surface waters to regional pesticide usage and water flow. The use of pesticides to control weeds, insects and other pests is widespread in southern Manitoba because it is considered essential for increased crop production by the majority of agricultural producers. The Canadian prairie region is a much drier environment than the US midwest and, therefore, atmospheric deposition processes may be of greater importance than runoff. Measurements of pesticides in surface water samples and the atmospheric compartments, air and precipitation from a small southern Manitoba watershed were performed between 1993 and 1996, and in the Red River and its tributaries between 1993 and 1995, to establish the significant pathways of pesticide entry into surface waters in southern Manitoba.

Atmospheric levels of PCBs are typically lower than observed for current use pesticides during application periods (Hoff et al., 1992a). Atmospheric concentrations of PCBs have been identified as a significant source of contamination in large lakes (McConnell et al., 1996; Hornbuckle et al., 1995; Achman et al., 1993; Iwata et al., 1993; Baker and Eisenreich, 1990). The concentrations of PCBs in Manitoba river waters have been below method detection limits in previous monitoring studies, although they have been detected in river sediments and in aquatic invertebrates (Chacko et al., 1991). PCB levels in both surface water and atmospheric compartments in a small watershed in southern Manitoba also were established as part of this study to determine which deposition pathways were significant in comparison to current use pesticides.

2. LITERATURE REVIEW

The objective of this thesis was to describe the transport and deposition of current use pesticides and polychlorinated biphenyls (PCBs) to surface waters via atmospheric compartments: air and precipitation. The review of literature, however, has been restricted to the 16 pesticides under investigation in the research program and to PCBs in abiotic compartments. These chemicals were chosen for study because they were either a) extensively used products in southern Manitoba or b) not widely used in Manitoba, but widely used in the neighbouring US states or c) belong to a class of pesticides known to persist in soil and subject to long range transport and deposition. This review of the literature supports the research goals, in that it describes previous studies that have discussed the pathways by which pesticides and PCBs may be deposited to surface waters. In addition, observations on the levels of these pesticides and PCBs in surface water, air and precipitation are discussed. Emphasis has been placed on recently reported literature (late 1980s - 1990s).

2.1 Pathways of Pesticides and PCBs to Surface Waters

2.1.1 Surface Runoff

Surface runoff generally has been considered to be the most important mechanism of pesticide loss from treated fields. During periods of rain or snow melt, the available water may exceed the soil infiltration capacity and lead to surface runoff events which can transport

pesticides off site (Hillel, 1982). Pesticides lost from field surfaces during overland flow events are available for entry into rivers, streams and lakes. Pesticides are considered to be available for loss through surface runoff if they are present in the top one cm of the soil (Leonard, 1988). Losses through this pathway include dissolved and particle sorbed phases (Squillace and Thurman, 1992; Leonard, 1988). The highest concentrations of pesticides detected in runoff generally occur in the first significant runoff event following application (Wauchope, 1978). Climatic conditions, soil properties and characteristics of the pesticide all influence the amount of chemical lost via runoff (Wauchope, 1978). Because surface runoff occurs during periods when water exceeds soil infiltration capacity, rainfall intensity and duration have a direct impact on runoff losses (Hillel, 1982). Soil texture can also influence the rate of runoff. For example, higher runoff occurs on fine textured soil than on coarse textured soils because of increased soil infiltration in coarse textured soils (Buttle and Harris, 1991; Leonard, 1988). Surface crusting and compaction of soil reduces infiltration rates, thereby resulting in increased runoff (Hillel, 1982). Elevated water content in soil and slope of land additionally result in increased runoff potential. Chemical specific factors such as water solubility, persistence or biodegradability and soil sorption characteristics will determine the degree of pesticide loss during overland flow periods (Wauchope and Leonard, 1980). Pesticide formulations and application rates have been shown to affect losses during runoff events, with wettable powders resulting in greatest losses (Wauchope and Leonard, 1980). Tillage practices have little effect on pesticide losses through surface runoff, however, banded applications reduce pesticide concentrations in runoff (Gaynor et al., 1995).

Many studies have been performed to determine the significance of surface runoff

losses, relative to applied levels. Pesticide losses through surface runoff are considered catastrophic if they exceed 2% of applied levels during any single event (Wauchope, 1978). Generally, losses are found to be <1% of applied amounts (Leonard, 1988).

Pesticide losses from treated fields via surface runoff have been studied in many regions of Canada (Cessna et al., 1997; Gaynor et al., 1995; Gaynor and van Wesenbeeck, 1995; Waite et al., 1992). In a small prairie watershed in Saskatchewan, pesticide concentrations were higher in runoff (<0.05 - 2.0 $\mu\text{g/L}$) from agricultural fields than in ponds (<0.05 - 0.51 $\mu\text{g/L}$) receiving overland flow runoff (Waite et al., 1992). In the same study, pesticide concentrations in surface waters were below levels measured in groundwater samples (<0.05 - 4.9 $\mu\text{g/L}$), indicating infiltration of these chemicals from surface water was not the source for pesticides detected in groundwater (Waite et al., 1992).

Pesticide runoff has been studied extensively for many years and losses from agricultural fields can be estimated using models such as CREAMS (Chemicals, Runoff and Erosion from Agricultural Management Systems) (Knisel, 1980), which was developed for the US Department of Agriculture and SWRRB (Simulator for Water Resources in Rural Basins), which is a US Environmental Protection Agency (EPA) model. These models are based on soil water balance. The main equation in the SWRRB model is:

$$SW_t = SW + P - Q - ET - O - QT \quad [1]$$

where SW is the starting soil moisture and SW_t is the soil moisture at time t , following a rainfall event, P is equal to the amount of rainfall received, Q is the amount of runoff, $ET =$

evapotranspiration, O = the percolation below the root zone and QR = the amount of return flow (SWRRB Manual, 1985). Many of these models, including SWRRB, can be used to estimate the amount of pesticide leached into the soil profile in addition to runoff.

The pesticide component used in the SWRRB model includes equations for describing pesticide deposition to soil and plant interception of sprayed material. The amount of pesticide reaching the soil (PE) is determined using the relationship:

$$PE = PA \cdot \alpha \quad [2]$$

where PA is the actual amount applied and α is the fraction of the pesticide actually reaching the ground, resulting from losses via spray drift and volatilization. The total amount of chemical reaching the soil is also related to the fraction of ground covered by plants with the relationship:

$$FP = GC \cdot PE \quad [3]$$

where GC is the fraction of the ground covered by plants, which is a function of leaf area index and FP = the fraction of pesticide intercepted by the plants. The amount of pesticide reaching the ground (GP) is then determined by the relationship:

$$GP = PE - FP. \quad [4]$$

Increased amounts of pesticide are expected to reach the ground during storm events and, therefore, the amount of washoff (WO) may be estimated for a pesticide by:

$$WO = WOF \cdot FP \quad [5]$$

where WOF is the fraction of pesticide washed off of foliage (SWRRB Manual, 1985). Pesticide degradation in the soil and on plants is calculated using first order kinetics.

The model output includes daily precipitation, runoff, sedimentation yield and amount of pesticide leached. Separate estimates of the amount of pesticide in both the dissolved phase and sorbed to sediment in runoff is also reported, in addition to evapotranspiration, percolation, peak runoff rate, water yield, return flow storage and soil water (SWRRB Manual, 1985).

2.1.2 Leaching

Loss of pesticides as a result of movement through the soil profile into the water table has been studied for many years. Leaching occurs when the water entering the soil profile exceeds the soil-water deficit, therefore, the amount of water in excess of the deficit will lead to downward movement, or leaching (Rao, et al., 1988). Soil texture and moisture level in addition to pesticide factors such as persistence (i.e., half-life) in soil, and soil sorption coefficients (K_d), are controlling variables in the downward movement of pesticides through the soil profile. Increased soil microbial activity will reduce the pesticide movement through the soil profile, however, the result may be leaching of pesticide metabolites (Jayachandran et al., 1994). Pesticide soil adsorption will reduce downward movement, through binding

to soil particles in the soil profile (Rao et al., 1988).

Potential contamination of groundwater has been a concern in many regions, particularly where groundwater sources are used for drinking water. Groundwater return flow may contribute to surface water concentrations of pesticides if groundwaters themselves are contaminated. In the US midwest, where pesticides frequently have been detected in groundwater samples, a large study was conducted to determine levels of highly used products and their major degradation products in well water (Kolpin et al., 1996). Herbicide metabolites were most frequently detected in well water samples, rather than the parent compound (Kolpin et al., 1996). Jayachandran et al. (1994) determined atrazine, and its major degradation products deethylatrazine (DEA) and deisopropylatrazine (DIA), levels in tile drainage and groundwater samples collected in Iowa and found that Σ atrazine losses ranged from 1.2-1.4% of applied levels. The ratio of DEA to atrazine (DAR), in soil water samples has been used to determine the source of herbicide contamination (Adams and Thurman, 1991). Nonpoint source contamination, such as leaching, was indicated by high DAR values, corresponding to increased time for soil microbes to degrade atrazine. A low DAR value, conversely indicated elevated levels of atrazine to that of DEA, which would only be possible in situations where the microbial populations have not had an opportunity to degrade atrazine, therefore, indicating point source contamination (Adams and Thurman, 1991). In another study, inverse relationships between sulfate and chloride concentrations with herbicide concentrations indicated surface runoff, rather than groundwater contributions was the major pathway to the Minnesota River (Schottler et al., 1994).

Another nonpoint source of pesticide contamination results from drift during

pesticide application. Although the majority of chemical lost via spray drift is deposited within a short distance from the treated area, some remains in the atmosphere available for transport downwind of the treated region (Majewski and Capel, 1995). Many factors affect the level of spray drift, however, the major considerations are method of application, formulation type and specific equipment (Majewski and Capel, 1995).

Volatilization of pesticides from treated fields, surface waters and plant surfaces may occur, resulting in the introduction of chemicals into the troposphere. The degree of loss via this mechanism is related to a chemical's vapour pressure and its availability for volatilization which is dependent upon its rate of diffusion below the soil surface (Majewski et al., 1993).

2.1.3 Atmospheric Pathways

Atmospheric concentrations of pesticides and other persistent organic pollutants (POPs) are generally found at elevated levels in regions where they are used, however, long range transport of chemicals from regions of use to non-target areas has been observed (Hillery et al., 1997; Stern et al., 1997; Oehme et al., 1996; Hoff et al., 1992a; Hoff et al., 1992b). Pesticides and other persistent organic chemicals, including PCBs, present in the overlying atmosphere may be deposited directly to water surfaces through one of three pathways: precipitation, dry deposition and gas absorption (Figure 2.1) (Eisenreich and Strachan, 1992). Deposition of chemicals to soil and plant surfaces may occur, rather than to water surfaces, which may ultimately contribute to contaminant loads of surface waters draining a watershed (Figure 2.1). Atmospherically deposited contaminants are available to move into surface waters via runoff during overland flow events, associated with both the

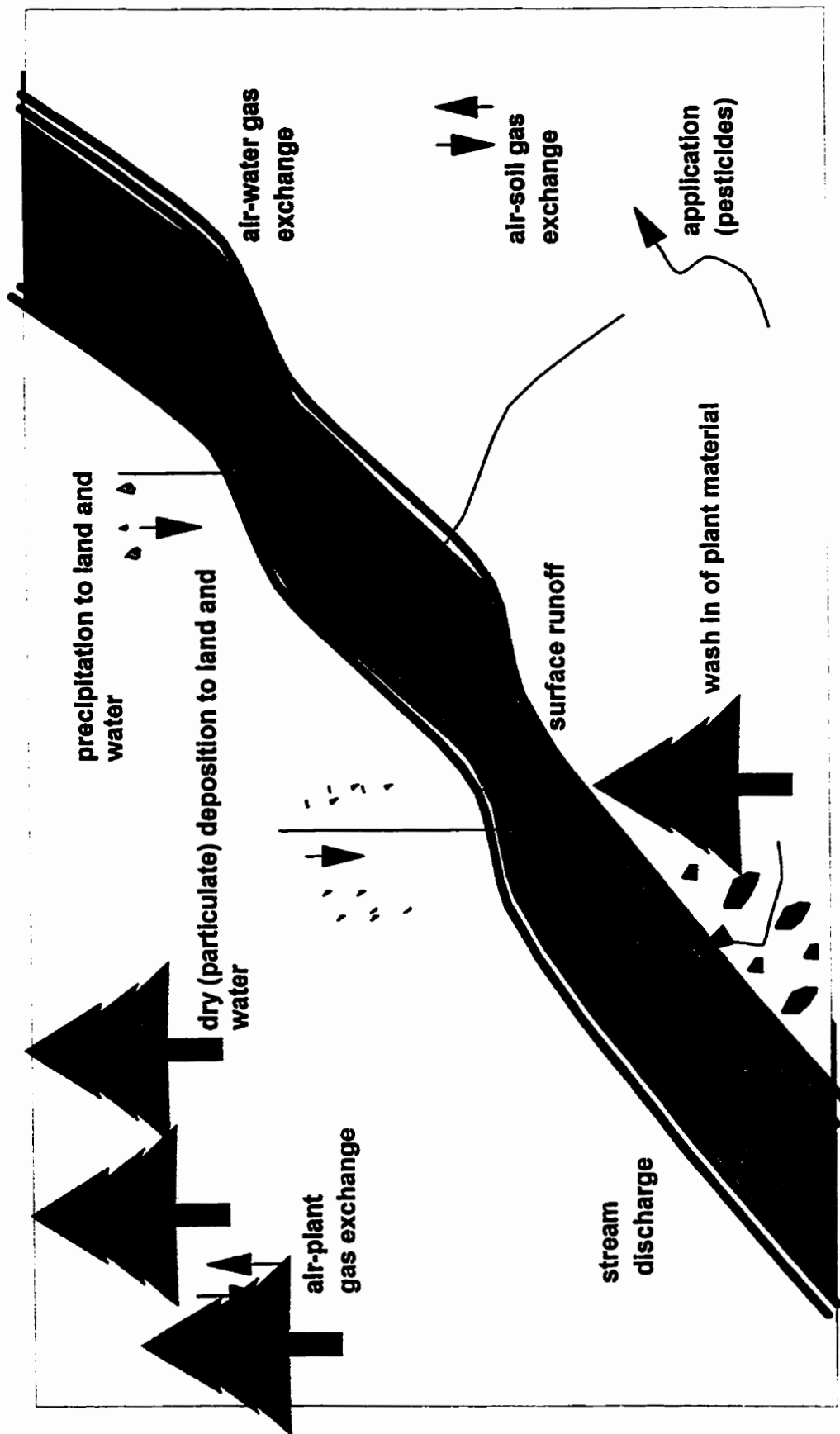


Figure 2.1 Pathways of chemical movement into rivers or stream systems.

particulate and dissolved phases, or sorbed to plant material. Presently, the majority of studies examining atmospheric deposition have been performed using highly persistent chemicals, such as the older organochlorine insecticides and PCBs, although atmospheric deposition of current use pesticides is becoming increasingly well studied (Hoff et al., 1996; Goolsby et al., 1995; Eisenreich and Strachan, 1992).

2.1.3.1 Washout via Precipitation. Removal of chemicals from the atmosphere can occur through wet deposition present as rainfall, snowfall or during fog events in both the gas phase and associated with particulates (Figure 2.2) (Hoff et al., 1996; Poster and Baker, 1996; Hoff et al., 1995; Schomburg et al., 1991). Chemicals present in the vapour phase may be dissolved into water droplets. This process may occur during both droplet formation and as the droplet falls through the air column, known as in-cloud scavenging and below cloud scavenging, respectively (Poster and Baker, 1996). In general, the dissolution of organic chemicals in the vapour phase is inversely related to a compound's air-water partition coefficient, or Henry's Law Constant (H) (Bidleman, 1988). If H is sufficiently high, the chemical in the vapour phase will remain in the air, rather than be dissolved into water droplets, and only those chemicals associated with particles in the atmosphere would be subject to washout during precipitation events (Bidleman, 1988).

Particle scavenging is highly variable and is dependent upon meteorological factors, cloud physics, in addition to particle sizes in the air column and chemical composition of the particles themselves (Bidleman, 1988; Franz and Eisenreich, 1993). Washout of organic chemicals on particles is generally more efficient on smaller particles (Bidleman, 1988). Scavenging rates increase as particle size increase theoretically, however, this does not

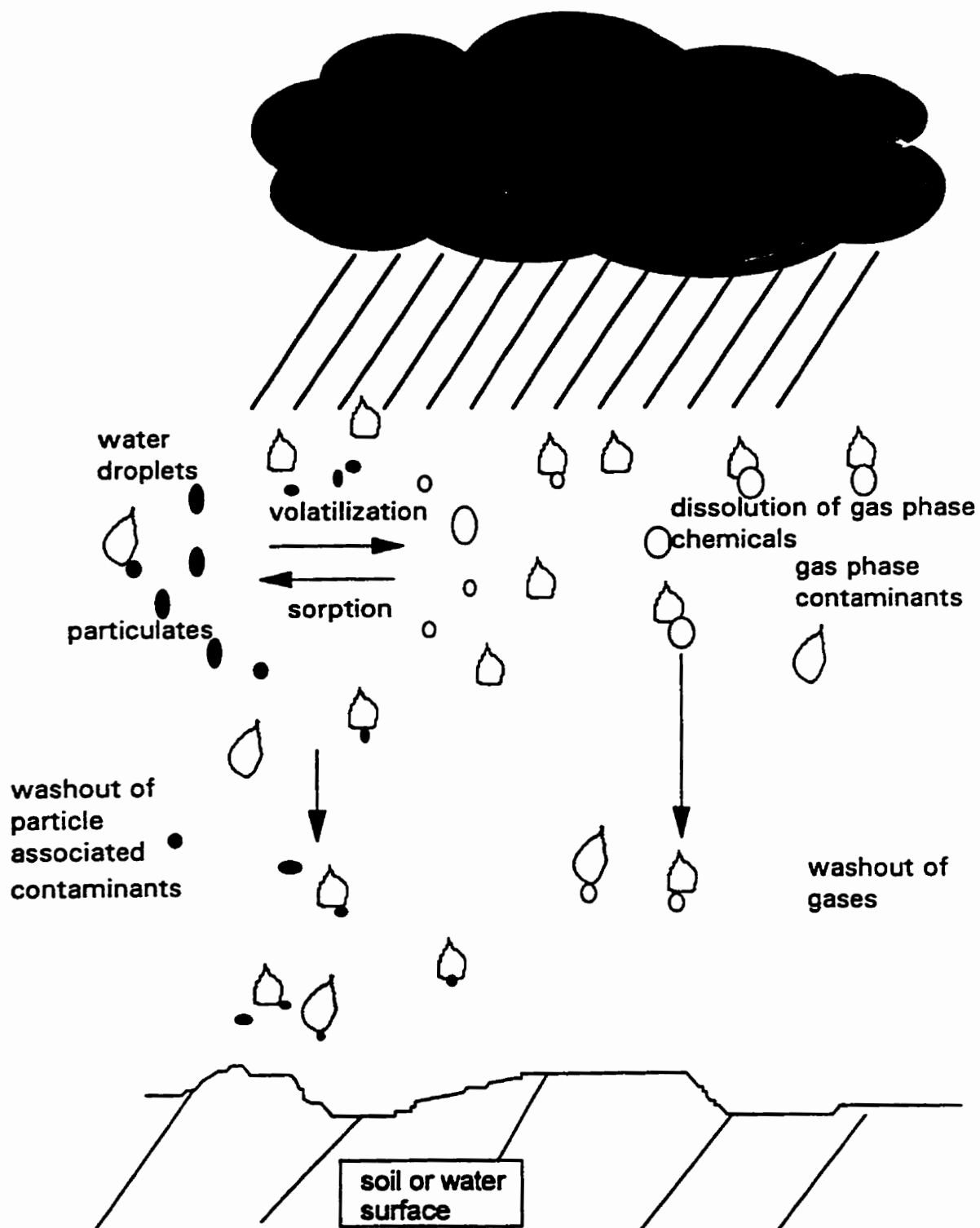


Figure 2.2 Removal of atmospheric species in the gas phase and associated with particles via wet deposition.

always occur (Poster and Baker, 1997). Below cloud scavenging of particles has been shown to decrease as the particle size increases (Franz and Eisenreich, 1993). Efficient scavenging of submicron particles have been shown to occur during rainfall events, which contradicts theoretical estimates (Poster and Baker, 1997). The enrichment of organic chemicals in fog water was observed in part due to the presence of submicron particles in the fog in a Californian study (Schomburg et al., 1991). These conflicts between theoretical and observed washout of particles have yet to be resolved.

Although the majority of wet deposition studies have been performed with rainfall, organic chemicals are efficiently scavenged by snowflakes due to their large surface area and low temperatures (Hoff et al., 1995). Snowflakes undergo change as they pass through the air column and continue to change after they have fallen to a surface where they are subject to compaction, freezing and thawing (Hoff et al., 1995). Chemical (e.g., PCBs) concentrations are reduced in the snow pack relative to fresh snow samples (Gregor et al., 1996).

Deposition of organic chemicals associated with precipitation is the most straight forward atmospheric deposition process (Hoff et al., 1996). Although washout of organic compounds present in both the vapour and aerosol phases occurs, most studies collect both phases together. In general, deposition via precipitation is calculated using the equation (Eisenreich and Strachan, 1992):

$$N_{ppm} = \frac{C_{TP} \cdot \text{Sample Volume (L)}}{S.A. \cdot \# \text{ days sample was collected}} \quad (\text{ng/m}^2 \cdot \text{d}) \quad [6]$$

where N_{ppm} = depositional flux via precipitation, C_{TP} = chemical concentration in precipitation (Σ particle and dissolved phases; ng/L) and S.A. = collection surface area (m^2).

2.1.3.2 Dry Deposition. Deposition of contaminants from the atmosphere occurs via unidirectional dry deposition, which involves removal of chemicals associated with particulate matter, and bidirectional gas exchange (McVeety and Hites, 1988). Dry deposition rates are dependent upon a number of factors, including mass to particle size ratios, total particulate mass, wind speed, turbulence in the atmosphere, surface roughness, erodibility of surfaces, potential sheltering effects and physical-chemical properties of the contaminant (Pirrone et al., 1995; Noll et al., 1985). The atmospheric boundary layer above water surfaces, such as lake environments, differs from that over land surfaces which result in differences in dry depositional rates (Holsen et al., 1997).

Larger particles are known to settle out of the atmosphere more rapidly than smaller particles (Noll et al., 1985). Dry deposition rates have been estimated from air particle concentrations measured on filters, however, rates are generally underestimated using these techniques (Holsen et al., 1993; Holsen et al., 1991). A number of surrogate collection surfaces have been used in dry deposition studies, including inverted frisbees and coated flat plates, although no standard surface has been established (Koester and Hites, 1992; Noll et al., 1990; Noll et al., 1988).

Measurements using a Noll Rotary Impactor, where coarse particles are accurately determined, have shown that >95% of dry deposition of crustal elements, anthropogenic metals and PCBs are associated with particles $>6.5 \mu m$ (Holsen et al., 1997; Holsen et al., 1993). This indicates that accurate estimates of large particles are necessary in the

determination of organic contaminants associated with dry deposition.

Although direct measurement of dry deposition (Figure 2.3) of pesticides and POPs is difficult, estimates have been possible using relationships between measured air concentrations, estimated particle deposition rates, and fractions of a chemical associated with the particle phase over a given surface area (Eisenreich and Strachan, 1992). The equation used to estimate dry deposition is:

$$N_{dry} = C_{TA} \cdot \phi \cdot V_d \cdot S.A. \quad (\text{ng/m}^2 \cdot \text{d}) \quad [7]$$

where N_{dry} = dry deposition flux, C_{TA} represents the air concentration (Σ aerosol and vapour phase)(ng/m³), the fraction of chemical associated with the particle phase = ϕ , depositional velocity of particles = V_d (cm/s) and S.A.(m²) = surface area over which dry deposition estimates are made. Frequently, particle sizes are not determined and, therefore, the depositional velocity rate is generally taken to be 0.2 cm/s although it is known to be more representative of smaller particles (Eisenreich and Strachan, 1992).

The fraction of the chemical associated with the particulate phase has generally been estimated using the Junge-Pankow relationship (Eisenreich and Strachan, 1992):

$$\phi = \frac{(c \cdot \theta)}{P_L^* + (c \cdot \theta)} \quad [8]$$

where $c = 17.2 \text{ Pa} \cdot \text{cm}$, θ is the surface area of particles per unit volume of air (cm²/cm³) and P_L^* = subcooled liquid vapour pressure. Estimates of θ have been determined for urban,

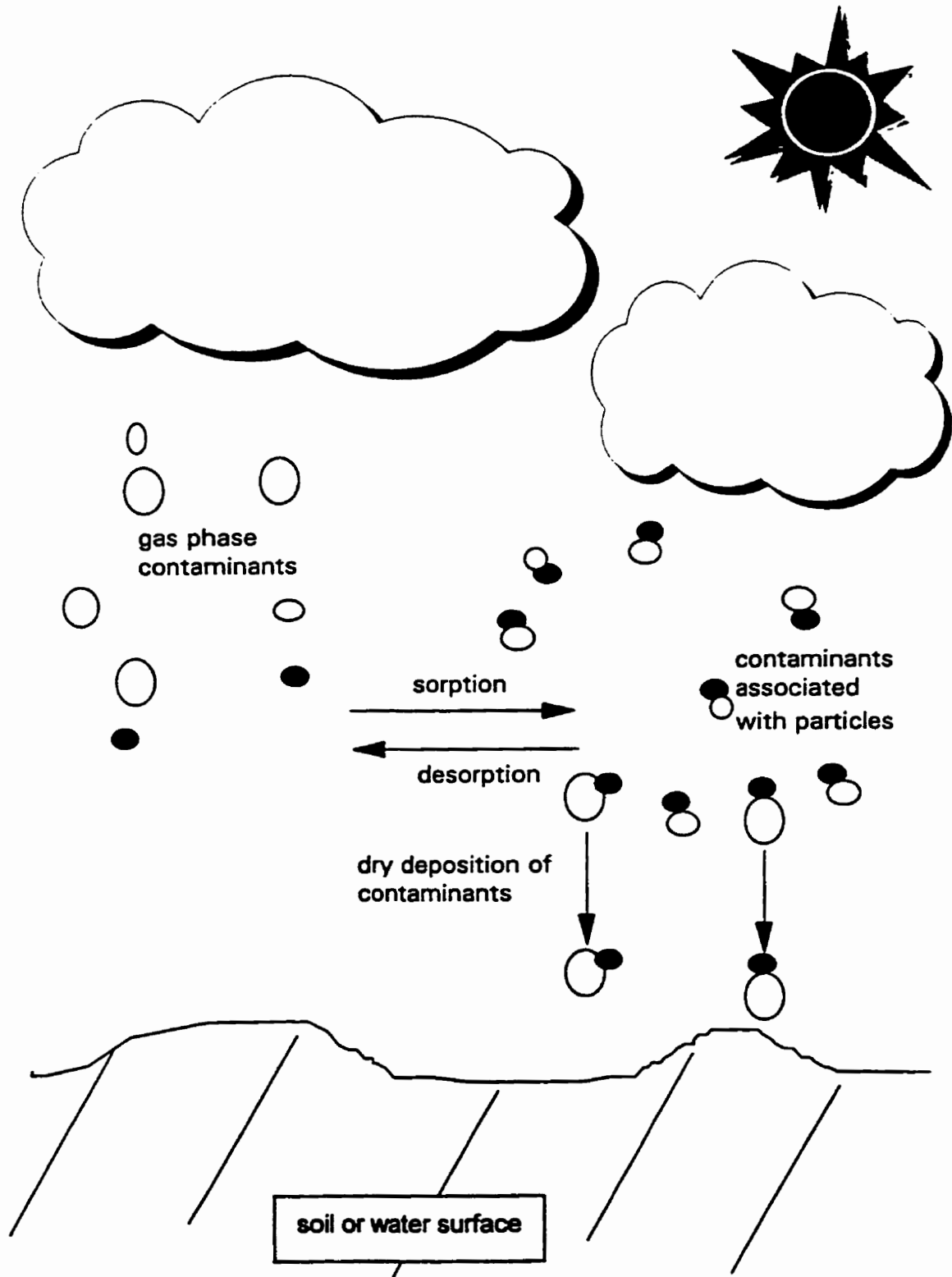


Figure 2.3 Removal of atmospheric species via dry deposition.

background and background plus local sources (Bidleman, 1988). Dry deposition estimates for organic contaminants, such as PCBs, are consistently higher during warmer periods (Koester and Hites, 1992; Holsen et al., 1991; McVeety and Hites, 1988). These observations correspond to the seasonality of PCBs in the vapour phase.

Recently, the octanol-air partition coefficient (K_{OA}) has been used as a method of determining organic contaminant partitioning behaviour between the gas and particle phase (Harner and Bidleman, 1996; Harner and Mackay, 1995). Octanol previously has been used as a surrogate for lipid material, which may sorb organic contaminants in aquatic systems. A comparison of the relative concentration of a pesticide in octanol and in water, known as the octanol-water partition coefficient (K_{OW}) can be used to predict a pesticide's potential for bioconcentration. Until recently, K_{OA} has been estimated using the ratio of K_{OW} with the dimensionless air-water partition coefficient:

$$K_{OA} = \frac{K_{OW} \cdot RT}{H} \quad [9]$$

where R = gas constant ($J/mol \cdot K$) and T = temperature (K). However, estimates using K_{OW} are not as accurate as direct measurement of K_{OA} because the K_{OW} represents the octanol phase saturated with water and water saturated with octanol, and H is measured for pure water (Harner and Bidleman, 1996). Estimation of K_{OA} can be performed using the relationship:

$$K_{OA} = \frac{s_l^o}{(p_l^o/RT)} \quad [10]$$

where s°_L and p°_L are the solubility in octanol and subcooled liquid vapour pressure, respectively. Measurements of K_{OA} may be used to determine the partitioning of hydrophobic chemicals between the air and lipid material directly (Tolls and McLachlan, 1994). K_{OA} is based on equilibrium condition of partitioning between these two phases, at a specific temperature, therefore, a linear relationship between $\log K_{OA}$ and p°_L should yield slopes near -1 (Simik et al., 1998). Field measurements have resulted in slopes shallower than -1. Several factors have been used to account for these differences which include: increasing concentration during sampling, decrease in temperature during sampling, nonequilibrium, nonexchangeability, varying differences between enthalpies of desorption and volatilization, varying number of sites available for adsorption and varying activity coefficients in organic matter within a class of compounds (Simik et al., 1998). Based on results of a large dataset from Chicago and southern Lake Michigan, the energy terms (enthalpies and activity coefficients) are the major factors in determining the slope of $\log K_{OA}$ and p°_L (Simik et al., 1998).

2.1.3.3 Gas Exchange. Movement of pesticides and other POPs across the air/water interface has been well studied in lake and ocean environments, however, there are limited data on gas exchange of chemicals across the air-water interface of flowing surface waters such as rivers or streams. Gas exchange occurs in both directions, resulting in absorption or volatilization of chemicals from the water surface. The dominant model currently used in the estimate of gas exchange across the air-water interface is the two-film model (Figure 2.4) (Bidleman and McConnell, 1995; McConnell et al., 1993; Schwarzenbach et al., 1993). The surface renewal model (Figure 2.5), an adaptation of the two-film model, applies the two-

film theory to flowing waters but has not been widely utilized (Schwarzenbach et al., 1993; O'Connor and Dobbins, 1958).

On either side of the air-water interface there exists a boundary layer (Figures 2.4 and 2.5). Both models include diffusivity parameters to represent molecular diffusion of organic chemicals through both sides of this boundary layer. In the two-film model, the water-side transfer velocity (v_w) is proportional to the diffusivity parameter (D_w), but in the surface renewal model v_w is proportional to the square root of D_w (Eisenreich et al., 1997). The actual v_w determined in the two film model is based upon diffusivity and wind speed taken at the 10 m height (u_{10}) using the relationship (Schwarzenbach et al., 1993):

$$v_w(\text{chemical}) = D_w(\text{chemical}) \cdot (4 \times 10^{-5} u_{10}^2 (\text{m/s}) + 0.0004). \quad [11]$$

In shallow flowing streams, the water depth and current will influence the chemical movement in the water layer and, therefore, v_w is estimated in the surface renewal model using the relationship (O'Connor and Dobbins, 1958):

$$v_w(\text{chemical}) = [D_w(\text{chemical}) \cdot \text{water velocity (cm/s)/water depth(cm)}]^{0.5}. \quad [12]$$

Air-side transfer velocities (v_a) are determined similarly using both models, utilizing wind speed at the 10 m height above the water surface (u_{10}). The air side transfer velocity of water has been found to correspond to the relationship (Schwarzenbach et al, 1993):

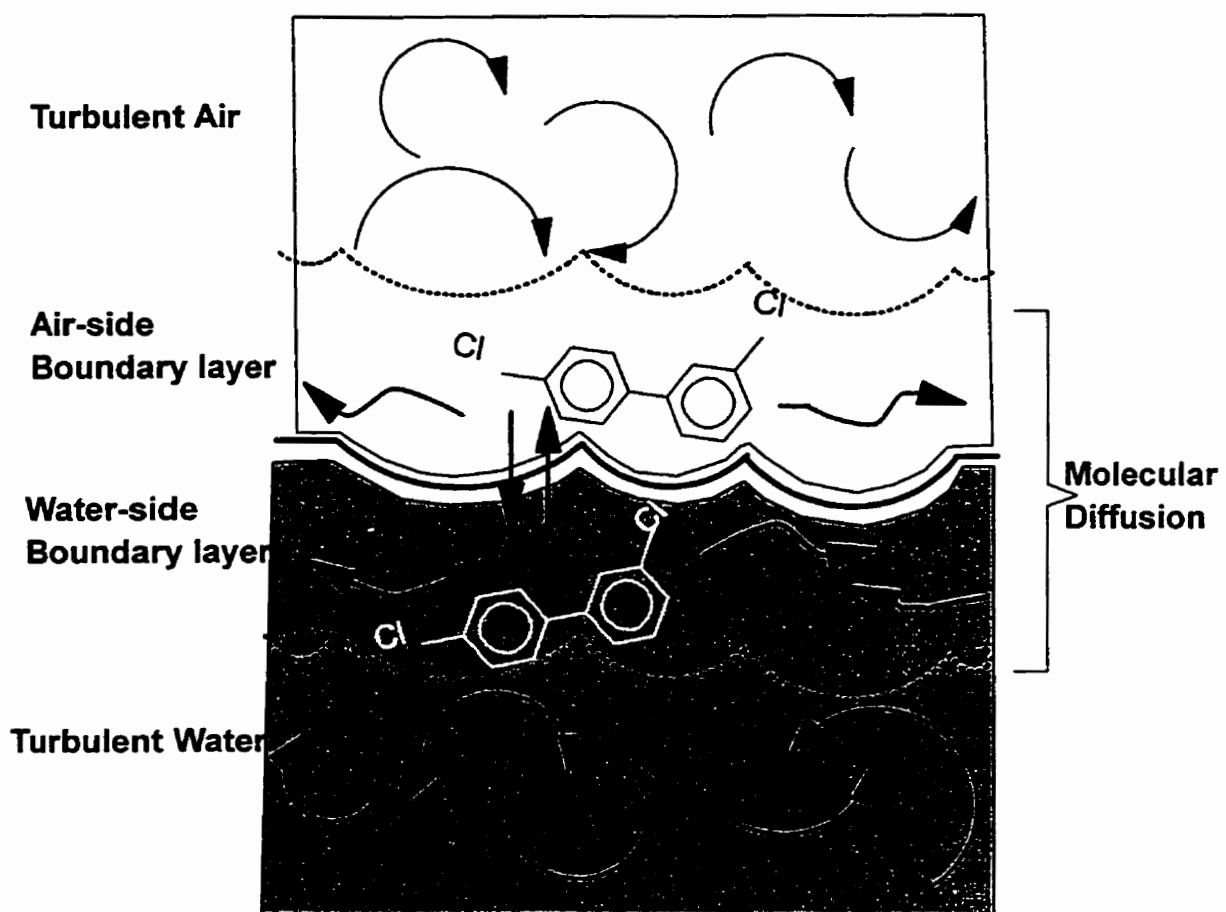


Figure 2.4 The two-film model for gas exchange of organic contaminants.

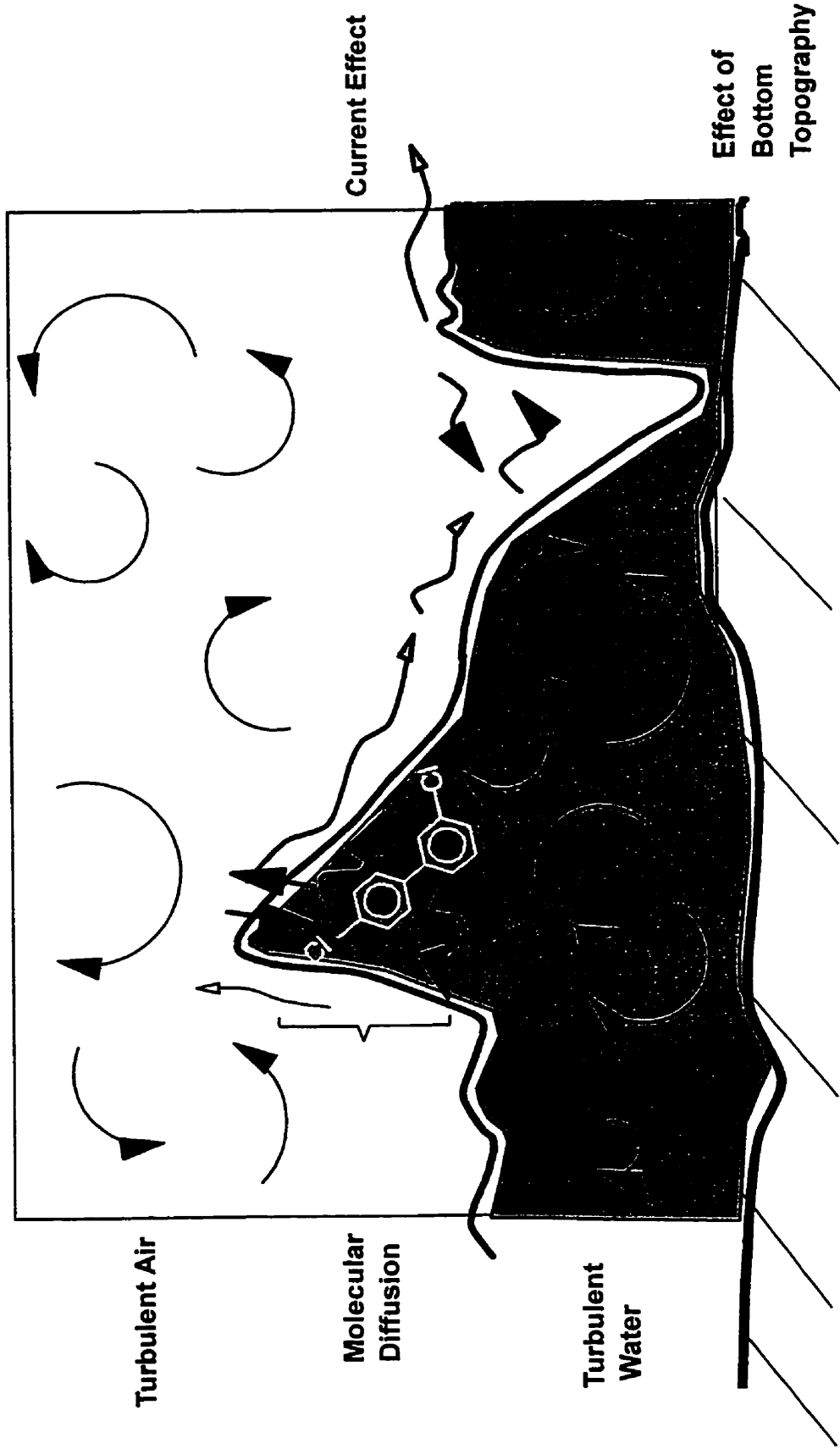


Figure 2.5 The surface renewal model for gas exchange of organic contaminants.

$$v_a(\text{H}_2\text{O}) = 0.2u_{10} (\text{m/s}) + 0.3 (\text{cm/s}). \quad [13]$$

For organic chemicals, v_a values are calculated by extrapolation using diffusivity ratios with v_a for water (Schwarzenbach et al., 1993).

$$v_a(\text{chemical}) = v_a(\text{H}_2\text{O}) [D_a(\text{chemical})/D_a(\text{H}_2\text{O})]^{0.67} \quad [14]$$

and diffusivity of the organic chemical is estimated using the molecular weight ratio:

$$D_a(\text{chemical})/D_a(\text{H}_2\text{O}) \approx [\text{MW}(\text{H}_2\text{O})/\text{MW}(\text{chemical})]^{0.5}. \quad [15]$$

The two models combine both air-side and water-side transfer velocities to establish the overall transfer velocity using the relationship (Schwarzenbach et al., 1993):

$$1/v_{\text{tot}} = 1/v_w + 1/v_a' \quad [\text{where } v_a' = v_a (H/RT)] \quad [16]$$

using temperature corrected H and where R = gas constant and T = temperature (K).

Gas exchange flux is then calculated using the overall mass transfer velocity in both models with the equation (Schwarzenbach et al., 1993):

$$N = v_{\text{tot}} (C_w - C_a/K_H) \quad (\text{ng/m}^2 \cdot \text{d}) \quad [17]$$

where $K'_H = H/RT$. By convention, the chemical is being absorbed by the water if N is negative and chemical volatilization occurs when N is positive (McConnell et al., 1993).

Gas exchange estimates have been performed in the Great Lakes region for POPs such as the hexachlorocyclohexanes (HCHs), polycyclic aromatic hydrocarbons (PAHs) and PCBs (Hornbuckle et al., 1995; Hornbuckle et al., 1994; Achman et al., 1993; McConnell et al., 1993; Baker and Eisenreich, 1990). Deposition of chemicals has been found during periods of cool temperatures, however, volatilization is the dominant direction of semivolatile organic contaminant gas exchange in the Great Lakes, corresponding to warmer temperatures observed in the summer months.

A depositional flux was observed for both α -HCH and chlorinated bornanes, while volatilization was observed for PCBs, chlordanes and hexachlorobenzene during a cruise of Lake Baikal in June 1991 (McConnell et al., 1996). Gas exchange estimates of the HCHs in a lake on Cornwallis Island in the North West Territories, however, indicated a volatilization rather than depositional flux (Falconer et al., 1995).

Water temperature is an important factor in the determination of flux direction because of its influence on H (McConnell et al., 1993). In large water bodies, such as the Great Lakes, the degree of mixing of the water column is also important (McConnell et al., 1993).

2.2 Pesticides

Pesticides are used extensively in the Canadian prairies for control of weeds and insects. Greater than 20 million kilograms of herbicides alone are applied in the region (southern Manitoba, Saskatchewan, Alberta) annually (Grover et al., 1997). In southern Manitoba, 900,000 kg of phenoxyacid herbicides (e.g., MCPA) and 165,000 kg of dinitroanilines (e.g., trifluralin) are applied annually (Agriculture Canada, unpublished data). Pesticide losses from treated areas may lead to the contamination of surface waters or groundwaters causing a decrease in water quality for such uses as irrigation and drinking water, in addition to possible adverse effects on aquatic organisms. Residues of these chemicals may be transferred from the site of application through both direct and indirect mechanisms. Direct loss from treated areas may occur through spray drift during product application or volatilization from treated fields (Muir, 1991). Indirect methods of pesticide loss include washoff of pesticides from treated fields via surface runoff during rain events or snow melt, leaching through the soil profile into groundwater, wind erosion of soil particles and atmospheric transport of pesticides (Glotfelty et al., 1990).

2.2.1 Pesticide Contamination of Surface Waters

Contamination of surface waters by agricultural chemicals including pesticides has been the focus of a number of recent reviews. Harker et al. (1997) reviewed monitoring data from the Canadian prairies to assess nonpoint effects of agriculture on water quality. Harker et al. (1997) concluded that there was no large body of evidence indicating widespread

contamination of surface and groundwater as a result of agricultural activity on the prairies, based on the Canadian water quality guidelines (Table 2.1). Although pesticides have been detected in surface waters within the prairie region, most products are found at levels below Canadian water quality guideline values (Harker et al., 1997). A review of Alberta surface water quality found that herbicides have been detected in streams and rivers in Alberta (Alberta Agriculture Food and Rural Development, 1998), however, in general, the pesticide levels were below water quality guideline values for the protection of freshwater aquatic life (Alberta Agriculture Food and Rural Development, 1998). The same reviews found that pesticide concentrations are elevated in prairie dugouts during spring melt and runoff periods in the Canadian prairies (Alberta Agriculture Food and Rural Development, 1998; Harker et al., 1997).

Currie and Williamson (1995) examined pesticide data, which had been collected in southern Manitoba river systems over the past three decades, for long term trends and for exceedences of Canadian water quality guideline values. Guideline values were exceeded in < 1% of sample collections. While these data represent results of long term monitoring programs within Manitoba, sampling of these rivers was restricted to monthly, seasonal or annual collection. Relationships between application of pesticides and occurrence of pesticides in river systems could not be established with these limited data.

Triazine herbicides dominate the measurements of current use pesticides in surface water reported in the US, Canada and western Europe during the late 1980s and 1990s. These chemicals are persistent in the environment and are relatively water soluble (Wauchope et al., 1992). These characteristics of triazines increase both residence time in

Table 2.1 Canadian water quality guidelines for the protection of freshwater aquatic life for the 16 pesticides in this review (CCREM, 1987).

Chemical	Guideline Value (ng/L)
Alachlor	- ^a
Atrazine	2000
Bromoxynil	5000
Chlorpyrifos	3.5 ^b
Chlorthal dimethyl	- ^a
Cyanazine	2000
2,4-D	4000
Dichlorprop	- ^a
Diclofop methyl	6100
Ethalfuralin	- ^a
MCPA	2600 ^c
Metolachlor	8000
Terbuthylazine	- ^a
Triallate	240
Triclopyr	- ^a
Trifluralin	100
ΣPCBs	1

^ano guideline value

^bdraft interim value

^call forms of this product

the environment and mobility, which promotes their movement to surface waters. Triazines are widely used for broadleaf and grass weed control in corn, which is grown extensively in the US midwest and central Canada, although they are only a minor use product on the Canadian prairies (Beck et al., 1992). Atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] is generally the most widely reported compound of the triazine herbicides, owing to its widespread use. Atrazine concentrations in Quebec rivers as high as 37 $\mu\text{g/L}$ were reported during 1986-87 (Maguire and Tkacz, 1993). Atrazine measurements from the same rivers in 1991 and 1992 were lower (0.04 - 29 $\mu\text{g/L}$) (Berryman and Giroux, 1994). Atrazine was observed in three major rivers in Ontario with a detection frequency of 62 - 99% and maximum concentrations exceeded 5 $\mu\text{g/L}$ (Frank and Logan, 1988). Usage of atrazine in these southern Ontario watersheds was approximately one order of magnitude greater than 2,4-D [(2,4-dichlorophenoxy)acetic acid] and MCPA [(4-chloro-2-methylphenoxy)acetic acid] (Frank et al., 1988). In Alberta and Manitoba, atrazine was detected less frequently in surface waters than in Quebec and Ontario, where it is used more extensively (Currie and Williamson, 1995). Reported concentrations of atrazine in Manitoba rivers range between <0.05 and 6.6 $\mu\text{g/L}$ (Currie and Williamson, 1995). Levels of atrazine in the Stephenfield reservoir in southern Manitoba remained at <0.5 $\mu\text{g/L}$ during 1987-88 (Beck et al., 1992).

In the US midwest, atrazine was found at maximum concentrations during the postplanting period, prior to harvest (Thurman et al., 1992). Atrazine was detectable throughout the study (0.23 - 108 $\mu\text{g/L}$) although concentrations during the preplanting and harvest periods were 20 times less than the postplanting period (Thurman et al., 1992). In

27% of the samples collected in Arkansas, atrazine concentrations exceeded the US lifetime health advisory level ($3 \mu\text{g/L}$), a nonregulatory health-based reference concentration of pesticides in drinking water considered to be safe based on a lifetime exposure (Senseman et al., 1997). Only 4% of the Arkansas surface water samples, however, were found to exceed the US EPA maximum contaminant level for atrazine, where maximum concentrations ($10.5 \mu\text{g/L}$) were consistent with pre-emergence and post-emergence herbicide applications (Senseman et al., 1997). In Colorado, atrazine was present throughout a study of stream systems draining agricultural and urban regions. Concentrations of atrazine in the agricultural drainage system ranged from $0.012 - 5.4 \mu\text{g/L}$, however, the maximum concentration observed in the urban surface water remained at the detection limits ($0.009 \mu\text{g/L}$) (Kimbrough and Litke, 1996). In a large scale study of pesticides in US midwestern reservoirs, Scribner et al. (1996) reported the highest concentrations of atrazine generally occurred during the summer months. Maximum atrazine concentrations observed in the Minnesota River were observed during the first major discharge event following application in both 1990 and 1991 (2100 and $800-900 \text{ ng/L}$, respectively) (Schottler et al., 1994). In two lakes in Nebraska, one of which received water from surface runoff and the other mainly from groundwater discharge, atrazine concentrations were observed early in June (Spalding et al., 1994). Higher concentrations of atrazine ($17.4 \mu\text{g/L}$) were observed in the lake with surface runoff contributions than the lake with groundwater discharge contributions ($1.01 \mu\text{g/L}$) (Spalding et al., 1994).

Numerous studies to determine pesticide loadings in the Mississippi River have been performed in recent years. The Mississippi River drains a major part of the agricultural land

from the US midwest and is subject to contamination through contributions from tributaries, surface runoff, groundwater contributions in addition to atmospheric deposition. Atrazine concentrations were determined to be at maximum levels during May and June in the Mississippi River and its tributaries, corresponding to application time (Larson et al., 1995). Concentrations dropped to near or below detection limits in August and September in the Mississippi River, due to reduced river flow and the lack of chemical applications during that period (Larson et al., 1995). A number of cruises along the Mississippi River demonstrated that atrazine levels accumulated with contributions from the tributaries (Pereira et al., 1992). Although atrazine applications were similar between 1987 - 1989, low stream loads were found during 1987-1988, due to drought conditions that produced little runoff indicating that herbicide transport in river systems is affected by the hydrologic cycle during a given field season (Pereira and Rostad, 1990). In the following year, which was considered wet, much higher loads of atrazine and its degradation product were observed in the Mississippi River (Pereira and Rostad, 1990).

Cyanazine [2-[[4-chloro-6-(ethylamino-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile], like atrazine, is not widely used in the Canadian prairie region. It is used, however, in eastern Canada and in the US midwest. In eastern Canada, cyanazine was detected in <20% of the samples collected in three tributaries of the Great Lakes during the mid 1980s (Frank and Logan, 1988). The maximum concentration of cyanazine observed in Quebec agricultural areas in 1992 and 1993 was detected in the L'Acadie River (4.8 µg/L) (Berryman and Giroux, 1994). Cyanazine levels were considered more seasonal than atrazine residues in the Minnesota River drainage basin, due to its shorter half-life in soil (Table 2.2)

(Schottler et al., 1994). Although maximum cyanazine concentrations (6.5 $\mu\text{g/L}$, in June and early July) were higher than that observed for atrazine in the Minnesota River, it decreased to <10 ng/L by August during both 1990 and 1991 (Schottler et al., 1994). Thurman et al. (1992) found cyanazine at maximum concentrations (61 $\mu\text{g/L}$) in surface waters from the US midwest during the postplanting period, similar to results determined for atrazine. Water samples were collected along the Mississippi River and its tributaries following a major rainfall event which occurred after herbicide applications had been performed in late May 1990. During this event cyanazine was detected at maximum concentrations (4.5 $\mu\text{g/L}$) in the Wabash River, a tributary rather than in the Mississippi River itself (Moody and Goolsby, 1993). In four Vermont streams that were sampled following runoff producing rainfall events throughout the 1992 and 1993 agricultural seasons, cyanazine concentrations ranged from 0.1 - 6.9 $\mu\text{g/L}$ (Gruessner and Watzin, 1995). Cyanazine was present in surface water samples collected in two of three tributaries of Chesapeake Bay at maximum concentrations in June, (108 and 210 ng/L, Susquehanna and Potomac Rivers, respectively), while maximum concentrations in the James River were observed in May (25 ng/L) (Foster and Lippa, 1996). Although terbuthylazine [6-chloro-*N*-(1,1-dimethylethyl)-*N*'-ethyl-1,3,5-triazine-2,4-diamine] has not been as widely studied and reported in the literature as atrazine or cyanazine, it has been detected in the Mississippi River and its tributaries (Pereira et al., 1992). Terbuthylazine concentrations in the river Elbe in northern Germany were found to range from <110 - 140 ng/L (Bester et al., 1995).

Table 2.2 Physical properties of the pesticides under investigation (Wauchope et al., 1992).

Pesticide	Water Solubility (mg/L)	Half-life in Soil (d)	Soil Sorption (Koc)	Subcooled Liquid Vapour Pressure (Pa) ^a	Henry's Law Constant (Pa·m ³ /mol) ^a
Alachlor	240	15	170	4.10×10^{-3}	2.10×10^{-3}
Atrazine	33	60	100	1.22×10^{-3}	2.52×10^{-4}
Bromoxynil (phenol)	130	7	190	2.88×10^{-2}	1.07×10^{-3}
Chlorpyrifos	0.4	30	6070	4.13×10^{-3}	2.22
Chlorthal-methyl (Dacthal; DCPA)	0.5	100	5000	4.19×10^{-3}	2.21×10^{-1}
Cyanazine	170	14	190	6.23×10^{-6}	3.02×10^{-7}
2,4-D	890	10	20	1.31×10^{-3}	1.99×10^{-3}
Dichlorprop	350	10 ^b	170	4.70×10^{-3}	6.39×10^{-6}
Diclofop methyl	0.8	30	16000	4.7×10^{-3}	1.47×10^{-2}
Ethalfuralin	0.3	60	4000	2.35×10^{-2}	13.0
MCPA	825	25	110	2.32×10^{-4}	4.80×10^{-3}
Metolachlor	530	90	200	2.37×10^{-3}	9.28×10^{-4}
Terbutylazine	8.5 ^c	^d	^d	2.99×10^{-3}	4.06×10^{-3}

Triallate	4	82	2400	1.77×10^2	1.12
Triclopyr	440 ^b	46 ^b	1.5 ^b	3.52×10^3	1.37×10^4
Trifluralin	0.3	60	800	1.62×10^2	16.4

^acalculated

^bester

^cWorthing and Hance, 1991

^ddata not available

Alachlor [2-chloro-2',6'-diethyl-*N*-(methoxymethyl)acetanilide] is a pre-emergent herbicide used to kill grasses and broadleaf weeds in both corn and soybeans (Kolpin et al., 1996). In the Minnesota River, alachlor reached maximum seasonal concentrations in mid-June, prior to water flows reaching peak levels (Schottler et al. 1994). These results indicate that alachlor, similar to atrazine, is quickly mobilized and transported to rivers from treated regions during precipitation events (Schottler et al., 1994). The detection frequency of alachlor in the tributaries of Chesapeake Bay was consistently lower than that of the triazine herbicides, although maximum concentrations were observed in June in both the Susquehanna and Potomac Rivers (Foster and Lipka, 1996). Alachlor was detected in the Mississippi River and its tributaries in a study of surface waters from the summer of 1991 extending into spring 1992. Concentrations observed in the autumn sampling period (October-November) were much lower than during the spring and summer sampling events (Pereira and Hostettler, 1993). In a broad survey of reservoirs in the US midwest, alachlor was found to be the second most frequently detected herbicide, next to atrazine (Scribner et al., 1996). Alachlor was detected in 3.2, 0.7 and 5.4% of the samples collected from the Grand, Saugeen and Thames Rivers in Ontario, between 1981-85 (Frank and Logan, 1988). During this period alachlor was used within Canada. In 1985, however, alachlor was removed from the Canadian market and in a recent monitoring program of rivers in Quebec, alachlor was not detected (Berryman and Giroux, 1994).

Metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] is structurally similar to alachlor, however, it has a greater water solubility (Table 2.2). Metolachlor was more persistent than alachlor in surface waters from

the US midwest, however, maximum concentrations of alachlor exceeded metolachlor during the postplanting period (51 and 40 $\mu\text{g/L}$, respectively) (Thurman et al., 1992; Thurman et al., 1991). The median concentration of metolachlor increased by an order of magnitude in river systems, during the postplanting period, with a reduction to near preplanting concentrations by harvest (Thurman et al., 1991). Metolachlor was present in all four Vermont streams sampled in 1992 and 1993 and concentrations were similar to atrazine levels in all but one of the rivers (Gruessner and Watzin, 1995). Seasonal temporal trends for metolachlor were similar to alachlor, with maximum concentrations in rivers occurring in spring and summer, with reduced concentrations in fall periods (Pereira and Hosttetter, 1993). Metolachlor was one of the most frequently detected herbicides in the tributaries of Chesapeake Bay between 1992 and 1993 (Foster and Lippa, 1996). Maximum metolachlor concentrations in the Susquehanna and Potomac rivers were observed in June, however, a major runoff event in April produced the highest seasonal concentrations in the James River (Foster and Lippa, 1996). Metolachlor was detected in three major river basins in Ontario and detection frequency was related to the time of application of the herbicide (Frank and Logan, 1988). During the 1992-1993 water quality monitoring program in Quebec, metolachlor was present in 76% of the samples collected and concentrations ranged from $<0.1 - 21 \mu\text{g/L}$ (Berryman and Giroux, 1994).

The phenoxyacid herbicides such as MCPA and 2,4-D are relatively non-persistent in soil (Wauchope et al., 1992) (Table 2.2). These chemicals are used extensively in the Canadian prairie region. In a study of prairie lakes in Saskatchewan, 2,4-D was found in 78% of water samples collected, but MCPA was detected in $<10\%$ of the same samples

(Donald and Syrgiannis, 1995). 2,4-D was one of the most commonly detected herbicides in rivers in Manitoba (<0.05 - 7.7 $\mu\text{g/L}$) (Currie and Williamson, 1995). Phenoxyacid herbicides in Danish stream systems were present at elevated concentrations during the post application period for the region (Morgensen and Spliid, 1995). Maximum concentrations observed in these streams were 7.3, 6.6 and 2.8 $\mu\text{g/L}$ for MCPA, 2,4-D and dichlorprop [(RS)-2-(2,4-dichlorophenoxy)propionic acid], respectively.

Diclofop methyl [(RS)-2-[4-(2,4-dichlorophenoxy)phenoxy]propionic acid-methyl ester] was the second most frequently detected herbicide in farm dugouts on the Canadian prairies (Grover et al., 1997), however, it was rarely detected in Manitoba rivers (Currie and Williamson, 1995). The maximum concentration of diclofop methyl reported in Manitoba rivers was 4.0 $\mu\text{g/L}$ (Currie and Williamson, 1995). Frank and Logan (1988) also did not detect diclofop methyl in two major rivers in Ontario, although its use in the local watersheds was known to occur.

Although bromoxynil [3,5-dibromo-4-hydroxybenzonitrile] is not a phenoxyacid herbicide, it is applied in combination with MCPA for broadleaf weed control and has been detected in surface waters during and extending beyond regional application periods. Bromoxynil was detected in water collected from farm dugouts in Saskatchewan most frequently during summer sampling events, extending from late May into July, which corresponds to application periods for this compound (Grover et al., 1997). Concentrations observed in Saskatchewan surface waters ranged from <0.05 $\mu\text{g/L}$ to a maximum of 0.33 $\mu\text{g/L}$ (Grover et al., 1997). In Manitoba river systems, bromoxynil concentrations determined as part of routine water quality monitoring programs over a 30 year period of

record ranged from below detection ($<0.01 \mu\text{g/L}$) to $2.4 \mu\text{g/L}$ (Currie and Williamson, 1995). In Danish stream waters, bromoxynil was detected in 13% of samples collected from a region characterized by a clay soil, however, it was only detected in 3.5% of the samples collected from a region with sandy soils (Morgensen and Spliid, 1995). Maximum concentrations in surface waters draining the clay soil region also exceeded observations in the sandy region (0.53 and $0.03 \mu\text{g/L}$, respectively). (Morgensen and Spliid, 1995).

Dinitroaniline herbicides are used widely for pre-plant and pre-emergence weed control in small grains in the US and Canadian prairies. These herbicides are detected in surface waters periodically, however, they are not present at elevated concentrations. Senseman et al. (1997) reported a detection frequency of 0.4% for trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine] in Arkansas surface waters. Trifluralin was detected in only two of the 256 samples collected at a maximum concentration of $1.3 \mu\text{g/L}$ (Senseman et al., 1997). Between 1992 and 1994, trifluralin was detected in 1.4% of water samples and 5% of particulate samples collected in the Mississippi River, at the Gulf of Mexico (McMillin and Means, 1996). Concentrations in suspended sediment samples (22 pg/L) were an order of magnitude greater than in the dissolved phase (2.8 pg/L). Trifluralin was detected in 2-14% of lake water samples collected in agricultural regions of Nebraska and maximum concentrations ranged from $0.09 - 0.11 \mu\text{g/L}$ (Spalding et al., 1994). In Colorado, trifluralin concentrations were higher than ethalfluralin [*N*-ethyl-*N*-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine] concentrations in agricultural regions ($<0.012 - 0.11$, $<0.013 - 0.073 \mu\text{g/L}$, respectively) and temporal trends of these chemicals in streams reflected regional application periods (Kimbrough and Litke, 1996). Neither

chemical was detected in urban areas in the Colorado study. Trifluralin was detected most frequently in samples collected during spring sampling in Saskatchewan farm dugout water (Grover et al., 1997), corresponding to application times for the dinitroaniline herbicides. The maximum trifluralin concentration observed in the two year study (1988 - 1989) was 0.11 $\mu\text{g/L}$ (Grover et al., 1997).

Triallate [S-(2,3,3-trichloro-2-propenyl)bis(1-methylethyl)carbamoate] is another pre-emergence herbicide used for wild oat control applied in spring and fall that has been detected in surface waters. Triallate was detected in samples collected in farm dugouts on the Canadian prairies during both spring and fall periods, with concentrations below detection limits during the summer months (Grover et al., 1997). Maximum seasonal concentrations (0.87 $\mu\text{g/L}$) were observed during the spring, although frequency of detection was higher in fall samples in Saskatchewan dugouts (Grover et al., 1997). Although triallate is used for agricultural purposes, it was not detected in streams draining agricultural regions, but was present in streams (<0.008 - 0.036 $\mu\text{g/L}$) from urban regions in Colorado (Kimbrough and Litke, 1996). Similarly, triallate was not detected in either stream in the Stephenfield drainage basin in southern Manitoba, although it is used within this agricultural region (Beck et al., 1992).

Triclopyr [3,5,6-trichloro-2-pyridyloxyacetic acid] is mainly used as a forestry herbicide, however, there are small uses for control of broadleaf weeds in non-agricultural settings. It has been detected in a few rivers in Manitoba (<0.02 - 0.83 $\mu\text{g/L}$) (Currie and Williamson, 1995). Triclopyr was not detected in river waters collected from agricultural regions of Quebec during a two-year sampling program (Berryman and Giroux, 1994).

The organophosphorus insecticide chlorpyrifos [*O,O*-diethyl- *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] is used for Wheat Midge (*Sitodiplosis mosellana*) and Bertha Armyworm (*Mamestra configurata*) (*Wlk.*) control in southern Manitoba, however, it has not been reported in river waters from this region (Currie and Williamson, 1995). This may be a function of very high detection limits (0.8 µg/L) for this compound in most studies (Currie and Williamson, 1995). In Quebec rivers, however, chlorpyrifos was detected in samples collected in June of both 1986 and 1987 and the maximum concentration reported was 6.2 ng/L (Maguire and Tkacz, 1993). Chlorpyrifos was detected (<0.03 -0.55 µg/L) in one of the 13 rivers sampled in a more recent survey of Quebec surface waters (Berryman and Giroux, 1994). Chlorpyrifos is ranked as the second most frequently applied insecticide in Colorado for agricultural use and was detected in streams draining agricultural land (<0.008 - 0.22 µg/L) as well as in surface water samples collected from urban regions (<0.008 - 0.30) (Kimbrough and Litke, 1996). The detection of chlorpyrifos in urban areas may be a function of use in municipal insect control programs or in domestic pesticide products.

Chlorthal dimethyl (DCPA, dacthal) [2,3,5,6-tetrachloro-1,4-benzenedicarboxylic acid, dimethyl ester] is registered for use in Canada for control of crabgrass and annual grasses, although its use in Manitoba has not been reported (Manitoba Agriculture, unpublished data). It has been detected in surface waters in Manitoba, however, detection frequency for this compound is below 2% (Currie and Williamson, 1995). In Colorado, this product is widely used for weed control in onion fields and has been detected in streams draining agricultural regions at elevated concentrations (0.033 - 100 µg/L) and in urban

regions, although at lower concentrations ($<0.005 - 0.29 \mu\text{g/L}$) (Kimbrough and Litke, 1996). In the US midwest, chlorthal dimethyl was not detected in near surface aquifers, however, metabolites for this compound frequently were detected (Kolpin et al., 1996).

This review has described many studies on the measurements of pesticide concentrations in surface and groundwaters. Generally, the reports have been limited to either short term intensive studies or longer term low frequency monitoring. Intensive sampling programs, which were developed to determine temporal trends throughout the agricultural season, generally have been restricted to one year of measurements. Several cruises of major rivers systems have been reported, however, these sampling expeditions are expensive and are, therefore, limited to intensive sampling campaigns over an annual cycle, again restricting the capacity to determine accurate temporal patterns of pesticides. Although samples may be collected as frequently as daily, one field season alone is not sufficient to establish temporal trends because of the variability of meteorological conditions, which for a given year may alter pesticide degradation rates and loadings to surface waters. Water quality monitoring programs such as those conducted in the prairie region (Alberta Agriculture Food and Rural Development, 1998; Currie and Williamson, 1995), have developed a long period of record, although the sample collection frequency is limited to monthly, seasonal or annual events. The data from these types of programs cannot be used in the determination of seasonal trends or loadings of pesticides.

2.2.2 Pesticides in the Atmosphere

2.2.2.1 Air. Most of the early research on pesticides in air was performed in fields or regions where pesticide use was known. Only recently have measurements of current use pesticides in areas remote from use been conducted. Post-application volatilization is a source of pesticides available for both local and global transport (Whang et al., 1993). This process can account for losses of up to 90% of applied levels of some pesticides within days of application (Majewski et al., 1993). Pesticide volatilization is dependent mainly on its vapour pressure at the soil or water surface, the air-water partitioning for the chemical, in addition to the rate at which it moves away from the surface, e.g., leaching. A number of other factors may contribute to pesticide volatilization losses. These include the type of formulation and application technique used, the degree of sorption to the application surface, soil moisture content and temperature, the nature of the air-surface interface, soil tillage practices and micrometeorological conditions above the soil surface (Majewski and Capel, 1995).

Volatilization losses of soil applied pesticides have been modelled, based on the assumption of a linear equilibrium partitioning of the chemical between the vapour, liquid and sorbed phases. Jury et al. (1983) developed a model for screening the environmental behaviour, including volatilization from soil, of pesticides and other organic chemicals based on their physical and chemical properties. The general assumptions of the model are that soil properties and water content remain constant, adsorption isotherms and H values are linear with concentration, initial pesticide incorporation has occurred uniformly and volatilization losses of the pesticide and water are limited by gaseous diffusion through the stagnant air

boundary layer. Pesticide degradation follows first order kinetics. Above the stagnant layer of air, the pesticide concentration is considered to be zero. The chemicals that fit this model are generally highly soluble in water and can accumulate at the soil surface following convective movement of evaporating water. Jury et al. (1983) have used the model to determine volatilization of lindane and 2,4-D from soil. In further work, Jury et al. (1984) found that pesticide volatilization was controlled mainly by its H , which controls how much the boundary layer restricts volatilization from soil, and chemicals could be categorized based on the extent of limitation that the boundary layer had on volatilization rates.

The triazine and acetanilide herbicides are more frequently reported in air than other types of herbicides due to the extensive use and the persistence of these chemicals. Pesticide levels in air samples consistently are elevated during regional application times. Soil moisture also has been shown to be important in the regulation of herbicide volatilization from soil. Volatilization losses of atrazine were found to increase under moist soil conditions in a study performed in eastern Maryland (Glotfelty et al., 1989). Irrigation resulted in increased concentrations of atrazine in the air through evaporation of irrigation water which transports the atrazine off the soil surface (Clendening et al., 1990).

Measurements of atrazine in air have been performed in North America and Europe. Air concentrations of atrazine in Maryland ranged from 0.1 - 20 ng/m³, maximum concentrations were observed during local corn planting periods (Glotfelty et al., 1990). Elevated levels of atrazine in air samples were observed during use periods for regions south of the sampling location and prior to local application periods (Glotfelty et al., 1990). Gas phase concentrations were found to contribute 95% of total atrazine levels (Glotfelty et al.,

1990). Atrazine was detected in both the gas and particulate phase of air samples collected at a site removed from direct agricultural activity in North Dakota, concentrations ranged from 5.6–46 pg/m³ (Hawthorne et al., 1996). Air concentrations of atrazine ranged from 1.9 - 37 pg/m³ in the boreal forest in northwestern Ontario, an area which is remote from pesticide use (Muir and Grift, 1995).

Atrazine was not detected in air samples collected in an Italian forest between 1988 and 1989 (Trevisan et al., 1993). However, in France triazine herbicides were present in 85% of the samples collected in a rural region within a few hundred metres from triazine treated land. Atrazine levels in air ranged from <0.03 - 2 ng/m³ with maximum concentrations occurring in early May, coinciding with agricultural activity (Chevreuil et al., 1996). Atrazine was not detected in precipitation or river water samples in Japan, although it was detected in air samples (0.32 ng/m³) during sample collection in 1992 (Haraguchi et al., 1995).

Cyanazine was detected in air samples (<0.03 - 4 ng/m³) in France where maximum concentrations occurred in early May which corresponded to regional application times (Chevreuil et al., 1996). In contrast to atrazine, cyanazine was only detected in the particulate phase of air during a single sampling event in the US (22 pg/m³) (Hawthorne et al., 1996). Maximum terbuthylazine concentrations were lower than reported for cyanazine in a French study (3 and 4 ng/m³, respectively) (Chevreuil et al., 1996). Maximum concentrations of atrazine and cyanazine were observed in early May, however, terbuthylazine maximum levels were detected in late May (Chevreuil et al., 1996).

The acetanilide herbicides also have been reported in air samples, although not as

extensively as the triazine herbicides. Alachlor has been more widely reported than metolachlor. Volatilization studies with alachlor indicate a similar loss mechanism as that of atrazine. Alachlor was found to volatilize from soil surfaces under moist conditions and a reduction in volatilization occurred corresponding to drying of soil (Glotfelty et al., 1989). A diurnal variation in volatilization was observed for alachlor, however, this did not occur for atrazine (Glotfelty et al., 1990). Alachlor and metolachlor were detected in air samples in Maryland (0.06 - 7.3 and 0.07 - 1.7 ng/m³, respectively) and seasonal patterns corresponded to regional applications (Glotfelty et al., 1990). Greater than 98% of these herbicides were detected in the vapour phase (Glotfelty et al., 1990). Alachlor and metolachlor were observed in air samples collected in a region remote from agricultural activity (6.7 - 87 and 32 - 81 pg/m³ alachlor and metolachlor, respectively), although maximum concentrations were lower than observed for use regions (Muir and Grift, 1995). Maximum air concentrations of alachlor (2.02 ng/m³) in an Italian forest were detected in May (Trevisan et al., 1993).

Although the phenoxyacid herbicides are not as persistent in the environment as the triazines or acetanilides and have lower vapour pressures, they have been reported in air. Phenoxyacid concentrations in atmospheric samples were elevated during regional uses of these products in Saskatchewan (Waite et al., 1995). Hawthorne et al. (1996) only detected MCPA and 2,4-D in the particulate phase of air samples collected in North Dakota in 1992 and 1993. 2,4-D concentrations observed were two orders of magnitude higher than MCPA (1770 and 70 pg/m³, respectively) (Hawthorne et al., 1996). Although dichlorprop was an analyte in the North Dakota study, it was not detected in air during 1992 or 1993 (Hawthorne

et al., 1996). 2,4-D was detected in air samples (<1 - 33 pg/m³) in northwestern Ontario, although samples were collected in a region removed from agricultural activity (Muir and Grift, 1995). The phenoxyacid herbicides 2,4-D and MCPA were detected in air samples (10 - 477 and 69 ng/m³, respectively) collected in Natal, South Africa. MCPA was only present in one sample and triclopyr was not detected throughout the sampling period (Sandmann et al., 1991). Although bromoxynil is not a phenoxyacid herbicide, it is frequently applied in formulations with the phenoxyacids. Bromoxynil was detected in air samples (<7 - 37 ng/m³) collected near known application sites in an air monitoring program in California (Baker et al., 1996).

Dinitroanilines are highly volatile, pre-emergent herbicides that have been detected in air samples from many regions. Air concentrations of trifluralin ranged from <1 - 78 pg/m³ in a remote location in northwestern Ontario between 1990 and 1992 (Muir and Grift, 1995). Hawthorne et al. (1996) reported trifluralin in both the vapour and particulate phase, however, >95% was present in the gas phase of air samples collected in North Dakota. Maximum concentrations (700 pg/m³) were observed in samples collected in the fall, despite this product generally being used as a pre-emergent herbicide. In North Dakota, up to four treatments of trifluralin are used within a growing season (Hawthorne et al., 1996). Levels of trifluralin reported in Italy ranged from below detection limits (1.17 ng/m³) to 5.6 ng/m³, with maximum concentrations occurring in May (Trevisan et al., 1993). In Japan, trifluralin was detected in air during 1992 (0.21 ng/m³) although it was not present in precipitation samples collected over the same period (Haraguchi et al., 1995). Volatilization studies with trifluralin and triallate have shown that losses of these chemicals increase with soil moisture

(Majewski et al., 1993). Diurnal patterns in volatilization flux were observed corresponding to daily drying of the soil (Majewski et al. 1993).

Chlorthal dimethyl, although not widely reported in the literature, has been studied in air samples as part of a volatilization study. Maximum concentrations of chlorthal dimethyl were found on the first day following application of the chemical after irrigation had taken place (Ross et al., 1990). Chlorthal dimethyl levels were found in the vapour phase under wet conditions and, conversely, associated with soil particles during dry conditions (Ross et al., 1990). During this study, an increase in volatilization was observed when wetting of the soil occurred, through irrigation or rain events (Ross et al., 1990). Chlorthal dimethyl was not detected in air samples collected in Japan (Haraguchi et al., 1995).

Chlorpyrifos levels in California were present at maximum concentrations during the peak of its application period (Zabik and Seiber, 1993). Concentrations of chlorpyrifos were found to decrease with increasing elevation, based on results from three elevation levels (<1.4 - 3900, <1.4 - 76 and <0.7 pg/m³ at 114, 533 and 1920 m, respectively). Schomburg et al. (1991) reported higher chlorpyrifos concentrations in agricultural rather than non-agricultural regions. McConnell et al. (1997) detected chlorpyrifos in 100% of the air samples collected in Chesapeake Bay, lowest concentrations were observed in samples collected during March (2-3 pg/m³) and maximum levels were observed in June (95 pg/m³).

2.2.2.2 Precipitation. Pesticides and other POPs may be removed from the atmosphere through association with rain during precipitation events and have been detected in wet deposition in the form of rain, fog and snow (Figure 2.2) (Poster and Baker, 1997; Gregor

et al., 1996; Goolsby et al., 1995; Capel et al., 1991; Gregor and Gummer, 1989; Glotfelty et al., 1987). There have been a few studies performed where pesticide loadings were determined in precipitation over the course of the rainfall event. Pesticide concentrations were found to decrease in rainwater as the precipitation period increased (Capel, 1991; Richards et al., 1987). Although many classes of pesticides have been detected in precipitation, triazine and acetanilide herbicides are the most frequently reported in the literature (Goolsby et al., 1997).

In a large study of pesticides in precipitation, atrazine and alachlor were present with increased detection frequency and in higher concentrations in the US midwest where these products are widely used, relative to regions where there is limited use of these products (Goolsby et al., 1997; Goolsby et al., 1995). Pesticide concentrations were highest in precipitation samples following regional application periods (Goolsby et al., 1994; Glotfelty et al., 1990). Bulk precipitation samples collected in Iowa indicated washout from the atmosphere of four of the most highly used herbicides in the region (atrazine, alachlor, metolachlor and cyanazine), however, trifluralin, which is applied to a large area of the sampling region, was not detected in rain samples throughout the study (Nations and Hallberg, 1992).

Triazine herbicide levels were below detection limits in snow samples collected between January and March in Switzerland, but they were detected in rainfall and maximum concentrations were observed in May and June (175 and 600 ng/L, respectively) following regional application (Buser, 1990). Bulk precipitation samples collected throughout the year in Maryland had detectable atrazine residues, although concentrations in winter were 1% of

the summer observations (Glotfelty et al., 1990). Although air samples collected in Japan had detectable levels of atrazine, it was not detectable in precipitation samples (Haraguchi et al., 1995).

Long range transport can result in the deposition of atrazine to areas of non-use. Despite restrictions on atrazine use in Germany, it was detected in precipitation samples collected at three sites (Seibers et al., 1994). Atrazine was detected in all precipitation samples collected in northern Germany and maximum concentrations were observed in rainfall samples collected at the end of May at two of the four sampling stations, which corresponded to atrazine use in the Netherlands and may indicate long range transport (Bester et al., 1995). Atrazine was detected at maximum concentrations ($1.99 \mu\text{g/L}$) in an Italian forest in June (Trevisan et al., 1993). Muir and Grift (1995) reported atrazine in precipitation at concentrations ranging from below detection limits (0.03 ng/L) to maximum levels (51 ng/L) in a region remote from atrazine use.

Terbuthylazine was detected in all precipitation samples collected in northern Germany during 1993 (Bester et al., 1995). Maximum concentrations ($>300 \text{ ng/L}$) were observed in rain samples collected at the end of May for two of the four sampling locations in the study. At a third location, maximum concentrations were observed during the beginning of June. The maximum concentrations of terbuthylazine in precipitation corresponded to local use periods for this chemical and decreased as distance between areas of use and sampling stations increased (Bester et al., 1995).

Alachlor was reported in precipitation samples collected in Italy, with maximum concentrations ($0.81 \mu\text{g/L}$) occurring in October (Trevisan et al., 1993). In the US, bulk

precipitation samples were collected throughout the year, however, alachlor was only present in samples collected between April and July (Glotfelty et al., 1990). Both alachlor and metolachlor were present in precipitation samples for short periods, following local applications. Alachlor also was detected in precipitation samples collected in northwestern Ontario, at a sampling station removed from pesticide use (Muir and Grift, 1995).

The phenoxyacid herbicides, MCPA and dichlorprop, were detected in precipitation in Norway at maximum concentrations during regional application periods (320 and 250 ng/L, respectively) (Lode et al., 1995). 2,4-D was present in precipitation in the boreal forest region of northwestern Ontario at concentrations ranging from <0.06 - 410 ng/L (Muir and Grift, 1995). In northern Italy, 2,4-D was below detection levels in precipitation, however, dichlorprop was detected (<0.058 - 1.81 $\mu\text{g/L}$) (Trevisan et al., 1993).

Trifluralin was one of the most frequently detected herbicides in precipitation in the same Italian study (Trevisan et al., 1993). It was not present, however, in Japanese rainfall samples, despite its presence in air samples collected at the same time (Haraguchi et al., 1995). Trifluralin concentrations ranged from <0.02 - 3.5 ng/L in northwestern Ontario rainfall (Muir and Grift, 1995), but in a study in Saskatchewan, trifluralin was not detected in any of the atmospheric samples collected (Waite et al., 1995). Triallate, another highly volatile compound was present in 53% of atmospheric samples collected on the prairies (Waite et al., 1995).

Chlorpyrifos was not observed in rainfall collected in Iowa despite its use regionally (Nations and Hallberg, 1992). Similarly, although chlorpyrifos is used in Germany, it was not detected in any precipitation samples collected between 1990 and 1992 (Seibers et al.,

1994).

2.3 Polychlorinated Biphenyls

PCB use has been restricted in North America since the late 1970s, however, they continue to be detected in atmospheric compartments, as well as in surface waters owing to their persistence in the environment (McConnell et al., 1996). PCB persistence in environmental matrices generally increases with increased number of chlorine atoms (Mackay et al., 1992).

PCBs are known to bioaccumulate in the fatty tissue of organisms (Bernhoft et al., 1994). The greatest accumulation in organisms occurs with congeners containing five to seven chlorines (Coulston and Kolbye, 1994). Movement of PCBs from liver and body fat to the brain has been shown to occur during reproduction and loss in body mass, resulting in higher PCB concentrations in the remaining lipid tissues (Henriksen et al., 1996).

The literature on biological effects of PCBs is very large and has been reviewed recently by Ahlborg et al. (1994) and Safe (1990). It will be summarized very briefly here. PCBs have been shown to produce sublethal effects in mammals and birds (Hutzinger et al., 1983). Studies with mink exposed to oral doses of PCBs have resulted in reproductive failure (Aulerich and Ringer, 1977; Bleavins et al., 1980). A reduction in fertility resulting from elevated levels of POPs, particularly PCBs, has been observed in both harbour and ringed seals from the Baltic Sea (Olsson et al., 1992; Helle et al., 1976a; Helle et al., 1976b). Similarly, a decrease in the reproductive performance in birds has been observed due to high

PCB levels (Delzell et al., 1994 ; Barron et al., 1995; Bosveld and van den Berg, 1994).

Other sublethal effects of PCB exposure have been observed including elevations in cytochrome P-450 dependent monooxygenases in mammals and fish (Tanabe et al., 1994). Immune system suppression has been observed in laboratory organisms exposed to PCBs including birds and mice, resulting in increased susceptibility to infections (Nikolaidis et al., 1988*a*; Nikolaidis et al., 1988*b*; Vos et al., 1988).

2.3.1 PCB Contamination of Surface Waters

PCBs have been detected in rivers, lakes and ocean environments, in the dissolved phase and in association with sediment particles and colloidal matter (Fox et al., 1996; Baker and Eisenreich, 1986; Capel and Eisenreich, 1985). Accumulation of PCBs on suspended particles in surface waters is known to occur due to their hydrophobic nature. PCB concentrations in water increase at the sediment-water interface as a result of resuspension from bottom sediments (Baker et al., 1991). Concentrations of PCBs and other hydrophobic organic chemicals associated with colloidal matter result in apparently increased dissolved phase measurements (Baker and Eisenreich, 1986). Dissolved phase levels of PCBs should, therefore, be corrected for the fraction bound to colloids (Jeremiason et al., 1997).

Sediment cores of two fluvial lakes along the St. Lawrence River were dated and measured for organic contaminant loads, including PCBs (Carignan et al., 1994). PCB concentrations in sediments in both Lake St. Francis and Lake St. Louis reflected PCB use periods, with concentrations near detection levels prior to 1950. Concentrations increased during the late 1950s, extending to 1963 (Carignan et al., 1994). Another peak in PCB

concentrations was observed in 1970, followed by a marked decrease in loadings. Couillard (1982) reviewed PCB data from the St. Lawrence region and found that both Lake St. Francis and Lake St. Louis were the most contaminated area in the region. PCB concentrations in Lake St. Louis sediments averaged 150 $\mu\text{g}/\text{kg}$, however, concentrations in river sediments contained 75-140 $\mu\text{g}/\text{kg}$ (Couillard, 1982).

In a determination of PCBs in Siskiwit Lake, a small lake on Isle Royale within Lake Superior, the average ΣPCB concentration in water samples was 2.3 ng/L (Swackhamer et al., 1988). Siskiwit Lake had PCB concentrations averaging 2.5 times higher than were observed in other regions of Lake Superior (Swackhamer et al., 1988). Similarly, Capel and Eisenreich (1985) observed elevated PCB concentrations in western regions of Lake Superior relative to other regions of the lake. Similarly, PCB concentrations were higher in the southern region of Lake Michigan, relative to levels in the northern part of the lake. Elevated levels in the southern part of Lake Michigan may be due to inputs from the Chicago area (Cotham and Bidleman, 1995). The Fox River, which receives discharge from 13 paper mills and 5 municipal wastewater treatment facilities, deposits PCB loadings into Green Bay (Hornbuckle et al., 1993). This heavy PCB load contributes to the elevated concentrations observed in Green Bay relative to the northern part of Lake Michigan (Hornbuckle et al., 1993).

In a number of other studies, regional differences in PCB concentrations have been observed in large lake systems. The highest concentrations of PCBs in Green Bay were observed in the lower bay area, near the mouth of the Fox River (Achman et al., 1993) and a decrease in concentration was observed corresponding to an increase in the distance from

the river mouth.

Similarly, Iwata et al. (1995) observed a change in congener contributions in Lake Baikal water samples collected from the centre of the lake compared to regions closer to the shoreline. The lower chlorinated congeners were the dominant homolog groups contributing to Σ PCBs in the central part of Lake Baikal, however, samples collected from other regions were dominated by the tetra- through hexachlorinated congeners (Iwata et al., 1995). The lower chlorinated homologs are dominant in surface water in the central part of Lake Baikal due to atmospheric contributions, however, nearer to shore, contributions from watershed runoff and river discharge altered congener contributions. Sovol, the PCB mixture used in Russia, contained the higher chlorinated congeners, which were deposited into regions where they could be transported into the lake via surface runoff and river inputs (Iwata et al., 1995).

In many studies, PCB concentrations in surface waters were dominated by the lower chlorinated homolog groups (Jeremiason et al., 1997; Hornbuckle et al., 1995; Achman et al., 1993; Baker and Eisenreich, 1990). Baker and Eisenreich (1990) reported that the congener profile of PCBs in Lake Superior was similar to observations in air samples collected from the region, dominated by the tri- and tetrachlorinated congeners. Achman et al. (1993) similarly determined that the tri- and tetrachlorinated congeners were dominant in Green Bay surface waters. In cruises of Lake Michigan between 1991 and 1993, the tri- and tetrachlorinated congeners represented 27% and 29%, respectively, of Σ PCBs present in the dissolved phase (Hornbuckle et al., 1995). In two lakes from a remote region in northwestern Ontario, the trichloro- and tetrachlorinated congeners were the largest contributors to Σ PCB loadings (Jeremiason et al., 1997). Lower PCB concentrations also

were observed in Lake Baikal samples collected in the northern basin, than in the south during a cruise in June, 1991 (McConnell et al., 1996). Surface water samples were dominated by the penta- and hexachlorinated congeners, similar to observations reported by Iwata et al. (1995). Surface runoff from soils contaminated by Sovol mixtures into lake waters contributed to these elevated levels of the higher chlorinated congeners. Σ PCB concentrations (560 ± 180 pg/L) in the dissolved phase observed by McConnell et al. (1996) in Lake Baikal were higher than reported by Iwata et al. (1995), which ranged between 18 and 590 pg/L.

Average total PCBs observed in Lake Superior were 547 ± 366 pg/L in 1986 based on analysis of 35 congeners (Baker and Eisenreich, 1990). In a more recent study of Lake Superior, Σ PCB concentrations were reduced to 180 pg/L (Jeremiason et al., 1994). Total PCB concentrations (460 - 8000 pg/L) observed in the dissolved phase of Green Bay water samples appear to be much higher than reported for Lake Superior by Baker and Eisenreich (1990), however, 50 more congeners were included in Σ PCB estimates (Achman et al. 1993). Jeremiason et al. (1997) measured similar PCB concentrations in two northwestern Ontario lakes (300 pg/L) as those observed in Green Bay. Seasonality in PCB levels was observed in the northwestern Ontario lakes with maximum concentrations occurring between May and June.

Iwata et al. (1993) reported Σ PCB results from a global survey performed between 1989 and 1990 in which samples were collected in 18 seas and in the Pacific, Atlantic and Indian Oceans. The lowest mean Σ PCB concentration (dissolved) was observed in the Southern Indian Ocean (8.3 pg/L) and the highest in the Mediterranean Sea (27 pg/L). PCB

congener composition in surface waters were found to differ between regions from the higher and lower latitudes (Iwata et al., 1993). Based on the results of this survey, tropical Asia is a significant emission source of PCBs.

PCB concentrations measured in the ship canal of the Hamilton Harbour were measured at two depths (Fox et al., 1996). PCBs present in the dissolved phase represented 30 -70% of Σ PCBs determined in surface water samples (Fox et al., 1996). Reported concentrations in the upper layer were higher than in the lower layer (6300 - 11400 pg/L and 4000 - 8900 pg/L, respectively). Concentrations reported are the sum of 13 congeners analyzed in the study (Fox et al., 1996). Much greater concentrations would be expected if a larger group of congeners were determined.

Maximum Σ PCB concentrations in the Fox River (150 ng/L) were observed near the DePere dam during sample collection between 1988 and 1993 as compared to previous measurements when PCB concentrations exceeded 250 ng/L (Velleux et al., 1995). Contamination of the river waters as they entered Green Bay was found to originate from river bed sediments. Velleux and Endicott (1994) found that a 60% increase in PCB transport occurred between the DePere dam and the river mouth into Green Bay, due to resuspension of river sediments. PCBs were generally associated with the particulate phase in the Fox River upon entry into Green Bay.

A high variation in PCB water concentrations was observed among tributaries of Lake Michigan. Higher Σ PCB concentrations were observed in outlet channels which pass through the urban and industrial regions of Calumet and Chicago (>200 ng/L) (Marti and Armstrong, 1990). These extremely high concentrations were similar to levels reported in

the 1970s when PCBs were in use. Average PCB concentrations in these river systems were higher than observed in lake waters (7 - 103 ng/L) , although a high degree of variation was observed (Marti and Endicott, 1990). Factors contributing to the high variability were reported to be fluctuations in local sources, river discharge, sediment resuspension and differences in the rate of release from sediments (Marti and Endicott, 1990).

Monitoring programs in the Canadian prairie region have detected PCBs in prairie river systems. Of 18 water samples collected on the prairies, PCBs were detected in one sample (5.7 ng/L) which was collected from the Qu'Appelle River in Saskatchewan (Chacko et al., 1991). PCBs were below detection (3.3 ng/L) in all other water samples collected from rivers in Manitoba and Saskatchewan, which may be a result of the high method detection limits for PCBs in the monitoring program. PCBs, however, were detected with greater frequency in macrophytes and forage fish from these river systems, including the Red River at Emerson, Manitoba (Chacko et al., 1991).

2.3.2 PCBs in the Atmosphere

2.3.2.1 Air. PCBs are present in the atmosphere throughout the world. The majority of PCBs measured in air have been found in the vapour phase, rather than associated with particulates (Manchester-Neesvig and Andren, 1989). The fraction of PCBs associated with the aerosol phase was shown to be consistent throughout the year, with no seasonal variation, in one of the earlier studies on PCB loadings in the Great Lakes region (Swackhamer et al., 1988). However, seasonal variation in air concentrations of PCBs has been observed in more recent studies (Jeremiason et al., 1997; Monosmith and Hermanson, 1996; Hoff et al., 1992a; 1992b).

Air measurements in North America have shown that the lower chlorinated (di- through tetrachlorinated) congeners contribute the greatest amount of PCBs, rather than the less volatile, higher chlorinated compounds (Jeremiason et al., 1997; Hornbuckle et al., 1994; Achman et al., 1993; Swackhamer et al., 1988). Iwata et al. (1995), however, found that air concentrations of Σ PCBs were dominated by the tetra- through hexachlorinated congeners in the Lake Baikal region. These differences in homolog contribution to air levels were attributed to the congener profile of the Sovol mixtures used in Russia (Iwata et al., 1995). Air concentrations observed the previous year in the Lake Baikal region were dominated by the lower chlorinated congeners, similar to North American observations (McConnell et al., 1996). Regional vapour phase concentrations observed by Iwata et al. (1995) also were lower than reported by McConnell et al. (1996) (9-23 and 113-1387 pg/m^3 , respectively). The 1991 samples were collected during warmer temperatures, resulting in the higher concentrations observed by McConnell et al. (1996).

In an intensive sampling program, Hoff et al. (1992a) measured PCBs and a variety of halogenated pesticides in air near the Great Lakes region, at Egbert Ontario. An annual trend in air concentrations was observed for PCBs in the Egbert study, where concentrations ranged from $<1 \text{ pg}/\text{m}^3$ - $2000 \text{ pg}/\text{m}^3$ (Hoff et al., 1992a). Higher Σ PCB concentrations were observed in the summer than in the winter months corresponding to ambient air temperatures. Hoff et al. (1992b) found good correlations between vapour phase air concentrations and inverse temperature indicating the source of PCBs was volatilization from surfaces. This was the first study that had been performed throughout the year with a high resolution sampling schedule. In most sampling programs, samples have been collected with

high frequency for a short duration or at low frequency over extended periods.

Vapour phase concentrations have been correlated with air temperature in a number of studies following the work of Hoff et al. (1992*b*). Total PCB levels in North Dakota, at a location removed from industrial activity, were $<50 \text{ pg/m}^3$ (Hawthorne et al., 1996). Although no correlation was developed in the study, elevated concentrations were observed during periods with higher temperatures (Hawthorne et al., 1996). A significant inverse relationship between ΣPCB concentration and air temperature ($r^2=0.52$) was developed at the Experimental Lakes Area in northwestern Ontario, where maximum concentrations (330 pg/m^3) were observed in early July 1994 (Jeremiason et al., 1997).

Air concentrations of PCBs were determined at three locations in the Great Lakes region with one site located close to urban activity and the other two being more remote (Hillery et al., 1997). Gas phase concentrations were similar to levels reported by other researchers (mean values $89 - 370 \text{ pg/m}^3$). Air concentrations were significantly correlated with air temperatures using Clausius-Clapeyron type relationships, similar to observations reported by Hoff et al. (1992*b*) (Hillery et al., 1997). Additional factors (e.g., wind speed and direction) were added to the relationship between concentrations and air temperature in an effort to further explain seasonal fluctuations in PCB levels, however, these additional parameters only improved the correlation slightly (Hillery et al., 1997).

No significant relationship between vapour phase concentrations and temperature, however, was observed by Achman et al. (1993) in the Great Lakes region, although concentrations were within the range reported by other researchers ($250 - 2300 \text{ pg/m}^3$). Similarly, no correlations between air temperature and PCB concentrations were established

in air samples collected from both urban and rural settings in France. The highest concentrations were observed during periods of air temperature exceeding 18°C and low levels corresponded to temperatures below 13°C (4900 pg/m³ and 300 pg/m³, respectively) (Chevreuil et al., 1996). The lack of relationship in the French study was attributed to variable air mass origins (Chevreuil et al., 1996).

In a comparison between PCB levels at a rural site with air concentrations from urban Chicago, differences between homolog contributions to ΣPCB loadings were observed (Cotham and Bidleman, 1995). The penta- through heptachlorinated congeners contributed the largest amount to total PCB levels in air at the rural site at Green Bay, while the lower chlorinated congeners contributed to the largest extent to Chicago air levels (Cotham and Bidleman, 1995). Air concentrations observed ranged from 300 - 1000 pg/m³, similar to other reported results for the region (Cotham and Bidleman, 1995).

Spatial differences in ΣPCB concentrations were observed along the coast of Lake Michigan (Monosmith and Hermanson, 1996). Although PCB concentrations at Traverse Bay (75 - 2013 pg/m³) were higher than observed at Saginaw (206 - 1080 pg/m³) and Sault Ste. Marie (28 - 883 pg/m³), concentrations were similar to other remote areas of the Great Lakes region. PCB concentrations were higher during the summer months than at the colder temperatures experienced in winter along Lake Michigan (Monosmith and Hermanson, 1996).

In the United Kingdom, air samples were collected from four urban areas during 1991 and 1992 for determination of PCB concentrations. PCB concentrations were highest in London (3850 pg/m³), the largest urban centre under investigation (Halsall et al., 1995).

Maximum air concentrations observed ranged between 112 - 3850 pg/m³, similar to concentrations reported in studies in the Great Lakes region of Canada (Halsall et al., 1995). The dominant homolog groups in air samples were the lower chlorinated congeners in each region. Elevated PCB levels were observed during the warmer summer months (Halsall et al., 1995).

A long term sampling program was established in the Canadian and Russian Arctic to measure POPs including PCBs in air. Mean Σ PCB concentrations (100 congeners) for 1993 ranged from 17 - 34 pg/m³ (Stern et al., 1997). In this study, weak relationships between air temperature and PCB concentrations were observed, similar to the observations in Norwegian air samples (Stern et al., 1997; Oehme et al., 1996). The lack of relationship between PCB concentrations and air temperature is in contrast to observations in the Great Lakes region. Stronger correlations are expected in the Great Lakes Region because it is much closer to PCB sources than the sites in Norway and the Arctic (Stern et al., 1997; Oehme et al., 1996).

Although many studies report similar levels of Σ PCBs in atmospheric samples, direct comparison is not always possible or accurate. PCB concentrations reported may be totals of a few congeners (e.g., eight (Halsall et al., 1995); Oehme et al. 1996), however, other reported PCB levels may be the result of contributions from 90 or more congeners (Stern et al., 1997). In general, seasonal concentration patterns have been observed in temperate zones, however, relatively few studies have determined the relationship between air temperature and vapour phase PCB concentrations. Without these data, it is difficult to compare between reported temporal trends.

Although contaminant loadings in the atmosphere have been determined for many years, true temporal definition is quite limited. Hoff et al. (1992a) have reported a year long sampling program with high resolution (two-day cycle), however, few sampling regimes continue throughout all seasons annually. The Integrated Atmospheric Deposition Network (IADN) in the Great Lakes region is one of the long term studies where sample collection has been performed on an annual cycle, for a period of years (Hillery et al., 1997). The reported program in the Arctic is rare in that it provides high resolution sampling (weekly sample collection), in combination with numerous years of data (Stern et al., 1997).

2.3.2.2 Precipitation. PCBs have been detected in precipitation samples collected from a wide range of locations studied in North America (Offenberg and Baker, 1997; Capel et al., 1991; Gregor and Gummer, 1989). PCB concentrations in snow samples from the Canadian Arctic ranged between 0.2 and 1.76 ng/L, however, the majority of observations resulted in Σ PCB levels of <1 ng/L (Gregor and Gummer, 1989). In subsequent measurements of PCBs in the Arctic, snow samples collected on a weekly basis at two locations were found to contain higher Σ PCB concentrations than snow pack samples from the same regions (Gregor et al., 1996). PCB concentrations in snow from sampling sites at Mould Bay and Eureka ranged from 7 ng/L to >20 ng/L and 17.6 to 32.5 ng/L, with average concentrations of 14 and 23.7 ng/L, respectively (Gregor et al., 1996). Average concentrations observed in snow pack samples, however, were 5.7 and 3.1 ng/L, for Mould Bay and Eureka, respectively (Gregor et al., 1996).

Capel et al. (1991) measured PCBs during foggy periods between September and December in Switzerland. Reported concentrations were 7 - 22 ng/L, a total of 31 congeners

measured. Deposition of PCBs associated with fog was estimated to be 100 times greater than deposition through rainfall during this study (Capel et al., 1991).

In the Great Lakes region, many studies have detected PCBs in precipitation samples. Maximum PCB concentrations in precipitation samples from a Lake Michigan sampling site (7.2 ng/L) were lower than observed at an urban Chicago location (189 ng/L) (Offenberg and Baker, 1997). Congeners associated with particles rather than in the vapour phase were dominant in precipitation samples collected. As with the other sites, maximum Σ PCB concentrations observed were 8.14, 32.4 and 32.4 ng/L at Fayette State Park, Peninsula State Park and Green Bay, respectively (Franz and Eisenreich, 1993). Although PCBs were measured between October and May, no seasonal trends were observed, in contrast to the seasonality observed in air PCB levels. Similar homolog profiles were present in rain and snow samples with the lower chlorinated congeners dominating Σ PCB concentrations (Franz et al., 1993; Swackhamer et al., 1988). Swackhamer et al. (1988) measured higher PCB concentrations in precipitation at Isle Royale in Lake Superior, although fewer congeners were measured than have been reported in the more recent studies.

3. A MULTI-YEAR STUDY OF FOUR HERBICIDES IN SURFACE WATER OF A SMALL PRAIRIE WATERSHED

3.1 Abstract

Temporal trends of three phenoxy- herbicides (2,4-D, dichlorprop and MCPA) and bromoxynil were determined in the South Tobacco Creek, which drains a 70 km² agricultural watershed near Miami, Manitoba, over a four-year sampling program. The quantities of all pesticides used in the watershed and their application times were accurately recorded with the cooperation of landowners. Herbicide concentrations in South Tobacco Creek ranged from <0.01 ng/L to a maximum concentration of 680 ng/L for 2,4-D and reflected local application times. Spring melt contributions were important when no significant runoff events occurred late in the previous growing season. Discharge of these herbicides in the South Tobacco Creek was calculated to be < 0.01% of their quantities used within the watershed. No correlation was found between the water quality parameters: total organic carbon, total nitrogen and total phosphorus and herbicide concentrations in South Tobacco Creek. Total nitrogen and phosphorus, however, were correlated to water flow, indicating runoff and groundwater sources rather than atmospheric. We concluded that detailed temporal patterns of herbicides and nutrients could only be established if high sampling frequency was maintained during such critical periods such as application periods and during major runoff events. An unexpected finding was that herbicide levels were not related to runoff losses,

but instead they did correspond to elevated levels in precipitation and air measured within the watershed.

3.2 Introduction

The phenoxyacid and phenolic type herbicides are widely used in the Canadian prairie region and in the northern Great Plains of the US, adjacent to Canada. Estimates of 2,4-D [(2,4-dichlorophenoxy)acetic acid], MCPA [(4-chloro-2-methylphenoxy)acetic acid], dichlorprop [(RS)-2-(2,4-dichlorophenoxy)propionic acid] and bromoxynil [3,5-dibromo-4-hydroxybenzotrile] use in southern Manitoba during the late 1980s were 495, 595, 253, and 55 tonnes per year, respectively (Environment Canada, 1990). Monitoring programs in both the US (Zaugg et al., 1995) and in Canada (Currie and Williamson, 1995) include measurements of the phenoxyacid and phenolic herbicides, although the results have not been as widely reported in surface waters as results for the more persistent compounds, such as atrazine. Currie and Williamson (1995) found 2,4-D to be the most frequently detected herbicide in southern Manitoba river waters. The acidic/phenolic compounds, including 2,4-D, MCPA, dichlorprop and bromoxynil, have been detected in both western Canada and US surface waters (Donald and Syrgiannis, 1995; Tornes and Brigham, 1994; Beck et al., 1992; Muir and Grift, 1987) and in atmospheric compartments (Waite et al., 1995; Hawthorne et al., 1996), despite their relatively short persistence in soil (Table 3.1).

The temporal pattern of herbicides in surface water systems has been shown to be highly seasonal and variable between years (Pereira and Hostettler, 1993). Maximum

concentrations of 2,4-D in the Red River at Emerson, Manitoba occur during March and June, annually (Tornes and Brigham, 1994), which correspond to spring runoff and application periods. Seasonal maximum concentrations of 2,4-D and MCPA in surface waters draining agricultural watersheds in Georgia and Alabama occur in April and May, respectively, which coincide with the majority of local use of these chemicals (Hippe et al., 1994). Variability in results may reflect changes in use patterns of a chemical, in addition to differences in meteorological conditions between growing seasons.

Table 3.1 Comparison of the chemical properties of the well-studied neutral compound atrazine with three phenoxyacid and one phenolic herbicide used in this study. (Wauchope et al., 1992).

Herbicide	Water Solubility	Half-life (d)	Soil Sorption (Koc)
Atrazine	33	60	100
Bromoxynil (phenol)	130	7	190
2,4-D	890	10	20
Dichlorprop	350	10 ^a	170
MCPA	825	25	110

^aester

The present study was performed in the South Tobacco Creek Watershed in southern Manitoba, near the town of Miami. The South Tobacco Creek Watershed (49°19'28"N, 98°21'50"W) (Figure 3.1) is a 70 km² agricultural watershed which originates in the Pembina Hills of Manitoba. The creek draining this watershed flows down an escarpment and drops

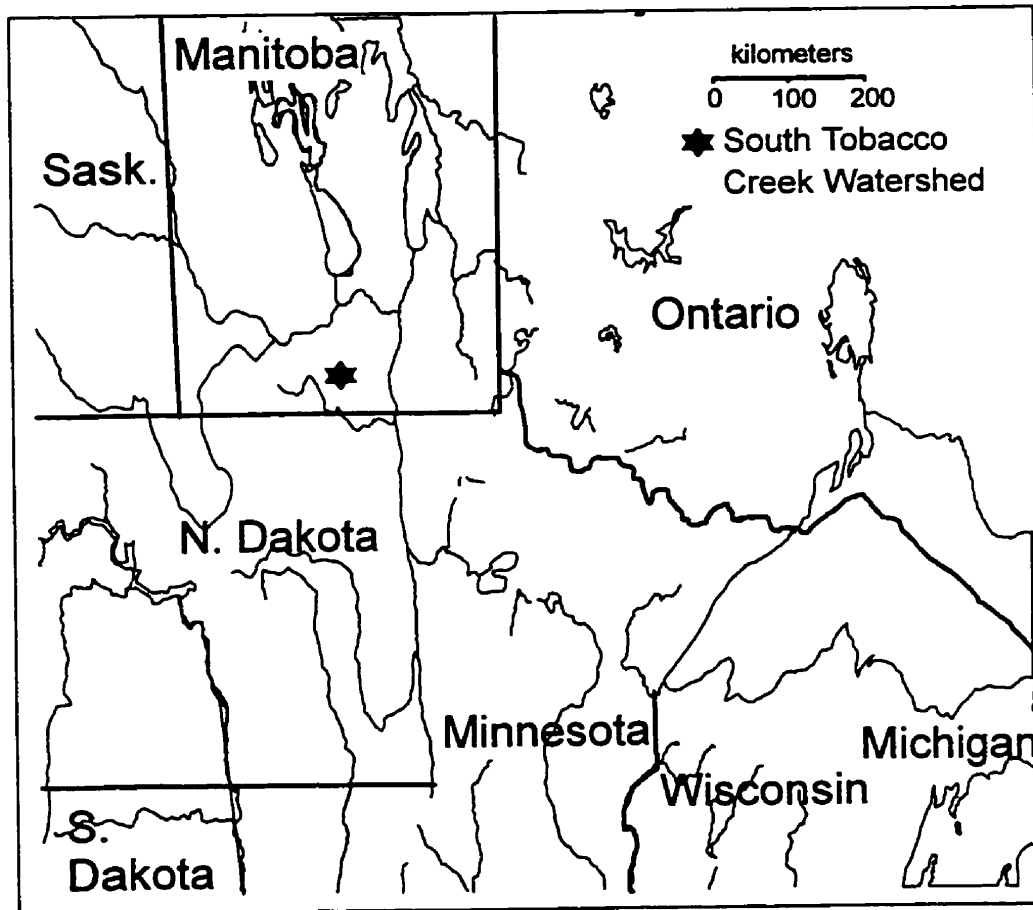


Figure 3.1 Location of the South Tobacco Creek Watershed.

approximately 130 m over an eight km distance (Yarotski, 1996). Landuse within the watershed is well-characterized and both meteorological information for the watershed and hydrological data for the creek draining this region were available (Yarotski, 1996; Miller, 1995; Miller, 1994; Water Survey of Canada, 1994-1996). With the cooperation of landowners and the Prairie Farm Rehabilitation Agency (PFRA), we were able to obtain detailed landuse practices which included cropping practices and pesticide application information. Details of the formulation applied and rate of application, on a field by field basis was provided by the landowners for each year of the study. Application data were recorded on a weekly basis to ensure that correlations between local use and levels detected in the creek water would be possible. Each of the four herbicides discussed here were among the top 10 chemicals applied within the South Tobacco Creek Watershed, each year of the study. The creek banks are surrounded by forested strips, which may act as a buffer zone from rinsing of equipment after application of herbicides or spray drift during application.

The purpose of this study was to develop relationships between use patterns and concentrations of four of the major herbicides applied within the South Tobacco Creek Watershed and to determine the relative losses via discharge for these chemicals. Additionally our aim was to determine whether relationships between herbicide or nutrient levels and water flow existed in this watershed. In a companion paper (Rawn et al., 1998a (Chapter 4)) we examined precipitation and air concentrations of the same four herbicides. This program was part of a larger study of levels and sources of pesticides in the South Tobacco Creek Watershed (Rawn, 1998).

3.3 Materials and Methods

3.3.1 Sample Collection

Creek water samples were collected over a four year period, 1993-1996 at the outflow of the watershed near Miami. In the first three years of the study, 18 L water volumes were collected in stainless steel containers, using a submersible pump in the centre of the creek. Samples were collected on a weekly (1994-5) and biweekly (July - October 1993) sampling schedule from spring melt through freeze up. During 1996, 2 L samples were collected every second day during the local pesticide application period (June - July). Samples were transported to the lab and stored at 4°C until samples were processed. Samples were filtered under pressure using pre-cleaned 1 μ m GFA filters prior to extraction. Water samples (1 L) were collected for water chemistry parameters including total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), conductivity and non-filterable residue (NFR), sulfate (SO₄⁻) and chloride (Cl⁻) by lowering a weighted sample bottle into the centre of the water flow.

Automated water samplers (American Sigma Inc, New York, USA) were setup for runoff collection during periods of overland flow from two cropped fields, known as the Twin Watershed (Figure 3.2). No runoff events occurred and the samplers were not triggered during the pesticide application period. Autosamplers also were setup at two sites on South Tobacco Creek to collect samples during periods of high water flow caused by spring melt or heavy rain events. Daily water flow was recorded at the Environment Canada hydrometric station in South Tobacco Creek near Miami, MB and at the Twin Watershed site during

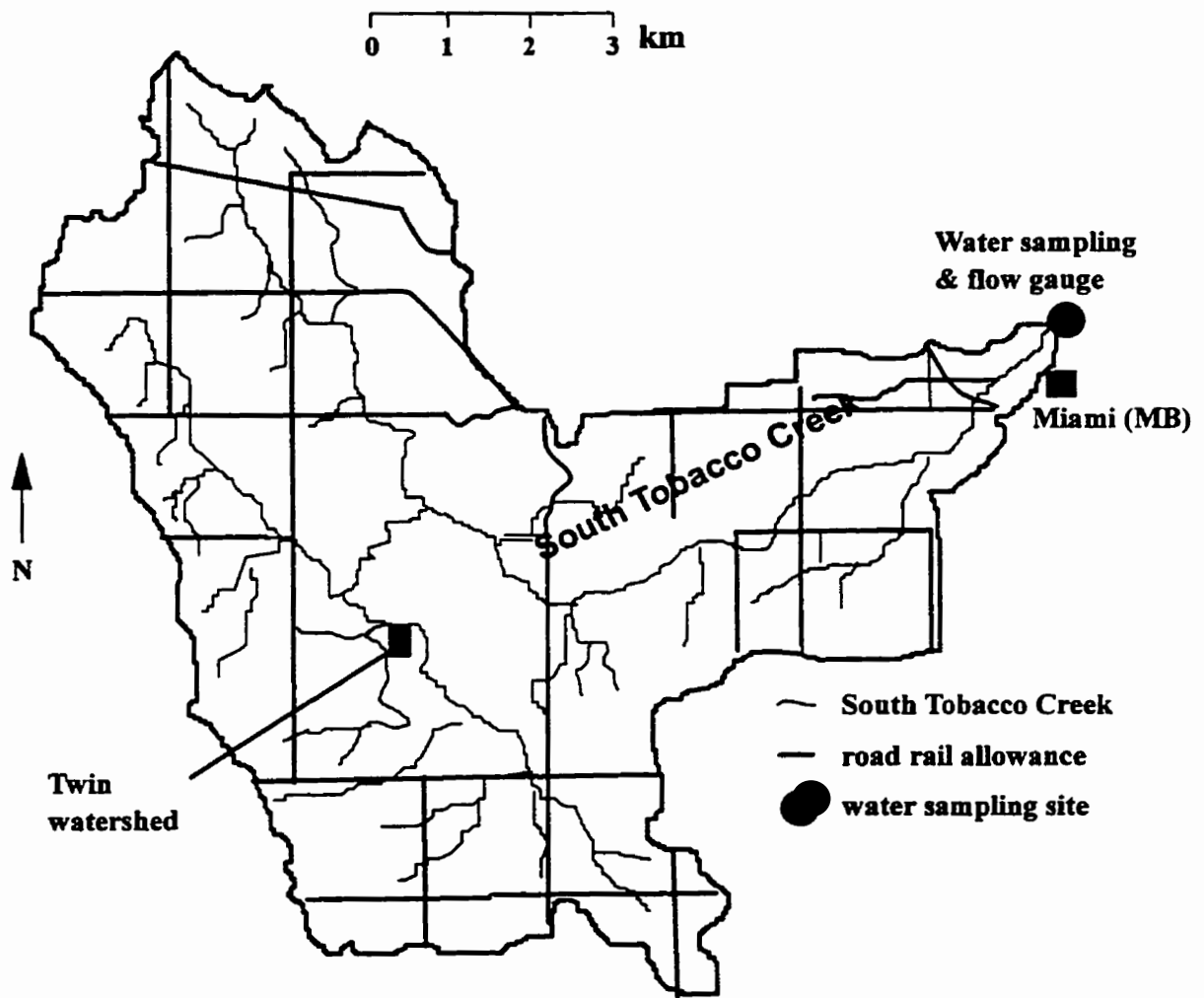


Figure 3.2 Map of the South Tobacco Creek Watershed.

periods of water flow.

3.3.2 Sample Analysis

Dissolved herbicides were extracted using a broad spectrum approach for both acidic and neutral compounds (e.g., 2,4-D and atrazine). Large volume samples were adjusted to pH 2 using sulphuric acid and mixed with dichloromethane (DCM) to extract acid herbicides followed by adjustment to pH 10 using 10 M NaOH to extract the hydrophobic organics. During 1996, 2 L samples were extracted following an adaptation of the USGS method (Burkhardt and Werner, 1994), using pre-conditioned solid phase extraction cartridges packed with Carbo-pack B (Supelco Sigma-Aldrich Canada Ltd.). Cartridges were eluted with 1 mL methanol, 6 mL 80:20 DCM:methanol followed by 8 mL 0.2% trifluoroacetic acid in 80:20 DCM:methanol. Sample extracts were evaporated to small volumes and methylated using freshly prepared diazomethane. Extracts were cleaned up using 5% deactivated Florisil, eluting with 20 mL hexane to remove polychlorinated biphenyls, followed by 85 mL, 18% ethyl acetate (EtAc) in hexane. The acid and phenolic herbicides were then analyzed as methyl ester derivatives after derivatization with diazomethane. Sample extracts were analysed by high resolution gas chromatography-low resolution mass spectrometry (Select Ion Monitoring) (Hewlett Packard 5971 MSD) using a 60 m x 0.25 μ m DB-5 column with helium as the carrier gas. Detection criteria were the correct ratios of two characteristic ions and retention times. Herbicides were quantified using external standard solutions and corrected for volume changes using PCB-104. Blanks of "Super Q" water were analyzed with each batch of samples. Average spike recoveries of triplicates analyses at both 10 ng/L and 100 ng/L for 18 L volumes were 26%, 115%, 52% and 65% for MCPA, dichlorprop,

2,4-D and bromoxynil, respectively. Spike recoveries for 2 L volumes were 59%, 100%, 77% and 70%, for MCPA, dichlorprop, 2,4-D and bromoxynil, respectively. Detection limits for 18 L volumes were calculated to be 7, 10, 11 and 15 pg/L for dichlorprop, MCPA, 2,4-D and bromoxynil, respectively, using instrument detection limits plus three times the standard deviation of the lowest concentration analysis (Keith, 1991). TOC, TN, TP loadings in South Tobacco Creek were measured following standard colorimetric techniques for nutrient analysis (Environment Canada, 1997).

Discharge of each chemical from this agricultural watershed via the South Tobacco Creek was calculated for each complete season of study (1994 and 1995) and for 1996, between late May extending into August. For purposes of discharge calculation during 1994 and 1995, MCPA, 2,4-D and bromoxynil concentrations were corrected for recovery efficiency. Discharge was calculated as the product of herbicide concentration and water flow for each day (Larson et al., 1995). Herbicide concentrations were estimated by linear interpolation for days when sampling was not performed and concentrations below detection limits were assigned a value of zero (Larson et al., 1995) in all discharge calculations. The daily discharge values were summed for the sampling season (March - end of October), to give the total seasonal discharge values.

3.4 Results

3.4.1 Temporal Patterns

South Tobacco Creek water ranged in TOC from 6.8 to 43 mg/L and in pH from 6.7 to 8.0, during the course of the study. Total nitrogen ranged from 0.3 to 4.3 mg/L and TP ranged from 0.05 to 2.9 mg/L. Nutrient loadings in South Tobacco Creek were elevated during high flow periods corresponding to overland flow caused by spring melt and heavy rains (Figure 3.3). Lower levels of TOC, TN and TP were observed during periods of reduced flow.

Distinct seasonal concentration patterns were observed for MCPA, dichlorprop, 2,4-D and bromoxynil over the four years of the study (Figures 3.4 - 3.7). These patterns may be divided into the spring, when snowmelt and runoff from fields occurred, the application period and the post-application period, which extended to freeze up and snow cover. In general, the highest herbicide concentrations corresponded to the period of application for each chemical within the watershed. The 1994 field season was relatively dry with no runoff events occurring over the growing season. The South Tobacco Creek was dry for an extended time between late July and early September in 1994. Rain events in October produced overland flow within the watershed, however, pesticide loss from fields during that time was not initially considered to be important due to the long period of time between application of chemicals and rain events. However, because of the unusually low herbicide levels observed in the 1995 spring melt, the fall runoff event in 1994 may have been more

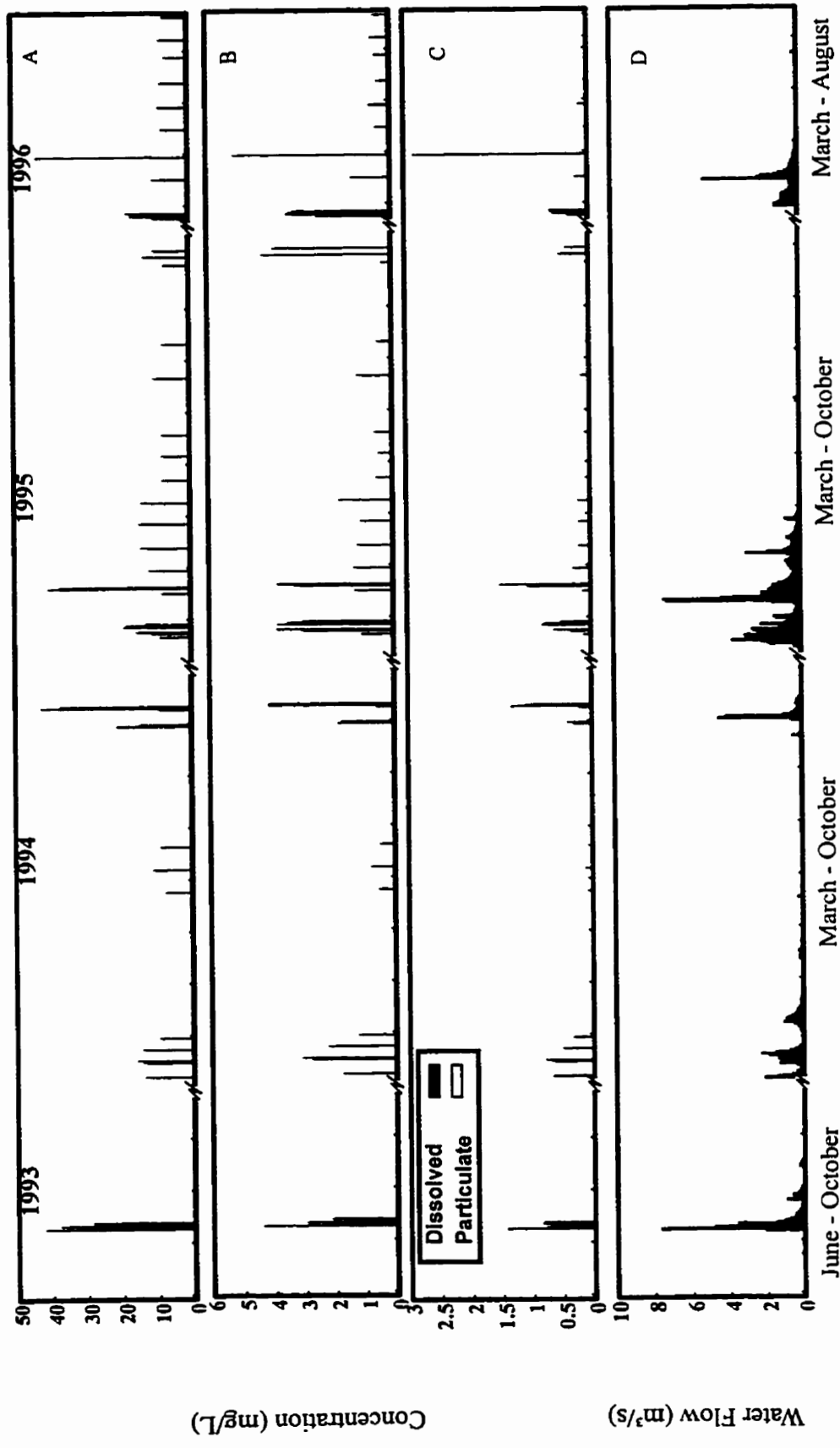


Figure 3.3 Nutrient loading in the South Tobacco Creek 1993-1996. A) Total organic carbon, B) Total nitrogen, C) Total phosphorus. Water flow is indicated in D.

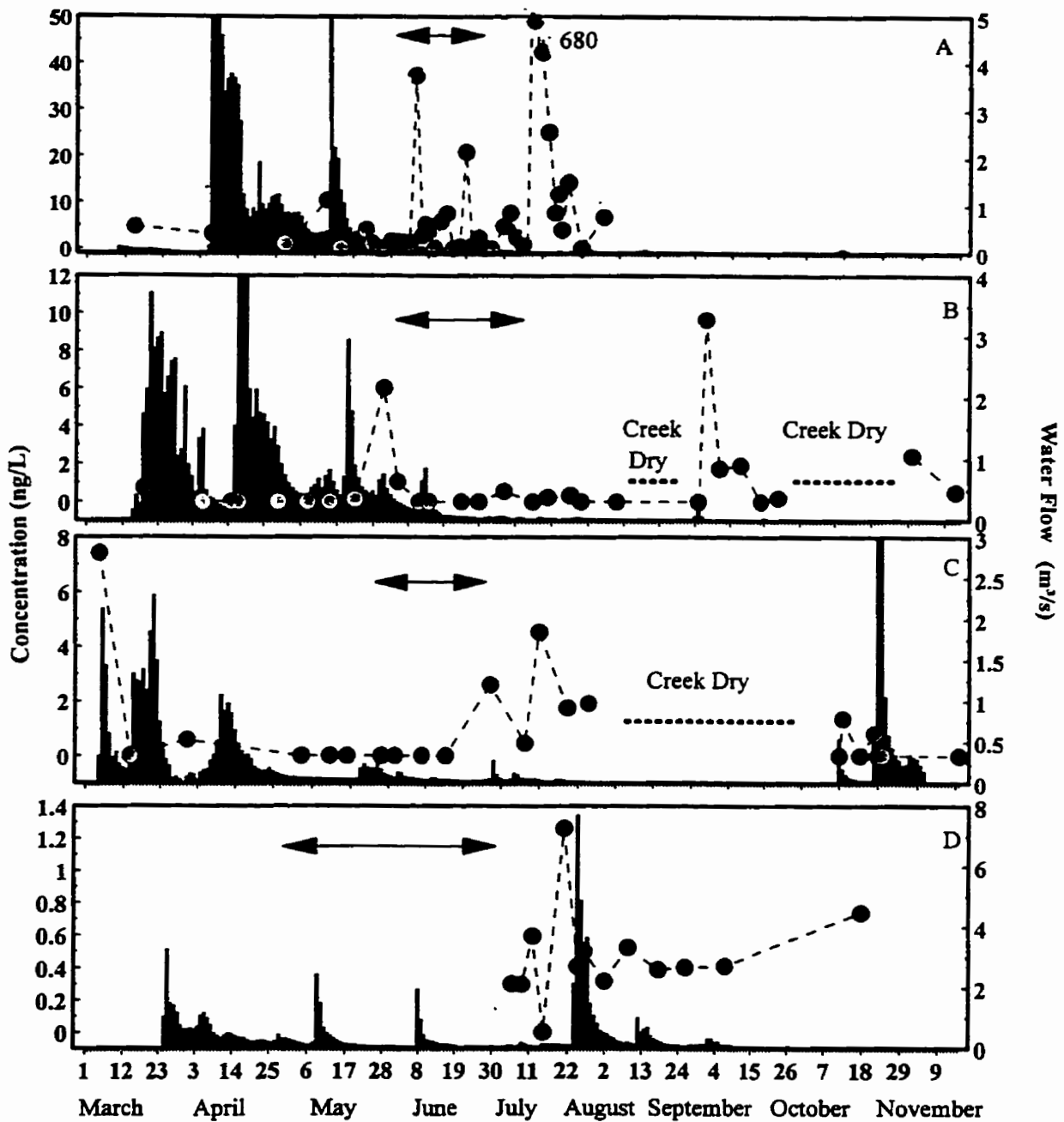


Figure 3.4 2,4-D concentrations in the dissolved phase of the South Tobacco Creek. A) 1996, B) 1995, C) 1994 and D) 1993. Water flow is indicated by the bar graph, scale on the right. (Dry periods are indicated by ---; application period indicated by ↔). NOTE: Concentration scale differences between A,B,C and D.

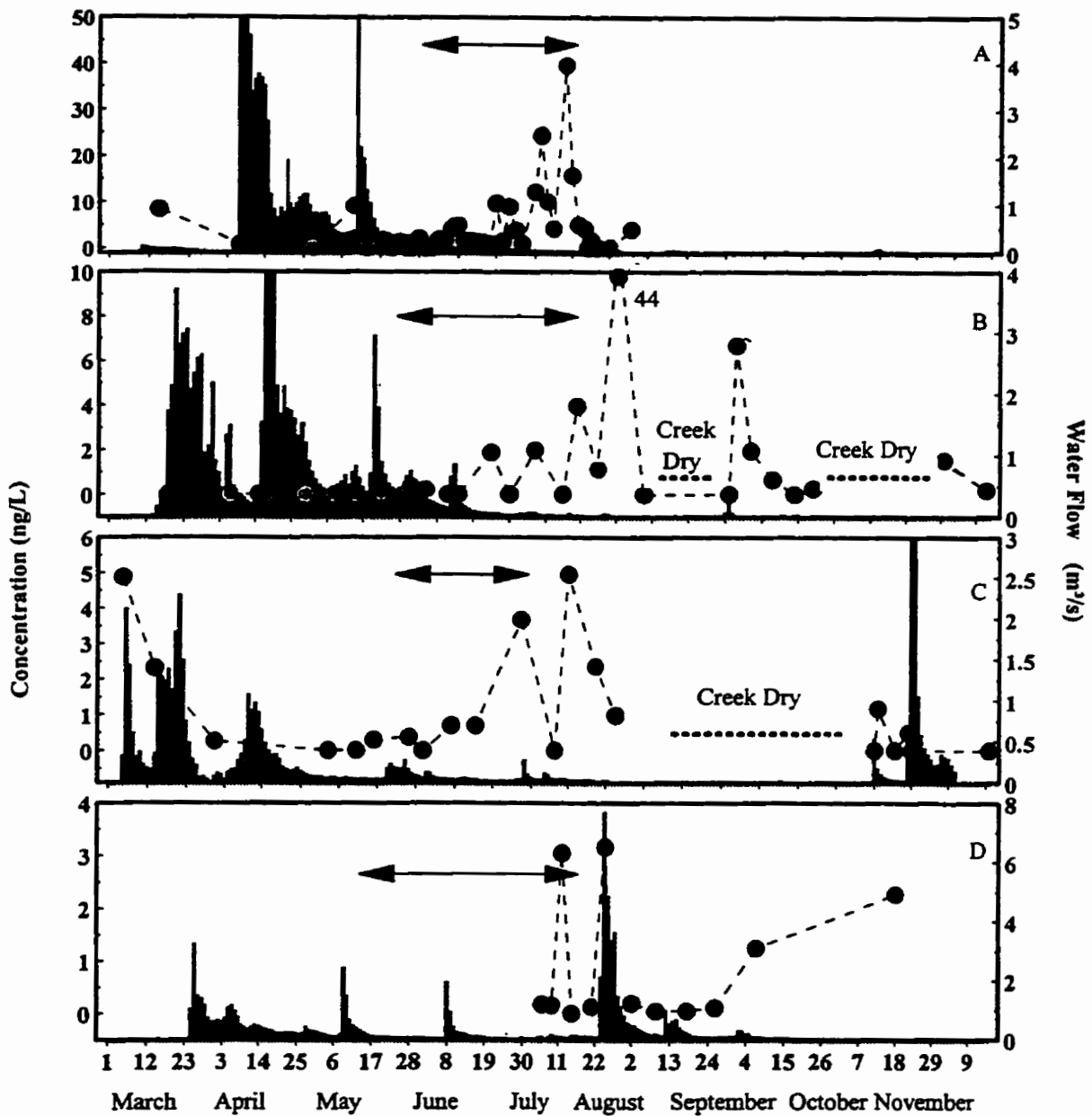


Figure 3.5 MCPA concentrations in the dissolved phase of the South Tobacco Creek. A) 1996, B) 1995, C) 1994 and D) 1993. Water flow is indicated by the bar graph, scale on the right. (Dry periods are indicated by - - -; application period indicated by ↔). NOTE: Concentration scale differences between A,B,C and D.

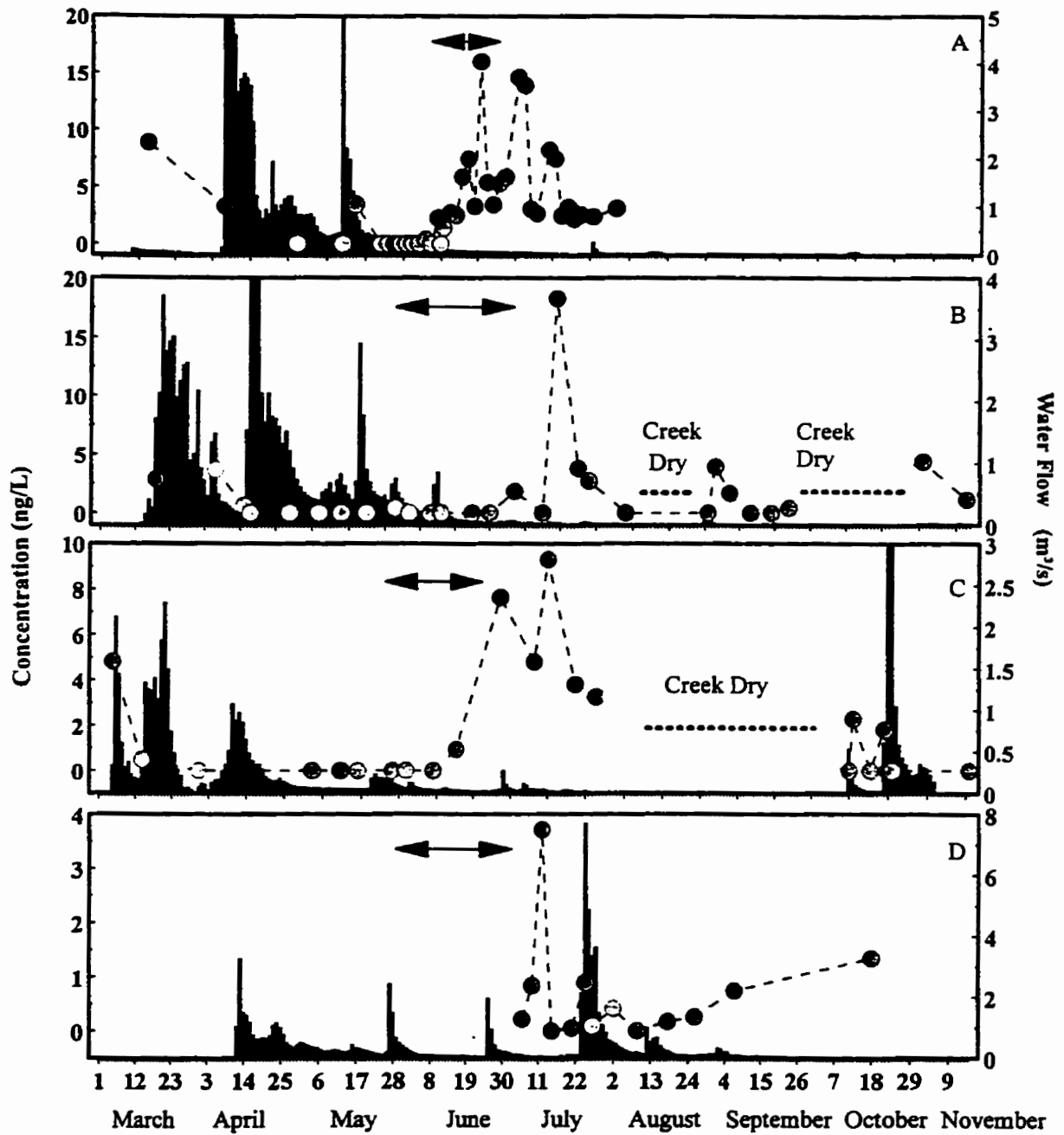


Figure 3.6 Dichlorprop concentrations in the dissolved phase of the South Tobacco Creek. A) 1996, B) 1995, C) 1994 and D) 1993. Water flow is indicated by the bar graph, scale on the right. (Dry periods are indicated by - - -; application period indicated by ↔). NOTE: Concentration scale differences between A,B,C and D.

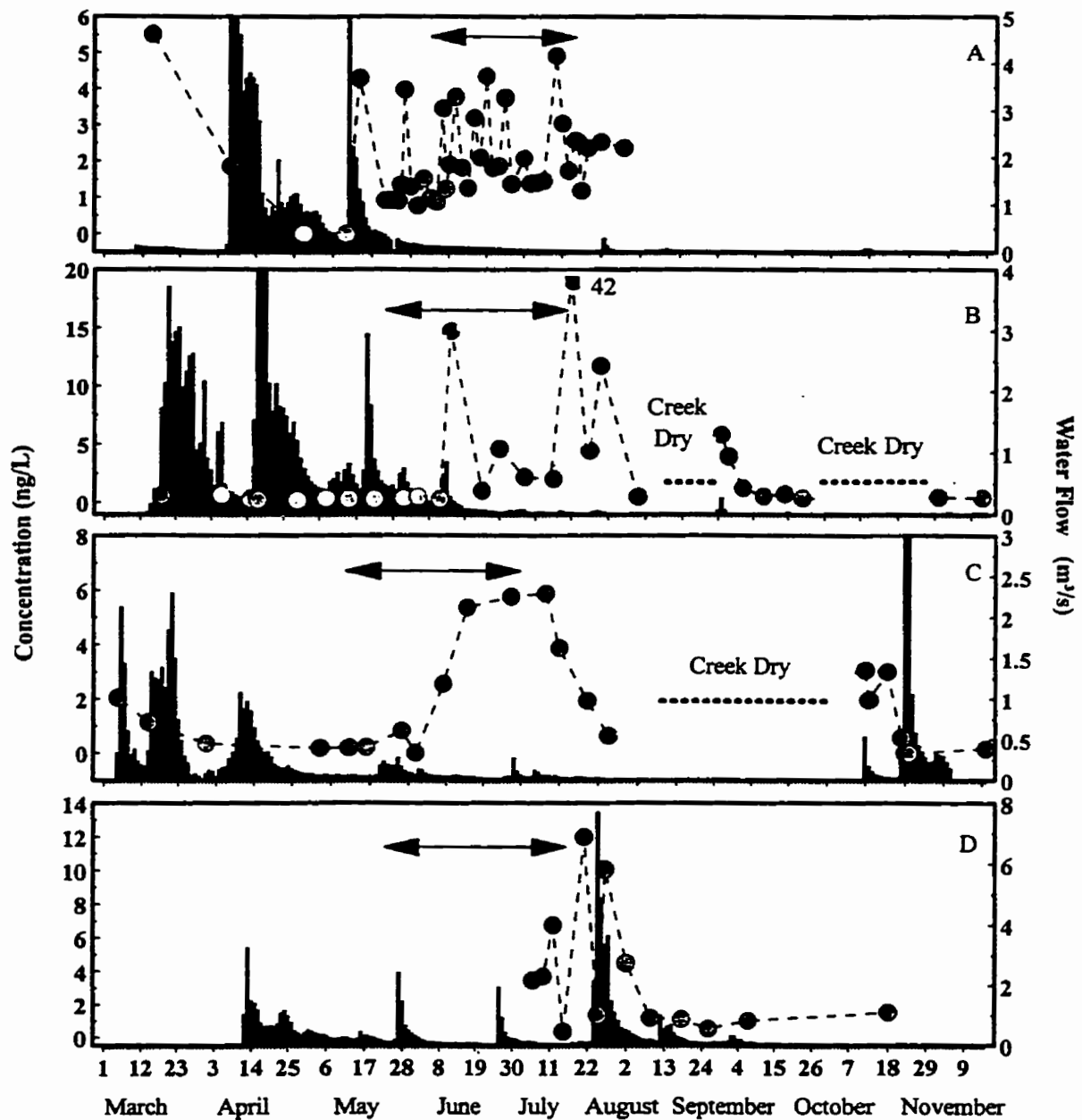


Figure 3.7 Bromoxynil concentrations in the dissolved phase of the South Tobacco Creek. A) 1996, B) 1995, C) 1994 and D) 1993. Water flow is indicated by the bar graph, scale on the right. (Dry periods are indicated by - - -; application period indicated by \leftrightarrow). NOTE: Concentration scale differences between A,B,C and D.

significant than originally considered. The 1995 field season was not as dry as the previous year, but, there were two short intervals when South Tobacco Creek did not flow. South Tobacco Creek was flowing throughout the sampling period in 1996.

3.4.2 Herbicides in Runoff from the Twin Watershed

Runoff samples were obtained during the spring melt period of each year (1994-1996) at the Twin Watershed site (Figure 3.2), however, only two major rainfall events produced mid-season runoff over the four-year duration of this study. 2,4-D (282 g/L) and dichlorprop (300 g/L) were applied as an emulsifiable concentrate to the field during the 1994 growing season at a rate of 1.75 L/ha. None of these herbicides were applied to the Twin Watershed fields in 1993, 1995 or 1996. During the 1993 runoff event, MCPA was detected in runoff water at a maximum concentration of 2 ng/L while maximum levels of dichlorprop, 2,4-D and bromoxynil were 0.3, 1 and 1.2 ng/L, respectively (Table 3.2). Runoff collections during the late season event in 1994 resulted in elevated concentrations of 2,4-D (13 ng/L) and dichlorprop (20 ng/L). Bromoxynil (2 ng/L) was detected in runoff water at lower concentrations and MCPA was measured at 9 ng/L in a single sample over this runoff event. MCPA was detected at < 1 ng/L in all other samples collected during the late October rainfall event.

3.4.3 Herbicides in Spring Runoff

The seasonal maximum concentration of 2,4-D (7.4 ng/L) (Figure 3.4C) was observed in the first sample collected in the spring of 1994. A near maximum concentration of MCPA was observed in the same sample (4.9 ng/L) (Figure 3.5C). Dichlorprop and bromoxynil concentrations were elevated during the spring of 1994, but seasonal high concentrations for

Table 3.2 Herbicide concentrations observed in field runoff events at the Twin Watershed site.

Chemical	Year	Concentration Range (ng/L)	Season	Type of Runoff	Duration of Event (d)	# of Samples Collected from each Field
Bromoxynil	1993	0.4 - 1.2	Summer	Rain	3	2
	1994	<0.015 - 0.2	Spring	Snowmelt	4	2
		<0.015 - 2.0	Autumn	Rain	3	6*
	1995	0.15 - 0.2	Spring	Snowmelt	3	4
	1996	<0.015 - 5.0	Spring	Snowmelt	3	4
2,4-D	1993	0.3 - 1.0	Summer	Rain	3	2
	1994	<0.011 - 0.8	Spring	Snowmelt	4	2
		<0.011 - 13	Autumn	Rain	3	6*
	1995	<0.011 - 0.6	Spring	Snowmelt	3	4
	1996	<0.011 - 7.0	Spring	Snowmelt	3	4
Dichlorprop	1993	<0.01 - 0.3	Summer	Rain	3	2
	1994	<0.01	Spring	Snowmelt	4	2
		<0.01 - 20	Autumn	Rain	3	6*
	1995	<0.01 - 0.9	Spring	Snowmelt	3	4
	1996	<0.01 - 9.2	Spring	Snowmelt	3	4
MCPA	1993	0.3 - 2.0	Summer	Rain	3	2

1994	<0.01 - 9.0	Spring	Snowmelt	4	2
	<0.01 - 2.5	Autumn	Rain	3	6*
1995	<0.01	Spring	Snowmelt	3	4
1996	<0.01 - 3.5	Spring	Snowmelt	3	4

*1 sample collected from each field, 5 timed interval samples collected from an individual field

both of these herbicides occurred in early July (Figures 3.6C and 3.7C, respectively).

MCPA residues were below detection limits in the samples collected during the spring melt period in 1995. Elevated levels of dichlorprop (2.9 ng/L March 17th; 3.7 ng/L April 3rd) were observed in the early spring samples, while 2,4-D and bromoxynil were present at < 1 ng/L.

All four of the herbicides were found at elevated concentrations in the first sample collected in 1996 (Figures 3.4A-3.7A). Both MCPA and dichlorprop concentrations exceeded 8 ng/L (8.4 and 8.8 ng/L, respectively). 2,4-D was found to be 4.7 ng/L and the concentration of bromoxynil was 5.5 ng/L in this sample. Concentrations of each herbicide decreased from this event, to at or near detection limits until later in the growing season, corresponding to regional application periods.

3.4.4 Application and Post-Application Period

Application of bromoxynil and MCPA commenced in late May and local application of dichlorprop and 2,4-D did not begin until early June. Dichlorprop and 2,4-D applications were completed by the end of June, but, bromoxynil and MCPA spraying was not completed until one to two weeks later each year.

Herbicide concentrations were elevated throughout July 1993, but dropped rapidly to < 1 ng/L following heavy rain events between July 25th and 27th of that field season. We did not begin sampling until June in 1993 and thus the herbicide temporal profiles were not well established during that field season.

In 1994, concentrations of each herbicide remained low in May and June. Seasonal maximum levels were observed for MCPA, dichlorprop and bromoxynil between July 7th and

11th (5, 9.3, and 5.9 ng/L, respectively). Although the seasonal maximum was detected in spring melt samples, the highest concentration of 2,4-D during the growing season was similarly observed July 11th (4.5 ng/L) (Figure 3.4C), after application of this chemical was completed within the watershed. Concentrations of MCPA, dichlorprop and bromoxynil remained at elevated levels in South Tobacco Creek for a longer period than was observed for 2,4-D. Although the maximum concentration of dichlorprop (Figure 3.6C) in South Tobacco Creek was higher than either bromoxynil or MCPA in 1994, it was detected in very few of the water samples. Bromoxynil and MCPA were detected throughout the sampling season in creek water.

In 1995, temporal patterns of three compounds bromoxynil, dichlorprop and MCPA were similar to those observed in 1994, however, maximum concentrations of bromoxynil and MCPA were much higher than those for dichlorprop. Seasonal maxima in 1995 were observed during July for each of these compounds and the concentrations measured in water samples were higher than during the previous year. The maximum seasonal 2,4-D concentration measured was 9.6 ng/L August 21st (Figure 3.4B). The highest level of dichlorprop was found on July 8th (18.3 ng/L) (Figure 3.6B). The maximum bromoxynil concentration (41.6 ng/L) (Figure 3.7B) observed during 1995 coincided with the dichlorprop maximum concentration. The highest concentration of MCPA (Figure 3.5B) was detected in the sample collected July 17th (44.2 ng/L). Dichlorprop concentrations were relatively low (≤ 4 ng/L) within a one week interval both prior to and following the date where maximum levels were observed during 1995. Similar patterns were obtained for bromoxynil and MCPA, showing isolated occurrences of high herbicide concentration in the creek water.

From these results we concluded that increased frequency was necessary for complete definition of temporal trends of these pesticides.

During 1996, the sampling frequency was increased to every two days. Rapid changes in creek water concentrations of 2,4-D, dichlorprop and MCPA were observed over a one-week to ten day period during the local herbicide application time. Both dichlorprop and bromoxynil were found at the highest levels during the growing season on June 30th (16 and 4.3 ng/L, respectively), whereas the MCPA maximum concentration was detected in the sample collected July 22nd (39 ng/L) (Figure 3.5A). The maximum level of 2,4-D was obtained similarly on July 22, 1996. The 2,4-D concentration (680 ng/L) on that date was the highest observed concentration of any analyte in South Tobacco Creek water through the duration of the study. The highest herbicide concentrations observed in South Tobacco Creek, however, were one to two orders of magnitude below the Canadian water quality guideline values (Table 3.3) for the protection of freshwater aquatic life, where such values exist. Only one sample throughout the entire sampling regime exceeded proposed German guideline values for protection of freshwater aquatic life for 2,4-D (Table 3.3).

3.5 Discussion

Spring melt is the major source of surface water runoff in southern Manitoba. Each of the four herbicides was found at elevated concentrations in samples collected during spring melt and runoff periods in March, but levels were reduced to near detection limits in April during both 1994 and 1996. This pattern was not observed in the 1995 field season and may

be attributed to the late October rain event in 1994, which produced overland flow causing residual herbicides to be washed into the South Tobacco Creek. Less herbicide residue was available for runoff in the spring of the following season.

Table 3.3 Comparison of Canadian and German guideline values for protection of freshwater aquatic life with maximum concentrations (ng/L) measured in South Tobacco Creek (CCREM, 1987).

Chemical	Freshwater Aquatic Life Guideline Value		Maximum Concentration Observed
	Canada	Germany ^a	
Bromoxynil	5000	- ^b	41.6
2,4-D	4000	20 ^b	680
Dichlorprop	- ^c	- ^c	18.3
MCPA	4200	500 ^b	44.2

^aDieter Schudoma (Federal Environmental Agency, Berlin, Germany), personal communication, 1997

^bunder derivation

^cno water quality guideline value exists at present

Maximum concentrations of these herbicides in South Tobacco Creek were found during and extending beyond local applications. Based on the lack of activation of automated samplers at the Twin watershed site and on observations of local landowners, no runoff events occurred during this interval in 1994-96. Thus, it is unlikely that elevated herbicide concentrations in creek water were due to overland flow events. However, elevations in herbicide concentrations were similarly observed in both ambient air and precipitation samples

over this period. Higher phenoxyacid and bromoxynil concentrations were consistently observed in creek water coinciding with elevated levels of these herbicides in air and precipitation, during the 1994-1996 field years (Figures 3.8-3.10). Therefore, the most likely source of these chemicals is via the atmospheric deposition processes, rain, dryfall and gas exchange. The temporal concentration trends of the four herbicides throughout the field season observed in this study were similar to the pattern of 2,4-D observed in the Red River (Tomes and Brigham, 1994). Elevated concentrations of 2,4-D in the Red River at Emerson, Manitoba occur in March and maximum seasonal concentrations occur in June corresponding to use in North Dakota (Tomes and Brigham, 1994). Similarly, seasonal maximum concentrations of 2,4-D and MCPA were observed during April and May, respectively, corresponding to local application times in the southern US (Hippe, et al., 1994). Muir and Grift (1995) reported 2,4-D in a lake in the Experimental Lakes Area, near Kenora, in the boreal forest of Northwestern Ontario where atmospheric sources are the sole contributor. 2,4-D, MCPA, dichlorprop and bromoxynil all were detected in Danish surface waters samples (Mogensen and Spliid, 1995) at frequencies and time of year corresponding to regional use.

Phenoxyacid and bromoxynil concentrations were not correlated to flow nor the water chemistry parameters: conductivity, TN, TP, TOC, SO_4^- , Cl^- and NFR ($r^2 < 0.11$). There were, however, significant correlations between the nutrient levels: TOC ($r^2 = 0.52$; $p < 0.001$), TN ($r^2 = 0.42$; $p < 0.001$) and TP ($r^2 = 0.47$; $p < 0.001$) with creek water flow (Figure 3.3A, B and C, respectively). Nutrient levels in South Tobacco Creek were greatest during the high flow periods, spring melt and heavy rain events late in October, 1994. This differs from

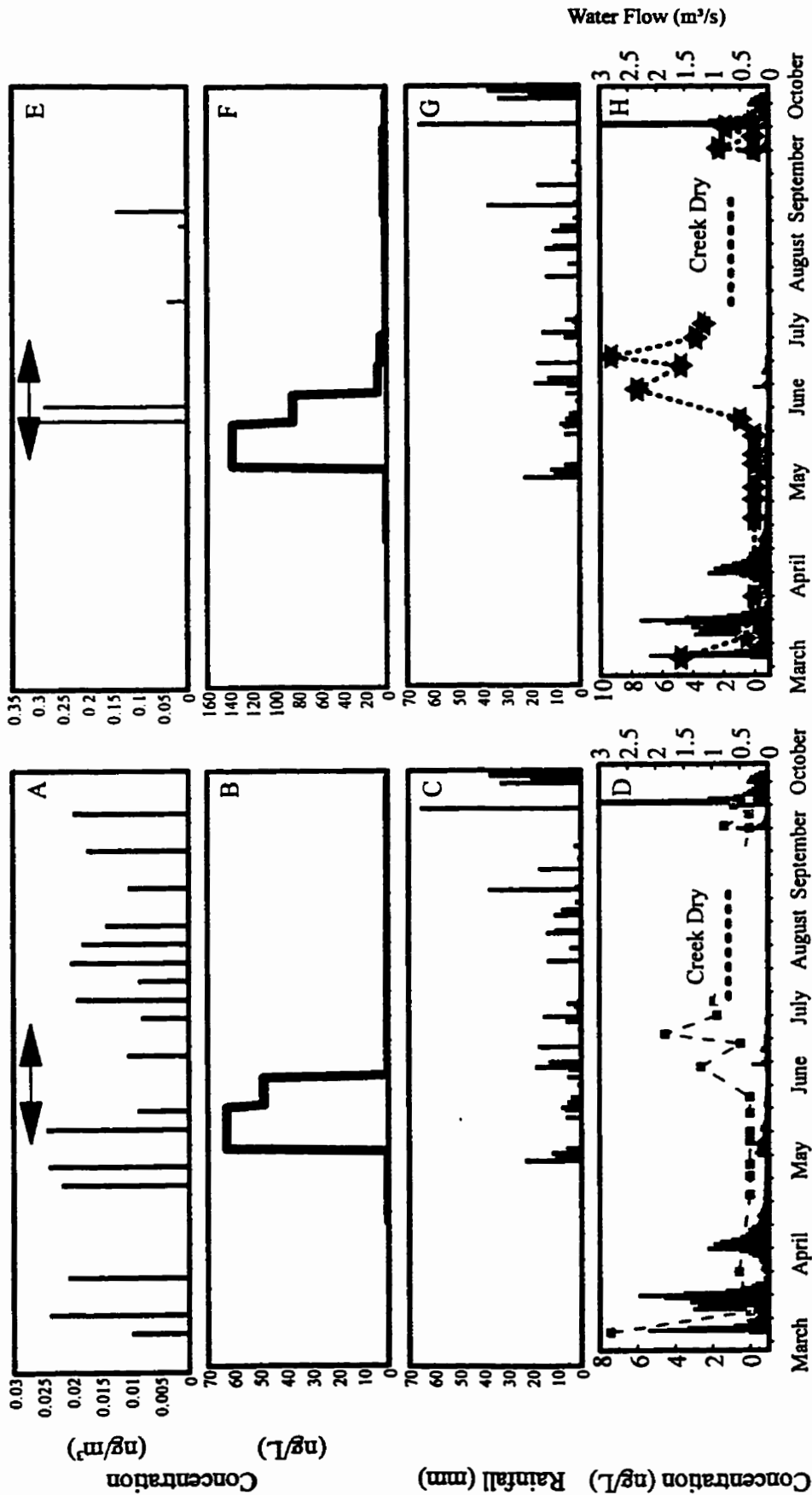


Figure 3.8 2,4-D (A-D) and dichlorprop (E-H) concentrations in 1994 in the South Tobacco Creek Watershed. A&E) air, B&F) precipitation, D&H) creek water. Water flow is indicated by the bar graph, scale on the right. (Dry periods are indicated by - - ; application period indicated by ↔). Rainfall is indicated in panel C&G. NOTE: Concentration scale differences for each panel.

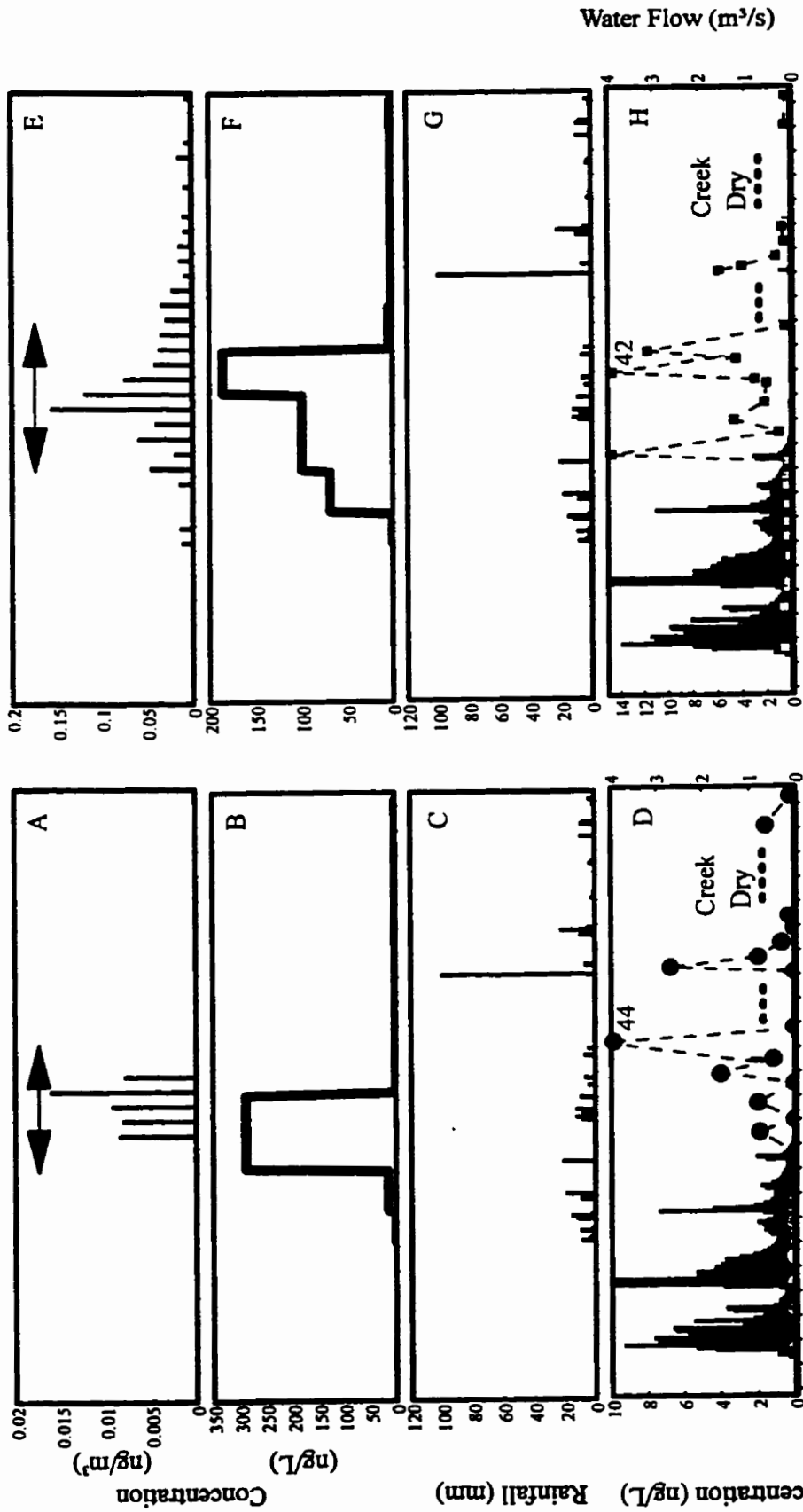


Figure 3.9 MCPA (A-D) and bromoxynil (E-H) concentrations in 1995 in the South Tobacco Creek Watershed. A&E) air, B&F) precipitation, D&H) creek water. Water flow is indicated by the bar graph, scale on the right. (Dry periods are indicated by - -; application period indicated by ↔). Rainfall is indicated in panel C&G. NOTE: Concentration scale differences for each panel.

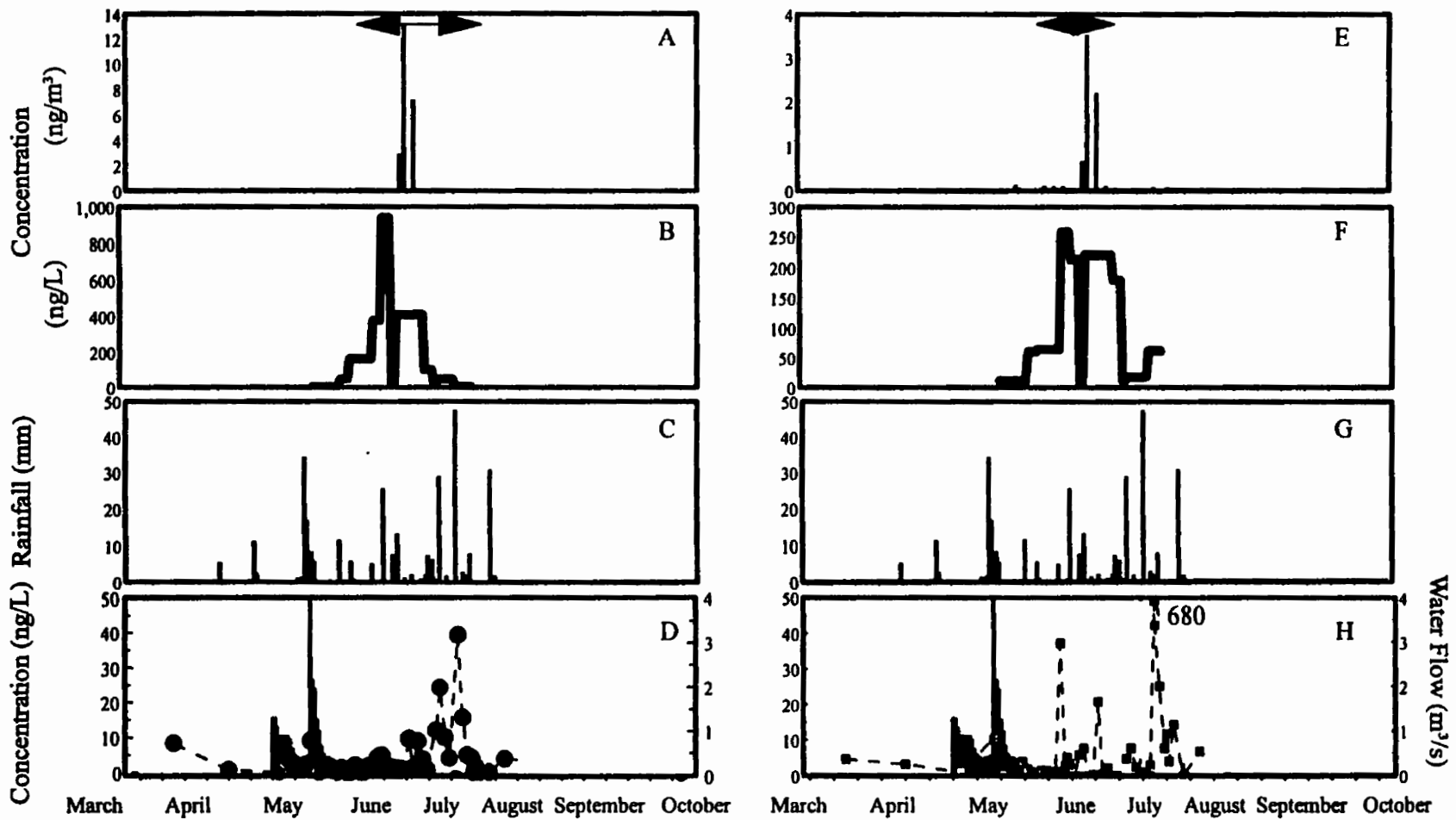


Figure 3.10 MCPA (A-D) and 2,4-D (E-H) concentrations in 1996 in the South TobaccoCreek Watershed. A&E) air, B&F) precipitation, D&H) creek water. Water flow is indicated by the bar graph, scale on the right. (Dry periods are indicated by - - -; application period indicated by ↔). Rainfall is indicated in panel C&G. NOTE: Concentration scale differences for each panel.

nitrate- nitrogen levels in tributaries of the Mississippi River which showed little response to rainfall (Goolsby et al., 1991).

Inverse relationships between herbicide concentrations and SO_4^{2-} and Cl^- levels have been used to indicate surface water inputs into the Minnesota River (Schottler et al., 1994). No correlation was found between SO_4^{2-} and Cl^- levels and any of the four herbicides ($r^2=0.0006 - 0.02$) in the present study.

Estimates of the quantity of each herbicide discharged via South Tobacco Creek ranged from 3 - 28 g (Table 3.4). Discharge levels of bromoxynil, 2,4-D, dichlorprop and MCPA via South Tobacco Creek were $< 0.01\%$ of the amounts applied within the watershed. However, underestimation of seasonal creek herbicide discharge is likely, particularly for the 1994 and 1995 field seasons. The weekly sampling protocol used over these years was proven insufficient, with respect to the development of well defined temporal trends for these herbicides in South Tobacco Creek water. Several isolated "spikes" in herbicide concentrations were observed through the first three years of this study. This indicated that we were missing important movement of these herbicides in South Tobacco Creek and lead to changes in our sampling strategy. The need for high frequency sampling was confirmed with the 1996 data. Concentration profiles in 1996 showed that herbicide levels can change dramatically within a one week period. Although sampling was limited to a short interval, rather than throughout the entire field season in 1996, discharge estimates of 2,4-D increased an order of magnitude over the 1994 and 1995 values. Larson and coworkers (1995) reported a similar under prediction of pesticides lost via discharge from the Mississippi River basin.

Table 3.4 Seasonal discharge via South Tobacco Creek compared with amounts of each chemical applied within the South Tobacco Creek Watershed.

Chemical	1994		1995		1996	
	Discharge (g)	Applied (kg)	Discharge (g)	Applied (kg)	Discharge (g)	Applied (kg)
Bromoxynil	5.42 ^a ±1.63	295	10.1 ^a ±3.02	292	2.95±0.89	275
2,4-D	6.89 ^a ±2.07	417	6.39 ^a ±1.92	342	27.7±8.30	473
Dichlorprop	3.27±0.98	312	8.85±2.66	275	2.72±0.82	387
MCPA	18.3 ^a ±5.74	511	4.07 ^a ±1.22	852	10.8±3.24	985

^acorrected for % recovery

3.6 Conclusions

This dataset provides a detailed account of the seasonal trends of the phenoxyacid and phenolic herbicides in surface waters, over a four year period. We found that, under a variety of environmental conditions, in a region where they are heavily used, the phenoxyacid and phenolic herbicide concentrations in creek water do not exceed Canadian guideline levels for the protection of freshwater aquatic life. In most years of the study, the maximum concentration for each herbicide detected in creek water corresponded to the local application time for each chemical and levels remained elevated for up to a month, followed by a rapid decrease in concentration. Spring runoff losses from treated fields also resulted in a brief increase in chemical concentrations.

An unexpected finding was that the highest levels of herbicides in creek water corresponded to elevated herbicide levels in air and precipitation throughout the growing season, during periods when no known runoff events occurred. This suggests that atmospheric deposition is a major source of these chemicals to the water surface. No correlation existed between elevated herbicide levels and water flow, in contrast to nutrient levels which indicates different sources for these two groups. The nutrients appear to enter South Tobacco Creek via runoff and groundwater movement, rather than via atmospheric processes.

High frequency sampling over a focussed period around local application times is necessary to follow herbicide temporal concentration patterns. Without strategic sampling schedules, monitoring programs are subject to missing important riverine herbicide

movement.

Calculated discharges of the herbicides from the catchment were about 1% of the amount applied.

4. A MULTI-YEAR STUDY OF FOUR HERBICIDES IN AIR AND PRECIPITATION FROM A SMALL PRAIRIE WATERSHED

4.1 Abstract

Temporal trends of three phenoxyacid herbicides: 2,4-D, dichlorprop and MCPA and the phenolic herbicide: bromoxynil, were determined in ambient air and precipitation over a four year period within a well defined watershed in southern Manitoba. Air concentrations ranged from below detection limits to 3.5, 1.0, 13 and 2.0 ng/m³, for 2,4-D, dichlorprop, MCPA and bromoxynil, respectively. The herbicides under investigation were four of the highest use herbicides in the South Tobacco Creek Watershed and were present in both air and precipitation samples at maximum concentrations during periods of local use. Concentration patterns for each herbicide in precipitation were similar each year of the study. Of the four herbicides, precipitation fluxes were greatest for MCPA in the watershed and the surrounding region. Although bromoxynil and dichlorprop were less widely used than 2,4-D, bromoxynil precipitation fluxes exceeded those of 2,4-D in 1993 and 1994, and dichlorprop precipitation fluxes were greater than 2,4-D in 1994. Elevated levels of these herbicides in creek water samples were observed during periods of high concentration in both atmospheric compartments, despite the lack of surface runoff events within the watershed over that period.

4.2 Introduction

The atmosphere has been shown to be an important source of persistent organic pollutants (e.g., organochlorine insecticides) to surface waters (McConnell et al., 1996; Iwata et al., 1995; McConnell et al., 1993). These compounds have been shown to be transported from regions of use into non-target areas prior to deposition (Stern et al., 1997; Hoff et al., 1996). The majority of the work performed has examined atmospheric deposition to lakes (Honrath et al., 1997; Jeremiason et al., 1994; Achman et al., 1993), rather than to watersheds and riverine environs.

Atmospheric sources of current use herbicides, however, have been less well studied. Herbicide losses from treated fields to surface waters have been thought to occur mainly as a result of runoff during rain events and spring thaw periods or groundwater movement (Fischer et al., 1995; Muir and Grift, 1995; Schottler et al., 1994; Leonard, 1988). Volatilization of pesticides from treated fields has been shown to occur within the first weeks following application (Glotfelty et al., 1989; Grover et al., 1985). Recently, several studies have examined herbicide presence in atmospheric compartments as a source of contamination of regions outside of the target area (Goolsby et al., 1997; Chevreuil et al., 1996; Trevisan et al., 1993; Capel, 1991; Glotfelty et al., 1987). In general, the study of atmospheric deposition of herbicides has been focussed on the persistent, highly used classes, such as the triazines, acetanilides and phenyl ureas (Goolsby et al., 1997; Rawn et al., 1998*b* (Chapter 5); Chevreuil et al., 1996; Nations and Hallberg, 1992; Buser, 1990; Chevreuil and Garmouma, 1993; Richards et al., 1987). Very few studies have examined phenoxyacid or phenolic

herbicides in these compartments. This may be a result of their characteristic short half-life in soil and low volatility (Wauchope et al., 1992).

In the Great Plains region of western Canada and north central USA, phenoxyacid and phenolic herbicides are widely used for control of broadleaf weeds in cereal crops (Anonymous, 1996; Donald and Syrgiannis, 1995; Gianessi and Anderson, 1995*a*; Gianessi and Anderson, 1995*b*). Atmospheric samples collected in this region have shown the presence of many of these chemicals (Waite et al., 1995; Hawthorne et al., 1996). Hawthorne et al. (1996) found seasonal maximum concentrations of 2,4-D and MCPA levels in air samples from an agricultural region of North Dakota corresponded to regional application times. Elevations in MCPA levels in ambient air in California also were found to correspond to regional use patterns (Woodrow et al., 1990). There has been little work to define long term temporal patterns of these chemicals in atmospheric compartments.

Less is known about phenoxyacid and phenolic herbicides in precipitation. MCPA and dichlorprop were detected in rain samples collected during 1992 and 1993 at two sites in Norway (Lode et al., 1995). Temporal patterns of these herbicides in rain samples corresponded to local application. Maximum concentrations of MCPA and dichlorprop detected in precipitation were 320 ng/L and 250 ng/L, respectively (Lode et al., 1995). MCPA and dichlorprop both were detected in the rainwater in an Italian study, however, 2,4-D was not detected in any rainfall sample collected between April and late October during 1988 (Trevisan et al., 1993). Although there have been numerous studies to determine more persistent herbicides e.g., atrazine in precipitation in the US (Goolsby et al., 1993), we are not aware of any similar reports on phenoxyacid/phenolic herbicides in precipitation.

The purpose of the present study was to determine the concentrations and fluxes to surface waters of three phenoxyacids (2,4-D, dichlorprop and MCPA) and one phenolic (bromoxynil) herbicide from ambient air and precipitation, in a small agricultural watershed in southern Manitoba. Ambient air and precipitation samples were collected within the well defined 70 km² agricultural South Tobacco Creek Watershed (49°19'28"N, 98°21'50"W), previously described in Rawn et al.(1998c (Chapter 3)). Landuse data for the entire watershed were obtained with the cooperation of landowners. The dataset provided information on applied chemicals, which included rate of application, for each field on a weekly basis, for all years of the study.

4.3 Materials and Methods

4.3.1 Sample Collection

Air and precipitation were sampled over a four year period (1993-1996) to determine pesticide levels in two atmospheric compartments. The sampling program was designed to collect large volumes of air and precipitation in order to measure locally used pesticides and those entering the watershed via long range transport. Sampling of atmospheric compartments began in June 1993. Atmospheric sample collection in 1994 and 1995 began in early May, prior to the commencement of any local spraying of 2,4-D, dichlorprop, MCPA or bromoxynil. In 1996, a more intensive sampling regime, limited to use periods (June-July) for the chemicals of interest was followed.

Air samples were collected using a high volume air sampler (General Metalworks PS-

1) using polyurethane foam plugs (PUF) with a GF/A glass fibre filter to trap particulate matter. Filters were prepared for use by heating for 18 hours at 265°C. PUF plugs were pre-cleaned by Soxhlet with hexane for 24 h prior to use. Approximately 350 m³ of air was drawn through the sampling unit over a 24 h period every 6 days during the early part of the growing season. Later in each field season, samples were collected every 12 days. Samples were collected June-October 1993, May-November, 1994 and May-October 1995. During 1996, air samples were collected (24 h) on a two-day cycle. PUFs were placed in sealed glass jars and stored at 4°C until extraction and analysis. Filters were placed in “Whirl pak” polyethylene bags and stored at 4°C until extraction and analysis.

Rainfall was collected using an automated wet-only sampler (0.2025 m²) (Meteorological Instrument Centre, Mississauga, ON) located in the geographical centre of the watershed. Rain collected over two week periods (1993-1995) was stored in 18 L stainless steel soft drink cans. Rain water was filtered through a glass wool plug at the bottom of the collection basin for removal of large particles. Dichloromethane (DCM) was added to the tanks as a preservative. Sample volumes ranged from 3 to 18 L. During 1996, the precipitation sampler was checked for rain water every second day and samples were taken when rainwater was present. Sample volumes ranged from 1 - 8 L in the 1996 field season.

4.3.2 Sample Analysis

A broad spectrum approach was used for sample analysis to analyse both acid and neutral herbicides (e.g., 2,4-D and atrazine). Atrazine results are reported elsewhere (Rawn et al., 1998*b* (Chapter 5)). PUFs were extracted using Soxhlet with DCM for 4 h. Deuterated (d₃) 2,4-D was used as an internal recovery standard which was added at the

extraction step.

Precipitation samples were extracted in the sampling containers using DCM. Precipitation samples were extracted following the method for creek water samples described in the first paper in this series (Rawn et al., 1998c (Chapter 5)). All analytes were quantified using gas chromatography-mass spectrometry (Hewlett Packard 5971 MSD) using a 60 m x 0.25 μ m DB-5 column with helium as the carrier gas. Detection criteria were the correct ratios of two characteristic ions and retention times. Herbicides were quantified using external standard solutions and corrected for volume changes using PCB-104. Blank PUFs, filters and blanks of "Super Q" water were analysed with each batch of samples. Sample blanks for PUF and filter samples were collected once every sixth sample throughout the period of study. Herbicide levels were below detection limits in blank samples. Herbicide recoveries from PUF plugs were 100%, 95%, 72% and 85% for MCPA, dichlorprop, 2,4-D and bromoxynil, respectively. Recoveries of herbicide spikes into water sample blanks were reported previously (Rawn et al., 1998c (Chapter 3)). Precipitation fluxes for these herbicides to the South Tobacco Creek and land surfaces of the watershed were calculated for each year of the study. For purposes of flux calculation during 1993 - 1995, MCPA, 2,4-D and bromoxynil concentrations were corrected for recovery efficiency.

Detection limits were calculated to be 7, 10, 11 and 15 pg/L for 18 L volumes of precipitation; and 1.9, 2.1, 2.7 and 2.9 pg/m³ based on 350 m³ air samples, for dichlorprop, MCPA, 2,4-D and bromoxynil, respectively, using instrument detection limits plus three times the standard deviation of the lowest concentration analysis (Keith, 1991).

4.4 Results

4.4.1 Air

Maximum concentrations of each herbicide in both air and precipitation occurred during periods of local use for all years of the study. MCPA was detected primarily in the vapour phase (Figure 4.1A-D) (Table 4.1). However, maximum concentrations in 1993 were observed June 21st, where 98% of MCPA was associated with particles. In all years except 1995, MCPA was detectable, although at low concentrations, during periods when there was no local use of this chemical. This may be a result of regional use. Dichlorprop levels similarly reflected local use patterns (Figure 4.2A-D). In 1993, all dichlorprop residues detected in air samples were associated with particles (Figure 4.2D), however, in 1994-1996, the majority of dichlorprop was in the vapour phase. During 1994, dichlorprop was applied to the field adjacent to our air sampler, but the maximum dichlorprop concentration was detected in the sample collected prior to that application. Temporal patterns of 2,4-D (Figure 4.3A-D) in air do not appear as clearly defined as either of the other phenoxyacid herbicides or bromoxynil. 2,4-D maximum concentrations were lower than all other analytes during the 1993-1995 field years. The seasonality of 2,4-D in air was least obvious in 1994 (Figure 4.3C), when this chemical was applied to the field adjacent to the sampling station. By sampling on a two-day cycle in 1996, seasonal patterns were more clearly discerned and reflected local use (Figure 4.3A).

Differences between patterns of bromoxynil (Figure 4.4A-D) and those of the phenoxyacids were observed in all field seasons. Distinct seasonal patterns reflecting local

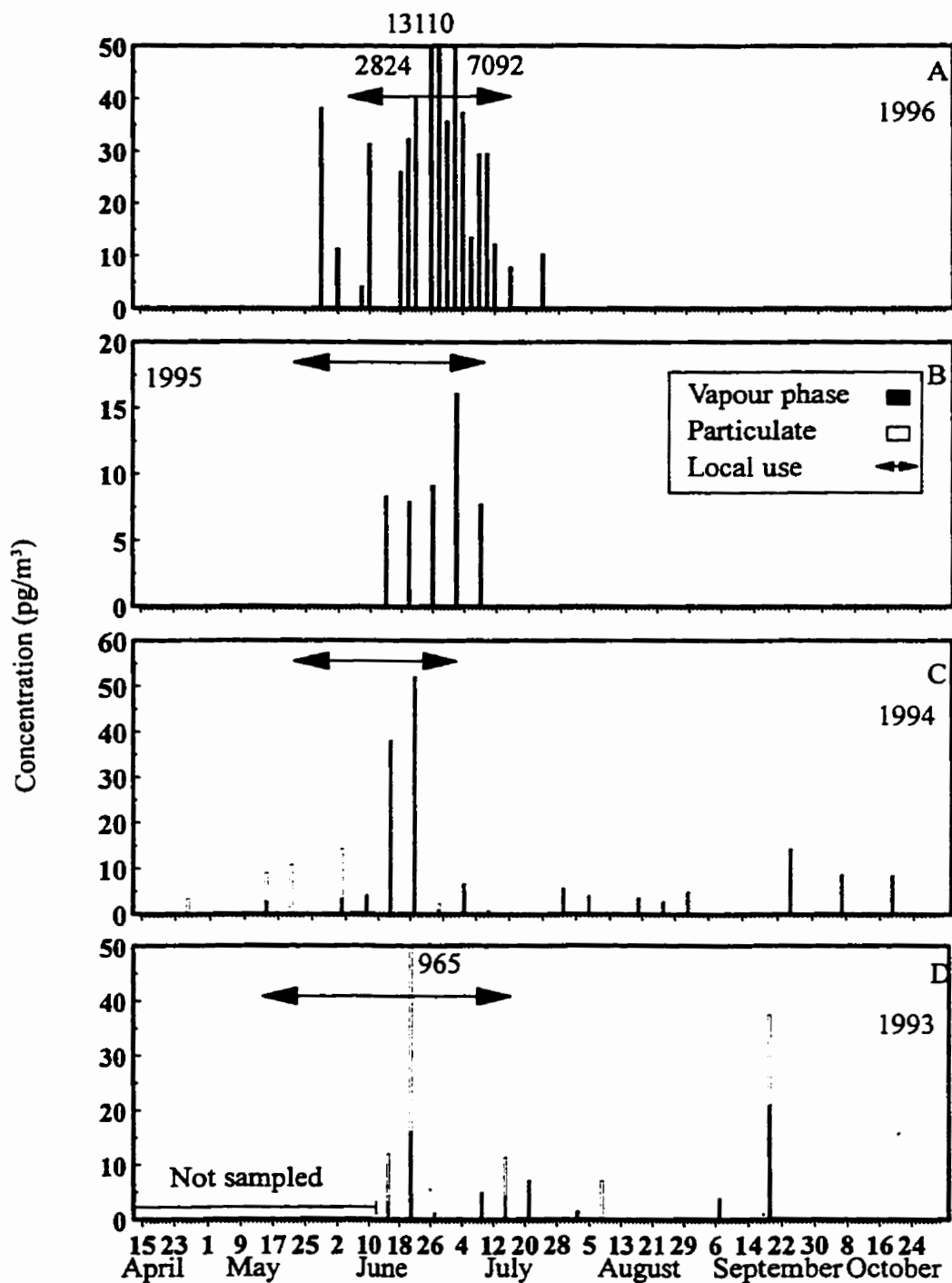


Figure 4.1 MCPA concentrations in air (Σ vapour and particulate phases) in the South Tobacco Creek Watershed. A) 1996, B) 1995, C) 1994 and D) 1993. Sampling frequency was every 6 d from May-September and reduced to every 12 d until the end of October (1993-1995); in 1996 sampling frequency was every 2 d in June and July. NOTE: Sampling commenced in June 1993. Application period indicated by \leftrightarrow .

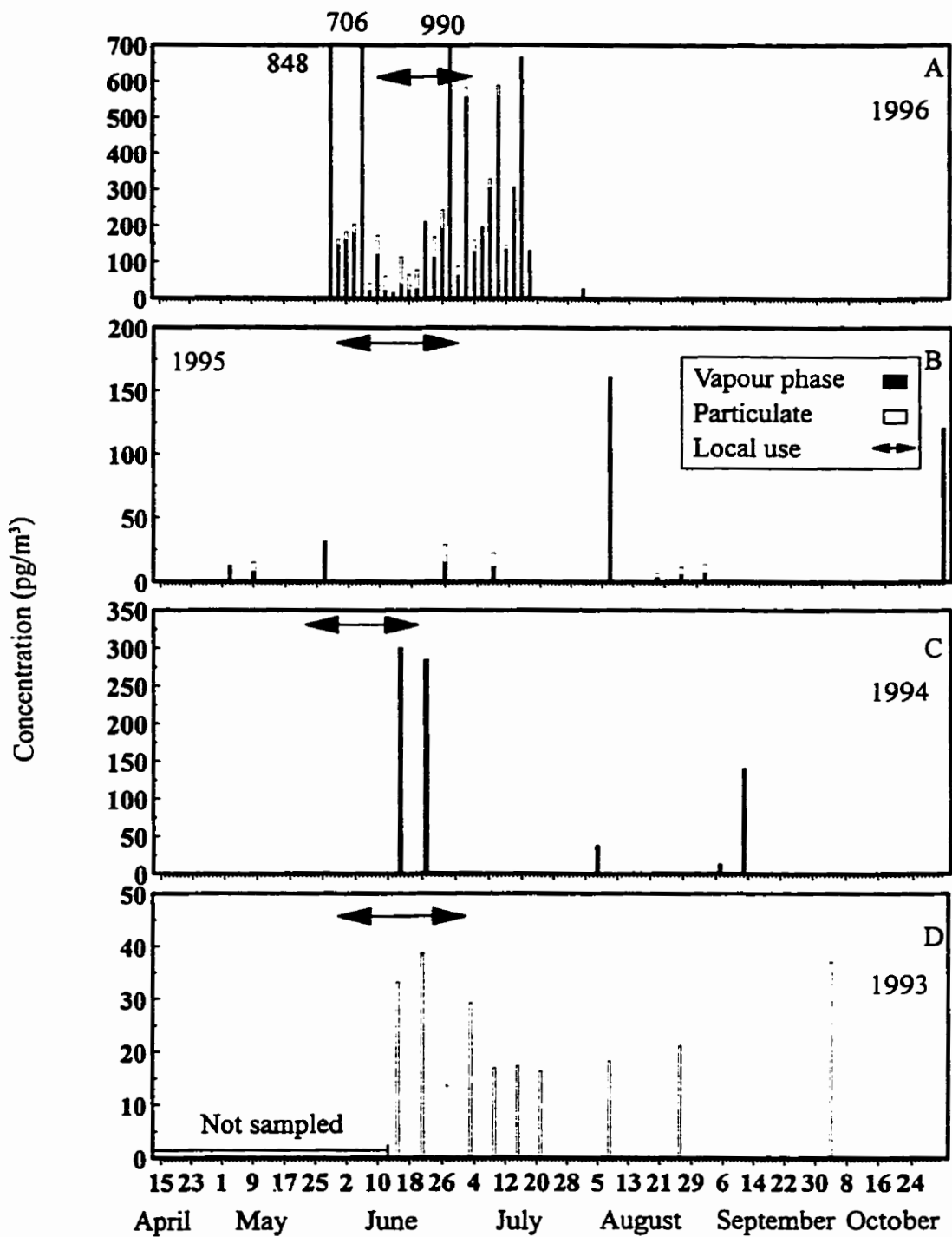


Figure 4.2 Dichlorprop concentrations in air (Σ vapour and particulate phases) in the South Tobacco Creek Watershed. A) 1996, B) 1995, C) 1994 and D) 1993. Application period indicated by \leftrightarrow .

Table 4.1 Maximum concentrations (pg/m³) of each herbicide observed in ambient air (vapour and particle phase); [date of maximum concentration].

Year	Bromoxynil		2,4-D		Dichlorprop		MCPA	
	Vapour	Particle	Vapour	Particle	Vapour	Particle	Vapour	Particle
1993	470	110	29	31	ND ^a	39	21	950
	[21/6]	[15/6]	[21/6]	[21/6]		[21/6]	[19/9]	[21/6]
1994	240	280	24	26	300	17	52	11
	[19/6]	[1/6]	[1/7]	[31/7]	[19/6]	[11/10]	[19/6]	[20/5;1/6]
1995	66	130	20	18	160	15	16	ND ^a
	[2/7]	[26/6]	[1/8]	[8/7]	[7/8]	[26/6]	[2/7]	
1996	1600	440	3500	41	930	6	13000	8
	[28/6]	[28/6]	[21/6]	[14/6]	[28/6]	[24/6]	[28/6]	[16/7]

^aNot Detected

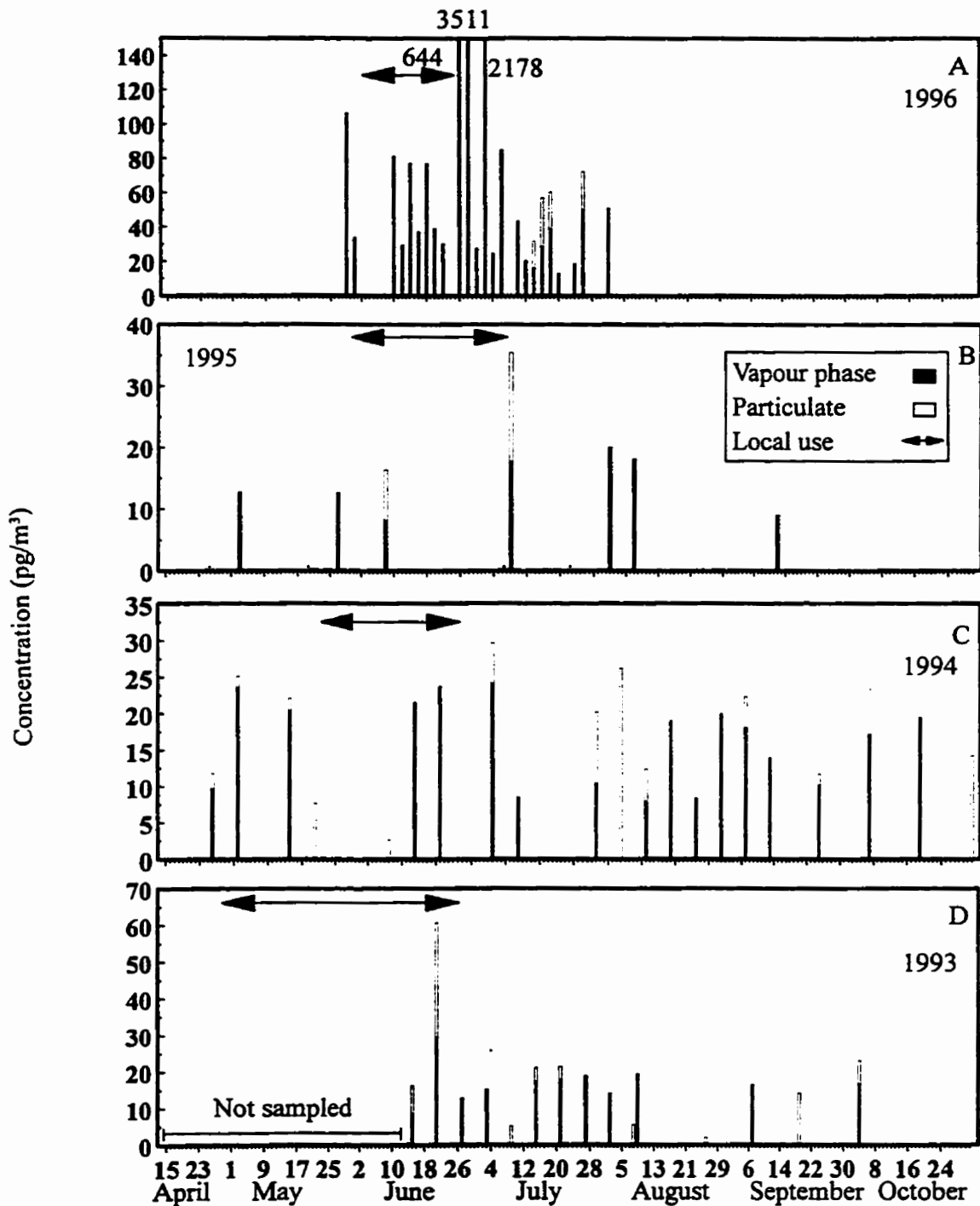


Figure 4.3 2,4-D concentrations in air (Σ vapour and particulate phases) in the South Tobacco Creek Watershed. A) 1996, B) 1995, C) 1994 and D) 1993. Application period indicated by \leftrightarrow .

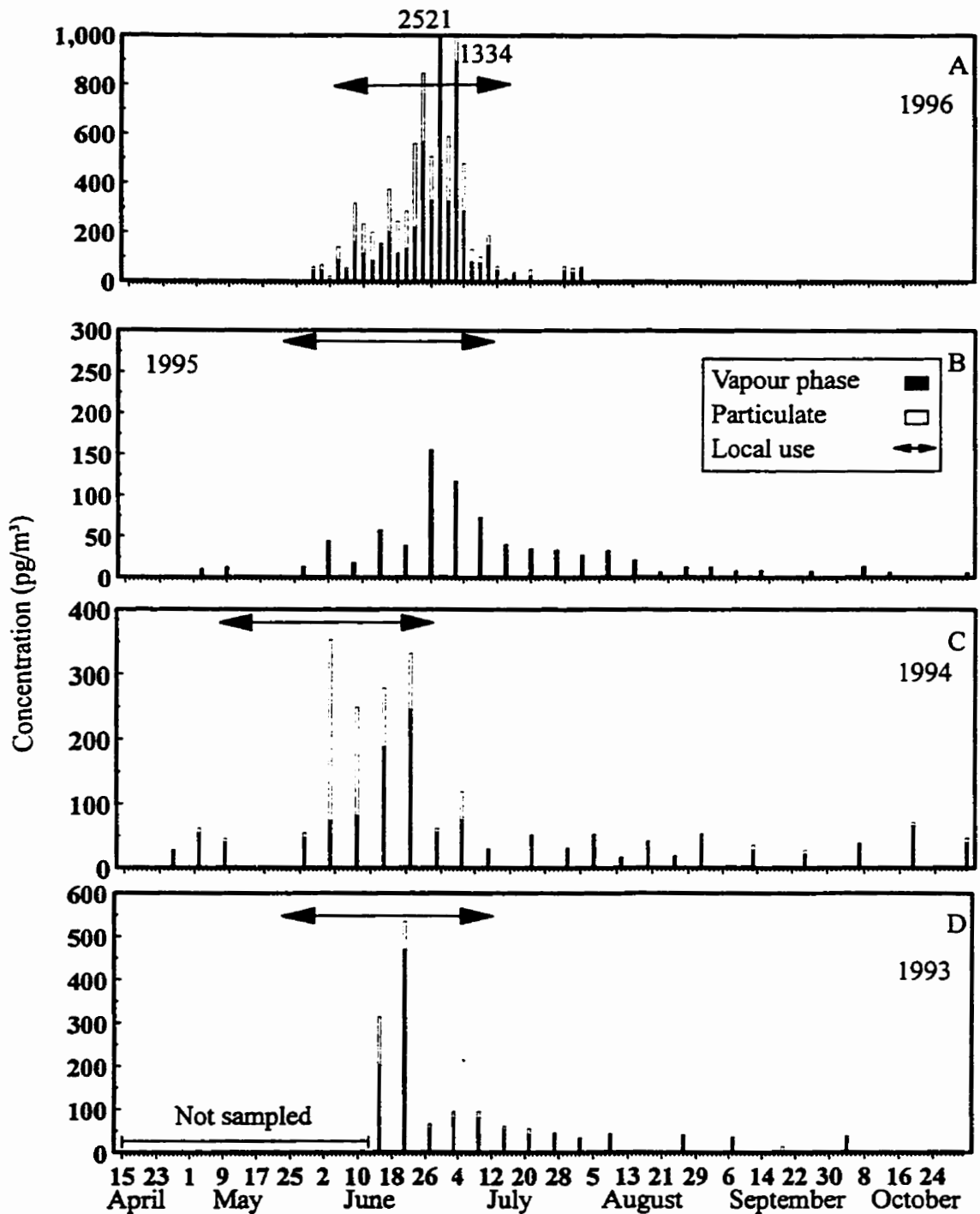


Figure 4.4 Bromoxynil concentrations in air (Σ vapour and particulate phases) in the South Tobacco Creek Watershed. A) 1996, B) 1995, C) 1994 and D) 1993. Application period indicated by \leftrightarrow .

use were observed each year of the study. Contributions of bromoxynil associated with particles occurred throughout the field season (Figure 4.4A-D). Maximum concentrations of bromoxynil in air were higher than 2,4-D and dichlorprop in the 1993-1995 field years. Bromoxynil concentrations in air were higher than all of the phenoxyacid herbicides in both 1994 and 1995, despite the fact that less bromoxynil was used in the watershed than all of the phenoxyacids (Rawn et al., 1998c (Chapter 3)). Dichlorprop application was marginally lower than bromoxynil in 1995 (Rawn et al., 1998c (Chapter 3)).

4.4.2 Precipitation

Concentration profiles for bromoxynil, 2,4-D, dichlorprop and MCPA in precipitation were very similar each year (Figure 4.5-4.6). Maximum concentrations of each chemical in 1994 were found in late May and early June. This is the period of the most intense application of these chemicals in the South Tobacco Creek Watershed, based on information provided by the landowners. Concentrations in rain samples were at, or near, detection limits prior to this sampling period. A gradual decrease in concentrations of the herbicides was observed for bromoxynil, dichlorprop and MCPA (Figures 4.5 and 4.6). 2,4-D was detected only during late June 1994 (Figure 4.6). Maximum concentrations of 2,4-D were lower than the maxima determined for each of the other analytes.

The temporal pattern of bromoxynil in precipitation during the 1995 season differed from the other chemicals. Elevated bromoxynil concentrations (Figure 4.5) were observed in the sample collected in early May, whereas, 2,4-D, dichlorprop and MCPA were not detected in rainfall samples until June 1995. Bromoxynil was found in four of the eight samples collected over the season, while the others were below detection limits at all but two

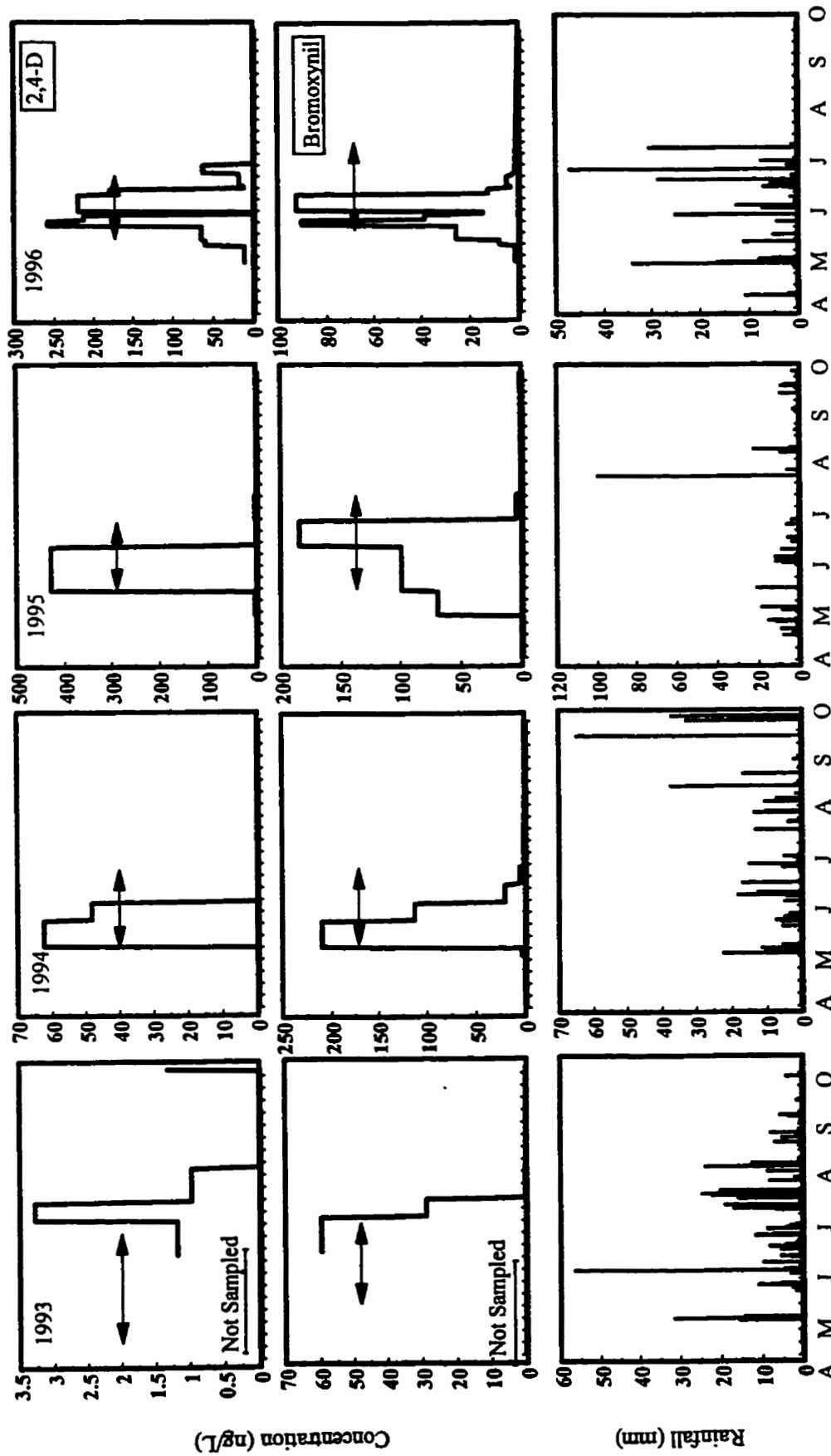


Figure 4.5 2,4-D and bromoxynil concentrations in precipitation in the South Tobacco Creek Watershed 1993-1996. Corresponding seasonal rainfall is shown in bottom panels.

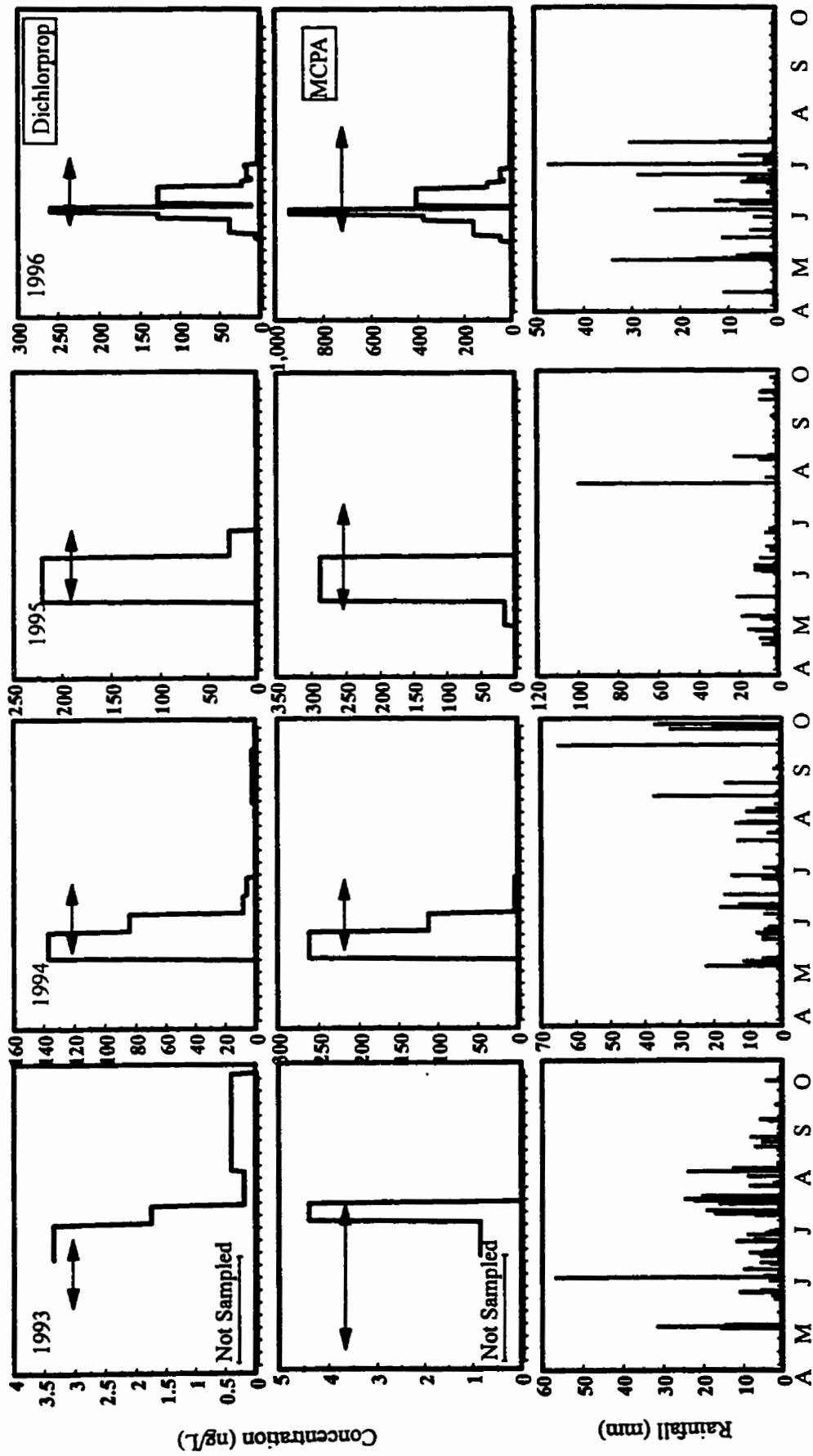


Figure 4.6 Dichloroprop and MCPA concentrations in precipitation in the South Tobacco Creek Watershed 1993-1996. Corresponding seasonal rainfall is shown in bottom panels.

sampling times. The concentration patterns for each herbicide virtually overlapped during the 1996 sampling season. Because lower volumes were sampled in 1996, greater frequency was possible which resulted in a near event-based sampling. The higher concentrations of MCPA may be due to less dilution with continued rainfall after initial washout from the atmosphere. Much higher concentrations of MCPA (Figure 4.6) were observed in precipitation during this field year, compared with previous seasons' data. Maximum concentrations of all chemicals were found during the same time frame as previous years, although the temporal resolution was improved for each of the herbicides.

4.5 Discussion

Temporal trends of each of these herbicides in both air and precipitation reflected local use throughout the study. These chemicals persisted for only short periods, compared with other current use chemicals such as atrazine (Rawn et al., 1998*b* (Chapter 5)) or chlorthal dimethyl (dacthal) (Rawn, 1998) measured at this site. In previous work at this site, we found elevated levels of atrazine in air when the air mass originated in the US and passed over the midwest states (Rawn et al., 1998*b* (Chapter 5)). Goolsby et al. (1997) have detected atrazine and alachlor in precipitation samples outside of use regions. Rawn et al. (1998*b* (Chapter 5)) reported atrazine in both air and precipitation samples collected from northwest Ontario and southern Manitoba, two regions where there is limited atrazine use.

Concentrations of the phenoxyacid herbicides in air were not related to the origin of the air mass above the South Tobacco Creek Watershed during sampling events in this study.

Air mass back trajectory analyses were performed for two consecutive sampling events in June, 1994 when the concentration of phenoxyacid herbicides and bromoxynil were elevated in air. During the 12 h period prior to sampling on June 13, 1994, the air mass above the watershed was slow moving, situated above the region (Figure 4.7A). However, the air mass above the watershed during the following sampling period moved into the watershed from South Dakota during the 12 h period prior to sample collection (Figure 4.7B). Therefore, while long range transport from distant agricultural regions may contribute to phenoxyacid concentrations in air, local sources appear to be the major contributor.

No significant correlations between air temperature and concentrations of MCPA, dichlorprop, 2,4-D and bromoxynil existed based on air data collected over the entire sampling regime. Similarly, no relationships existed between air temperature and vapour concentrations for these herbicides during the period of regional application ($r^2 = 0.07 - 0.24$), based on 1993-1996 sampling data. This lack of correlation also suggests that the source of these herbicides is current uses, rather than volatilization from surfaces. Good correlations between air temperature and vapour phase concentrations of semi-volatile organic chemicals are thought to be indicative of revolatilization from soil and plant surfaces (Hoff et al., 1992). These relationships have been shown to occur for PCBs and other organochlorine compounds in temperate regions (Hillery et al., 1997; Rawn et al., 1998*d* (Chapter 7); Hoff et al., 1992*b*).

Temporal patterns and concentrations of phenoxyacids in atmospheric compartments in other published work compare well with results in the present study. Strongly seasonal distribution of the phenoxyacid herbicides, dichlorprop and MCPA has been observed in

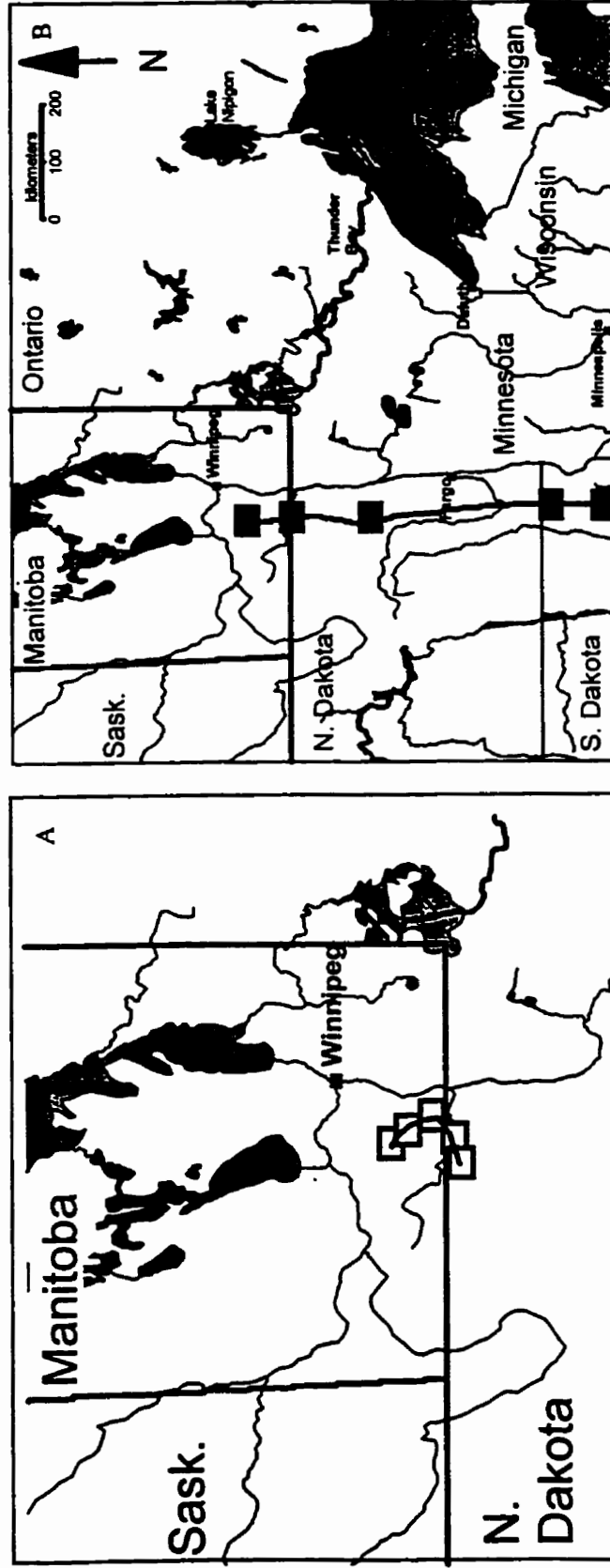


Figure 4.7 24 hour air mass trajectories prior to sampling event on A) June 13, 1994 and B) June 19, 1994. Phenoxoyacid herbicides and bromoxynil concentrations were found at elevated levels on both days.

Norwegian rain (Lode et al., 1995). Maximum concentrations of MCPA and dichlorprop were 320 and 250 ng/L, respectively, collected over the same one week interval in mid-June, 1992. 2,4-D was not detected in precipitation samples collected in Italy during 1988 (Trevisan et al., 1993), however, both MCPA and dichlorprop were detected. Dichlorprop was detected in an isolated sample, collected in mid-September, whereas MCPA was present in rainfall samples collected in both July and September (Trevisan et al., 1993). 2,4-D was consistently detected in rain samples collected between March and October, 1987 in a South African study to a maximum concentration of 430 $\mu\text{g/L}$ (Sandmann et al., 1991), three orders of magnitude higher than observed in the present study.

Temporal trends of the herbicides in air followed similar trends to those observed in other studies, with detection of these chemicals occurring during local use periods. Hawthorne et al. (1996) observed both MCPA and 2,4-D in air samples collected at non-farmed sites, in an agricultural region of North Dakota during the 1993 and 1994 field seasons. Maximum concentrations reported for MCPA and 2,4-D were observed in 1993, 70 and 1770 pg/m^3 , respectively (Hawthorne et al., 1996). Temporal patterns coincided with application times for the region (Hawthorne et al., 1996). Extremely high levels of 2,4-D were observed in South African air samples collected between September and December, 1987 (Sandmann et al., 1991), where the maximum concentration reported was 60 ng/m^3 . In an examination of airborne pesticides in California, MCPA levels were present in ambient air samples throughout regional use periods corresponding to sampling times (Woodrow et al., 1990). MCPA levels in air declined with the completion of local use of this herbicide (Woodrow et al., 1990).

Although concentrations observed in North Dakota were within the range of levels determined in this study, these chemicals were reported to be associated with particles, with no contribution from the vapour phase (Hawthorne et al., 1996). Hawthorne et al. (1996) collected air samples at locations removed from field applications of pesticides, thereby eliminating spray drift and volatilization from treated fields as a source. Also, by using a total suspended particulate sampling head equipped with quartz filters for air sampling, Hawthorne et al. (1996) observed large soil particles ($< 50\mu\text{m}$) on the filter surfaces. These larger particles may have contributed to sorption of the phenoxyacid herbicides, removing these compounds from the vapour phase prior to air reaching the PUF plug in the sampler. Although soil particles were observed on filter papers from the present study, our sampling head, which is similar to those used in the Integrated Atmospheric Deposition Network (IADN) program, is known to discriminate against particle sizes $>10\mu\text{m}$ (Hoff et al., 1996) and may explain the differences in sampling efficiency. Additionally, the sampler in the present study was centrally located in the watershed where local applications of the herbicides occurred within 0.2 -5 km of the sampling station. These differences in sampler design and particle collection efficiency as well as location of sampler relative to where herbicides were applied may have resulted in the differences in particle/vapour ratios for the phenoxyacid herbicides between the present study and Hawthorne et al. (1996).

Seasonal precipitation fluxes were calculated for each herbicide (Table 4.2) for each year of the study by the following equation which relates chemical concentrations to precipitation volume collected, corrected for surface area (S.A.) and duration over which the samples were collected:

$$N_{\text{pptn}} = \frac{C_{\text{TP}} \cdot \text{Sample Volume (L)}}{\text{S.A.} \cdot \# \text{ days sample was collected}} \text{ ng/m}^2\text{-d.} \quad [1]$$

The amount of each herbicide added directly to the South Tobacco Creek via rainfall (Table 4.3) has been related to discharge losses reported previously (Rawn et al., 1998c (Chapter 3)) for the 1994 (May-October) through 1996 (June-July) field seasons. The percent of discharge that precipitation contributes is highly variable for each chemical. Direct precipitation is responsible for less than 50% of herbicide levels discharged via South Tobacco Creek with the exception of MCPA in 1994 and 1995 and 2,4-D in 1995. Because the temporal resolution in 1996 was 2 d, rather than biweekly as in the previous years, the 1996 results reflect more accurately the precipitation contributions to discharge. The creek water depth was low during the period of elevated herbicide concentrations in South Tobacco Creek in the 1994-1996 agricultural growing seasons. During the interval of high herbicide concentrations, there were no overland flow events observed by landowners in the watershed and autosamplers equipped to respond to increased water flows were not triggered (Rawn et al., 1998c (Chapter 3)). Therefore, wash in of herbicides via rainfall runoff could not be identified as the route of entry for these compounds. Maximum concentrations in creek water corresponded to elevated herbicide levels in the two atmospheric compartments; precipitation and air (Rawn et al., 1998c (Chapter 3)). Precipitation may have scavenged airborne herbicides and deposited these compounds directly into the water column. Deposition of these herbicides to the land surface of the watershed was greater than two orders of magnitude higher than the discharge losses (Table 4.2). The fate of these herbicides deposited to the watershed is unknown, however, they may have been degraded,

Table 4.2 Seasonal precipitation fluxes (g) to the South Tobacco Creek water surface^a and the land surface of watershed^b.

Chemical	1993	1994	1995	1996
bromoxynil	0.65 ± 0.21 [840±270]	1.24 ± 0.40 [1600±510]	1.17 ± 0.37 [31±10]	0.34 ± 0.11 [460±150]
2,4-D	0.08 ± 0.03 [110±35]	0.40 ± 0.22 [520±170]	1.87 ± 0.60 [2400±770]	1.2 ± 0.38 [1500±480]
dichlorprop	0.03 ± 0.01 [34±11]	0.46 ± 0.59 [600±200]	0.54 ± 0.17 [700±220]	0.70 ± 0.22 [800±260]
MCPA	0.11 ± 0.03 [140±45]	2.94 ± 0.85 [3800±1200]	2.64 ± 0.84 [3400±1100]	2.1 ± 0.67 [2500±800]

^aSouth Tobacco Creek estimated to be 58409 m²

● standard error associated with the determination of precipitation concentrations

^bland surface of watershed = 76341591 m², fluxes to land surface area are given in parentheses

Table 4.3 The contribution of herbicide inputs via precipitation to total discharge^a (%) from the South Tobacco Creek.

Chemical	1994 (May-October)	1995 (May-October)	1996 (June-July)
bromoxynil	35 ± 16	18 ± 7.8	12 ± 5.1
2,4-D	11 ± 4.9	56 ± 25	4.3 ± 1.9
dichlorprop	14 ● 6.2	6.1 ● 6.2	26 ± 11
MCPA	62 ± 27	256 ± 113	19 ● 8.5

^a% of what would have landed directly to water surface of the South Tobacco Creek via precipitation

● standard error of precipitation concentrations and discharge estimates

similar to degradation losses in soil. (Wauchope et al., 1992). Deposition of these compounds directly to the water surface through precipitation contributed significantly to South Tobacco Creek discharge losses (Table 4.3). Additionally, herbicides in air may have contributed to herbicide loadings in the creek water through gas absorption. During both wet and dry periods, deposition of herbicides may also have occurred through association with dryfall (Hoff et al., 1996).

The dynamics of the phenoxyacid herbicides, 2,4-D, dichlorprop and MCPA, and the phenolic herbicide bromoxynil in the atmosphere are not well understood. These chemicals are applied as amines, esters or salts of the acid or phenol and may be present in one of several forms. These chemicals have very low vapour pressures resulting in low volatility, however, they have been found in atmospheric compartments previously and in the present study.

We previously found that gas absorption of atrazine was a significant pathway of entry to the South Tobacco Creek (Rawn et al., 1998*b* (Chapter 5)). This estimation was not possible for the phenoxyacid herbicides and bromoxynil due to the lack of data on the physical properties for these compounds. The calculation of gas absorption or volatilization of these chemicals at the air-water interface requires Henry's Law Constant and dry deposition requires subcooled liquid vapour pressure values (Eisenreich and Strachan, 1992). Vapour pressures of the phenoxyacid and phenolic herbicides are often estimated based on the ester or salt forms of these chemicals. These compounds, however, are detected in atmospheric samples in the acid or free phenol form. Vapour pressure values reported for the free acid or phenol frequently are recorded as less than a given value, e.g., dichlorprop (acid and salts)

$<1 \times 10^{-7}$ mmHg; bromoxynil (parent phenol) $<1 \times 10^{-5}$ mmHg (Wauchope et al., 1992). These herbicides are dissolved in creek water at pHs above their known pK_a values (Rawn et al., 1998c (Chapter 3); Wauchope et al., 1992) and, therefore, are present in the water column in their freely dissociated forms, which further complicates the estimates of their chemical dynamics.

4.6 Conclusions

Although these phenoxyacid and phenolic herbicides are considered to be non-volatile, they were present in both gas and particle phases and precipitation in this study. Their presence in atmospheric compartments was generally restricted to use periods within the South Tobacco Creek Watershed. Phenoxyacid levels in South Tobacco Creek water follow concentration patterns of these herbicides in precipitation more closely than air concentration patterns. The temporal distribution of bromoxynil in the creek water corresponds to both the air and precipitation concentration patterns. The behaviour of bromoxynil in ambient air differs from the phenoxyacids. Bromoxynil is present in air samples over longer periods than was observed for 2,4-D, dichlorprop or MCPA each year of the study. Bromoxynil was found in both the gas and particle phase throughout the season, whereas phenoxyacids were restricted mainly to the vapour phase. Although bromoxynil use was less than that of the phenoxyacid herbicides within the South Tobacco Creek Watershed, precipitation fluxes were greater. Accurate vapour pressure values for the appropriate forms of these phenoxyacid and phenolic herbicides are required to enable estimates of gas exchange to water surfaces and

deposition associated with dryfall.

The high sampling frequency which we employed in 1996 resulted in more accurate determination of the temporal patterns of herbicides in atmospheric compartments. Accurate physical property measurements also are required to further examine gas absorption, dryfall and contributions to discharge of the phenoxyacid and phenolic herbicides. In general, high frequency sampling is required for these chemicals which have short residence times.

5. ATMOSPHERIC TRANSPORT AND DEPOSITION, AN ADDITIONAL INPUT PATHWAY FOR ATRAZINE TO SURFACE WATERS

5.1 Abstract

This paper reviews the current literature observations of atrazine in precipitation and ambient air and evaluates the importance of atmospheric deposition to surface waters using measurements of atrazine in water, air and precipitation at two locations where this chemical is not used. Precipitation was found to be an important route of entry into aquatic systems, particularly during periods when extensive regional use of atrazine occurs. Gas exchange and dry deposition were estimated using established methods and gas exchange was found to be the primary dry process of atrazine deposition to surface waters.

5.2 Introduction

Surface runoff losses from treated fields and groundwater contamination have been traditionally viewed as the main sources of the triazine herbicides to rivers (Muir and Grift, 1995). There has been little attention paid, until recently, to the role of atmospheric contributions to surface waters by current use herbicides, particularly in agricultural regions. In the most comprehensive study to date, Goolsby et al. (1994) have measured atrazine in precipitation samples from both agricultural and non-agricultural regions of the US.

Maximum atrazine concentrations in precipitation samples collected through midwestern and northeastern US were observed in May and June during 1990 and 1991 (Goolsby et al., 1995). Atrazine deposition via precipitation and gas exchange was examined in the Chesapeake Bay region (Glotfelty et al., 1990), based on bulk rain and ambient air levels. From this and previous studies, Glotfelty et al. (1990) concluded that seasonal high atrazine concentrations in surface waters resulted from runoff contamination, whereas atmospheric deposition was responsible for low-level, widespread contamination year round. Although the triazines have been detected in precipitation and air, there has been little research to examine dry deposition and gas exchange of these chemicals (Figure 5.1), or the relative importance of each of these pathways to surface waters. The objective of this paper is to review existing information on atrazine in precipitation and air, and to evaluate the importance of atmospheric deposition pathways.

Triazines are relatively non-volatile (Table 5.1), which may be the reason why volatilization losses and atmospheric transport of these chemicals have not been studied as extensively as surface runoff losses. Atrazine losses in the vapor phase from treated fields in a southern California study were found to be 0.16% during the first 3 days of the experiment (Clendening et al., 1990). Atrazine losses through volatilization from treated fields in Maryland, however, were found to be 2.4% (Glotfelty et al., 1989). Surface runoff losses of pesticides are considered catastrophic if they exceed 2% of applied levels in a single event (Wauchope, 1978). In 1989, 1.7% of the atrazine applied in the US Midwest was estimated to have been transported via runoff to the Gulf of Mexico (Pereira et al., 1992). Thus, overall atrazine losses via volatilization may be similar to runoff losses.

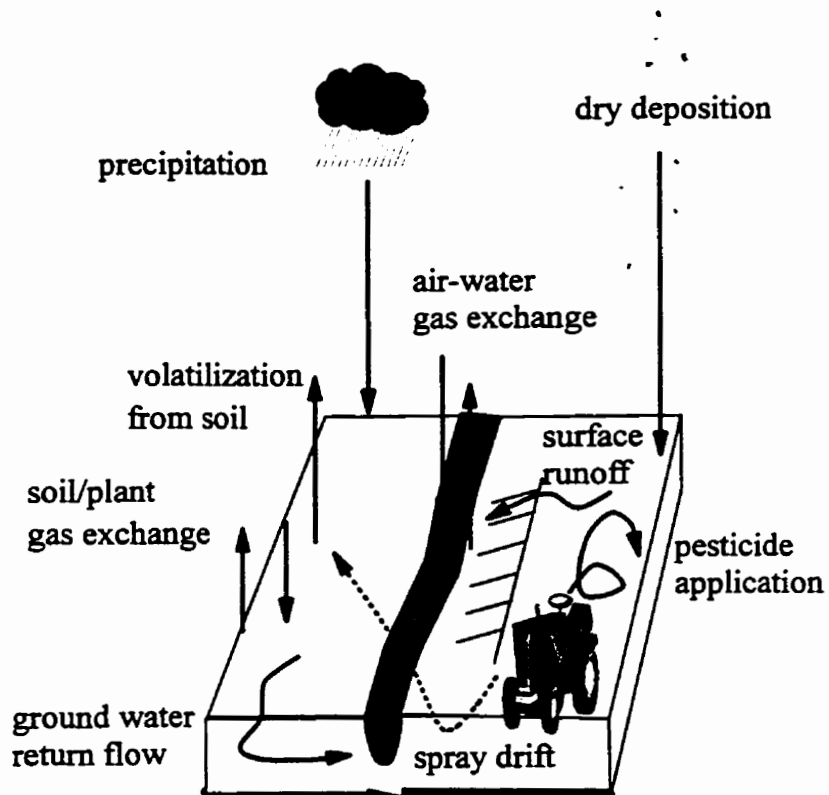


Figure 5.1 Atmospheric inputs and loss pathways of atrazine in agricultural watersheds.

Seasonal trends of atrazine in precipitation have been found, generally corresponding to application times (Richards et al., 1987). Goolsby and coworkers (1994) found temporal patterns of atrazine in rainwater samples fit closely to the trends in water previously observed for the Mississippi River. The highest observed concentrations were detected in samples collected during application times from regions where greatest atrazine use occurred. Atrazine was found infrequently in areas where it is not used, such as Maine and parts of Michigan. When detected in these areas, it was at much lower concentrations than observed in high use regions (Goolsby et al., 1994).

Table 5.1 Physical/chemical properties related to atmospheric behaviour of triazines.

Chemical	Molecular Weight ^a g/mol	Water Solubility ^a mg/L (T°C)	Subcooled Liquid Vapor Pressure ^b VP _L , mPa	Melting Point ^a °C	Henry's Law Constant ^c Pa·m ³ /mol
Atrazine	215.7	33 (25)	1.22 x 10 ⁻³	174	2.52 x 10 ⁻⁴
Simazine	201.7	6.2 (25)	6.23 x 10 ⁻⁶	225-7	9.59 x 10 ⁻³
Terbutryn	241.4	25 (20)	2.99 x 10 ⁻³	104-5	2.70 x 10 ⁻³

^a(Shiu et al., 1990)

^bCalculated using the relationship: $(VP_{\text{liquid}}/VP_{\text{solid}}) = \exp[6.81 (T_{\text{Melting point}}/T-1)]$
(Schwarzenbach et al., 1993)

^c(Wauchope et al., 1992)

Recent atrazine measurements in several European countries also show seasonal trends in precipitation and evidence of long range transport. Although atrazine use was reduced in Switzerland in 1988, detectable levels of atrazine were found in precipitation samples collected during 1988 and 1989 (Buser, 1990) (Table 5.2). Detectable levels of

Table 5.2 Recent observations of atrazine in precipitation.

Location	Concentration Range (ng/L)	Duration of Study	Maximum Concentration Observed	Reference
Ontario, Canada	<10 - 445	Apr. '91 - Sept. '92	May '92	Hall et al., 1993
Midwestern - Eastern US	<50 - 16,000	Mar. '90 - Sept '91	June '90, '91	Goolsby et al., 1994
Iowa, US	<100 - 40,000	Oct. '87 - Sept. '90	June '89	Nations and Hallberg, 1992
Minnesota, US	<20 - 2,000	Mar. - Nov. '89	May '89,	Capel, 1991
		Mar. - Apr. '90	June '90	
Northeastern US	<50 - 1,500	Apr. - Aug. '85	May '85	Richards et al., 1987
Northern Germany	<10 - 113	Mar. '90 - Mar. '92	May '90, '91	Seibers et al., 1994
North Sea Germany	<3 - 140	Apr. - Jul. '93	May '93	Bester et al., 1995
France	< 5 - 140	Mar. '91 - Feb. '92	April - May '91	Chevreuil and Garmouma, 1993
Switzerland	<0.1 - 600	Feb. '88 - Jul. '89	May - June '89	Buser, 1990
Italy	<100 - 1,990	May - Oct. '88	June '88	Trevisan et al., 1993
Norway	<10 - 86	Jun. - Sept. '92/'93	May '93	Lode et al., 1995

atrazine were found in approximately 25% of the precipitation samples collected in Germany, both prior to, and following, the ban on atrazine use in 1991 (Seibers et al., 1994). Atrazine was detected in precipitation samples at four locations in Northern Germany, however concentrations were not found to be significantly different between agricultural, urban and coastal sites (Bester et al., 1995) and no seasonal or spatial differences in atrazine concentrations were observed. Atrazine was not registered for use in Germany throughout the duration of the latter study. Maximum atrazine concentrations in rainwater samples collected near an Italian forest were $1.9 \mu\text{g/L}$, with temporal trends reflecting local high use intervals (Trevisan et al., 1993). Combined wet and dryfall concentrations of atrazine were found at maximum levels in early spring in a rural area of France (Chevreuil and Garmouma, 1993). In Paris, however, the highest observed levels were found during sampling in June, 1991 (Chevreuil and Garmouma, 1993). Atrazine residues in Norwegian rain samples collected during 1993 were detectable during early to mid-May sampling times (Lode et al., 1995), four years following its removal from the market in Norway. In all cases, highest concentrations observed in precipitation samples reflected local or regional atrazine application.

Atmospheric deposition of semivolatile organic contaminants (SOCs) also occurs via dry processes which can be separated into gas exchange and particle associated deposition (Figure 5.1). There has been limited research to estimate relative contributions of SOC's through each of the pathways. Estimates of atrazine associated with the dryfall component were made for the Great Lakes region by Eisenreich and Strachan (1992) using total air concentrations (vapor + particle). Particle deposition is a function of both the size and mass

of a particle, in addition to nonchemical factors such as the wind speed, temperature and surface characteristics (Majewski and Capel, 1995). The majority of work in this area has been performed for persistent organochlorine compounds, rather than current use herbicides. For some chemicals, relationships between concentration associated with the particles and ambient air temperature have been developed (Eisenreich and Strachan, 1992; Bidleman and Foreman, 1987).

As far as we are aware, there have been no direct measurements of atrazine in dry deposition although several authors have measured total precipitation and dryfall using uncovered precipitation collectors (Seibers et al., 1994; Chevreuil and Garmouma, 1993; Nations and Hallberg, 1992). Representative measurement of dry deposition is difficult to perform. Many devices have been used to measure dryfall and have resulted in the bias toward one particle size or another. Inverted frisbee and coated flat-plate samplers were used in the determination of polychlorinated dibenzo-*p*-dioxin (PCDD) and -furan (PCDF) dry deposition fluxes (Koester and Hites, 1992). Koester and Hites (1992) concluded that frisbee and flat plate collectors were less efficient than water surfaces, based on mass balance estimates.

Knowledge of depositional velocity (V_d) and particle surface areas (S.A.), used in the calculation of the fraction associated with the particle phase (ϕ) are critical for estimating dry deposition. V_d is dependent upon the fraction of coarse or fine particles in air available for dry deposition (Noll et al., 1988). Estimates of particle S.A. from rural and urban regions differ by greater than one order of magnitude (Bidleman, 1988). Surface area estimates are used in combination with subcooled liquid vapor pressure (VP_L) to estimate the fraction of

a given SOC associated with the particle phase using the Junge-Pankow model (Pankow, 1987).

There have been far fewer measurements of atrazine in air than in precipitation (Table 5.3). Concentrations of atrazine in air have generally been reported to be low, or non-detectable ($< 1 \text{ ng/m}^3$). Particle-associated or vapor phase atrazine was not detected in ambient air samples collected in Italy (Trevisan et al., 1993). This may have been a function of the high detection limit 1.6 ng/m^3 for atrazine. In Paris, air samples collected between April and June contained detectable levels of atrazine in the vapor phase (Chevreuil and Garmouma, 1993) at levels (0.05 ng/m^3) very near detection limits (0.03 ng/m^3), when observed. In a Japanese study of pesticides in ambient air, atrazine was detected during both spring and summer sampling times (Haraguchi et al., 1994), but only in the vapor phase ($0.2\text{-}0.32 \text{ ng/m}^3$), with no contribution from the particulate phase. Ambient air measurements of atrazine ranged between $0.1\text{-}20 \text{ ng/m}^3$ in the Wye River region, near Chesapeake Bay and varied seasonally. Five percent of the atrazine concentration detected in ambient air was associated with the particle phase during the warmer sampling times and increased particle-bound atrazine was observed during winter sampling events (Glotfelty et al., 1990). Seasonal differences in ambient air levels of atrazine were observed in the Wye River region, with winter samples containing approximately 1% of observed summer values. Alachlor and metolachlor, two other herbicides used in this region, were limited temporally to local use times in ambient air samples, whereas both atrazine and simazine were detected throughout the year (Glotfelty et al., 1990). Glotfelty and coworkers (1990) concluded that the source of high pre-application atrazine levels resulted from long range transport from southern states,

Table 5.3 Atrazine in ambient air.

Location	Concentration Range (ng/m ³) [where available]	Duration of Study	Fraction Associated with Particle Phase	Reference
Ontario, Canada	0.002 - 0.037	May '90 - Sept. '92	not determined	Muir and Grift, 1995
Midwest, US	0.008 - 20	Mar. '81 - Oct. '82	0.05 - summer 0.32 - winter	Glottfelty et al., 1990
Japan	0.2 - 0.32	Jul. '91, Apr. '92	0	Haraguchi et al., 1994
Italy	<1.6 (not detected)	May - Oct. '88	not determined	Trevisan et al., 1993
France	0.05	Mar. '91 - Feb. '92	0	Chevreuil and Garmouma, 1993

where atrazine application occurred during March and April. Based on the measured atrazine concentrations in each of the wetfall, ambient air and Chesapeake Bay surface waters, atrazine deposition via gas exchange from the atmosphere to the river was considered important (Glotfelty et al., 1990).

In the following sections we examine the relative importance of atmospheric contributions of the triazine herbicide atrazine via individual atmospheric pathways based on data from two locations; one in the centre of the agricultural region of Manitoba, and the other at a remote location, within a boreal forest in northwestern Ontario.

5.3 Materials and Methods

5.3.1 Watershed Description

The South Tobacco Creek Watershed (49°19'28"N, 98°21'50"W) (Figure 5.2) is a 70 km² agricultural watershed in southern Manitoba. Detailed landuse information is available including weekly pesticide application information within the watershed, details of the formulation applied and rate of application, on a field by field basis. A survey of 41 landowners over the past five years show that there has been no atrazine application within this watershed. South Tobacco Creek, which drains the watershed ranged in dissolved organic carbon from 6.5 to 68 mg·L⁻¹ and in pH from 6.7 to 8.0, during the course of the study.

At the Experimental Lakes Area, lake and atmospheric samples were collected in a boreal forest in northwestern Ontario 50 km east of Kenora, ON (49°45'N, 93°47'W) (Figure

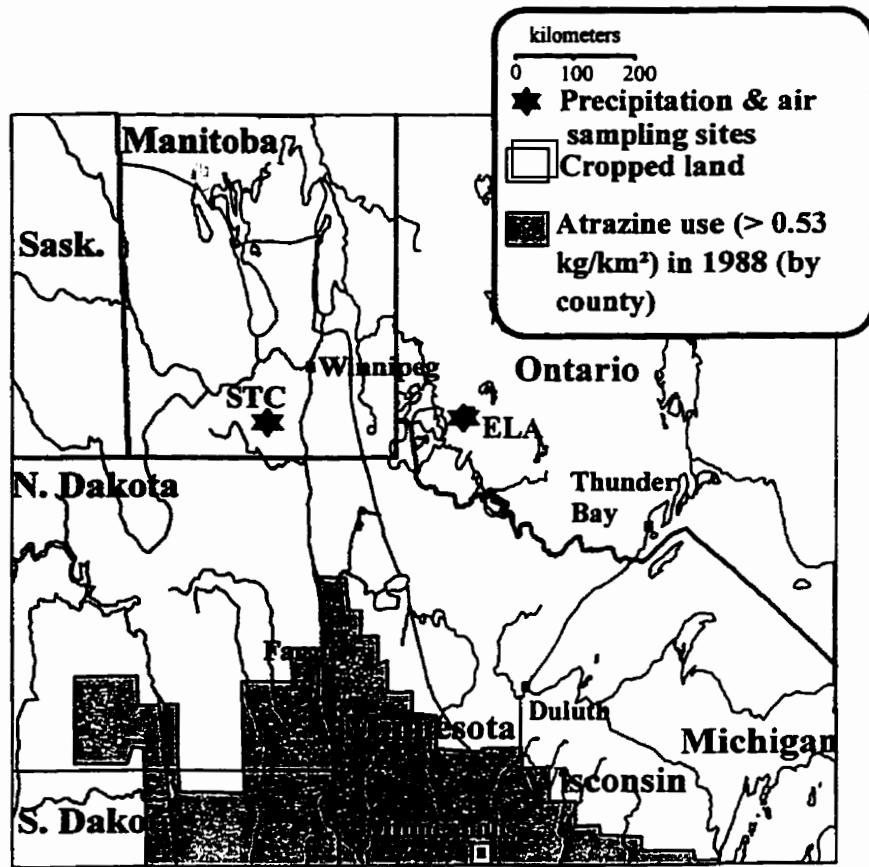


Figure 5.2 South Tobacco Creek Watershed and Experimental Lakes Area locations.

5.2). This location is in a remote area, at least 100 km from the nearest agricultural area and 1000 km from the US “corn belt”.

5.3.2 Sample Collection

South Tobacco Creek Watershed: Air, precipitation and creek water were sampled over a three year period, from 1993-1995 to determine pesticide levels in each of the compartments. The sampling program was designed to collect large volumes of air, precipitation and creek water in order to determine locally used pesticides and those entering the watershed via long range transport.

Air samples were collected using a high volume (General Metalworks PS-1) PUF sampler with a GF/A glass fibre filter to trap particulate matter. Filters were prepared for use by heating for 18 hours at 265°C. PUF plugs were pre-cleaned by Soxhlet with hexane for 24 h prior to use. Approximately 350 m³ of air was drawn through the sampling unit over a 24 h period every 6 days during the early part of the growing season, sampling commenced in June 1993. Samples were collected every 12 days later in the field season, annually. Samples were collected June-October 1993, May-November, 1994 and May-October 1995. PUFs were placed in sealed glass jars and stored at 4°C until extraction and analysis. Filters were placed in “Whirl pak” bags and stored at 4°C until extraction and analysis.

Rainfall was collected, using an automated wet-only (0.2025 m²) sampler (Meterological Instrument Centre) in the centre of the watershed, continuously over two week periods in 18 L stainless steel transfer tanks. Sample volumes ranged from 3 to 18 L. Rain water was filtered through a glass wool plug at the bottom of the collection basin, for removal of large particles and dichloromethane (DCM) was used as a preservative.

Creek water was collected using a submersible pump in the centre of the creek and pumping 18 L into stainless steel containers. Samples were filtered under pressure through precleaned 1 μm GFC glass fibre filters. Samples were collected on a weekly (1994-5) and biweekly (beginning in July 1993) sampling schedule, from spring melt through freeze up. Experimental Lakes Area: Air and precipitation samples were collected throughout the 1995 field season. Air samples were collected for a 24 h period on a 12 day cycle using a PS-1 high volume air sampler. Precipitation samples were collected on a continuous basis from May to October 1995, using an automated wet-only sampler. Sample containers were exchanged on a monthly basis through the season.

5.3.3 Sample Analysis

A broad spectrum approach was used for sample analysis to analyse both acid and neutral herbicides (e.g., 2,4-D and atrazine). PUFs were extracted using Soxhlet with DCM for 4 h. Deuterated (d_3) atrazine was used as an internal recovery standard which was added at the extraction step.

Creek water and precipitation samples were extracted in the sampling containers using DCM. Creek water samples were filtered (1 μm glass fibre) prior to extraction. Water was adjusted to pH 2 to extract acid herbicides and phenolics and then taken to pH 10 to recover hydrophobic organics. Extracts were evaporated to small volumes and methylated using freshly prepared diazomethane. Cleanup was performed using 5% deactivated Florisil, eluting with 20 mL hexane to remove polychlorinated biphenyls, followed by 85 mL, 18% ethyl acetate (EtAc) in hexane. Using this procedure, the acid and phenolic herbicides were analysed as methyl ester derivatives and results will be reported elsewhere. Atrazine was

quantified using gas chromatography-mass spectrometry (Hewlett Packard 5971 MSD) using a 60 m x 0.25 μm DB-5 column with helium as the carrier gas. Detection criteria were the correct ratios of two characteristic ions and retention times. Herbicides were quantified using external standard solutions and corrected for volume changes using PCB-104.

5.3.4 Quality Assurance

Blank PUFs, filters and blanks of "Super Q" water were analysed with each batch of samples. PUF and air filter samples were corrected for internal standard recoveries. Average internal standard recovery for precipitation and creek water was 107%. Water and precipitation results were not corrected for d_5 -atrazine standard recoveries. Desethylatrazine (DEA) was detected in water and precipitation, although recovery from water may be inefficient using liquid-liquid partitioning, resulting in lower observed concentrations in the present study (Thurman, E.M., U.S. Geological Survey, Lawrence, KA. personal communication, 1996), therefore, DEA concentrations are not reported for precipitation or creek water samples.

5.4 Results and Discussion

5.4.1 Air

Temporal patterns of atrazine in ambient air were similar between the South Tobacco Creek Watershed (STCW) and the Experimental Lakes Area (ELA) sites (Figure 5.3). Atrazine concentrations at the ELA location were generally lower than those measured in the STCW. Maximum concentrations were detected at both sites during mid-June sampling times

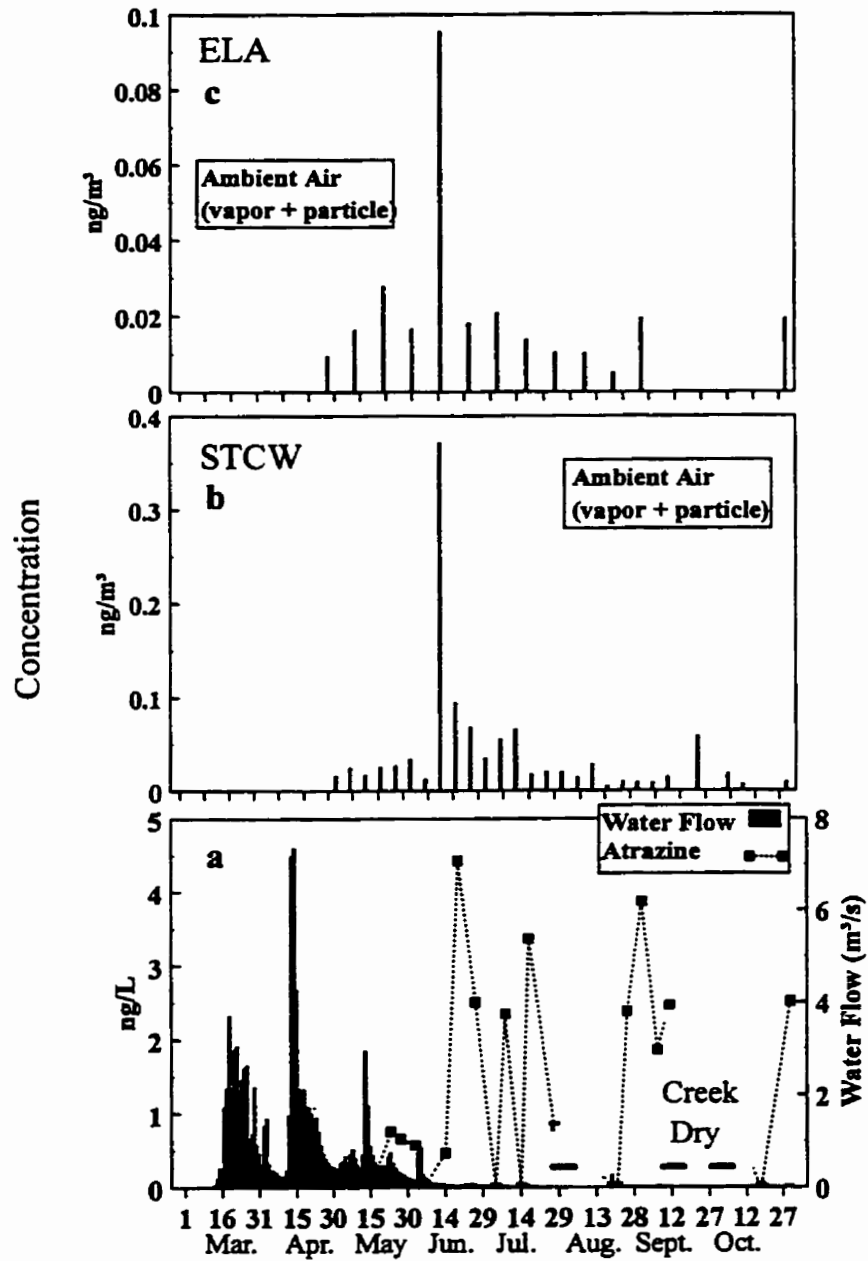


Figure 5.3 Atrazine concentrations - 1995 a) in creek water (ng/L) in South Tobacco Creek, b) in ambient air (ng/m³) in the South Tobacco Creek Watershed and c) in ambient air (ng/m³) at the Experimental Lakes Area.

(0.3 ng/m³ STCW; 0.09 ng/m³ ELA). Atrazine presence in ambient air reflected its probable use pattern, with maximum values obtained during the period between May and July when high herbicide use would be expected (Figure 5.3). Hoff and coworkers (1992a) found a similar pattern for trifluralin levels in air samples collected in southern Ontario.

5.4.2 Water

Atrazine concentrations during the pre-application period were at or near detection limits (0.04 ng/L) in South Tobacco Creek water and remained at low levels until early June sampling times. Elevated concentrations were detected in the water column at most sampling times through June and July (Figure 5.3a). Temporal patterns of atrazine in the South Tobacco Creek follow similar trends to those determined in Roberts Creek (Iowa) which also drains a small (16 km²) watershed, where maximum concentrations were found in June (Kolpin and Kalkhoff, 1993). Maximum concentrations (8.9 µg/L) were much higher in Roberts Creek than observed in the southern Manitoba watershed, (4.4 ng/L) where no atrazine use occurred.

Maximum seasonal atrazine concentrations in South Tobacco Creek water coincided with seasonal maximum levels observed in ambient air and elevated levels in precipitation (Figure 5.4a,b). Low concentrations of atrazine were detected in creek water samples collected during spring runoff events. Similarly, 1994 results indicate low atrazine levels in South Tobacco Creek following an extended (July-early September) dry period. Maximum atrazine concentrations observed during the 1994 field season were found during the May sampling times, which corresponded to maximum concentrations in both precipitation and ambient air samples.

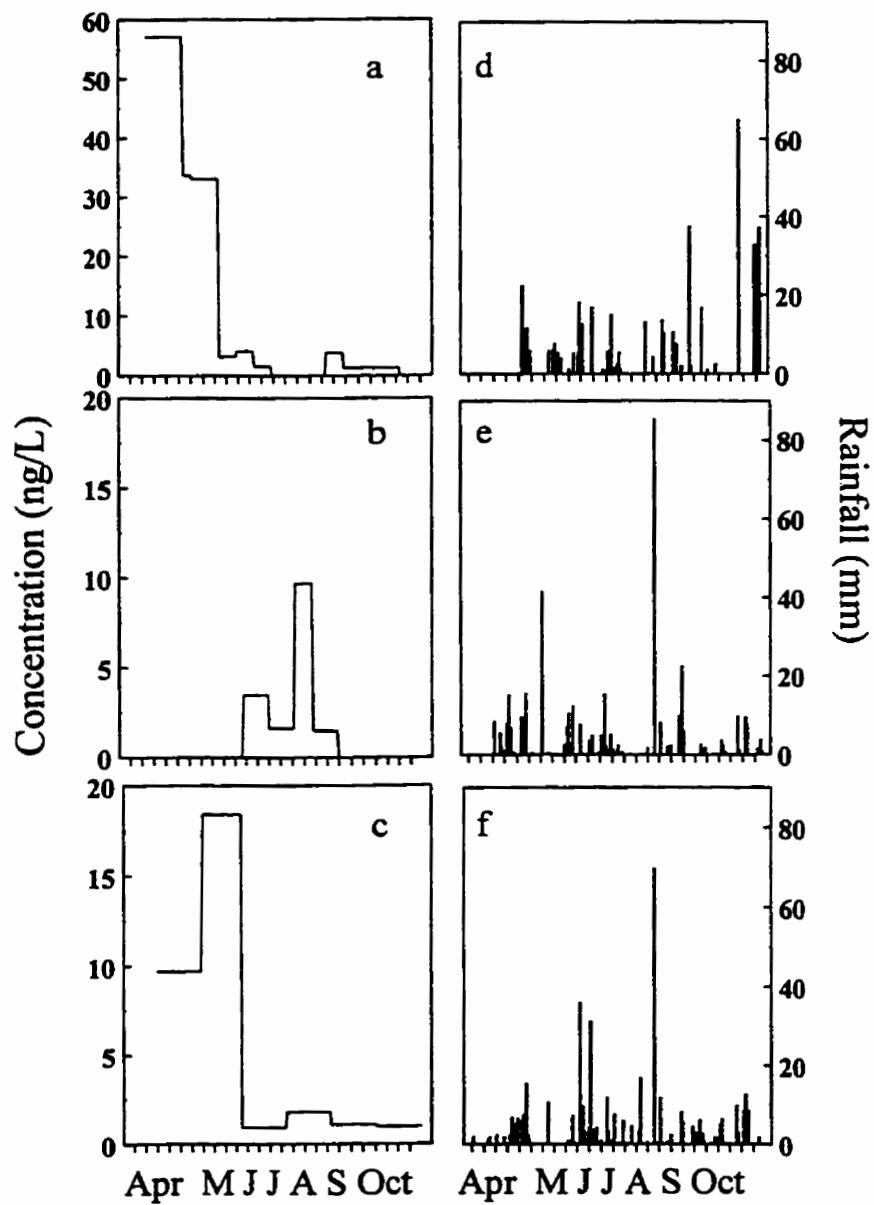


Figure 5.4 Atrazine concentrations (ng/L) in precipitation samples collected in the South Tobacco Creek Watershed: a) 1994; b) 1995; c) Experimental Lakes Area 1995; corresponding rainfall (mm) indicated in d) e) and f), respectively.

5.4.3 Precipitation

Seasonal patterns of atrazine in precipitation within the STCW varied between the 1994 and 1995 field seasons (Figure 5.4a,b). The 1994 pattern is in better agreement with the majority of other research. High atrazine levels in precipitation, during the period of application in areas of use, have been found in Germany (Seibers et al., 1994), Switzerland (Buser, 1990) and in the US (Richards et al., 1987; Goolsby et al., 1994). Glotfelty and coworkers (1990) found highest atrazine concentrations in rain samples prior to local application, which they attributed to atmospheric transport from more southern locations, where atrazine use began earlier in the year than in the Chesapeake Bay region. In this study, maximum observed atrazine concentrations were much lower during 1995 (10 ng/L) than 1994 value (57 ng/L). The 1995 pattern of atrazine in precipitation is similar to the observed pattern found for the first year of sampling by Hall and coworkers (1993), where maximum concentrations were found later in the field season (June), rather than during local application times at three sampling sites.

The trend in atrazine levels observed in precipitation at the remote ELA site and the STCW suggest different input sources. Atrazine concentrations at ELA correspond to sources from spring application (Figure 5.4c), similar to the 1994 determinations in the STCW. Temporal relationships within a precipitation event were not possible because rainfall was collected on a continuous basis for two to four weeks to obtain bulk rainfall samples. Precipitation weighted concentrations observed in this study for both sites, where atrazine is not used, were three to four orders of magnitude below values obtained in the high herbicide use areas in the US (Table 5.4).

Table 5.4 Precipitation weighted atrazine concentrations.

Location/Year/Reference	Atrazine Concentration	Weighted Concentration ^a
1993 STCW ^b	0.42 - 12.55	5.80
1994 STCW	<0.04 - 12.55	11.59
1995 STCW	<0.04 - 9.68	2.85
1995 ELA	0.9 - 18.41	5.64
1990 - 1992 ELA	<0.03 - 51	27.29
Muir and Grift, 1995		
Midwest US	-	200 - 400
Goolsby et al., 1994		
North Dakota 1990	<50 - 420	56.76 ^c
Goolsby et al., 1995		
Minnesota 1991	<50 - 440	43.89 ^c
Goolsby et al., 1995		
Iowa, Illinois and Indiana	-	600 - 1,000
Goolsby et al., 1994		

^aprecipitation weighted concentration = $\frac{\sum(\text{Precipitation}_{\text{amount}} \cdot [\text{atrazine}])}{\sum \text{Precipitation}_{\text{amount}}}$

^bbased on June-October sampling

^cestimated by taking atrazine levels reported to be below detection limits (50 ng/L) as 0.5 x detection limit concentrations (25 ng/L)

5.4.4 Sources

Air-mass back trajectories were performed by the Canadian Meteorological Centre, (Environment Canada) for five day periods at six hour intervals at the 900 mbar pressure level. Results from the 1994 field year indicated that elevated concentrations of atrazine were associated with air movement from the south. During the period of maximum atrazine in air

samples in 1995, air masses had moved in from the south, at both sampling sites (Figure 5.5a,b). Low concentrations of atrazine were generally observed in samples collected over periods when air masses entered from non-source regions.

Atrazine concentrations in the gas and particle phase were used to calculate the fraction of atrazine associated with the particle phase in order to estimate dry deposition. Previously Eisenreich and Strachan (1992) had estimated this fraction (ϕ) to be 0.75 during summer months and 0.85 during winter periods. The value obtained in the present study was much lower (0.40), based on 85 sampling observations producing detectable levels of atrazine in both vapor and particle phases, from both ELA and STCW (1993-1995). A wide range of atrazine in the gas/particle distribution was observed in ambient air samples (Figure 5.6a). Atrazine presence in the vapor phase was higher during periods of application, relative to particle phase levels (Goolsby, D.A., U.S. Geological Survey Lakewood, CO. personal communication, 1996). Problems with stripping of SOCs from filter surfaces during extended sampling times have been reported for highly volatile compounds, such as trifluralin (Hoff et al., 1992a), however, the vapor pressure of atrazine is sufficiently low (0.0399 mPa) and the total air volumes of $\sim 350 \text{ m}^3$ were small enough to suggest that this was not an important source of error.

Hoff and coworkers (1992b) plotted log concentrations of several SOCs against inverse temperature in Clausius-Clapeyron type plots and showed a clear relationship between ambient air concentration and temperature for several organochlorine insecticides. A similar Clausius-Clapeyron plot of vapor phase atrazine concentrations measured in this study with temperature, indicated a poor relationship between these parameters (correlation coefficient

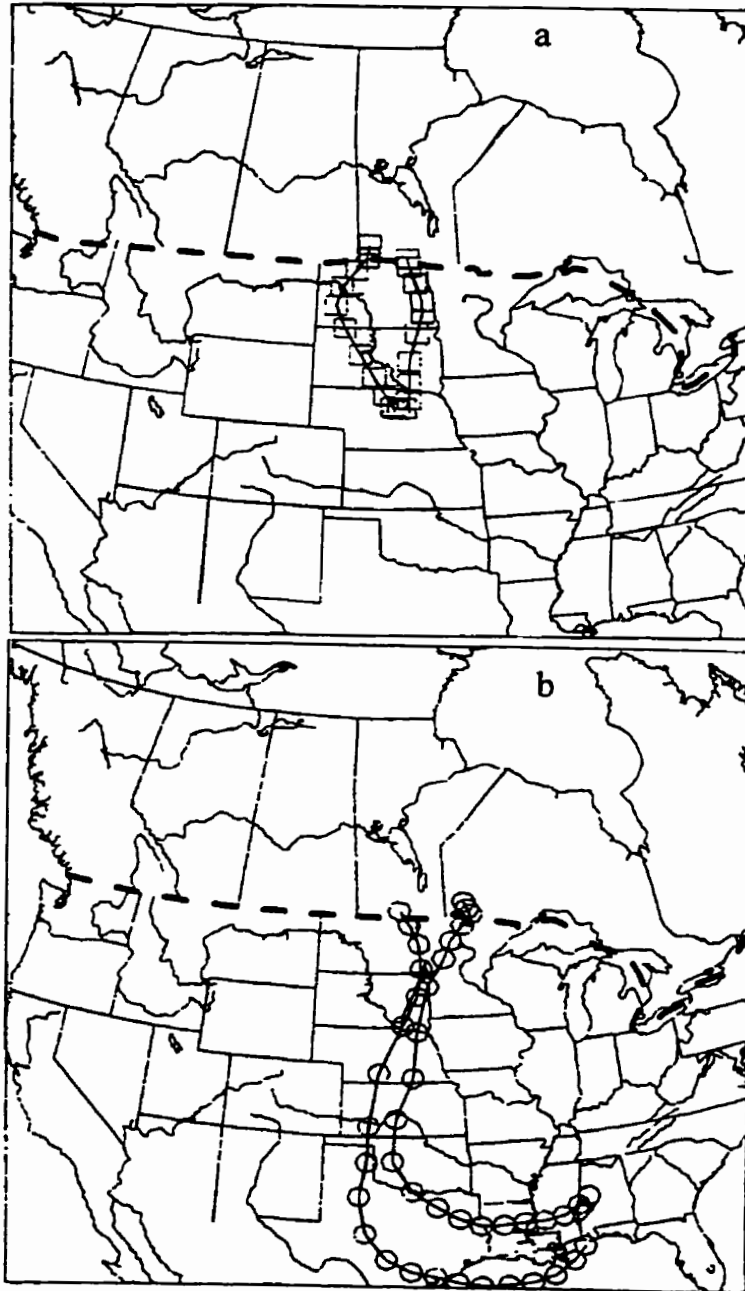


Figure 5.5 Air mass back trajectories a) to the South Tobacco Creek Watershed: June 14, 1995 (981 mbar); b) to the South Tobacco Creek Watershed and Experimental Lakes Area: June 20, 1995 (950 mbar).

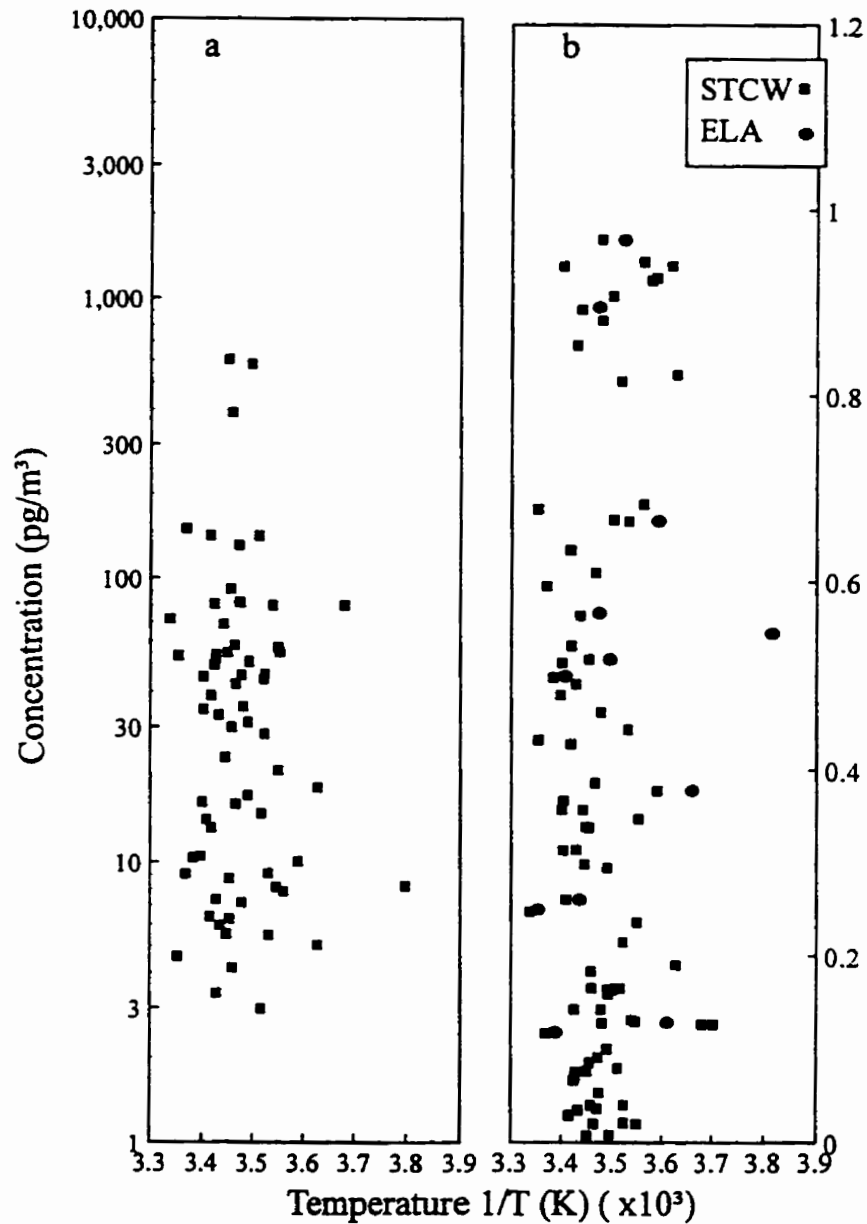


Figure 5.6 Atrazine temperature relationships: a) atrazine concentration in the vapor phase of ambient air; b) fraction of atrazine on particles. Data from the 1993 through 1995 sampling years at the South Tobacco Creek Watershed and measurements during 1995 at the Experimental Lakes Area site were used for the Clausius-Clapeyron type plot (a).

= 0.02) (Figure 5.6b) and suggests that atrazine sources are not temperature related. Sources at a distance removed from sampling sites appear to be controlling local concentration, not sorption/desorption processes.

5.4.5 Flux

Deposition via precipitation (N_{ppm}) to the STCW was calculated for each of the compartments under investigation, for both the 1994 and 1995 sampling seasons and for the ELA site for 1995, by relating atrazine concentration to the volume of precipitation collected, corrected for surface area and duration over which the sample was collected:

$$N_{ppm} = \frac{C_{TP} \cdot \text{Sample Volume (L)}}{\text{S.A.} \cdot \# \text{ days sample was collected}} \quad \text{ng/m}^2\text{-d} \quad [1]$$

where C_{TP} = atrazine concentration in precipitation (sum of particle and dissolved phases) and S.A. = collection surface area.

Deposition of atrazine from dry particles (N_{dry}) was estimated using the relationship (Eisenreich and Strachan, 1992):

$$N_{dry} = C_{TA} \cdot \phi \cdot V_d \cdot \text{S.A.} \quad \text{ng/m}^2\text{-d} \quad [2]$$

where the fraction of atrazine associated with the particle phase, ϕ , was taken to be 0.4, based on measured results in this study. Total atrazine concentrations (C_{TA}) in air (vapor + particle) were required for the dry deposition estimates. Particle size measurements were not performed in this study and, therefore, the deposition velocity (V_d) was taken to be 0.2 cm/s, which is more representative of small particles and used by Eisenreich and Strachan for

deposition estimates in the Great Lakes (Eisenreich and Strachan, 1992). The coarse particle fraction which has greater deposition velocity, (Noll et al., 1985) was not considered. Dry deposition estimates were calculated over a 1 m² surface area (S.A.).

Particle size distribution ratios and deposition velocities have been determined and used in flux estimates of metals (Holsen and Noll, 1992; Noll et al., 1990), however, similar results for organic contaminants are not available. Meteorological factors such as wind speed and direction, ground condition and atmospheric stability play an important role in the deposition of particles (Noll et al., 1985).

Gas exchange of organic contaminants between a water surface and the air above the water body can result in deposition of contaminants to the water system or export of the chemical from the water to the atmosphere. Gas exchange can be calculated for lake environments using the two-film model (Schwarzenbach et al., 1993). For small streams, where water depths are low and where bottom topography may affect the air-water interface, the surface renewal model can be used (Schwarzenbach et al., 1993). The total mass transfer velocity (v_{wt}) is calculated as two separate factors, air and water (v_a and v_w , respectively).

Air transfer velocities (v_a) were calculated using the relationship between water and wind speed at 10 m above the water surface (u_{10}): $v_a(H_2O) \approx 0.2 u_{10} (m/s) + 0.3 (cm/s)$ (Schwarzenbach et al., 1993) and extrapolated to the chemical of interest by the relationship:

$$v_a(\text{atrazine}) = v_a(H_2O) [D_a(\text{atrazine})/D_a(H_2O)]^{0.67}. \quad [3]$$

Atrazine diffusivity in air was estimated using a molecular weight ratio (Schwarzenbach

et al., 1993):

$$D_a(\text{atrazine})/D_a(\text{H}_2\text{O}) = [\text{MW}(\text{H}_2\text{O})/\text{MW}(\text{atrazine})]^{0.5} \quad [4]$$

The calculation of the transfer velocity in water (v_w) takes into account factors such as water currents and water depths which affect v_w in a small stream. Molecular diffusivities in water can be calculated, using oxygen as the reference compound because gas exchange of O_2 is only dependant on v_w and not v_a (Schwarzenbach et al., 1993). The transfer velocity of a shallow stream can be calculated using a relationship that includes water velocity and depth of the water (Schwarzenbach et al., 1993):

$$v_w = [(D_w(\text{atrazine}) (\text{cm}^2/\text{s}) \cdot \text{water velocity (cm/s)/water depth (cm)})^{0.5} \quad [5]$$

For a lake situation, the transfer velocity is calculated using wind speed at the 10 m height (u_{10}) (Schwarzenbach et al., 1993):

$$v_w = (D_w/D_w(\text{O}_2)) \cdot (4 \times 10^{-5} u_{10}^2 (\text{m/s}) + 0.0004). \quad [6]$$

Once the two transfer velocities (v_a and v_w) are known for a given compound, the overall transfer velocity (v_{tot}) $1/v_{tot} = 1/v_w + 1/v'_a$ [$v'_a = v_a(H/RT)$] can be calculated, where: H = Henry's Law Constant, R is the gas constant and T = temperature (K). This overall transfer velocity is then used to calculate the flux (N) by:

$$N = v_{tot} (C_w - C_a/K'_H) = N = C_a/K'_H \quad [\text{where: } K'_H = H/RT] . \quad [7]$$

Atrazine gas exchange across the air-water interface was calculated for South Tobacco Creek with the surface renewal model, using water flow and depths in combination with molecular diffusivities, as discussed above. Calculations of gas exchange were performed using air and water samples collected at approximately the same time. Gas exchange calculations required the estimation of the H for the temperatures over which samples were collected. H values were estimated from a linear regression, using the averages of several pesticide temperature:H relationships (Chernyak et al., 1996). Gas exchange with lake water at the ELA site was calculated using 1992 lake water data (Muir and Grift, 1995), in combination with the air data (Table 5.5) for atrazine taken from 1995, using the two film model, corrected for wind speed.

Seasonal fluxes from each of the precipitation, dry deposition and gas exchange pathways within the STCW during the 1993, 1994 and 1995 seasons are compared in Table 5.6. The 1995 precipitation flux in the South Tobacco Creek Watershed did not fit the trends observed in 1993 and 1994, flux values were much lower and the greatest flux via precipitation occurred during August. Flux values at ELA were greatest for precipitation samples collected in May and June. Maximum flux at the ELA site was an order of magnitude below maximum values estimated in the STCW during the 1994 field season. The results show that precipitation has the greatest relative contributions to atrazine flux at each of these locations. Gas exchange of atrazine is most important during the June-July period. Dry deposition is also greatest during June and July, when air concentrations of atrazine are at maximum values, however, dryfall is not predicted to be as important a route of entry as

either the precipitation or gas exchange pathways.

Table 5.5 Average monthly conditions and transfer velocities during sample times in the South Tobacco Creek Watershed (STCW) (1993-95) and the Experimental Lakes Area (ELA) (1995).

Month	STCW (Stream) ^{a,b}				ELA (Lake)		
	v_{tot} ($\times 10^{-5}$) m/d	Wind Speed $\text{m}\cdot\text{s}^{-1}$	Water Temperature $^{\circ}\text{C}$	Water Flow m^3/s	v_{tot} ($\times 10^{-5}$)	Wind Speed $\text{m}\cdot\text{s}^{-1}$	Water Temperature $^{\circ}\text{C}$
May	1.66	4.5	10	0.60	1.78	3.1	10
June	2.24	2.9	22	0.08	2.54	3.2	16
July	2.12	3.3	20	0.02	2.56	2.9	18
Aug.	2.19	3.4	17	0.09	2.02	1.9	19
Sept.	2.75	6.7	17	0.01	1.91	1.6	14
Oct.	1.76	2.8	3	0.02	1.38	1.9	9

^aassumes average stream width of 1.4 m

^bmonthly average depth range 0.02 - 0.29 m

Precipitation and gas exchange fluxes calculated for ELA were in the same order of magnitude as those calculated by Muir and Grift (1995) for ELA during 1992. Atrazine flux results in these regions, where there is zero atrazine use, indicate there can be deposition to the watershed and lake surface during all sampling times. Our atrazine gas exchange flux values indicated deposition to surface waters throughout the field season. McConnell and coworkers (1993) reported both deposition and export fluxes for α - and γ -HCH in the Great Lakes. Water temperature and degree of mixing of the water affect the direction of flux of SOC_s (McConnell et al., 1993), however, atrazine flux is likely to favour deposition rather than volatilization because of low H values.

Table 5.6 Seasonal (May - October) flux estimates for the South Tobacco Creek Watershed (STCW) 1994- 1995 with Experimental Lakes Area (ELA) results.

Location	Flux ng/m ²			
	Dry Deposition	Gas Exchange	Total Dry Process	Precipitation
1995 ELA	235	421	656	2006
1995 STCW	452	1200	1652	1269
1994 STCW	670	1151	1821	17245
1993 STCW*	506	812	1318	3101

*does not include May - June period, when potentially high precipitation concentrations would be observed in the present study.

Flux values for atrazine from other studies are not readily available, however, estimates based on atrazine measurements in precipitation can be made (Table 5.7). Precipitation inputs into Northern Germany are very close to the measured flux values of the present study. Atrazine use was banned in Germany during the study period (Bester et al., 1995), therefore, long range transport and deposition pathways may be similar to those in the present study. Flux values via wet deposition in Switzerland were higher than maximum annual values estimated for the sites where atrazine was not used. Higher flux values were estimated for the Great Lakes region (Eisenreich and Strachan, 1992). This area has significant local atrazine use and may receive inputs via atmospheric deposition and transport from the Midwest (Goolsby et al., 1994).

Numerous uncertainties in the dry deposition and gas exchange estimates exist, due to the wide range of observed results (e.g., gas/particle partitioning) or lack of knowledge of the physical properties (e.g., subcooled liquid vapor pressure and variation

Table 5.7 Comparison with other predicted or observed fluxes for atrazine.

Location	Flux ($\mu\text{g}/\text{m}^2\text{-yr}$)		Reference
	Wet	Dry	
Great Lakes	100	35	Capel, 1991
N. Germany	1-5	not determined	Trevisan et al., 1993
Switzerland	20	not determined	Buser, 1990
Minnesota	12	not determined	Goolsby et al., 1995
North Dakota	16	not determined	Goolsby et al., 1995
South Tobacco Creek	1.3-13.7	0.4-0.6	Present study
Experimental Lakes Area	2.7	0.2	Present study

of H with temperature). Dry deposition estimates are calculated by using estimated ϕ values, which can range between 0.1 and 0.9. Altering this value between the extremes would result in a 3-fold decrease or a 2-fold increase in dryfall estimates, from those obtained using the measured ϕ value (0.4) in this study. V_d of small particles sampled by high volume air samplers range between 0.1 and 0.8 cm/s (Holsen and Noll, 1992). Because each of these factors (ϕ and V_d) are linearly related to dryfall flux, their effect on uncertainty is additive (equation 2). The critical factor in dryfall estimations, is the ϕ value, because it has a greater range than V_d . Minor differences in gas exchange results were observed for South Tobacco Creek, when calculations were performed using the surface renewal model, which most accurately represents a moving stream (Schwarzenbach et al., 1993) or using the two-film model for this creek, indicating the air mass transfer coefficient (v_a) of these calculations drives gas exchange. Flux is temperature dependent (equation 7) through effects of temperature on H. However, sensitivity analysis showed that wind speed was a more critical

parameter because of its effect on $v_a(\text{H}_2\text{O})$. Therefore, the wind speed is the critical value in gas exchange flux calculations.

5.5 Conclusions

Although these results have been obtained for a region of low atrazine use, we believe they have relevance for estimating atrazine deposition in use areas. Atrazine was found in air, both gas and particle phase, precipitation and surface water throughout the field season in the present study. Temporal relationships correlated to atrazine use times in the US Midwest, although atrazine is not used in either of these sampling locations.

Atrazine concentrations in air and its partitioning to particles were not related to air temperature. This indicates that distant sources, rather than local sorption/desorption processes control the atrazine air concentration at these sites. Particle fraction estimates previously used for flux calculations may be high which could lead to overestimating dry deposition of atrazine at least for areas remote from major use.

Precipitation was found to be the most important route of entry of atrazine into a small lake in northwestern Ontario and into southern Manitoba surface waters. Results also indicate that dry processes, gas exchange and dry deposition contribute most significantly during the early part of the field season. The low concentrations of atrazine observed in each of these areas is indicative of regional or long range transport and deposition. Atrazine deposition via precipitation in southern Manitoba and southern Ontario is generally lower than found in the US, where atrazine use occurs. Dry deposition values estimated for the South

Tobacco Creek Watershed and the Experimental Lakes Area are also lower than the values determined for the Great Lakes region (Eisenreich and Strachan, 1992). There is considerable uncertainty in the dry deposition and gas exchange estimates. Nevertheless extrapolating to high use areas, by assuming concentrations in air are similar to those measured by Glotfelty et al. (1990), an additional 120% deposition of atrazine could be accounted for by gas exchange to water during the intensive use of the herbicide. We have not considered gas exchange to other surfaces, such as plants and soil nor the deposition of atrazine degradation products.

6. PESTICIDES IN THE RED RIVER AND ITS TRIBUTARIES IN SOUTHERN MANITOBA: 1993 - 1995

6.1 Abstract

Pesticide concentrations and loadings at three locations along the Red River and on seven of its tributaries in southern Manitoba were determined over a three year period. Samples (18 L) were collected on a biweekly schedule between spring and late autumn in 1994 and 1995 and triweekly throughout the initial year of the study (1993) between June and October. The pesticides detected in the highest frequency in the Red River tributaries generally were those used most extensively (e.g., MCPA). MCPA concentrations for all sites ranged from <0.01 - 990 ng/L. MCPA had the largest discharges of all herbicides in each tributary, although discharge loads were low compared to usage. However, in the Red River atrazine and alachlor were frequently detected in river water. Atrazine is widely used in the neighbouring US states although it was used only to a minor extent in Manitoba. Discharges of this chemical in the Red River were similar to loadings of the highly used and less persistent phenoxyacids. Alachlor, although not used in Canada, was present in the Red River at each sampling site (<0.060 - 150 ng/L), which reflected US usage of this product. Urban usage of chlorpyrifos, 2,4-D and MCPA contributed to loadings along the Red River. Pesticide concentrations generally were well below Canadian water quality guidelines in the Red River drainage basin, however, chlorpyrifos concentrations occasionally exceeded guideline limits.

6.2 Introduction

Nonpoint sources of pesticides to rivers include runoff losses from treated fields, groundwater movement and atmospheric inputs (Rawn et al., 1998c (Chapter 3); Senseman et al., 1997; Pereira et al., 1992; Leonard, 1988). Soil type, topography and climatic conditions can affect the movement of pesticides from target areas (Schottler et al., 1994; Pereira and Hostettler 1993). Additionally, physical and chemical properties of the pesticides, such as water solubility, partitioning to organic carbon (K_{oc}) and persistence, which vary widely among chemicals, can affect pesticide movement (Larson et al., 1995; Wauchope et al., 1992). Although pesticide movement into rivers and streams is well documented in the US midwest, the Great Lakes region and Chesapeake Bay, there are few intensive sampling programs to determine loadings in the rivers of western Canada. In Manitoba, routine monitoring programs have been limited to single monthly, seasonal or annual measurements at a limited number of locations (Currie and Williamson, 1995) making it difficult to accurately determine seasonal pesticide loading in river systems.

The Red River extends north from the US/Canada border to Lake Winnipeg in southern Manitoba (Figure 6.1). It has an effective drainage area of 148335 km² (Table 6.1). Pesticides are used extensively in the Red River drainage basin along the 252 km from the US/Canada border to its mouth at Lake Winnipeg (Agriculture Canada, 1980). On the US side of the border, the Red River also passes through primarily agricultural land along its 635

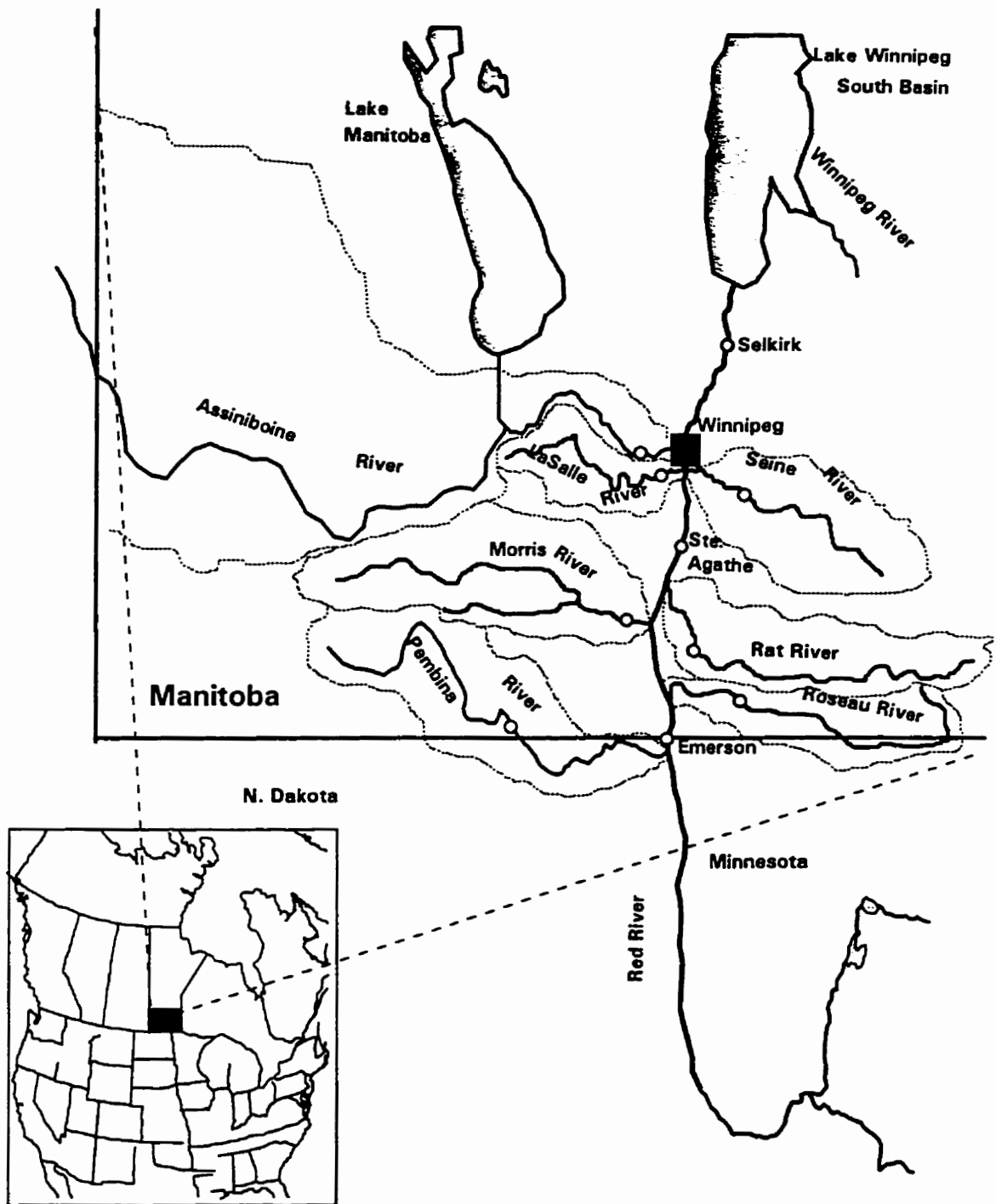


Figure 6.1 Red River drainage basin indicating sampling locations along the Red River and tributaries.

km length (Tornes and Brigham, 1994). Between the US/Canada border and its mouth at Lake Winnipeg, seven main tributaries contribute to the flow of the Red River.

The majority of the land in southern Manitoba is used for agricultural activity. Crops from this region are primarily grains and cereals. Corn is grown in the southern region of the basin, but only in limited amounts as the Red River passes increasingly northward.

Table 6.1 Effective drainage area of the tributaries on the Canadian side of the Red River (Agriculture Canada, 1996).

River	Drainage Area (km ²)
Assiniboine	60534.8
LaSalle	2278.7
Morris	3903.7
Pembina	5353.2
Rat	6082.8
Roseau	5770.2
Seine	1436.1

Phenoxyacid (e.g., 2,4-D [(2,4-dichlorophenoxy)acetic acid]), dinitroaniline (e.g., trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine]) and phenolic herbicides (e.g., bromoxynil [3,5-dibromo-4-hydroxybenzonitrile]) are most commonly used on these crops. 2,4-D was the most frequently detected herbicide in surface waters of Manitoba and MCPA [(4-chloro-2-methylphenoxy)acetic acid] was found in Manitoba river systems at higher concentrations than in surface waters from the other prairie provinces, based on water quality monitoring data for a 30-year period of record (Currie and Williamson, 1995). Based on

estimates of areas treated (Tornes and Brigham, 1994) and typical application rates, greater than 1.7 million kg of 2,4-D and 1.4 million kg of MCPA are applied annually within the US part of the drainage basin. Dinitroaniline products are widely used on the US side of the Red River drainage basin where in excess of 1.8 million kg of trifluralin alone are applied annually. In comparison, approximately 900,000 kg of phenoxyacid herbicides and 165,000 kg of trifluralin were applied annually in southern Manitoba (Agriculture Canada, unpublished data).

Approximately 135,000 kg and 146,000 kg of atrazine [6-chloro-*N*-ethyl-*N'*-(1-methyl ethyl)-1,3,5-triazine-2,4-diazine] and alachlor [2-chloro-2',6'-dimethyl-*N*-(methoxymethyl)acetanilide], respectively, are applied annually on the US side of the Red River drainage basin (Tornes and Brigham, 1994). In Manitoba, however, the use of atrazine is limited (10000 kg), due to the minor production of corn, and alachlor is not registered for use in Canada. Despite low uses of atrazine, this chemical was detected frequently in Manitoba rivers (Currie and Williamson, 1995). Discharges of neutral, persistent herbicides, such as atrazine and alachlor, have been widely determined for rivers in the US midwest and Great Lakes region (Larson et al., 1995; Schottler et al., 1994; Glotfelty et al., 1990; Frank and Logan, 1988). In comparison, while the phenoxyacid herbicides are widely used on cereals and grains and are frequently detected in river systems, discharge estimates for these compounds are rare in the literature (Currie and Williamson, 1995; Morgensen and Spliid, 1995; Berryman and Giroux, 1994; Frank and Logan, 1988).

A three-year study was conducted to determine pesticide loadings in the Red River and seven tributaries in southern Manitoba. The objectives of this study were to measure, as a reference, pesticide concentrations in the Red River as the river flowed into Manitoba, to

determine pesticide loadings and to compare the results with concentrations and discharges observed at other points along the Red. Additionally, we wanted to determine if a relationship existed between regional pesticide use and concentrations and discharges of major neutral, phenoxyacid and phenolic pesticide contaminants in these river systems. Based on work in the Red River previously reported by US Geological Survey, Environment Canada and Manitoba Environment (Currie and Williamson, 1995; Tornes and Brigham, 1994), we selected 16 pesticides (15 herbicides and one insecticide) for analysis. Pesticide loadings in the Red River at the Canadian border were determined at the Emerson sampling station and at two additional stations; Ste. Agathe, which is in the centre of the agricultural area and Selkirk, which is downstream of the City of Winnipeg (Figure 6.1).

6.3 Materials and Methods

6.3.1 Sample Collection

River water samples were collected from seven tributaries of the Red River (Figure 6.1) and three sites along the Red River. Water (18 L) was collected by lowering a submersible pump into the centre of channel flow and pumping into stainless steel soft drink cans. Rivers were sampled every three weeks during the first year of the study which began in June 1993. Samples were collected on a biweekly schedule from spring through freeze up during 1994 and 1995. Samples were sealed and transported to the lab where they were stored at 4°C until processed. Prior to extraction, water samples were filtered under pressure using pre-cleaned GFA filters (1µm). One litre water samples were collected for water

chemistry parameters including total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and pH by lowering a weighted sample bottle into the centre of stream flow.

6.3.2 Sample Extraction and Cleanup

Dissolved pesticides were extracted using a broad spectrum approach for both acidic and neutral compounds (e.g., 2,4-D and atrazine). Water samples were adjusted to pH 2 using sulphuric acid and mixed with dichloromethane (DCM) to extract acid herbicides followed by adjustment to pH 10 using 10 M NaOH, to extract the hydrophobic organics (e.g., polychlorinated biphenyls (PCBs)). Sample extracts were evaporated to a small volume and methylated using freshly prepared diazomethane. Extracts were cleaned up using 5% deactivated Florisil, eluting with 20 mL hexane to remove PCBs, followed by 85 mL, 18% ethyl acetate (EtAc) in hexane to elute the acid and phenolic herbicides (methyl derivatives).

6.3.3 Sample Analysis

Sample extracts were analysed by gas chromatography - mass spectrometry (Select Ion Monitoring) (Hewlett Packard 5971 MSD) using a 60 m x 0.25 μ m DB-5 column with helium as the carrier gas. Detection criteria were the correct ratios of two characteristic ions and retention times. Herbicides were quantified using external standard solutions and corrected for volume changes using PCB-104. Blanks of "Super Q" water were analyzed with each batch of samples. Average spike recoveries of triplicate analyses at both 10 ng/L and 100 ng/L for 18 L volumes and detection limits are reported in Table 6.2. All pesticides with <80% recovery were recovery corrected. Method detection limits for 18 L volumes were calculated using instrument detection limits plus three times the standard deviation of

the lowest concentration analysis (Keith, 1991). TOC, TN, TP loadings in each river system were measured following standard colorimetric techniques for nutrient analysis (Environment Canada, 1997).

Table 6.2 Pesticide recovery from spiked water samples and method detection limits for individual pesticides.

Pesticide	Average Recovery (%)	Method Detection Limit (ng/L)
Alachlor	84	0.060
Atrazine	86	0.042
Bromoxynil	65	0.015
Chlorpyrifos	112	0.082
Chlorthal methyl (Dacthal/DCPA)	80	0.013
Cyanazine	50	0.190
2,4-D	52	0.011
Dichlorprop	115	0.007
Diclofop methyl	57	0.023
Ethalfuralin	98	0.280
MCPA	26	0.010
Metolachlor	115	0.023
Terbutylazine	80	0.041
Triallate	86	0.040
Triclopyr	14	0.033
Trifluralin	99	0.023

6.3.4 Pesticide Use Estimates

Pesticide application data were provided by Manitoba Agriculture for each year of the study for all municipalities in the six smaller watersheds (Manitoba Agriculture, unpublished data). Landuse data were available for southern Manitoba through the Canadian census (Statistics Canada, 1996). The area treated with each pesticide on a municipality basis was overlaid on watershed boundaries (Manitoba Natural Resources, 1967) to estimate the pesticide treated area within each watershed. Based on this area, an estimate of the amount of pesticides used (kg) was calculated using products commonly applied to regional crops and assuming recommended application rates. A pesticide use estimate was not performed for the Assiniboine River watershed because the watershed basin extends into Saskatchewan and pesticide use data for the entire watershed were not available (Figure 6.1).

6.3.5 Discharge Estimates

Discharges of six major chemicals from the watersheds under investigation were calculated for both the 1994 and 1995 field years. For purposes of discharge calculation, MCPA, 2,4-D and bromoxynil concentrations were corrected for recovery efficiency. Discharge was calculated as the product of herbicide concentration and water flow for each day (Larson et al., 1995). Herbicide concentrations were estimated by linear interpolation for days when sampling was not performed and concentrations below detection limits were assigned a value of zero (Larson et al., 1995) in all discharge calculations. The daily discharge values were summed for the sampling season (March - end of October), to give the total seasonal discharge values.

6.4 Results

6.4.1 Pesticide and Nutrient Concentrations

Sixteen pesticides were frequently detected in waters of the Red River and its tributaries in southern Manitoba (Table 6.3). Pesticide concentrations were not correlated to water flow in any of the rivers under investigation in this study. Significant correlations between MCPA and bromoxynil ($r^2=0.25 - 0.93$; p-values $0.01 - <0.001$) were found in all tributaries with the exception of the Morris River (Table 6.4). Relationships between MCPA and bromoxynil concentrations were expected because they are applied during the same period of the agricultural season, frequently as a single formulation. Concentrations of the phenoxyacids MCPA and 2,4-D in river water also were correlated ($r^2= 0.22 - 0.97$; p-values $0.02 - <0.001$) in all rivers under investigation with the exception of the Roseau River (Table 6.4). No significant relationships existed between atrazine, chlorpyrifos and trifluralin concentrations with water flow or other pesticides. These differences are indicative of different use patterns for these compounds.

The pH of water from the river systems under investigation in this study were close to neutrality (Table 6.5). Total organic carbon, total nitrogen and total phosphorus levels in each river are reported in Table 6.5. The greatest pH range (6.74 - 9.21) was observed in the LaSalle River. Water flow was correlated with TN loadings in the LaSalle River ($r^2=0.44$) (Table 6.4). Weak correlations between water flow and TP ($r^2=0.25$) was found in the Morris River over the duration of the study. Nitrogen and phosphorus levels in all other rivers were not correlated to water flow. This contrasts with results from South Tobacco Creek which

Table 6.3 Pesticide concentrations (ng/L) in the Red River and tributaries.

Pesticide	1993 ^a				1994 ^b			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Assiniboine River	N = 6				N=12			
Alachlor	0.42	<0.060	<0.060	0.080	<0.060	<0.060	<0.060	<0.060
Atrazine	5.99	0.24	1.11	2.52	6.93	<0.042	2.05	2.71
Bromoxynil	21.6	0.32	5.10	7.46	15.7	0.29	1.27	2.55
Chlorpyrifos	13.2	<0.082	0.64	2.80	1.01	<0.082	<0.082	0.08
Chlorthal dimethyl	0.33	0.05	0.12	0.15	0.10	<0.013	0.06	0.05
Cyanazine	3.11	<0.19	<0.19	0.52	<0.19	<0.19	<0.19	<0.19
2,4-D	12.5	2.18	6.29	7.06	8.27	<0.011	1.40	2.02
Dichlorprop	14.3	0.14	3.09	4.78	2.92	<0.007	0.10	0.64
Diclofop methyl	2.56	<0.021	1.39	1.33	1.71	<0.023	0.06	0.46
Ethalfuralin	1.83	<0.28	<0.28	0.31	2.97	<0.28	<0.28	<0.28
MCPA	34.1	0.70	12.1	15.1	22.8	<0.010	1.91	5.26
Metolachlor	1.99	0.05	0.50	0.67	2.15	<0.023	<0.023	0.42
Terbutylazine	2.49	0.44	1.57	1.48	<0.041	<0.041	<0.041	<0.041
Triallate	4.61	<0.040	0.72	1.37	1.71	<0.040	0.15	0.60
Triclopyr	70.9	<0.033	1.10	12.5	<0.033	<0.033	<0.033	<0.033
Trifluralin	1.18	<0.023	<0.023	0.21	2.43	<0.023	<0.023	0.46

^atriweekly sample collection, June -October 1993

^bbiweekly sample collection, May-October 1994; March-October 1995

Pesticide	1995*				
	Maximum	Minimum	Median	Average	
Assiniboine River Alachlor	N=14 <0.060	<0.060	<0.060	<0.060	<0.060
Atrazine	1.40	0.12	0.59	0.65	
Bromoxynil	2.27	<0.15	0.17	0.42	
Chlorpyrifos	2.15	<0.082	<0.082	0.19	
Chlorthal dimethyl	0.08	<0.013	0.03	0.03	
Cyanazine	<0.19	<0.19	<0.19	<0.19	
2,4-D	2.12	<0.011	<0.011	0.16	
Dichlorprop	0.58	<0.007	<0.007	0.04	
Diolofop methyl	0.55	<0.023	<0.023	0.09	
Ethalfuralin	0.77	<0.28	<0.28	<0.28	
MCPA	2.49	<0.010	<0.010	0.25	
Metolachlor	0.46	<0.023	<0.023	0.12	
Terbutylazine	<0.041	<0.041	<0.041	<0.041	
Triallate	3.18	<0.040	0.20	0.57	
Triclopyr	1.84	<0.033	<0.033	<0.033	
Trifluralin	0.60	<0.023	0.26	0.25	

Pesticide	1993*				1994*			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
LaSalle River Alachlor	N=6 1.86	<0.06	0.37	0.54	N=12 <0.06	<0.06	<0.06	<0.06
Atrazine	7.05	0.43	5.56	3.72	15.7	0.92	3.29	4.35
Bromoxynil	35.21	0.69	5.38	9.30	66.4	0.41	1.84	12.4
Chlorpyrifos	2.91	0.09	0.62	0.97	1.27	<0.082	<0.082	0.19
Chlorthal dimethyl	0.31	0.05	0.12	0.16	0.18	<0.013	0.08	0.08
Cyanazine	2.90	<0.19	<0.19	0.45	2.74	<0.19	<0.19	0.23
2,4-D	31.0	2.32	4.32	11.7	22.6	<0.011	3.91	6.60
Dichlorprop	12.1	0.11	4.37	5.05	9.78	<0.007	0.64	2.27
Diclofop methyl	2.43	0.23	1.44	1.43	3.66	<0.023	0.91	1.10
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	0.36	<0.28	<0.28	<0.28
MCPA	57.5	0.45	8.12	20.1	987	<0.010	7.14	141
Metolachlor	1.4	<0.021	0.09	0.42	0.93	<0.023	<0.023	0.22
Terbutylazine	2.4	<0.041	0.61	1.19	0.40	<0.041	<0.041	<0.041
Triallate	10.2	0.64	2.35	3.22	4.32	0.36	0.66	1.41
Triclopyr	419.6	<0.031	38.3	131.4	56.3	<0.033	5.56	13.9
Trifluralin	<0.023	<0.023	<0.023	<0.023	0.43	<0.023	<0.023	0.12

Pesticide	1995*				
	Maximum	Minimum	Median	Average	
LaSalle River Alachlor	N=14 <0.060	<0.060	<0.060	<0.060	<0.060
Atrazine	7.05	0.34	1.17	1.99	
Bromoxynil	2.31	<0.015	0.32	0.74	
Chlorpyrifos	4.18	<0.082	<0.082	0.37	
Chlorthal	0.09	<0.013	0.05	0.05	
Cyanazine	0.43	<0.19	<0.19	0.03	
2,4-D	1.13	<0.011	<0.011	0.12	
Dichlorprop	0.56	<0.007	<0.007	0.08	
Dicofop methyl	1.41	<0.023	<0.023	0.19	
Ethalfuralin	0.97	<0.28	<0.28	<0.28	
MCPA	9.39	<0.010	<0.010	1.45	
Metolachlor	0.86	<0.023	0.06	0.18	
Terbuthylazine	<0.041	<0.041	<0.041	<0.041	
Triallate	1.36	<0.040	0.13	0.30	
Triclopyr	7.93	<0.033	<0.033	1.17	
Trifluralin	1.09	0.05	0.27	0.33	

Pesticide	1993 ^a				1994 ^a			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Morris River	N=6				N=11			
Alachlor	2.40	<0.060	<0.060	0.57	<0.060	<0.060	<0.060	<0.060
Atrazine	32.5	1.69	13.2	14.7	39.3	1.83	8.51	12.0
Bromoxynil	176	0.59	17.3	41.8	86.4	0.27	1.27	10.2
Chlorpyrifos	7.45	0.65	1.89	2.8	1.09	<0.082	<0.082	0.10
Chlorthal dimethyl	0.42	0.11	0.18	0.22	0.38	0.05	0.12	0.13
Cyanazine	0.56	<0.19	<0.19	0.09	2.38	<0.19	<0.19	0.65
2,4-D	50.5	2.27	10.3	16.1	14.4	<0.011	4.11	5.03
Dichlorprop	20.1	0.65	1.63	4.62	4.59	<0.007	1.20	1.51
Diclofop methyl	8.86	1.21	1.55	2.82	1.98	<0.023	0.77	0.68
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28
MCPA	423	<0.010	4.53	83.4	93.2	<0.010	28.1	27.1
Metolachlor	6.28	<0.023	1.23	1.77	4.77	<0.023	<0.023	1.06
Terbutylazine	3.17	0.07	0.73	1.17	<0.041	<0.041	<0.041	<0.041
Triallate	4.68	<0.040	1.12	1.53	1.74	<0.040	<0.040	0.54
Triclopyr	34.1	<0.033	0.57	6.50	41.1	<0.033	3.69	10.8
Trifluralin	8.17	0.16	0.42	1.76	3.40	<0.023	0.71	0.91

Pesticide	1995 ^a			
	Maximum	Minimum	Median	Average
Morris River Alachlor	N=14 0.22	<0.060	<0.060	0.02
Atrazine	32.4	0.94	4.22	7.93
Bromoxynil	4.99	<0.015	0.94	1.52
Chlorpyrifos	17.8	<0.082	<0.082	1.51
Chlorthal dimethyl	0.08	0.02	0.05	0.05
Cyanazine	1.81	<0.19	<0.19	0.13
2,4-D	0.70	<0.011	<0.011	0.12
Dichlorprop	1.06	<0.007	<0.007	0.16
Diclofop methyl	0.57	<0.023	<0.023	0.16
Ethalfuralin	0.84	<0.28	<0.28	<0.28
MCPA	2.67	<0.010	0.30	0.95
Metolachlor	1.04	<0.023	0.31	0.36
Terbutylazine	<0.041	<0.041	<0.041	<0.041
Triallate	1.26	0.05	0.39	0.50
Triclopyr	<0.033	<0.033	<0.033	<0.033
Trifluralin	1.32	<0.023	0.31	0.45

Pesticide	1993*				1994*			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Pembina River	N=6				N=12			
Alachlor	1.66	<0.06	0.19	0.40	<0.06	<0.06	<0.06	<0.06
Atrazine	2.82	0.46	1.63	1.64	3.34	<0.042	1.06	1.33
Bromoxynil	17.7	0.21	4.31	6.04	7.08	0.23	1.01	1.47
Chlorpyrifos	1.74	<0.082	0.32	0.53	1.61	<0.082	<0.082	0.18
Chlorthal dimethyl	0.17	<0.013	0.12	0.10	0.14	0.04	0.07	0.08
Cyanazine	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19
2,4-D	217	1.90	3.80	39.1	4.66	<0.011	0.60	1.15
Dichlorprop	3.69	<0.007	0.66	1.11	1.23	<0.007	0.43	0.43
Diclofop methyl	3.81	1.60	2.04	2.30	10.9	<0.023	0.43	1.62
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	2.45	<0.28	<0.28	0.24
MCPA	144	0.58	3.84	26.9	11.8	<0.010	2.19	3.32
Metolachlor	7.86	<0.023	0.40	1.62	0.26	<0.023	<0.023	0.02
Terbutylazine	4.20	<0.041	0.18	1.29	<0.041	<0.041	<0.041	<0.041
Triallate	16.9	<0.040	3.52	5.35	5.43	<0.040	1.62	1.56
Triclopyr	4.34	<0.033	0.73	1.16	6.70	<0.033	<0.033	0.63
Trifluralin	<0.023	<0.023	<0.023	<0.023	2.27	<0.023	<0.023	0.32

Pesticide	1995*				
	Maximum	Minimum	Median	Average	
Pembina River Alachlor	N=13 0.37	<0.060	<0.060	<0.060	<0.060
Atrazine	1.77	0.40	0.68	0.75	
Bromoxynil	5.87	0.06	0.40	0.82	
Chlorpyrifos	1.24	<0.082	<0.082	0.13	
Chlorthal dimethyl	0.07	<0.013	0.03	0.03	
Cyanazine	<0.19	<0.19	<0.19	<0.19	
2,4-D	1.11	<0.011	<0.011	0.16	
Dichlorprop	0.06	<0.007	<0.007	<0.007	
Diclofop methyl	0.67	<0.023	<0.023	0.14	
Ethalfuralin	0.38	<0.28	<0.28	<0.28	
MCPA	1.34	<0.010	0.37	0.36	
Metolachlor	14.4	<0.023	<0.023	1.17	
Terbutylazine	<0.041	<0.041	<0.041	<0.041	
Triallate	2.49	<0.040	0.38	0.73	
Triclopyr	1.07	<0.033	<0.033	0.08	
Trifluralin	0.43	0.18	0.24	0.26	

Pesticide	1993*				1994*			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Rat River	N=6				N=12			
Alachlor	0.62	<0.060	<0.060	0.17	0.35	<0.060	<0.060	0.06
Atrazine	5.19	<0.042	0.98	1.84	14.4	2.19	5.58	6.37
Bromoxynil	39.1	0.32	2.23	9.03	18.0	0.43	3.80	6.51
Chlorpyrifos	1.02	<0.082	0.38	0.45	1.01	<0.082	<0.082	0.08
Chlorthal dimethyl	0.29	0.05	0.10	0.11	0.30	<0.013	0.07	0.09
Cyanazine	<0.19	<0.19	<0.19	<0.19	7.58	<0.19	<0.19	1.11
2,4-D	35.2	1.66	7.47	14.8	6.82	<0.011	1.80	2.67
Dichlorprop	3.32	0.33	0.64	1.11	1.94	<0.007	<0.007	0.32
Diclofop methyl	7.46	0.45	1.07	2.30	1.30	<0.023	<0.023	0.38
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	1.24	<0.28	<0.28	<0.28
MCPA	24.2	<0.010	4.31	6.70	70.0	<0.010	7.41	21.2
Metolachlor	30.8	<0.023	1.03	6.05	7.78	<0.023	<0.023	0.91
Terbuthylazine	1.98	<0.041	<0.041	0.42	2.40	<0.041	<0.041	0.20
Triallate	4.82	<0.040	0.09	0.95	9.52	<0.040	<0.040	0.98
Triclopyr	32.1	<0.031	0.88	8.69	3.38	<0.033	<0.033	0.86
Trifluralin	<0.023	<0.023	<0.023	<0.023	2.12	<0.023	0.19	0.54

Pesticide	1995*			
	Maximum	Minimum	Median	Average
Rat River Alachlor	N=14 0.69	<0.060	<0.060	0.06
Atrazine	14.8	0.73	2.08	3.17
Bromoxynil	4.76	0.05	0.32	1.10
Chlorpyrifos	3.68	<0.082	<0.082	0.38
Chlorthal	0.08	0.01	0.04	0.04
Cyanazine	1.15	<0.19	<0.19	0.08
2,4-D	2.31	<0.011	<0.011	0.27
Dichlorprop	2.31	<0.007	<0.007	0.18
Diclofop methyl	0.19	<0.023	<0.023	0.02
Ethalfuralin	0.43	<0.028	<0.028	<0.028
MCPA	14.0	<0.010	0.19	1.25
Metolachlor	1.71	<0.23	0.49	0.57
Terbutylazine	<0.041	<0.041	<0.041	<0.041
Triallate	0.42	<0.041	0.06	0.11
Triclopyr	1.26	<0.033	<0.033	0.16
Trifluralin	0.35	0.14	0.21	0.24

Pesticide	1993 ^a				1994 ^a			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Roseau River Alachlor	N=6 1.21	<0.06	<0.06	0.23	N=12 <0.06	<0.06	<0.06	<0.06
Atrazine	16.4	0.49	4.24	5.86	5.72	<0.042	1.21	1.50
Bromoxynil	18.1	0.40	2.47	5.41	4.57	0.16	0.50	1.38
Chlorpyrifos	1.78	<0.082	0.24	0.48	0.52	<0.082	<0.082	0.04
Chlorthal dimethyl	0.17	0.12	0.14	0.14	0.21	<0.013	0.04	0.07
Cyanazine	0.41	<0.19	<0.19	0.07	<0.19	<0.19	<0.19	<0.19
2,4-D	53.7	0.64	5.55	18.8	38.5	<0.011	0.82	5.26
Dichlorprop	0.61	<0.007	0.10	0.21	0.59	<0.007	<0.007	0.05
Diclofop methyl	1.14	<0.023	0.62	0.59	1.27	<0.023	<0.023	0.23
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28
MCPA	217	0.32	1.47	38.2	11.8	<0.010	0.93	2.37
Metolachlor	1.05	<0.023	0.31	0.49	0.042	<0.023	<0.023	<0.023
Terbutylazine	2.18	<0.041	0.09	0.46	0.41	<0.041	<0.041	<0.041
Triallate	0.51	<0.040	0.12	0.17	1.41	<0.040	<0.040	0.26
Triclopyr	53.8	<0.033	1.60	10.1	51.1	<0.033	7.34	10.8
Trifluralin	<0.023	<0.023	<0.023	<0.023	2.59	<0.023	<0.023	0.61

Pesticide	1995				
	Maximum	Minimum	Median	Average	
Roseau River Alachlor	N=14 0.79	<0.060	<0.060	0.07	
Atrazine	13.1	<0.042	1.05	2.10	
Bromoxynil	13.2	<0.015	0.44	1.35	
Chlorpyrifos	0.47	<0.082	<0.082	0.05	
Chlorthal dimethyl	0.22	<0.013	0.05	0.06	
Cyanazine	<0.19	<0.19	<0.19	<0.19	
2,4-D	4.48	<0.011	<0.011	0.36	
Dichlorprop	<0.007	<0.007	<0.007	<0.007	
Diclofop methyl	0.32	<0.023	<0.023	0.02	
Ethalfuralin	0.55	<0.28	<0.28	<0.28	
MCPA	4.30	<0.010	<0.010	0.88	
Metolachlor	0.03	0.69	<0.023	0.07	
Terbutylazine	<0.041	<0.041	<0.041	<0.041	
Triallate	2.93	<0.040	<0.040	0.27	
Triclopyr	8.83	<0.033	<0.033	1.10	
Trifluralin	0.48	<0.023	0.24	0.27	

Pesticide	1993*				1994*			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Selne River	N=6				N=12			
Alachlor	1.31	<0.060	0.29	0.53	<0.060	<0.060	<0.060	<0.060
Atrazine	7.24	0.27	1.19	2.15	57.3	0.46	4.15	9.54
Bromoxynil	76.8	0.68	7.10	17.1	186	0.09	0.89	17.1
Chlorpyrifos	1.71	<0.082	0.52	0.72	<0.082	<0.082	<0.082	<0.082
Chlorthal dimethyl	0.36	0.08	0.10	0.17	0.17	0.02	0.06	0.07
Cyanazine	25.9	<0.19	<0.19	4.31	<0.19	<0.19	<0.19	<0.19
2,4-D	286	4.38	29.3	80.4	10.4	<0.011	2.29	3.40
Dichlorprop	22.5	<0.007	1.77	5.14	10.5	<0.007	0.14	1.47
Diclofop methyl	1.66	0.50	0.81	0.90	0.91	<0.023	0.24	0.33
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	2.08	<0.28	<0.28	<0.28
MCPA	29.6	<0.010	5.22	9.49	139	<0.010	1.21	18.9
Metolachlor	5.45	<0.023	0.89	1.64	1.61	<0.023	<0.023	0.20
Terbuthylazine	2.22	<0.041	0.50	0.84	<0.041	<0.041	<0.041	<0.041
Triallate	9.00	1.17	3.58	3.93	1.37	<0.040	<0.040	0.28
Triclopyr	7.89	<0.033	0.43	1.58	17	<0.033	<0.033	2.73
Trifluralin	<0.023	<0.023	<0.023	<0.023	2.15	<0.023	<0.023	0.52

Pesticide	1995*			
	Maximum	Minimum	Median	Average
Selne River	N=14			
Alachlor	<0.060	<0.060	<0.060	<0.060
Atrazine	96.4	0.90	2.09	15.6
Bromoxynil	6.01	0.06	0.48	1.03
Chlorpyrifos	4.16	<0.082	<0.082	0.41
Chlorthal dimethyl	0.10	0.01	0.04	0.05
Cyanazine	<0.19	<0.19	<0.19	<0.19
2,4-D	19.5	<0.011	<0.011	2.03
Dichlorprop	1.90	<0.007	<0.007	0.33
Diclofop methyl	0.82	<0.023	<0.023	0.06
Ethalfuralin	0.64	<0.28	<0.28	<0.28
MCPA	13.8	<0.010	<0.010	1.58
Metolachlor	0.87	<0.023	<0.023	0.12
Terbuthylazine	<0.041	<0.041	<0.041	<0.041
Triallate	0.73	<0.040	<0.040	0.13
Triclopyr	0.88	<0.033	<0.033	0.06
Trifluralin	0.49	<0.023	0.25	0.24

Pesticide	1993*				1994*			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Red River at Emerson	N=6				N=12			
Alachlor	50.9	<0.060	4.81	13.3	21.8	<0.060	1.25	3.78
Atrazine	52.4	2.04	8.37	16.8	116	1.46	20.2	32.1
Bromoxynil	41.5	0.43	14.0	18.3	264	0.55	1.81	26.8
Chlorpyrifos	2.06	<0.082	0.58	0.67	1.84	<0.082	<0.082	0.27
Chlorthal dimethyl	<0.013	<0.013	<0.013	<0.013	0.35	0.08	0.19	0.20
Cyanazine	<0.19	<0.19	<0.19	<0.19	30.5	<0.19	<0.19	9.21
2,4-D	56.8	0.36	12.3	19.0	54.9	<0.011	5.19	11.4
Dichlorprop	2.89	<0.007	0.59	0.85	4.39	<0.007	<0.007	0.56
Diclofop methyl	11.7	0.33	1.75	3.29	187	<0.023	1.95	20.5
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	0.73	<0.28	<0.28	<0.28
MCPA	139	0.86	16.3	34.1	667	<0.010	8.41	73.15
Metolachlor	205	2.06	22.3	48.2	73.4	1.06	14.1	22.1
Terbuthylazine	2.10	<0.037	0.50	0.69	3.75	<0.041	<0.041	0.31
Triallate	3.73	0.34	2.32	2.10	7.91	<0.040	1.24	2.18
Triclopyr	2.36	<0.033	0.54	0.83	5.17	<0.033	<0.033	1.11
Trifluralin	1.18	0.09	0.39	0.46	1.22	<0.023	0.39	0.50

Pesticide	1995*				
	Maximum	Minimum	Median	Average	
Red River at Emerson Alachlor	N=13 122	<0.060	0.79	10.3	
Atrazine	145	0.83	8.01	22.8	
Bromoxynil	79.1	0.41	0.99	7.96	
Chlorpyrifos	1.12	<0.082	<0.082	0.15	
Chlorthal dimethyl	0.08	0.01	0.05	0.05	
Cyanazine	23.1	<0.19	<0.19	2.83	
2,4-D	0.79	<0.009	<0.009	0.06	
Dichlorprop	0.84	<0.005	<0.005	0.06	
Diclofop methyl	0.64	<0.021	<0.021	0.09	
Ethalfuralin	1.15	<0.28	<0.28	<0.28	
MCPA	2.15	<0.010	<0.010	0.51	
Metolachlor	38.0	<0.021	8.84	11.7	
Terbuthylazine	1.72	<0.037	<0.037	0.14	
Triallate	21.2	<0.040	0.82	2.63	
Triclopyr	<0.033	<0.033	<0.033	<0.033	
Trifluralin	1.69	<0.023	0.57	0.66	

Pesticide	1993*				1994*			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Red River at Ste. Agathe Alachlor	N=6 114	<0.060	3.83	21.8	N=13 13.1	<0.060	1.93	3.66
Atrazine	41.8	6.69	9.29	14.3	97.1	4.60	21.9	31.2
Bromoxynil	75.4	0.25	25.6	29.3	139	0.32	2.24	16.3
Chlorpyrifos	2.46	<0.082	0.52	1.02	3.01	<0.082	<0.082	0.35
Chlorthal dimethyl	0.34	0.08	0.14	0.16	0.25	0.12	0.19	0.19
Cyanazine	<0.19	<0.19	<0.19	<0.19	98.1	<0.19	<0.19	12.0
2,4-D	47.6	0.88	8.83	19.7	65.7	<0.011	0.80	7.89
Dichlorprop	2.53	<0.007	0.95	1.14	0.93	<0.007	<0.007	0.22
Diclofop methyl	3.39	0.73	2.10	2.13	16.4	<0.023	2.28	3.91
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	0.53	<0.28	<0.28	<0.28
MCPA	118	<0.010	8.83	30.2	148	<0.010	3.78	18.5
Metolachlor	113	4.08	19.1	39.9	72.7	1.72	24.3	26.4
Terbutylazine	3.14	0.52	0.93	1.21	<0.041	<0.041	<0.041	<0.041
Triallate	5.15	1.31	1.75	2.23	5.07	<0.040	1.46	1.76
Triclopyr	8.49	<0.033	1.73	2.90	8.54	<0.033	<0.033	2.16
Trifluralin	<0.023	<0.023	<0.023	<0.023	1.85	<0.023	0.40	0.60

Pesticide	1995 ^a			
	Maximum	Minimum	Median	Average
Red River at Ste. Agathe Alachlor	N=13 117	<0.060	1.34	9.95
Atrazine	188	1.77	11.5	38.4
Bromoxynil	33.5	0.50	1.44	5.56
Chlorpyrifos	3.20	<0.082	<0.082	0.70
Chlorthal dimethyl	0.46	<0.013	0.05	0.10
Cyanazine	49.8	<0.19	<0.19	7.65
2,4-D	2.27	<0.011	<0.011	0.50
Dichlorprop	0.93	<0.007	<0.007	0.13
Diclofop methyl	3.93	<0.023	<0.023	0.79
Ethalfuralin	2.51	<0.28	<0.28	0.62
MCPA	4.25	<0.010	1.20	1.30
Metolachlor	81.2	<0.023	8.98	15.4
Terbuthylazine	2.16	<0.041	<0.041	0.24
Triallate	25.6	<0.040	1.26	4.50
Triclopyr	8.27	<0.033	<0.033	0.64
Trifluralin	3.23	<0.023	0.78	0.93

Pesticide	1993 ^a				1994 ^a			
	Maximum	Minimum	Median	Average	Maximum	Minimum	Median	Average
Red River at Selldrk Alachlor	N=6 150	<0.060	0.85	27.0	N=13 32.9	<0.060	1.02	3.82
Atrazine	33.2	0.08	6.02	9.91	145	<0.042	17.0	36.7
Bromoxynil	96.8	0.12	6.39	22.4	277	0.32	3.40	31.1
Chlorpyrifos	8.53	0.08	1.98	2.61	14.0	<0.082	0.17	2.13
Chlorthal dimethyl	0.29	0.08	0.16	0.17	0.58	0.07	0.20	0.24
Cyanazine	3.33	<0.19	<0.19	0.58	104	<0.19	<0.19	9.75
2,4-D	37.7	0.15	3.12	11.9	170	<0.011	9.73	29.2
Dichlorprop	2.77	<0.007	0.23	0.79	18.5	<0.007	0.69	2.10
Diclofop methyl	1.98	0.13	0.49	0.72	181	<0.021	2.93	18.3
Ethalfuralin	<0.28	<0.28	<0.28	<0.28	0.44	<0.28	<0.28	<0.28
MCPA	77.1	0.29	6.14	18.4	322	<0.010	12.1	57.4
Metolachlor	126	0.08	10.8	27.6	82.4	0.49	9.13	16.5
Terbuthylazine	<0.041	<0.041	<0.041	<0.041	1.55	<0.041	<0.041	0.18
Triallate	4.88	0.08	1.74	2.05	5.63	<0.040	0.48	1.06
Triclopyr	4.00	<0.033	1.42	1.64	15.6	<0.033	2.01	3.83
Trifluralin	<0.023	<0.023	<0.023	<0.023	2.24	<0.023	0.41	0.50

Pesticide	1995 ^a			
	Maximum	Minimum	Median	Average
Red River at Selldrk	N=14			
Alachlor	5.24	<0.060	0.40	1.27
Atrazine	65.3	2.95	7.26	11.8
Bromoxynil	13.7	0.86	1.28	3.71
Chlorpyrifos	3.59	<0.082	<0.082	0.60
Chlorthal dimethyl	0.52	0.03	0.06	0.09
Cyanazine	10.2	<0.19	<0.19	1.16
2,4-D	5.09	<0.011	<0.011	0.72
Dichlorprop	1.28	<0.007	<0.007	0.24
Dictofop methyl	2.24	<0.023	0.17	0.64
Ethalfuralin	2.04	<0.28	<0.28	0.45
MCPA	6.58	<0.010	2.44	2.47
Metolachlor	8.43	<0.023	5.09	4.76
Terbutylazine	0.36	<0.041	<0.041	0.03
Triallate	11.5	<0.040	0.94	2.11
Triclopyr	2.22	<0.033	<0.033	0.23
Trifluralin	1.78	<0.023	0.86	0.86

^atriweekly sample collection, June -October 1993

^bbiweekly sample collection, May-October 1994; March-October 1995

Table 6.4 Correlation coefficients between pesticides, nutrients and water flow in six watersheds.

Correlation	LaSalle			Morris			Pembina		
	N ^a	r ²	p-value	N ^a	r ²	p-value	N ^a	r ²	p-value
MCPA and Bromoxynil	26	0.90	<0.001	25	-. ^b	-. ^b	25	0.29	0.005
MCPA and 2,4-D	26	0.48	<0.001	25	0.35	0.001	25	0.49	0.001
TN and flow	16	0.44	0.005	15	-. ^b	-. ^b	15	-. ^b	-. ^b
TP vs flow	16	-. ^b	-. ^b	15	0.24	0.06	15	-. ^b	-. ^b

Correlation	Rat			Roseau			Seine		
	N ^a	r ²	p-value	N ^a	r ²	p-value	N ^a	r ²	p-value
MCPA and Bromoxynil	26	0.93	<0.001	26	0.25	0.01	26	0.87	<0.001
MCPA and 2,4-D	26	0.61	<0.001	26	-. ^b	-. ^b	26	0.22	0.01
TN and flow	13	-. ^b	-. ^b	1	-. ^{b,c}	-. ^{b,c}	18	-. ^b	-. ^b
TP vs flow	13	-. ^b	-. ^b	1	-. ^{b,c}	-. ^{b,c}	18	-. ^b	-. ^b

^anumber of samples

^bindicates no significant correlation p> 0.06

^cnot sufficient data to determine relationship

Table 6.5 Water quality parameters for the Red River and tributaries during 1993-1995.

River	pH	Total Organic Carbon (mg/L)	Total Nitrogen (mg/L)	Total Phosphorus (mg/L)
Assiniboine	7.26 - 8.66	10.46 - 16.64	- ^a	- ^a
LaSalle	6.74 - 9.21	10.87 - 18.43	0.48 - 5.68	0.188 - 0.793
Morris	7.30 - 8.55	12.27 - 15.49	0.81 - 5.11	0.047 - 0.815
Pembina	7.58 - 9.37	8.89 - 26.62	0.32 - 7.61	0.135 - 1.190
Rat	6.59 - 8.52	12.04 - 25.54	0.40 - 5.55	0.135 - 1.19
Roseau	7.49 - 7.97	16.32 - 38.30	0.22 - 1.25	0.053 - 0.224
Seine	6.67 - 8.63	9.20 - 24.87	0.41 - 11.84	0.019 - 0.59
Red at Emerson	7.57 - 8.49	8.40 - 22.40	- ^a	- ^a
Red at Ste. Agathe	7.27 - 8.59	15.95 - 18.11	- ^a	- ^a
Red at Selkirk	7.50 - 8.50	12.59 - 17.15	- ^a	- ^a

^adata not available

drains a small, well defined agricultural watershed in southern Manitoba (Figure 6.1) where nutrient levels (TOC, TN and TP) were correlated to water flow (Rawn et al., 1998c (Chapter3)). Correlations between pesticide concentrations and nutrient loads were not calculated due to limited data for the same sampling days.

6.4.2 Pesticide Use

MCPA was the product used in the greatest amounts of all active ingredients under investigation in this study (Table 6.6). Bromoxynil was generally the second most widely used product, although in the Pembina River watershed more trifluralin was used than bromoxynil. The large use of the phenoxyacid and phenolic pesticides in these watersheds is indicative of the typical crops grown in the region, namely oil seeds, wheat, barley and flax. Triazine herbicides were applied in each year of the study in all watersheds, however, the amounts used were approximately an order of magnitude below the most widely used products (Table 6.6). Within the tributary watersheds, an average of 332,000 kg of MCPA was applied each year of the study, but the average atrazine use in the same area was 11,700 kg.

Although alachlor is no longer registered for use in Canada, a similar product, metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methyl ethyl)acetamide], was used in four of the six watershed basins during at least one year of the study. Metolachlor use was also small compared with the use of the phenoxyacids (Table 6.6).

Chlorpyrifos [*O,O*-dimethyl- *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] use showed a marked increase during the 1995 growing season, relative to 1993 and 1994, in five of the six watersheds (Table 6.6). The LaSalle River watershed was the only drainage basin

Table 6.6 Estimates of the amount (kg) of pesticide used in six watersheds of southern Manitoba. (Manitoba Agriculture, unpublished data).

Pesticide	LaSalle	Morris	Pembina	Rat	Roseau	Seine
Atrazine						
1993	479	8698	91	2390	5121	1164
1994	265	7258	70	513	1164	245
1995	317	4510	119	515	1443	896
Bromoxynil						
1993	13978	30823	6515	11578	10234	8512
1994	13962	31776	6330	10009	10514	6045
1995	13064	35007	7271	12476	9044	5426
Chlorpyrifos						
1993	599	287	· ^a	196	37	87
1994	8768	7753	1256	129	37	39
1995	8599	24955	7913	6171	4288	1158
Cyanazine						
1993	442	10498	82	270	221	327
1994	688	16720	782	219	283	625
1995	554	9411	· ^a	640	926	303
2,4-D						
1993	10139	23204	69691	15949	2123	6650
1994	7950	20901	7318	8286	5391	6668
1995	9091	22416	9710	6285	3057	8348
Dichlorprop						
1993	5898	9616	2935	8606	908	4267
1994	4557	7444	3624	4980	622	3821
1995	4304	9583	6885	· ^a	684	5382
Diclofop methyl						
1993	763	1710	1156	301	594	405
1994	236	1068	585	468	206	129
1995	37	644	779	5190	36	659
Ethalfuralin						
1993	6093	27378	7218	8339	8431	3211
1994	5385	25607	6672	7721	16162	3512
1995	8167	21097	6000	4981	6997	1190
MCPA						
1993	53509	119317	33268	40211	41686	31300
1994	52196	119323	32020	37462	40350	29389
1995	62484	135034	38549	51217	43386	35577
Metolachlor						
1993	559	· ^a	· ^a	991	· ^a	1620
1994	386	· ^a	· ^a	539	· ^a	109
1995	459	· ^a	· ^a	· ^a	371	121
Triallate						
1993	2468	5266	4343	2886	1099	4426
1994	265	1619	2210	780	148	1263
1995	2414	1228	1315	511	· ^a	3790
Trifluralin						
1993	4671	36371	11446	1971	3294	1909
1994	4300	34202	12795	2341	4866	54
1995	4781	30195	10511	3255	2890	46

^apesticide use was not reported

that had a decrease in chlorpyrifos use to 8600 kg in 1995 from the 8800 kg applied during 1994. The increased amounts of chlorpyrifos during 1995 may be due to its use during an outbreak of Bertha Armyworm (*Mamestra configurata* (Wlk.)) in a broad region of southern Manitoba.

6.4.3 Temporal Trends

Distinct seasonal trends in pesticide concentration were observed for the phenoxyacid and phenolic compounds. Although spring melt and early summer rains result in the greatest runoff volumes in the Red River drainage basin (Tornes and Brigham, 1994), pesticides were not found at elevated levels during this period. Instead pesticides were present in river waters at maximum concentrations (Figure 6.2-6.7) during and extending beyond regional application periods (early May - end of June). While application periods were not known precisely in all watersheds, they were documented for the South Tobacco Creek Watershed (within the Morris River drainage basin) with the cooperation of landowners and assumed to apply for the entire region (Rawn et al., 1998c (Chapter 3)).

Pesticide concentrations in the rivers in southern Manitoba generally were lower during the 1995 sampling season than in 1994. Sample collection of the Red River and its tributaries commenced in March 1995, which was earlier than the 1994 sampling season. During the spring melt and runoff period, pesticides were not present at elevated concentrations. Temporal trends of pesticides between 1994 and 1995 were similar in that maximum concentrations generally were observed during and extending beyond regional applications times.

The phenoxyacid herbicides were frequently below the detection limit in 1995,

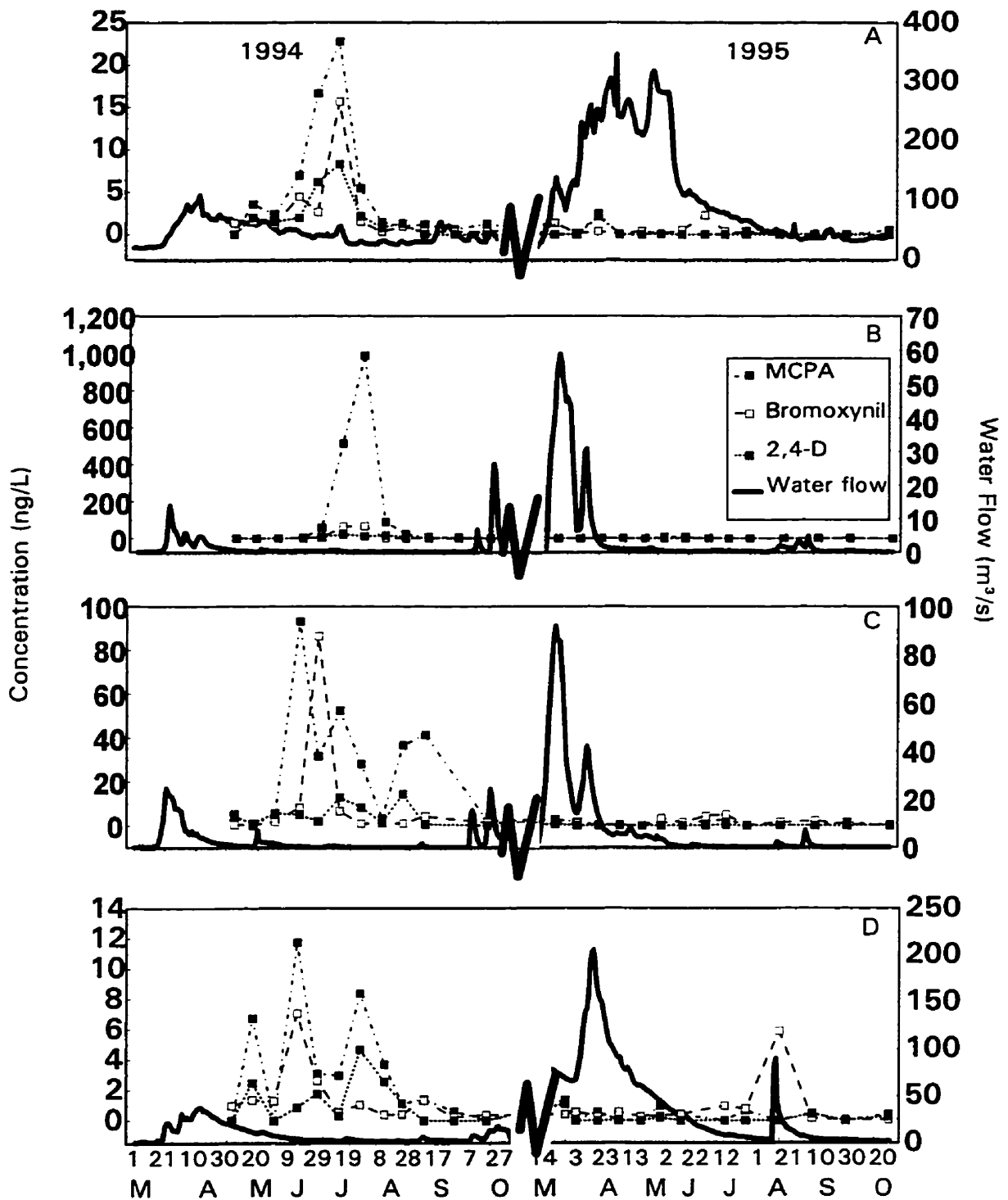


Figure 6.2. MCPA, bromoxynil and 2,4-D concentrations in A) the Assiniboine River, B) LaSalle River, C) Morris River and D) Pembina River during 1994 and 1995. Water flow is indicated on the right scale.

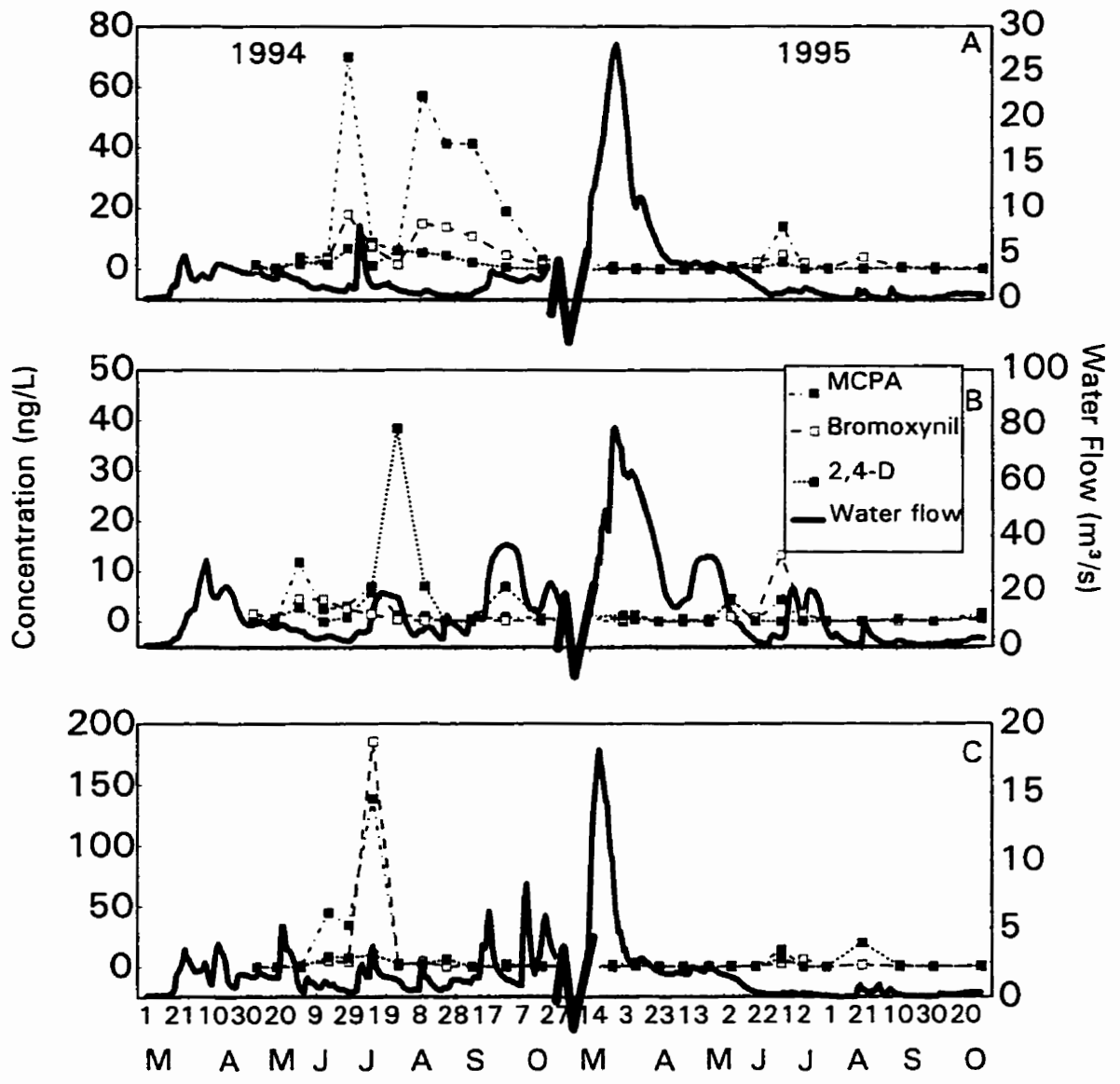


Figure 6.3. MCPA, bromoxynil and 2,4-D concentrations in A) the Rat River, B) Roseau River and C) Seine River during 1994 and 1995.

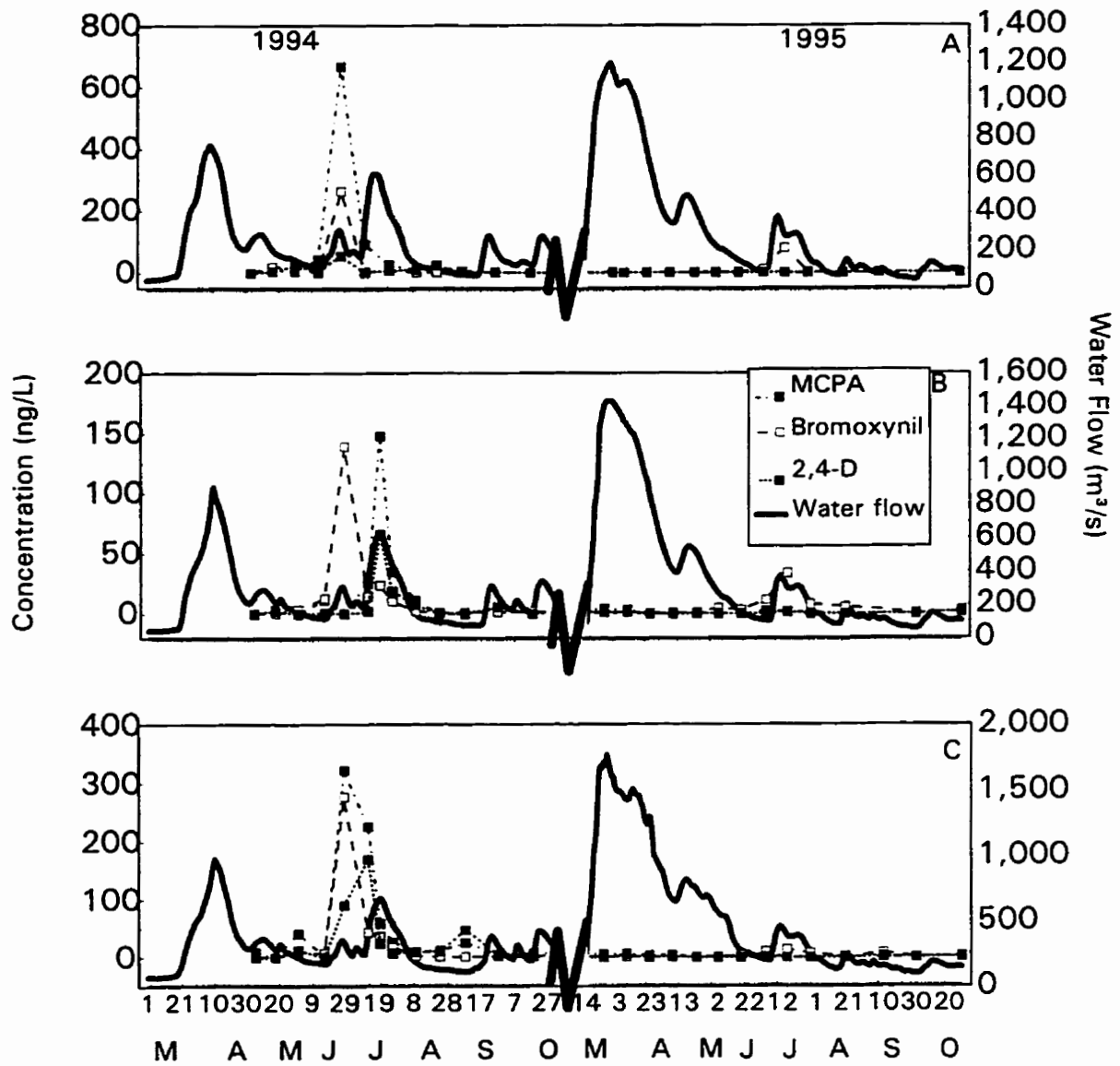


Figure 6.4. MCPA, bromoxynil and 2,4-D concentrations in the Red River at A) Emerson, B) Ste. Agathe and C) Selkirk during 1994 and 1995.

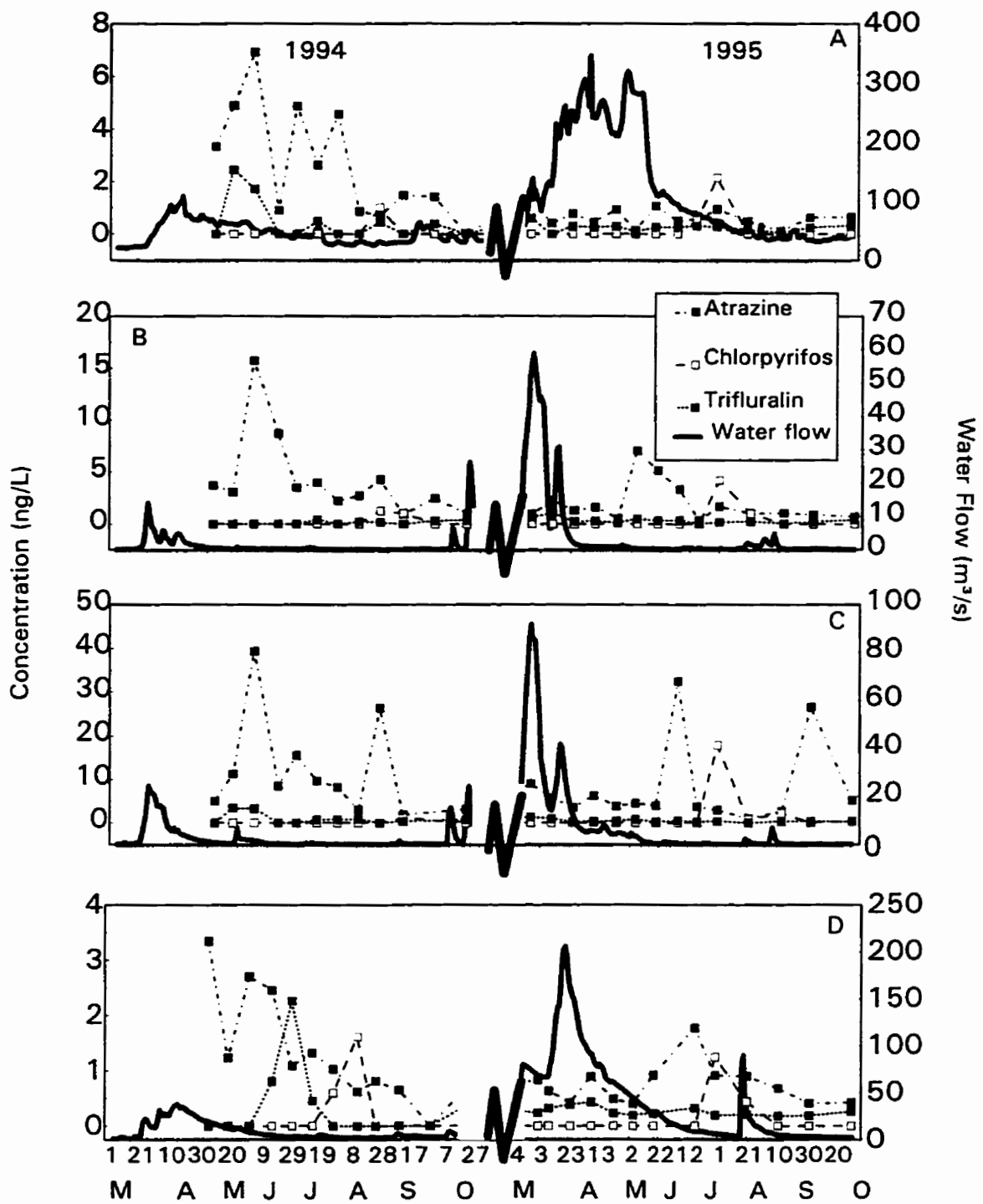


Figure 6.5. Atrazine, chlorpyrifos and trifluralin concentrations in A) the Assiniboine River, B) LaSalle River, C) Morris River and D) Pembina River during 1994 and 1995. Water flow is indicated on the right scale.

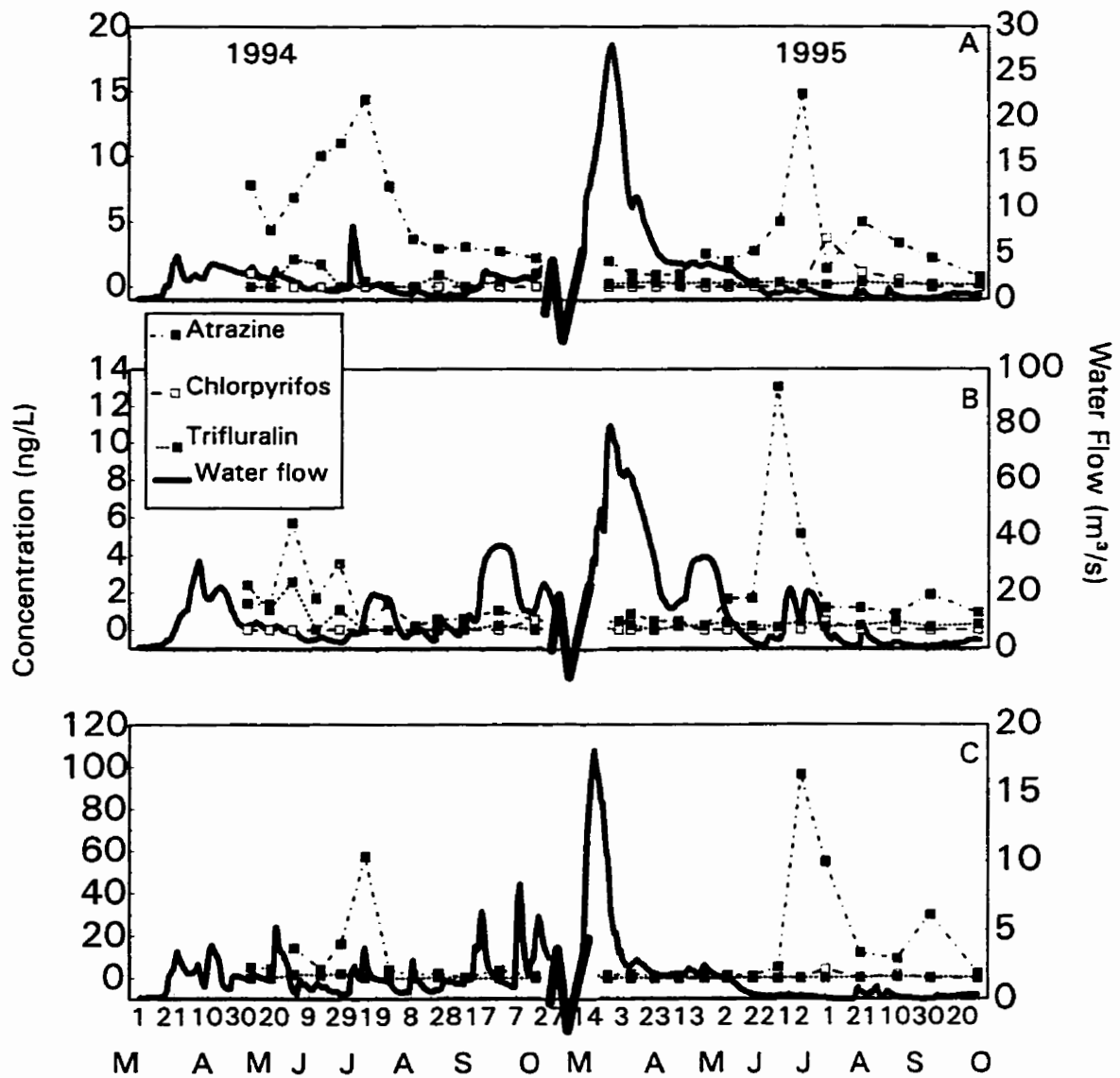


Figure 6.6. Atrazine, chlorpyrifos and trifluralin concentrations in A) the Rat River, B) Roseau River and C) Seine River during 1994 and 1995.

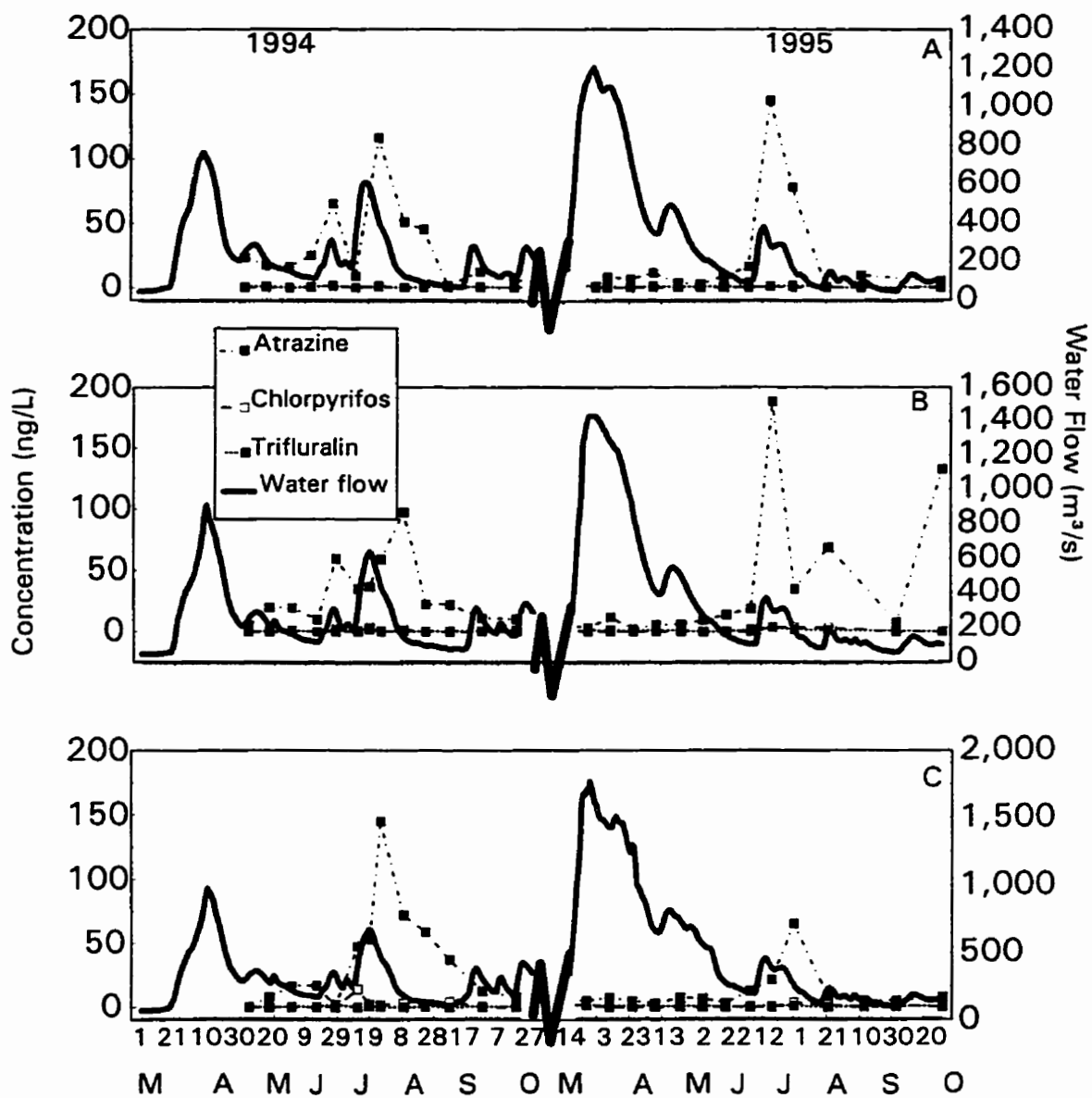


Figure 6.7 Atrazine, chlorpyrifos and trifluralin concentrations in the Red River at A)Emerson, B) Ste. Agathe and C) Selkirk during 1994 and 1995.

although water flow was higher in 1995 than in 1994. The lack of phenoxyacid detection may be related to their lack of persistence in soil which reduces their availability for loss via runoff and to dilution to below detection limits. Pesticide concentrations in southern Manitoba rivers were similar in 1993 and 1994.

Atrazine was detected at maximum concentrations between late May and early June 1994 in the Assiniboine, LaSalle, Morris, Pembina and Roseau Rivers. Atrazine concentrations in the Rat and Seine Rivers, however, were found at seasonal maximum values in July during 1994. Similarly, maximum concentrations of atrazine were observed in the Red River samples collected later in the field season. In 1993, atrazine generally was present at maximum concentrations in late July, coinciding with a heavy rainfall period producing overland flow. Although atrazine use is low in southern Manitoba, it is more widely used in the southern region of the Red River basin, in Minnesota and southern North Dakota (Gianessi and Anderson, 1995a; Gianessi and Anderson, 1995b; Tornes and Brigham, 1994). Elevated levels of atrazine in the Red River reflected US uses of the product as indicated by its detection (maximum atrazine concentrations at Emerson 57 and 96 ng/L, 1994 and 1995, respectively) in the Red River as it enters Canada. Atrazine is known to be quite persistent in water (Schottler et al., 1994). Movement of this chemical from the region of use in the southern Red River basin to areas at large distances from the site through water flow, is known to occur (Pereira et al., 1992; Thurman et al., 1991).

Chlorpyrifos use occurs later in the growing season (late July - early August) than herbicide applications and it generally was present in river systems during July and August, with very low levels during spring melt and runoff periods. During summer 1995, when the

greatest use of chlorpyrifos occurred in the three year period, concentrations were lower than in 1994 in all tributaries. This may have been due to dilution as a result of increased water flow during 1995.

6.5 Discussion

Although pesticide concentrations observed in the Red River at Emerson in this study were within the range observed in other studies, maximum concentrations were lower than in other reports (Currie and Williamson, 1995; Tornes and Brigham, 1994). For example, Tornes and Brigham (1994) reported atrazine concentrations ranging between <0.05 to 650 ng/L over the 14 year period of record, however, in the present survey maximum atrazine levels were found to be 145 ng/L during the 1995 sampling season. Reported concentrations of atrazine in Ontario rivers have exceeded 5 $\mu\text{g/L}$ (Frank and Logan, 1988). In the 1980s, maximum atrazine levels in Quebec exceeded 37 $\mu\text{g/L}$ (Maguire and Tkacz, 1993), however, more recent data found maximum atrazine levels in Quebec rivers of 29 $\mu\text{g/L}$ (Berryman and Giroux, 1994). Atrazine concentrations in the US midwest where its use is extensive exceeded 100 $\mu\text{g/L}$ (Thurman et al., 1992). Gruessner and Watzin (1995) reported maximum seasonal atrazine concentrations of 10 $\mu\text{g/L}$ in Vermont rivers. In France, concentrations exceeded 30 $\mu\text{g/L}$ (Tronczynski et al., 1993). In the largest tributaries of Chesapeake Bay, however, atrazine concentrations remained below 1 $\mu\text{g/L}$ (Foster and Lippa, 1996).

Maximum 2,4-D concentrations (0.8 - 57 ng/L) were observed in the Red River at Emerson between March and June which corresponded to regional application times. Beck

et al. (1992) reported 2,4-D in southern Manitoba rivers ranging in concentration from < 0.03 to $1 \mu\text{g/L}$.

Pesticide concentrations in Florida surface waters also reflected regional use patterns. The maximum concentration of 2,4-D observed in the Florida surface waters was $14 \mu\text{g/L}$ (Miles and Pfeuffer, 1997). Previous studies also have shown that pesticides are present in surface waters of agricultural watersheds at higher concentrations following local application periods (Rawn et al., 1998c (Chapter 3); Kimbrough and Litke, 1996; Hall et al., 1993). 2,4-D, bromoxynil and atrazine were three of the five most frequently detected herbicides in Manitoba surface waters in the 1980s (Currie and Williamson, 1995). These products also were present in the Red River and tributaries with a high degree of frequency in the current sampling program.

Dichlorprop was detected at each sampling station in the present study, however, concentrations only remained above detection limits for short periods close to application times each year. Dichlorprop concentrations exceeded bromoxynil levels in Danish streams ($2.8 \mu\text{g/L}$ and $0.53 \mu\text{g/L}$, respectively) (Morgensen and Spliid, 1995). In the Danish river systems, MCPA concentrations exceeded those of both dichlorprop and bromoxynil, where reported maximum concentrations of MCPA were $7.3 \mu\text{g/L}$ (Morgensen and Spliid, 1995).

Triallate was present in water from the Red River and its tributaries in the present study, with maximum concentrations occurring early in the agricultural season, corresponding to regional applications. Donald and Sygiannis (1995) found triallate in sediments, but not water samples collected in Saskatchewan lakes. In a study comparing surface waters draining agricultural areas with urban areas in Colorado, triallate only was detected in urban regions

(Kimbrough and Litke, 1996). Beck et al. (1992) did not detect triallate or diclofop methyl in small streams in southern Manitoba. Diclofop methyl was, however, detected in the Red River and tributaries in the present study. Similarly, Grover et al. (1997) detected diclofop methyl in Saskatchewan pond waters.

Maximum trifluralin concentrations (1 - 2 ng/L) were generally lower than observed for other herbicides in samples collected from the Red River and tributary sampling stations. Elevated trifluralin concentrations were observed early in the sampling season (March - early June), corresponding to the time of application for this chemical. Similarly, Kimbrough and Litke (1996) and Grover et al. (1997) found that trifluralin concentrations reflected seasonal use patterns. Lower frequency of detection and reduced concentrations of trifluralin also have been observed in Arkansas surface waters (Senseman et al., 1997).

Ethalfuralin was generally below detection limits (<0.28 ng/L) in southern Manitoba rivers, although it was detected occasionally in each river during the course of the present study at low concentrations (Table 6.3). In the Colorado study, ethalfuralin concentrations ranged from <13 to 73 ng/L in agricultural regions, but it was not detected in surface waters draining the urban areas (Kimbrough and Litke, 1996).

Although cyanazine was detected in both the Red River and tributaries, concentrations were generally <0.082 ng/L and, therefore, the temporal variation of this herbicide could not be defined. Cyanazine is a herbicide used widely in the US and is reported widely in surface waters. In the Minnesota River, a high degree of seasonality was observed for cyanazine compared to atrazine (Schottler et al., 1994). Concentrations of cyanazine in rivers of the US midwest were found to range from below detection limits to 61 µg/L, with

maximum concentrations observed in the post-planting period, prior to harvest (Thurman et al., 1992). Cyanazine concentrations observed in the tributaries of Chesapeake Bay and in Vermont rivers (4 - 108 ng/L, 6.9 µg/L, respectively) were lower than reported in the US midwest (Foster and Lippa, 1996; Gruessner and Watzin, 1995). Terbutylazine was rarely detected in the Red River or the six tributaries under investigation during 1993-1995. Terbutylazine is not as widely determined as cyanazine or atrazine, however, it was observed in the Mississippi River between 1987 and 1989 (Pereira et al., 1992).

In the present study, chlorpyrifos concentrations (<0.082 - 18 ng/L) were three orders of magnitude below the concentrations (6 µg/L) reported by Maguire and Tkacz (1993) for surface waters draining agricultural areas in Quebec. In Colorado, chlorpyrifos concentrations were higher in surface waters draining urban regions (<0.008 - 0.3 µg/L) than agricultural areas (<0.008 - 0.2 µg/L) (Kimbrough and Litke, 1996). In the present study, higher chlorpyrifos concentrations were observed downstream of the City of Winnipeg, a large urban centre (population 650,000) on the Red River.

Alachlor was frequently detected in the Red River throughout this study, however, it was generally below detection limits (0.060 ng/L) in each of the tributaries. Although alachlor is not registered for use in Canada, it is widely used in the US midwest and is observed in surface waters from that region. Schottler and coworkers (1994) reported maximum alachlor concentrations of 1.2 and 2.4 µg/L occurring in June 1990 and 1991, in the Mississippi River, respectively. Alachlor levels exceeded 50 µg/L in US midwest surface waters (Thurman et al., 1992) with maximum concentrations during the post-planting period. In the tributaries of Chesapeake Bay, concentrations ranged from 2 to 23 ng/L (Foster and

Lippa, 1996). Alachlor concentrations in the US were generally higher than observed for metolachlor in the early 1990s. During the post-planting period, maximum metolachlor concentrations in surface waters of the US midwest were 40 $\mu\text{g/L}$ (Thurman et al., 1992). In Arkansas surface waters, metolachlor concentrations ranged from $<0.1 \mu\text{g/L}$ to a maximum of 20 $\mu\text{g/L}$, however, in Vermont, river concentrations were only 10 $\mu\text{g/L}$ (Senseman et al., 1997; Gruessner and Watzin, 1995). Metolachlor maximum concentrations in Quebec rivers during the late 1980s were reported to be 5 $\mu\text{g/L}$ (Maguire and Tkacz, 1993). In this study, however, metolachlor concentrations in the Red River remained well below 1 $\mu\text{g/L}$.

Chlorthal dimethyl [2,3,5,6-tetrachloro-1,4-benzenecarboxylic acid] (dacthal, DCPA) was frequently detected, although at low concentrations ($<0.013 - 0.58 \text{ ng/L}$) in the present study. Chlorthal dimethyl was detected in Colorado river systems draining both agricultural (0.033 - 100 $\mu\text{g/L}$) and urban regions ($<0.005 - 0.029 \mu\text{g/L}$) (Kimbrough and Litke, 1996). In previous monitoring of Manitoba rivers, chlorthal dimethyl was detected in $< 2\%$ of the samples collected, but detection limits were much higher than in the present study (Currie and Williamson, 1995).

Triclopyr was not detected in the majority of Manitoba rivers, however, maximum concentrations reported were in the Turtle River (650 ng/L) over the period of record (Currie and Williamson, 1995). Similarly, in the present study triclopyr was infrequently detected in surface waters in southern Manitoba, which may be a function of low recoveries for this compound (Table 6.2).

6.5.1 Pesticide Loadings

Of the 16 pesticides measured in this program, six were selected for the determination

of seasonal pesticide discharge loadings in 1994 and 1995. Chlorpyrifos was the only insecticide under investigation. Phenoxyacid herbicides, trifluralin and bromoxynil were chosen for this detailed analysis because of their extensive use in southern Manitoba. Atrazine was included because it is persistent and was widely used within North Dakota and Minnesota, in the southern part of the Red River drainage basin, so it was potentially available for transport through to Lake Winnipeg. Although alachlor and chlorthal dimethyl were not used in southern Manitoba in any of the years of this study, they were included because of use in the neighbouring US states (Gianessi and Anderson, 1995*a*; Gianessi and Anderson, 1995*b*).

Discharges of the phenoxyacid herbicides were lower in the largest tributary, the Assiniboine River, and at each sampling point along the Red River in 1995 than in 1994, despite increased water flow in 1995 (Table 6.7 and 6.8). Similarly phenoxyacid concentrations were reduced in the Red River in July 1993 during a period of heavy rainfall which produced overland flow and high river flow. These results may be due to the rapid degradation of the phenoxyacids in soil and thus lower concentrations in runoff water. Therefore, concentrations may fall below method detection limits during high flow periods. Concentrations below detection limits resulted in discharge estimates of zero, although pesticide discharges might have been significant. The reduction in phenoxyacid concentration with increased water flow differs from results observed for the more persistent herbicides (e.g., atrazine). Atrazine loadings were generally higher in 1995 than 1994 in most of the tributaries.

MCPA had the greatest discharge in each of the river systems, consistent with its

Table 6.7 Seasonal discharge (m³) of water and estimates of discharge (g) of six pesticides in the tributaries of the Red River.

Discharge	Assiniboine	LaSalle	Morris	Pembina	Rat	Roseau	Selne
Water							
1994	9.57 x 10 ⁶	2.77 x 10 ⁷	9.06 x 10 ⁷	1.97 x 10 ⁸	4.17 x 10 ⁷	2.52 x 10 ⁸	3.78 x 10 ⁷
1995	2.34 x 10 ⁶	9.10 x 10 ⁷	1.54 x 10 ⁸	7.64 x 10 ⁸	7.98 x 10 ⁷	3.28 x 10 ⁸	3.57 x 10 ⁷
Atrazine							
1994	1743	20	133	123	164	0	233
1995	1402	111	780	454	166	338	77
Bromoxynil							
1994	1539	42	46	121	139	119	464
1995	820	36	110	477	29	214	12
Chlorpyrifos							
1994	58	0.43	2	7.2	1.7	9.3	0
1995	248	4.3	8	29	3.3	11	1.3
2,4-D							
1994	1194	25	27	80	52	1238	67
1995	665	0.60	30	43	5.5	147	19
MCPA							
1994	3114	411	178	265	438	288	425
1995	1090	9.0	180	219	29	192	26
Trifluralin							
1994	358	0.90	17	18	20	55	8.7
1995	514	52	104	216	15	61	4.4

Table 6.8 Seasonal discharge (m³) of water and estimates of discharge (kg) of nine pesticides at each sampling station in the Red River.

Discharge	Emerson	Ste. Agathe	Emerson + tributaries ^a	Selkirk	Ste. Agathe + tributaries ^b
River (km)	0	109		218	
Water					
1994	4.87 x 10 ⁹	5.30 x 10 ⁹		6.46 x 10 ⁹	
1995	6.54 x 10 ⁹	7.56 x 10 ⁹		1.05 x 10 ¹⁰	
Alachlor					
1994	15	14	- ^c	18	- ^c
1995	46	47	- ^c	11	- ^c
Atrazine					
1994	118	104	118	149	106
1995	99	156	100	88	157
Bromoxynil					
1994	87	58	87	133	60
1995	33	25	34	24	26
Chlorpyrifos					
1994	1.2	1.4	1.3	8.4	1.4
1995	0.54	2.9	0.56	4.0	3.1
Chlorthal dimethyl					
1994	0.56	0.60	- ^c	0.93	- ^c
1995	0.31	0.67	- ^c	1.1	- ^c
2,4-D					
1994	32	35	33	120	36
1995	0.31	4.2	0.49	11	4.9

MCPA					
1994	251	79	252	241	83
1995	2.4	11	2.8	32	12
Metolachlor					
1994	48	94	- ^c	70	- ^c
1995	76	86	- ^c	54	- ^c
Trifluralin					
1994	1.4	2.1	1.5	2.0	2.5
1995	3.0	9.1	3.2	9.2	9.6

^apesticide loadings at Emerson combined with loadings from the tributaries contributing to Red River levels between Emerson and Ste. Agathe (Morris, Rat and Roseau Rivers)

^bpesticide loadings at Ste. Agathe combined with loadings from the tributaries contributing to Red River levels between Ste. Agathe and Selkirk (LaSalle, Assiniboine and Seine Rivers)

^cloading not calculated for tributaries

more extensive use regionally, relative to the other products under investigation. Although atrazine was used to a much lower extent than MCPA in southern Manitoba, relatively large quantities of this chemical were discharged through the river systems. The Red River loadings of atrazine exceeded 140 and 80 kg, 1994 and 1995, respectively (Table 6.8). Chlorpyrifos discharge estimated for the Red River (Table 6.8) at Ste. Agathe (Figure 6.1) was greater in 1995 than in the 1994 agricultural season, corresponding to increased usage of this compound. The discharge in 1995 increased two fold while the usage in the watersheds south of Ste. Agathe increased by 4.5 times.

Alachlor and metolachlor loadings at each site along the Red River reflect the different sources of these two compounds. Alachlor loadings in the Red River were similar at all sites during 1994. In 1995, however, a decrease in alachlor concentration was observed between sampling sites at Emerson and Ste. Agathe compared with the Selkirk sampling station (46, 48 and 11 kg, respectively). The reason for this difference is unclear, however, it is possible that alachlor concentrations varied enough temporally that two week sampling intervals resulted in missing high levels. Metolachlor, unlike alachlor, is registered for use in Canada and had greatest concentrations in the Red River at the Ste. Agathe sampling station, which is centrally located in the agricultural region of southern Manitoba. The increase in metolachlor discharge along the length of the Red River corresponded well to contributions from tributaries (Table 6.8).

The percentage of atrazine applied in each watershed that was discharged generally was greater than that for the phenoxyacid and phenolic herbicides, (Table 6.9). This occurred despite the greater use of the phenoxyacid and phenolic chemicals. This may be a function

of atrazine's greater persistence in soil and water compared to the phenoxyacid pesticides (Muir 1991). The fraction of 2,4-D discharged, however, exceeded atrazine in the Pembina River during 1995 and the Roseau River in 1994. Although MCPA was the product used in the greatest amounts (Table 6.6) and was detected in river water frequently, discharge losses relative to use generally were lower than other herbicides. Percent discharge losses of chlorpyrifos were higher in the six small tributary watersheds during 1994 (Table 6.9), despite larger quantities used in the 1995 field year (Table 6.6).

The maximum losses of atrazine relative to applied levels (0.38%) determined in this study were generally lower than reported by Schottler et al. (1994) (0.33 - 0.62%) for the Minnesota River. Similarly, atrazine losses in the Mississippi River were greater than observed in the present study, relative to applied levels were 0.62% (Larson et al., 1995). Frank and Logan (1988) reported greater losses of atrazine (0.5 - 1.9%) relative to regional application levels from three rivers in Ontario. Similarly, MCPA and 2,4-D loss estimates reported in Ontario were greater (0.04 - 1.9% and 0.02 - 0.49%, respectively) than observed in the present study (Table 6.9). Chlorpyrifos discharge losses were 0.15% of applied levels in the Mississippi River basin, one order of magnitude above maximum losses in this study. Topography and soil type may explain this because the Red River basin is extremely flat, except in the Pembina River valley. Overland flow events are rare during summer months and rainfall is generally lower than observed in the US midwest cornbelt or the southern Great Lakes. During an unusually large rainfall producing runoff and major increases in the hydrograph of all the tributaries and the Red River in late July 1993, no large increase in pesticide concentrations were observed in the Red River. Fractional losses of 2,4-D, MCPA

Table 6.9 Discharge losses in the six small rivers as a percentage of quantities applied in each watershed during 1994-95.

Pesticide	LaSalle		Morris		Pembina	
	1994	1995	1994	1995	1994	1995
Atrazine	0.008	0.035	0.002	0.017	0.175	0.383
Bromoxynil	0.0003	0.0003	0.0001	0.0003	0.0019	0.0066
Chlorpyrifos	0.0002	0.0001	0.0	0.0	0.0006	0.0004
2,4-D	0.0003	0.0	0.0001	0.0001	0.0011	0.443
MCPA	0.0008	0.0	0.0001	0.0001	0.0008	0.0006
Trifluralin	0.0	0.011	0.0	0.0003	0.0001	0.0021

Pesticide	Rat		Roseau		Seine	
	1994	1995	1994	1995	1994	1995
Atrazine	0.0321	0.0322	0.0	0.0234	0.0951	0.0086
Bromoxynil	0.0014	0.0002	0.0011	0.0024	0.0077	0.0002
Chlorpyrifos	0.0013	0.0001	0.0251	0.0003	0.0	0.0001
2,4-D	0.0006	0.0001	0.0230	0.0048	0.0010	0.0002
MCPA	0.0012	0.0001	0.0007	0.0004	0.0014	0.0001
Trifluralin	0.0008	0.0005	0.0011	0.0021	0.0161	0.0095

and bromoxynil from the South Tobacco Creek Watershed in the western part of the Morris River watershed were within an order of magnitude of observed results in this program (Rawn et al., 1998a).

The cropped area relative to the total area in each watershed ranged from 52 - 89%. There was no relationship between fractional loadings of each pesticide with the amount of

cropped land. The Pembina and Roseau River basins, however, are thought to lose greater amounts of pesticides relative to applied levels due to increased resuspension of contaminated bed sediments and movement of highly erodible sediment relative to other Red River tributaries studied (Currie and Williamson, 1995). As anticipated, maximum fractional loadings of the pesticides were observed in the Pembina River basin, however, losses from the Roseau drainage were generally similar to all other watersheds under investigation (Table 6.9). These differences may have been observed due to the rolling topography in the Pembina watershed, compared to the flat land in the Roseau watershed.

6.5.2 Mass Balance

As the Red River flows from the Canada/US border into the middle of the agricultural region of southern Manitoba at Ste. Agathe, it receives pesticide loads from the connecting tributaries. Inputs from the Morris, Rat and Roseau Rivers all contribute to loadings measured at the Ste. Agathe sampling station. Chlorpyrifos, 2,4-D and trifluralin loads in the Red River at Ste. Agathe were higher than the sum of the loads at Emerson combined with inputs of the three contributing rivers by 125, 1741 and 564 g, respectively in 1994. These differences represent an elevation in discharge from expected loads by 9.1, 5.0 and 27%, for chlorpyrifos, 2,4-D and trifluralin, respectively. Similarly, in 1995 pesticide loads at Ste. Agathe were higher than anticipated from Emerson levels plus contributions of the three contributing tributaries. Differences were larger between expected and observed levels in 1995, where chlorpyrifos loads were 81%, 2,4-D 88% and trifluralin 65% higher at Ste. Agathe than could be explained by tributary inputs to Emerson loadings.

Although precipitation inputs of pesticides to each watershed result in runoff

contributions to riverine loads of these chemicals, the possibility exists for deposition directly to the water surface to occur. Increased loadings of herbicides in South Tobacco Creek, however, could be explained by deposition via precipitation directly to the river surface (Rawn et al., 1998a (Chapter 4); Rawn et al., 1998b (Chapter 5)). Based on data for pesticides in precipitation for the South Tobacco Creek during the 1994 and 1995 agricultural seasons (Rawn, 1998), chlorpyrifos, 2,4-D and trifluralin levels would have been increased by 31, 5 and 0.7 g, respectively in 1994 and by 1.3, 23 and 0.4 g, respectively, in 1995 due to direct atmospheric deposition via precipitation and dry deposition, assuming an average width of 200 m for the Red River. Therefore, direct deposition washin contributions of these chemicals do not alone explain the elevated loadings in the Red River at Ste. Agathe.

Chlorpyrifos, 2,4-D and MCPA levels also increased in the Red River between the Ste. Agathe and Selkirk sampling stations. Inputs of these chemicals from the Assiniboine, LaSalle and Seine Rivers which join the Red between the Ste. Agathe and Selkirk sampling locations do not completely account for the elevations in discharge observed at the Selkirk site (Table 6.8). Although deposition via precipitation and dry deposition to the water surface between these locations will contribute to loadings, contributions via these routes are small relative to tributary inputs, as discussed previously. Urban uses of 2,4-D, MCPA and chlorpyrifos within the City of Winnipeg is the most likely explanation for the increased pesticide concentration between the agricultural site at Ste. Agathe and the Selkirk station, beyond Winnipeg. Similarly domestic or urban uses of these chemicals in the rural towns along the river (e.g., Emerson, Morris, Ste. Agathe) may explain higher levels at Ste. Agathe. The higher than expected discharge values at Ste. Agathe also may be due to contributions

from non-monitored minor tributaries and drainage ditches along the Red River. The pesticide loadings of the tributaries may be underestimated as a result of additional inputs to the tributaries from the point of sampling to the junction with the Red River.

An additional input pathway of pesticides to surface waters is that of gas absorption. Gas exchange across the air-water interface has been shown to occur for many pesticides including atrazine, trifluralin and chlorpyrifos which may result in increased chemical loads in surface waters through absorption (Rawn, 1998; Rawn et al., 1998b; Schwarzenbach et al., 1993; Eisenreich and Strachan, 1992). Conversely, the possibility exists for loss of chemicals such as chlorpyrifos and trifluralin through volatilization from the water surface. Minor contributions through deposition of pesticides associated with dry particles (dry deposition) directly to the water surface is also known to occur (Rawn et al., 1998a (Chapter 4)).

6.5.3 Water Quality

All herbicide concentrations in the present study were below the Canadian (CCREM, 1987) water quality guideline values for the protection of freshwater aquatic life, where these guidelines are in place. Chlorpyrifos concentrations, however, exceeded the Canadian draft guideline for the protection of freshwater aquatic life (3.5 ng/L) (CCME, 1998) in the Assiniboine and Morris Rivers during the 1993 sampling season. During 1995, the year with a known outbreak of the Bertha Armyworm (*M. configurata*), chlorpyrifos levels exceed this guideline value in four of the seven sampled tributaries of the Red River (Table 6.3). Each year of the study, chlorpyrifos levels in the Red River at the Selkirk sampling station exceeded the draft water quality guideline objective for the protection of freshwater aquatic life. This site is the sampling point where pesticide contributions of the Assiniboine River and any

inputs from the City of Winnipeg to the Red River occur and prior to the entrance of the river into Lake Winnipeg.

6.6 Conclusions

This study is the first data set with reasonable temporal resolution for pesticides in southern Manitoba rivers and first to estimate seasonal loadings for pesticides both, in the Red River and tributaries. Pesticide concentrations in the Red River drainage basin in southern Manitoba reflected regional uses of these products and contributions from use on the neighbouring US states. Urban contributions may have resulted in increased pesticide loadings in the Red River at the sampling station downstream of Winnipeg city limits and may also explain higher levels at Ste. Agathe.

Discharge loadings of MCPA were the highest in each river system under investigation, however, relative to the amount of this chemical applied, losses were small. Although atrazine use was much lower than that of the phenoxyacid herbicides, atrazine discharge loadings were similar to these more widely used herbicides. Alachlor and dacthal were present in the Red River at all sampling locations although they were not used in southern Manitoba throughout the duration of this study. This suggests that pesticide concentrations in the Red River are heavily influenced by US usage of pesticides. Estimation of discharge was possible because of biweekly sampling. However, our study on the South Tobacco Creek (Rawn et al., 1998c) has shown that even greater frequency is necessary to get accurate loading estimates for periods when pesticides are being applied. Intensive sampling, not routine seasonal sampling of river waters, is required to determine temporal

trends and loadings of pesticides in surface waters.

Herbicide concentrations were well below Canadian water quality guideline values for the protection of freshwater aquatic life, where such values exist. Chlorpyrifos concentrations, however, occasionally exceeded draft water quality guideline values for the protection of freshwater aquatic life.

7. POLYCHLORINATED BIPHENYLS IN A RURAL WATERSHED IN THE SOUTHERN PRAIRIE REGION OF CANADA

7.1 Abstract

PCB concentration patterns were determined in air, precipitation and surface water in a small agricultural watershed (70 km²) in the Canadian prairies, with no known local source of these compounds. PCB concentrations were related to air temperature for lower chlorinated congeners and air mass back-trajectories indicated that elevated levels in ambient air were observed when air moved into the region from the south. Dissolved phase Σ PCB concentrations ranged from 20 - 6350 pg/L in creek water, air concentrations ranged from 1.4 - 751 pg/m³ and concentrations in precipitation ranged from 88 - 9703 pg/L. The stagnant layer (two-film) model and the surface renewal models were used to estimate PCB volatilization during both 1994 and 1995. The surface renewal model predicted greater volatilization losses than the two-film model, although the surface renewal model has been shown to under predict gas exchange in small turbulent streams. This suggests that for a small stream, the two-film model drastically under predicts gas exchange estimates. There was overall net deposition of PCBs to the South Tobacco Creek when precipitation and dry deposition inputs to the entire watershed were included. Similar levels of PCBs are exported from this watershed by both volatilization and stream discharge.

7.2 Introduction

Although use of polychlorinated biphenyls (PCBs) has been restricted in North America since the late 1970s, they are still present in both surface waters (McConnell et al., 1996; Pearson et al., 1996; Hornbuckle et al., 1994) and atmospheric compartments (Offenberg and Baker, 1997; Stern et al., 1997; Hoff et al., 1996). PCBs have long residence times in the environment and are subject to transfer from source regions to remote locations (Wania and Mackay, 1996). PCBs enter surface water via precipitation, dryfall and gas absorption and are also transferred from water to the overlying atmosphere through volatilization (McConnell et al., 1996; Iwata et al., 1995; Hornbuckle et al., 1994; Jeremiason et al., 1994; Baker and Eisenreich, 1990).

In temperate environments, PCB concentrations in air have been shown to vary annually with air temperature (Hillery et al., 1997; Hoff et al., 1992*b*). Revolatilization from plant and soil surfaces may be an important source of ambient air concentrations of PCBs (Wania and Mackay, 1996; Alcock et al., 1994; Hoff et al., 1992*b*). Air temperature limits volatilization rates and, therefore, regulates the amount of a chemical available for transport (Wania and Mackay, 1996). This contrasts with atmospheric concentrations of current-use pesticides that are present at elevated levels during periods of use (Glotfelty et al., 1990; Rawn et al., 1998*b* (Chapter 5)).

PCBs move between the overlying atmosphere and the water surface in both directions by gas exchange. The air-water gas exchange of PCBs and other persistent semivolatile organochlorine compounds (SVOC), notably the hexachlorocyclohexanes, is

relatively well studied (Ridal et al., 1996; Falconer et al., 1995; Jantunen and Bidleman, 1995; McConnell et al., 1993). Gas exchange has been modelled using different approaches, including the two-film and surface renewal models (Bidleman and McConnell, 1995).

The two-film model is the most widely used and has been described in detail in current reviews (Bidleman and McConnell, 1995; Schwarzenbach et al., 1993). The predominance of the two-film or stagnant layer model may be a function of the emphasis placed on gas exchange research in lake and ocean situations rather than riverine systems. Shallow streams are thought to have reduced air-water boundary layers due to water movement and turbulence in combination with effects of river bottom topography (Schwarzenbach et al., 1993). The surface renewal model differs from the two-film model in the way it estimates the water-side transfer coefficient. Like the two-film model, the surface renewal model includes factors to estimate the effect of molecular diffusivity on SVOC movement, but it also introduces additional parameters to incorporate effects of water velocity and depth. The surface renewal model is thought to under-predict true gas exchange in streams (Schwarzenbach et al., 1993).

It has long been recognized that tributaries contribute to loading of lakes by atmospherically derived SVOC contaminants (Eisenreich and Strachan, 1992; Hoff et al., 1996). Although PCB loadings in tributaries have been studied, emphasis has been on the determination of levels at the river mouth (Dolan et al., 1993). Mass-balance estimates in the Great Lakes include a tributary component, however, riverine loadings have been estimated from a limited number of samples (Hoff et al., 1996; Jeremiason et al., 1994).

The present study was established to determine the temporal trends of PCBs in both atmospheric samples and stream water within the South Tobacco Creek Watershed. The 70

km² watershed, near the town of Miami, originates in the Pembina Hills of Manitoba. The stream that drains the watershed flows down an escarpment which drops approximately 130 m over eight km (Yarotski, 1996). There are 42 large farming operations within the watershed. Apart from past minor uses in consumer products, e.g., fluorescent light ballasts, no local source of PCBs is known. We hypothesize, therefore, that PCBs in stream water would be related to air concentrations and precipitation inputs, similar to observations for current use pesticides (Rawn et al., 1998*a* (Chapter 4); Rawn et al. 1998*b* (Chapter 5); Rawn et al. 1998*c* (Chapter 3)). Our approach was to estimate PCB movement via gas exchange, deposition via precipitation and dryfall to the stream and to compare inputs and outputs to the stream draining the small, agricultural watershed in southern Manitoba, Canada.

7.3 Materials and Methods

7.3.1 Sample Collection

Air, precipitation and stream water were sampled in the South Tobacco Creek Watershed (Figure 7.1) during the 1994 and 1995 field seasons (May - October) to determine PCB levels in both atmospheric compartments and the receiving surface water. The sampling program was designed to collect large volumes of air, precipitation and South Tobacco Creek water simultaneously.

Air samples were collected using a high volume (General Metalworks PS-1) polyurethane foam plug (PUF) sampler with a GFA glass fibre filter to trap particulate matter. Filters were prepared for use by heating for 18 h at 265°C. PUF plugs were pre-cleaned by

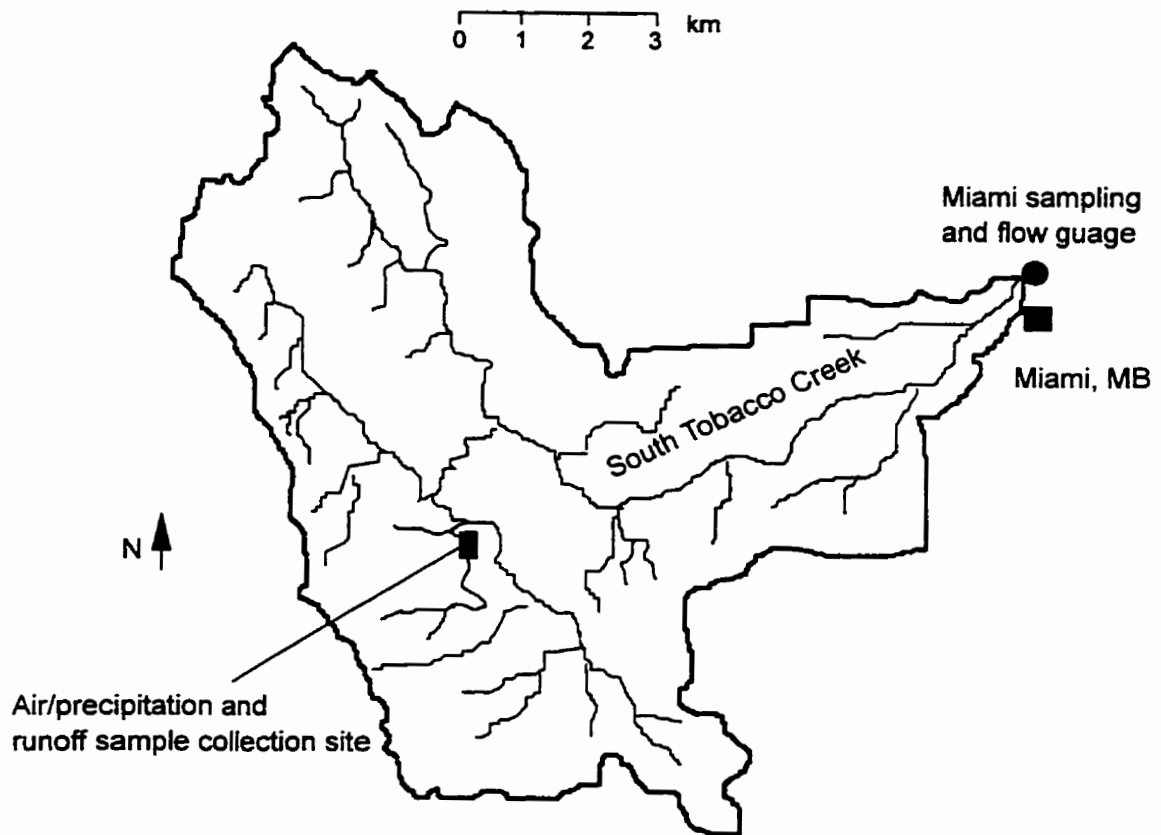


Figure 7.1 The South Tobacco Creek Watershed.

Soxhlet with hexane for 24 h prior to use. Approximately 350 m³ of air was drawn through the sampling unit over a 24 h period every 6 days during the early part of the agricultural season. Later in each field season, samples were collected every 12 days corresponding to the Great Lakes Integrated Atmospheric Deposition Network (IADN) sampling schedule (Hillery et al., 1997). PUFs were placed in sealed glass jars and stored at 4°C until extraction and analysis. Filters were placed in “Whirl pak” polyethylene bags and stored at 4°C until extraction and analysis.

Rainfall was collected using an automated wet-only sampler (0.2025 m²) (Meteorological Instrument Centre, Mississauga, ON) located in the geographic centre of the watershed. Rain was collected over two week periods in 18 L stainless steel soft drink tanks. Rain water was filtered through a glass wool plug at the bottom of the collection basin, for removal of large particles and dichloromethane (DCM) was added to the container as a preservative. Sample volumes ranged from three to 18 L.

Stream water samples (18 L) were collected by lowering a submersible pump into the centre of the stream and pumping into stainless steel containers. Although samples were collected during the spring melt and runoff period (March - April), weekly sampling was limited to the period between early May and freeze up in late October. Prior to extraction, samples were filtered under pressure using pre-cleaned 1 µm GFA filters.

Stream water (1 L) samples were collected by lowering a 1 L bottle into the centre of the stream throughout each field season to determine nutrient levels: total organic carbon (TOC), dissolved organic carbon (DOC), total nitrogen (TN) and total phosphorus (TP). Samples were transported to the lab and stored at 4°C until samples were processed.

7.3.2 Sample Analysis

PCB 30 was used as an internal recovery standard which was added to all samples at the extraction step. PUFs were Soxhlet extracted with DCM for four h. Stream water samples were extracted in sampling containers with DCM using a broad spectrum approach to include pesticides, as described by (Rawn et al., 1998*a* (Chapter 4); Rawn et al. 1998*b* (Chapter 5); Rawn et al. 1998*c* (Chapter 6)). Samples were adjusted to pH 2 using sulphuric acid to extract acid herbicides followed by adjustment to pH 10 using 10 M NaOH, to extract the hydrophobic organics including PCBs (Maguire et al., 1993). Precipitation samples were extracted following the method for stream water samples, except that filtration of rain water was not performed prior to extraction. To analyze suspended sediment, the filter papers used in the filtration of creek water samples collected from June and July, 1995 were mixed with anhydrous sodium sulfate and Soxhlet extracted using the method for PUF and air filter papers. Extracts were cleaned up using 5% deactivated Florisil, eluting with 20 mL hexane to remove PCBs, followed by 85 mL, 18% ethyl acetate (EtAc) in hexane to remove pesticides. All analytes were quantified using pressure programmed gas chromatography-mass spectrometry (Hewlett Packard 5971 MSD) using a 60 m x 0.25 μ m DB-5 column with helium as the carrier gas. Detection criteria were the correct ratios of two characteristic ions and retention times. PCBs were quantified using external standard solutions and corrected for volume changes using PCB-104. Method detection limits were calculated using instrument detection limits plus three times the standard deviation of the lowest concentration analysis (Keith, 1991). TOC, DOC, TN and TP loadings in South Tobacco Creek were measured following standard colorimetric techniques for nutrient analysis (Environment

Canada, 1997).

7.3.3 Data Analysis

Discharges of representative PCB congeners (CB 8, 18, 28, 64, 99, 138) for each season (1994-1995) via the South Tobacco Creek were calculated as the product of PCB concentration and water flow for each day (Larson et al., 1995). Concentrations were estimated by linear interpolation for days when sampling was not performed and concentrations below detection limits were assigned a value of zero in all discharge calculations (Larson et al., 1995). The daily discharge values were summed for the sampling season, commencing in March of each year, to give the total seasonal discharge values.

Daily average air temperatures were measured over the duration of the sampling period. Water temperatures were recorded at the time of sampling. The South Tobacco Creek is shallow (< 1 m depth) and water temperatures were determined to be close to air temperature (<5°C difference) throughout the sampling periods. Water temperatures were assumed to be equal to air temperatures when water data were not available. Regional wind speeds were used in the flux calculations. Although water samples were filtered, PCBs may have been bound to colloidal matter. The dissolved PCB congener concentrations were estimated by subtracting the DOC bound concentrations from the total. The fraction bound to colloidal matter was estimated from the mass fraction of DOC and the K_{oc} value for gas exchange estimates (Jeremiason et al., 1997).

7.3.4 Quality Assurance/Quality Control

Blanks of "Super Q" water were analyzed with each batch of samples. Dated (10,000 year old) well water samples were analyzed and the results for individual congeners were used

as blanks to correct PCB concentration in water and precipitation samples. The average recovery of PCB 30 spiked into distilled water (18 L) was $122 \pm 21\%$ (N=5). Blank PUFs and filter papers (collected every sixth sample) were analysed and used to blank correct results for air samples.

7.4 Results and Discussion

South Tobacco Creek, which drains the watershed, ranged in TOC from 6.8 to 43 mg/L and in pH from 6.7 to 8.0, during the study. TN ranged from 0.3 to 4.3 mg/L and TP ranged from 0.05 to 2.9 mg/L. DOC levels ranged from 6.4 to 15 mg/L during the 1994 and 1995 field seasons.

Water concentrations of Σ PCBs (dissolved and colloidal bound) ranged from 20 - 6350 pg/L (Table 7.1). The dissolved concentrations ranged from 5.5 to 1500 pg/L. Tetrachlorinated congeners were the dominant homolog group in South Tobacco Creek water samples in all months of the 1994 field season. However, in 1995, tri- and dichlorinated congeners were the largest component of Σ PCBs (Table 7.1) in water during August and September, 1995, respectively (Figure 7.2B). It was not possible to confirm this shift in congener profile during the late summer in 1994 because the South Tobacco Creek was dry for an extended period between the end of July until early October. Although PCB concentrations in stream water were not correlated with flow, maximum levels were observed in South Tobacco Creek during spring melt and runoff in 1995 (Figures 7.3 and 7.4).

Σ PCB concentrations on suspended sediments (June - July 1995) averaged $1900 \pm$

Table 7.1 Average PCB concentration in air (pg/m³), creek water (pg/L)^a and precipitation (pg/L) in the South Tobacco Creek Watershed during the 1994 and 1995 seasons.

Congener	Concentration							
	Air			Creek Water		Precipitation		
	Mean	Range	MDL ^b	Mean	Range	Mean	Range	MDL ^b
3	0.16	<DL - 0.8	0.2	10	<DL - 79	8.3	<DL - 70	3.0
4/10	0.26	<DL - 1.5	0.3	16	<DL - 59	26	<DL - 123	6.1
7	0.20	<DL - 0.9	0.2	3.4	<DL - 14	7.7	<DL - 59	4.6
6	0.81	<DL - 2.1	0.2	3.2	<DL - 26	11	<DL - 62	4.7
8/5	1.89	<DL - 6.1	0.33	11	<DL - 145	55	<DL - 331	6.0
19	0.61	<DL - 0.8	1.5	12	<DL - 13	15	<DL - 34	28
18	2.68	<DL - 11	0.4	14	<DL - 146	59	3.2 - 254	7.7
27/24	0.37	<DL - 1.5	0.2	3.4	<DL - 15	16	<DL - 200	4.8
16	2.05	<DL - 16	0.6	16	<DL - 205	49	<DL - 262	13
26	1.30	<DL - 9.7	0.3	5.5	<DL - 37	28	<DL - 162	6.8
25	0.48	<DL - 5.7	0.4	4.4	<DL - 12	5.6	<DL - 18	8.2
31	4.24	0.1 - 67	0.4	16	<DL - 208	59	<DL - 358	8.6
28	3.98	<DL - 58	0.4	14	<DL - 180	65	<DL - 371	8.6
33	4.67	<DL - 64	0.5	17	<DL - 198	74	<DL - 415	9.2
22	2.44	<DL - 36	0.5	7.0	<DL - 101	22	<DL - 107	9.0
45	0.72	<DL - 13	0.3	3.8	<DL - 26	4.2	<DL - 27	5.9
46	0.42	<DL - 4.8	0.4	4.6	<DL - 11	3.9	<DL - 2.9	7.9
52	7.90	<DL - 82	0.3	127	<DL - 671	129	<DL - 914	5.4

49	2.58	<DL - 49	0.3	21	<DL - 165	27	<DL - 219	6.5
47	1.74	<DL - 35	0.3	9.8	<DL - 113	38	<DL - 343	5.6
48	0.33	<DL - 0.5	0.6	6.1	<DL - 32	13	<DL - 96	12
44	4.52	<DL - 77	1.4	48	<DL - 321	60	0.9 - 354	28
42	1.72	<DL - 20	1.4	16	<DL - 42	40	<DL - 164	28
64	3.21	<DL - 37	0.3	13	<DL - 81	52	<DL - 233	6.7
40	0.78	<DL - 11	0.7	7.5	<DL - 20	17	<DL - 179	13
74	0.79	<DL - 17	0.6	13	<DL - 114	19	<DL - 119	12
70	3.75	<DL - 49	0.4	43	<DL - 452	71	<DL - 398	7.4
95	2.05	<DL - 14	0.4	68	<DL - 428	63	<DL - 385	7.1
66	1.53	<DL - 28	0.4	12	<DL - 171	28	<DL - 200	8.5
60	1.36	<DL - 21	1.3	13	<DL - 90	30	<DL - 221	25
84	0.62	<DL - 3.6	0.4	16	<DL - 98	18	<DL - 95	8.0
101/89	2.41	<DL - 11	0.5	53	<DL - 470	64	<DL - 395	8.9
99	0.85	<DL - 2.8	0.5	15	<DL - 111	22	<DL - 121	10
97	1.06	<DL - 2.9	0.7	14	<DL - 68	33	<DL - 173	13
87	1.86	<DL - 5.2	0.8	26	<DL - 181	48	<DL - 215	15
136	0.61	<DL - 1.7	0.8	8.7	<DL - 38	15	<DL - 63	16
110	4.01	<DL - 11	0.4	48	<DL - 369	102	<DL - 477	7.0
82	0.93	<DL - 2.3	1.3	13	<DL - 32	21	<DL - 70	26
151	0.67	<DL - 2.0	1.1	12	<DL - 54	19	<DL - 94	21
135	0.66	<DL - 1.6	1.2	10	<DL - 31	13	<DL - 26	22
149	2.05	<DL - 6.6	0.6	13	<DL - 156	75	<DL - 599	12
118	3.44	<DL - 1.2	1.7	26	<DL - 218	63	<DL - 261	34
134	0.66	<DL - 0.5	1.2	7.0	<DL - 10	12	<DL - 13	23

114	ND	-	2.1	ND	-	ND	-	41
131	ND	-	1.3	ND	-	14	<DL - 21	25
153	2.07	<DL - 6.5	0.7	11	<DL - 146	45	<DL - 236	14
132	1.36	<DL - 3.8	0.5	8.7	<DL - 47	31	<DL - 122	10
105	1.89	<DL - 3.9	1.7	19	<DL - 74	25	<DL - 113	32
141	0.78	<DL - 2.0	0.8	8.9	<DL - 34	14	<DL - 62	16
137	0.59	<DL - 0.9	0.8	8.4	<DL - 3.7	8.5	<DL - 2.1	16
130	0.61	<DL - 0.8	1.0	7.4	<DL - 8.9	ND	-	19
138/163	4.46	<DL - 13	0.5	12.5	<DL - 161	85	<DL - 427	9.9
158	0.49	<DL - 1.1	0.5	5.6	<DL - 19	7.0	<DL - 27	9.9
178	0.24	<DL - 0.3	1.4	13	<DL - 17	17	<DL - 35	26
129	0.61	<DL - 1.0	0.9	4.4	<DL - 6.1	10	<DL - 21	17
187	0.47	<DL - 1.4	0.8	9.3	<DL - 44	16	<DL - 59	16
183	0.47	<DL - 0.8	1.2	11	<DL - 19	14	<DL - 41	23
128	1.27	<DL - 3.2	0.7	8.6	<DL - 34	24	<DL - 136	14
185	0.33	<DL - 0.3	0.7	7.3	<DL - 12	7.7	<DL - 12	14
174	0.60	<DL - 1.1	1.4	12	<DL - 32	22	<DL - 63	26
171	0.43	<DL - 0.8	0.8	8.4	<DL - 22	19	<DL - 118	16
156	0.79	<DL - 1.7	0.7	7.4	<DL - 11	8.3	<DL - 23	13
201	0.95	<DL - 0.2	1.9	ND	-	ND	-	36
157	0.41	<DL - 0.5	0.8	ND	-	ND	-	16
172	0.51	<DL - 0.2	1.1	7.1	<DL - 9.1	ND	-	22
180	0.78	<DL - 1.9	1.2	13	<DL - 40	17	<DL - 96	23
193	ND	-	1.0	1.0	<DL - 3.2	ND	-	19
191	ND	-	1.2	14	<DL - 23	ND	-	24

200	ND	-	2.0	0.78	<DL - 2.8	ND	-	39
170	0.85	<DL - 1.4	1.3	13	<DL - 18	18	<DL - 139	25
190	0.53	<DL - 0.3	1.0	3.0	<DL - 3.1	13	<DL - 49	20
198	0.02	<DL - 0.2	3.4	ND	-	ND	-	65
199	0.04	<DL - 0.5	2.9	6.8	<DL - 16	ND	-	56
196	0.02	<DL - 0.3	3.3	4.3	<DL - 10	ND	-	65
189	ND	-	1.3	3.9	<DL - 4.3	ND	-	25
208	ND	-	6.2	ND	-	ND	-	120
195	ND	-	4.3	40	<DL - 45	ND	-	83
207	ND	-	7.2	ND	-	ND	-	140
194	ND	-	4.7	ND	-	ND	-	91
205	ND	-	4.5	ND	-	ND	-	88
206	ND	-	13	ND	-	ND	-	263
209	ND	-	15	ND	-	ND	-	299
ΣPCB	140	1.4 - 751	0.2-15	1839	20 - 6350	2872	88 - 9703	3-279

^astream water concentration not corrected for colloid binding

^bmethod detection limit

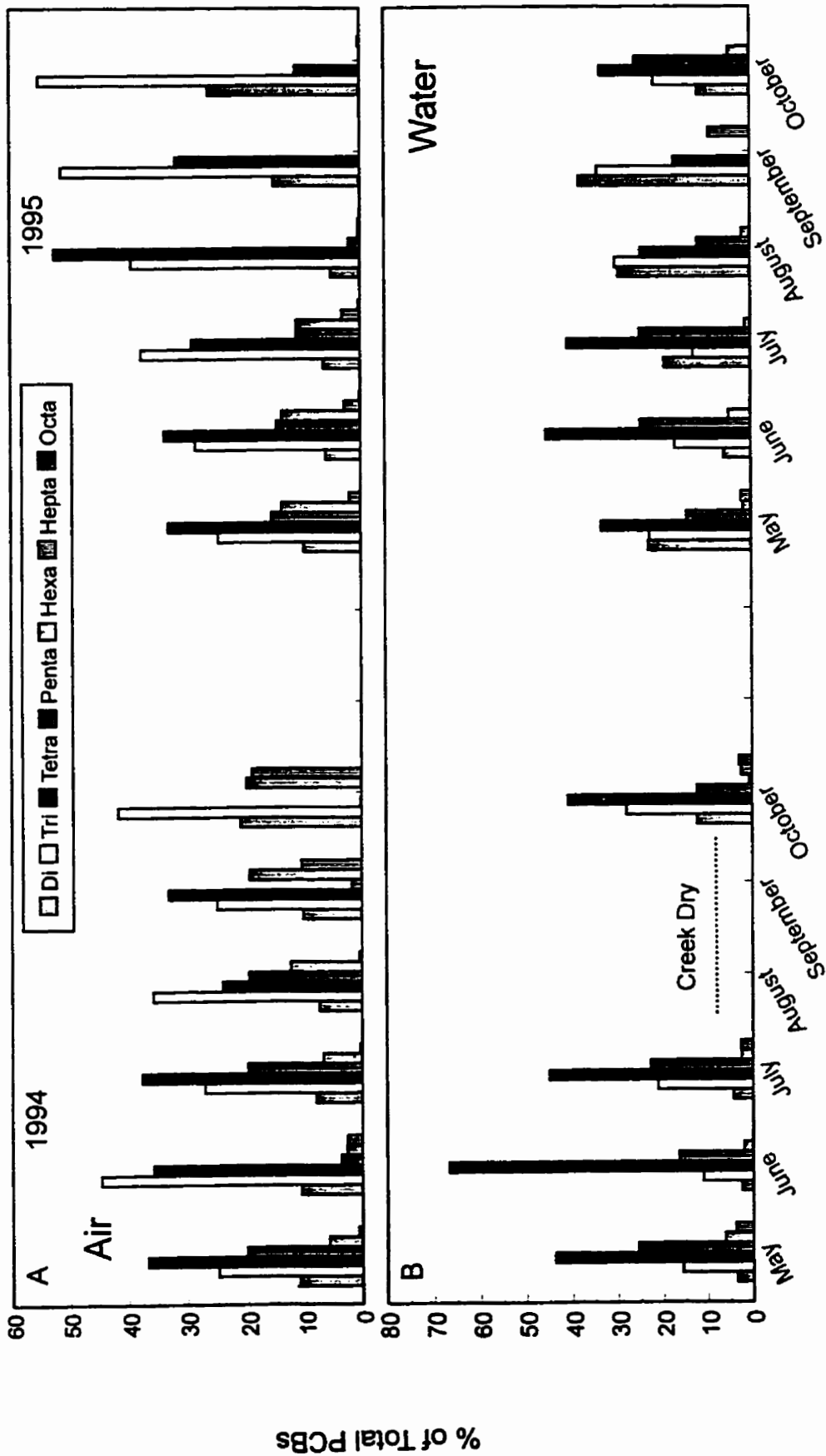


Figure 7.2 Relative contributions to total PCBs in the South Tobacco Creek Watershed.

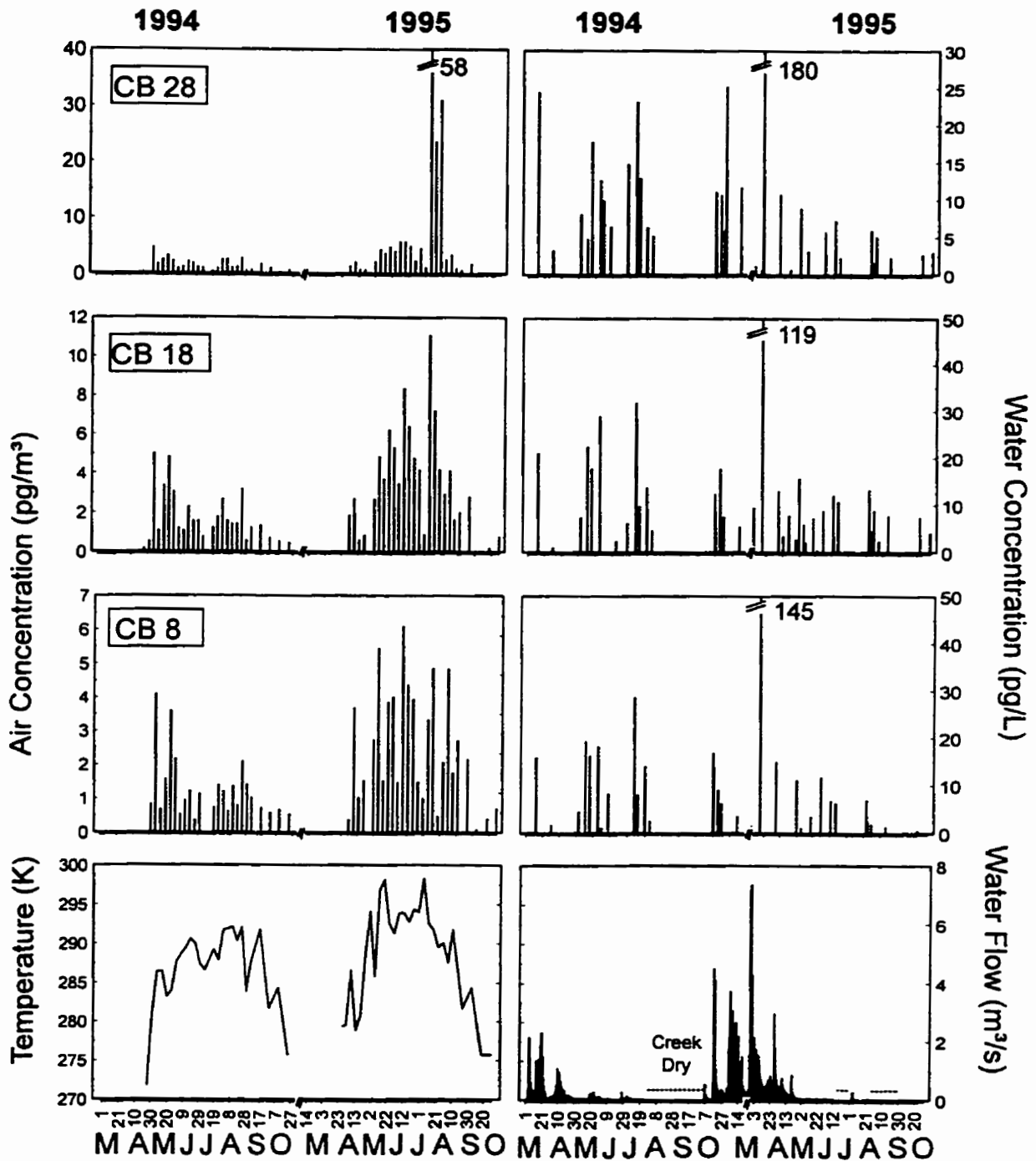


Figure 7.3 CB 8,18 and 28 concentrations in air and water in the South Tobacco Creek Watershed in 1994 and 1995. [air temperature (K) and water flow (m³/s) indicated in bottom panels]. Creek water concentrations are not corrected for colloidal contributions.

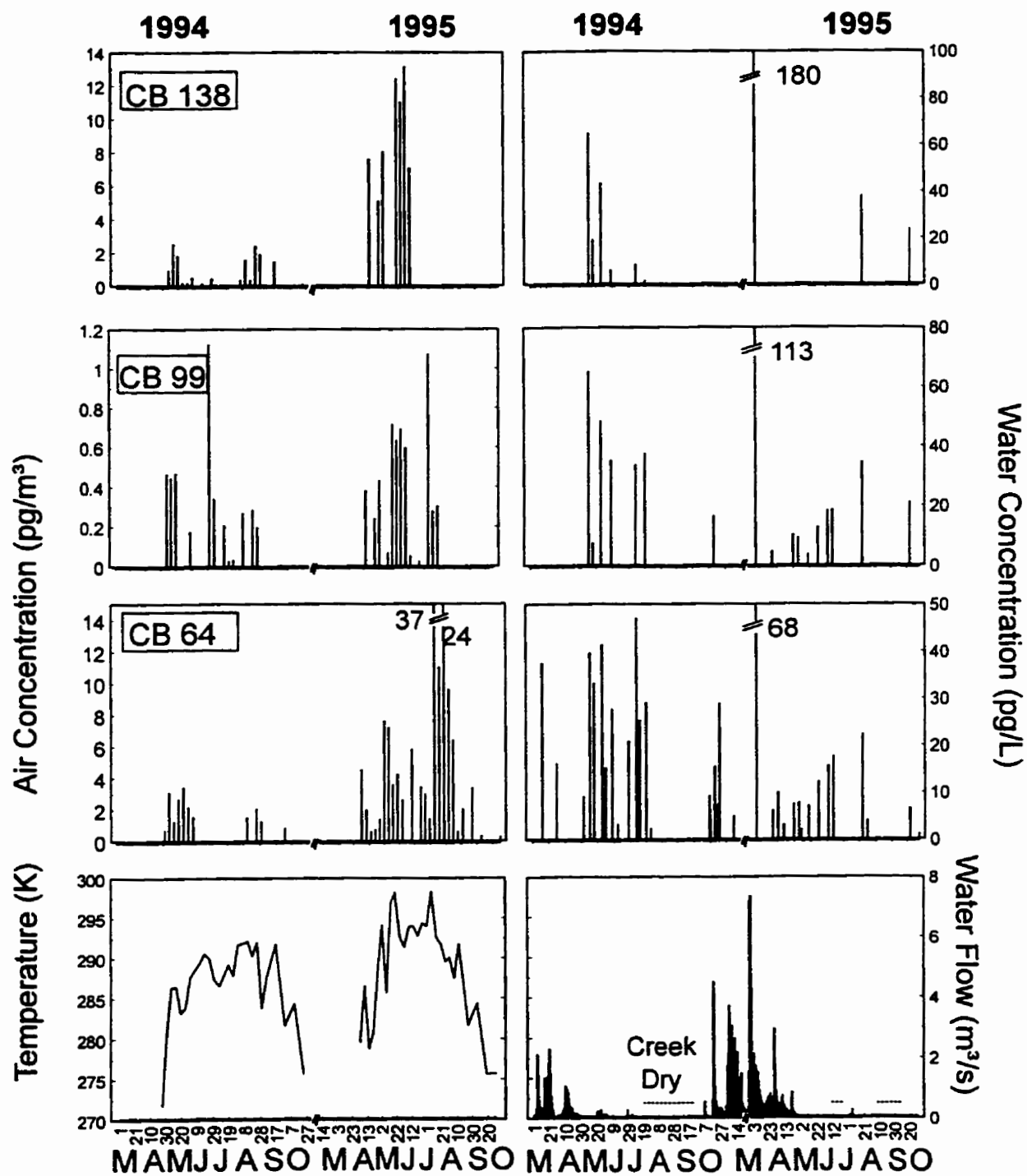


Figure 7.4 CB 64, 99 and 138 concentrations in air and water in the South Tobacco Creek Watershed in 1994 and 1995. [air temperature (K) and water flow (m³/s) indicated in bottom panels]. Creek water concentrations are not corrected for colloidal contributions.

1000 pg/L. Suspended sediments were dominated by the penta- and hexachlorinated homologs which averaged 35% and 42% of Σ PCBs, respectively. Combined contributions of the di- and trichlorinated homologs were <3% of Σ PCBs, while the tetra and heptachlorinated homologs contributed 9% and 10%, respectively.

Air concentrations of Σ PCBs ranged from 1.4 - 751 pg/m³ (Table 7.1). The tri- and tetrachlorinated congeners were the dominant homolog groups in vapour phase samples throughout the 1994 and 1995 seasons (Figure 7.2A). The highest monthly average concentration of Σ PCB in air (253 pg/m³) was observed in August 1995, which coincided with the highest average air temperature in 1995. The average monthly maximum observed Σ PCB levels in South Tobacco Creek water, however, were found in March 1995 and May and July of 1994.

Concentrations of Σ PCBs in precipitation ranged from 88 - 9703 pg/L (Table 7.1). The monthly average maximum Σ PCB concentrations in precipitation (4200 pg/L) were observed in August of 1994, during the period when South Tobacco Creek was dry. Higher concentrations in precipitation, based on monthly averages, were found throughout the 1994 sampling season than during 1995. Average annual precipitation-weighted Σ PCB concentrations were 2000 pg/L and 740 pg/L for 1994 and 1995, respectively, corresponding to the elevated PCB concentrations observed in precipitation samples during the 1994 field season. Precipitation weighted concentrations reduce the effect of sample dilution with increased volumes of precipitation thereby resulting in greater comparability between different temporal periods (Goolsby et al., 1993).

The higher chlorinated, more hydrophobic congeners were detected less frequently in both air and water samples. Air concentrations of PCBs during 1995 followed temperature patterns more closely than in 1994.

7.4.1 Air-Temperature Relationships

Specific congeners from each of the major homolog groups (di-, tri-, tetra-, penta- and hexa-; CB 8, 18 and 28, 64, 99 and 138, respectively) were chosen as representatives of the temporal patterns for each homolog group and illustrated with temperature and water flow in Figures 7.3 and 7.4. Significant correlations between PCB congener concentration and air temperature were found for a number of PCBs. Concentration:temperature relationships for most but not all PCB congeners were in good agreement with those reported by Hoff et al. (1992*b*) (Table 7.2). In general, the lower chlorinated congeners were found to correlate more closely to temperature. This may be a result of the difference between sampling stations. The South Tobacco Creek Watershed is further away from major industrial activity and urban areas than the site in southern Ontario used by Hoff et al. (1992). Hillery et al., 1997 also observed variability at a remote site on Lake Superior (Eagle Harbour). Additionally, sampling in the present study was limited to the period of May through to October, rather than throughout the entire year. In general, PCB concentrations observed in air samples from the South Tobacco Creek Watershed were similar to those at the nearest IADN site reported by Hillery et al., 1997 (Σ PCBs; 200 pg/m³, 1994; 130 pg/m³, 1995). PCB concentrations reported by Stern et al. (1997) for Arctic air samples during 1993-1994 generally were lower (1.7 - 148 pg/m³) than observed in the present study.

Table 7.2 Correlation parameters for PCBs [of the form $\log C \text{ (pg/m}^3\text{)} = b+m/T(K)$].

Congener	b ^a	m ^a	r ²	p-value	Study
8	8.4±2.5	-2383±730	0.18	<0.001	present study
18	14.8±2.0	-4175±577	0.45	<0.001	present study
28	16.3±3.2	-4619±922	0.28	<0.001	present study
	13.5±0.3	-3550±500	0.39		Hoff et al., 1992b
33	19.6±2.5	-5529±733	0.47	<0.001	present study
	18.1±0.3	-4920±560	0.51		Hoff et al., 1992b
52	9.5±3.1	-2540±891	0.10	<0.01	present study
	14.2±0.2	-3750±420	0.51		Hoff et al., 1992b
49	16.2 ±3.6	-4682±1059	0.23	<0.001	present study
	14.0±0.3	-3780±570	0.37		Hoff et al., 1992b
64	20.6±4.3	-5848±1229	0.39	<0.001	present study
99	3.5±4.3	1080±1244	0.01	<0.5	present study
	16.8±0.4	-4180±670	0.40		Hoff et al., 1992b
138	18.2±9.9	-5271±2847	0.13	<0.01	present study
151	19.4±5.5	5647±1597	0.22	<0.001	present study
	11.2±0.3	-3180±660	0.28		Hoff et al., 1992b
153	16.9±6.2	-4838±1787	0.14	<0.001	present study
	13.4±0.3	-3740±560	0.37		Hoff et al., 1992b
187	20.0±5.8	-5913±1684	0.19	<0.001	present study
	13.9±0.3	-3970±630	0.38		Hoff et al., 1992b

^a ± standard deviation

7.4.2 Sources

The maximum observed PCB concentration in ambient air was observed August 7, 1995 and much lower PCB concentrations were observed on August 1, 1995. Air-mass back trajectories for these dates were performed on a CRAY XMP computer: Atmospheric Environment Service (Dorval, PQ). Trajectories were computed at 950 mbar and the latitudes and longitudes of the air parcel over the South Tobacco Creek Watershed during the sample collection were plotted in six hour intervals backwards for a five day period, prior to the sampling events (Figure 7.5 A and B). The air mass over the South Tobacco Creek Watershed during the sampling event when very high Σ PCB concentrations were observed originated in the southern US (Figure 7.5A). The air mass present during the August 1, 1995 sampling interval had originated from the west, having settled over the Dakotas. In general, low PCB concentrations were observed in air samples collected during periods where air masses originated from the north and west, however, masses moving from the south, corresponded to consistently elevated PCB levels.

7.4.3 Air-water Gas Exchange

Air-water gas exchange calculations using both the two-film and surface renewal models were performed using paired water and air data from the South Tobacco Creek Watershed (Table 7.3). Both models have been described in detail elsewhere (Bidleman and McConnell, 1995; McConnell et al., 1993; Schwarzenbach et al., 1993; Baker and Eisenreich, 1990) and are described briefly here.

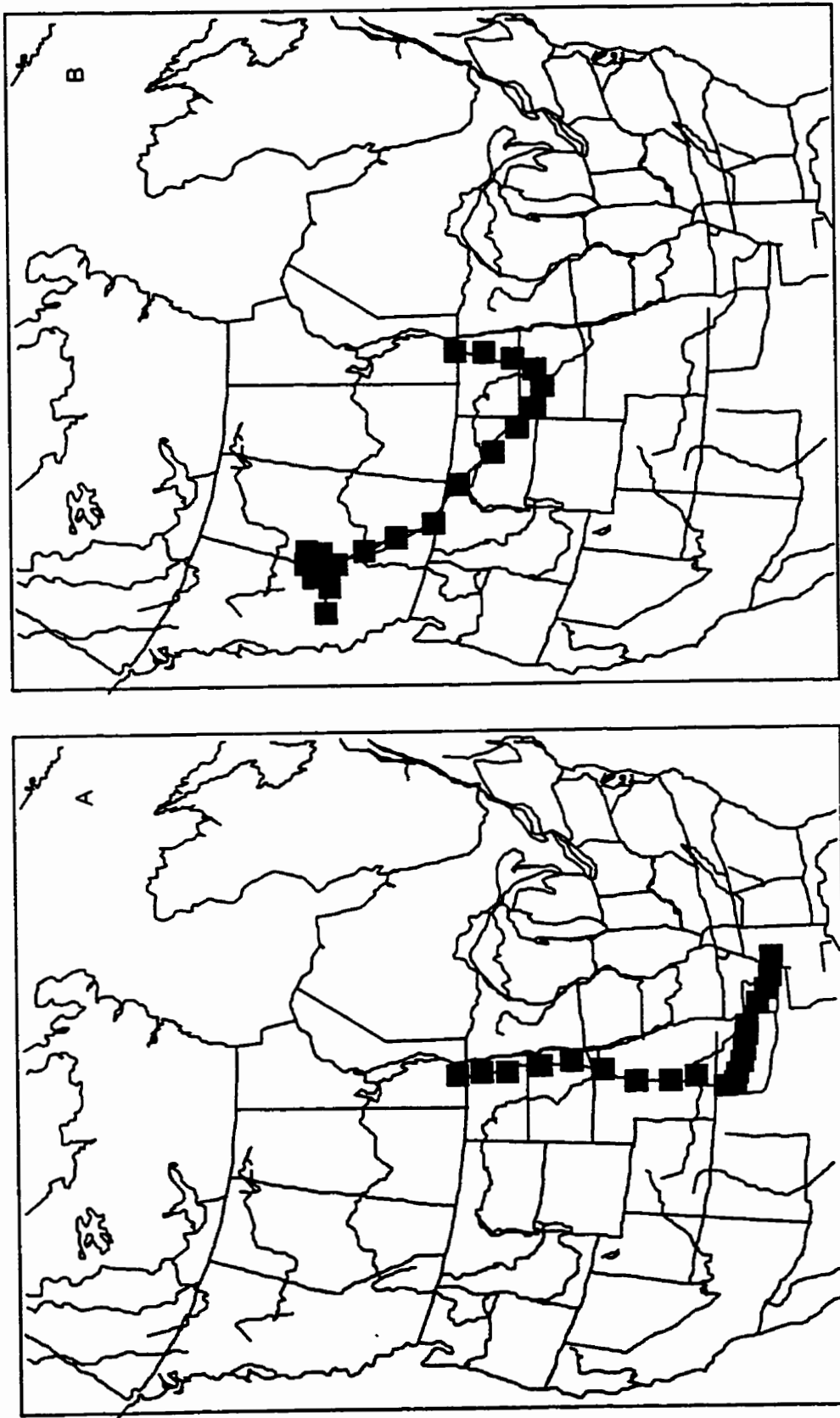


Figure 7.5 Air mass back-trajectories to the South Tobacco Creek Watershed. A) elevated PCB concentrations observed [August 1, 1995 sample], B) low PCB concentrations observed [August 7, 1995]. Points represent six hour intervals.

Table 7.3 Average monthly conditions during paired air-water sample collections in the South Tobacco Creek Watershed (1994-1995).

Month	Wind Speed (m/s)	Water Temperature (°C)	Water Flow (m/s)	Water Depth (m)
May	3.22	10.06	0.42	0.22
June	2.12	19.69	0.06	0.08
July	2.24	17.85	0.02	0.04
August	3.36	17.33	0.002	0.02
September	5.10	18.66	0.09	0.08
October	1.98	4.3	1.04	0.22

Diffusivity parameters are used in both the two-film and surface renewal models, to account for molecular diffusion of an organic chemical through both the water and air sides of the boundary layer. The water side transfer velocity (v_w) is proportional to the diffusivity parameter (D_w) using the two-film model, however, in the surface renewal model, v_w is proportional to the square-root of the diffusivity component (Eisenreich et al., 1997). The two-film model uses diffusivity in combination with wind speed to estimate the water side transfer velocity. The wind speed taken at the 10 m height (u_{10}) is used in the equation:

$$v_w(\text{PCB}) = (D_w(\text{PCB}) \cdot (4 \times 10^{-5} u_{10}^2 (\text{m/s}) + 0.0004)). \quad [1]$$

In a shallow stream, however, the water current and depth are thought to more greatly affect chemical movement in the water layer. Therefore, the water-side transfer coefficient in the

surface renewal model is estimated using the relationship (Schwarzenbach et al., 1993):

$$v_w(\text{PCB}) = [D_w(\text{PCB})(\text{cm}^2/\text{s}) \cdot \text{water velocity}(\text{cm}/\text{s})/\text{water depth}(\text{cm})]^{0.5} \quad [2]$$

For both models the air side transfer velocity (v_a) for organic chemicals is related to wind speed taken at the 10 m height (u_{10}) (Schwarzenbach et al., 1993) and has been determined for water molecules in the air above the boundary layer.

$$v_a(\text{H}_2\text{O}) \approx 0.2u_{10}(\text{m}/\text{s}) + 0.3 \text{ (cm/s)} \quad [3]$$

The air side transfer velocities for organic chemicals are calculated by extrapolation using diffusivity ratios with the air side transfer velocities for water (equation 3) (Schwarzenbach et al., 1993):

$$v_a(\text{PCB}) = v_a(\text{H}_2\text{O})[D_a(\text{PCB})/D_a(\text{H}_2\text{O})]^{0.67} \quad [4]$$

and diffusivity of the organic chemical is estimated using the molecular weight ratio:

$$D_a(\text{PCB})/D_a(\text{H}_2\text{O}) \approx [\text{MW}(\text{H}_2\text{O})/\text{MW}(\text{PCB})]^{0.5} \quad [5]$$

Both models combine water and air side contributions to determine the overall transfer velocity (v_{tot}) using the relationship:

$$1/v_{tot} = 1/v_w + 1/v_a' \text{ [where } v_a' = v_a(H/RT)\text{]} \quad [6]$$

using temperature corrected Henry's Law Constants (H) and where R = the Gas Constant and T is temperature (K).

Flux (N) estimates were calculated using the overall mass transfer velocity with the equation:

$$N = v_{tot}(C_w - C_a/K'_H) \text{ where } K'_H = H/RT. \quad [7]$$

PCB concentration in water is represented by C_w and PCB air concentration is C_a .

In general, export of PCBs via volatilization from the South Tobacco Creek was found to occur for most congeners throughout the period of water movement using both models (Table 7.4). PCB movement via gas exchange between South Tobacco Creek and the overlying atmosphere was dominated by the tetrachlorinated congeners. Seasonal flux patterns are similar between the di- and trichloro- groupings, as are the tetra- and pentachloro- congeners. A net deposition of the hexa- and heptachlorinated congeners was observed. Deposition of the octachlorinated congeners occurred during 1995 (Table 7.4).

Comparisons between flux estimates calculated using the two-film model with results from the surface renewal model consistently showed greater volatilization of PCBs when the surface renewal model was used (Table 7.4). However, the surface renewal model is thought to under-predict volatilization losses of organic compounds from water surfaces by 2 to 3 times based on field trials (Schwarzenbach et al., 1993). These results suggest that the two-

film model greatly underestimates gas exchange across the air-water boundary of shallow streams. Volatilization fluxes determined in the present study were within the range of those from the Great Lakes, however, maximum fluxes were higher in the present study (Table 7.5). Flux estimates for individual congeners in the present study using both models were within an order of magnitude of Lake Baikal results estimated using the two-film model (McConnell et al., 1996).

Table 7.4 Average^a PCB air-water gas exchange^b (ng/m²·d) across the South Tobacco Creek. (±S.D. of the six monthly averages).

Homolog	1994		1995	
	Two-film	Surface Renewal	Two-film	Surface Renewal
Di-	-3.4±2.1	-21±14	-8.4±3.9	-40±16
Tri-	-4.4±1.5	-22±9.3	-3.1±1.5	-15±6.7
Tetra-	-12.5±6.5	-41±25	-13±12	-49±54
Penta-	-3.2±1.9	-7.2±4.8	-3.8±5.0	-9.0±12
Hexa-	0.03±0.09	-0.11±0.16	1.3±1.8	1.9±2.9
Hepta-	0.03±0.05	0.05±0.07	0.2±0.3	0.4±0.5
Octa-	0±0.0005	0.0±0.0006	0.03±0.04	0.04±0.05
Total	-23±12	-91±52	-27±15	-111±78

^aaverage values based on samples collected May - October

^bnegative values indicate volatilization; positive values indicate deposition reported

One reason for higher fluxes in the present study is that water and air temperatures were higher than reported for other regions (Table 7.5). This contributes to increased volatilization from the water surface of the South Tobacco Creek relative to cold lake waters.

Table 7.5 Comparison of Σ PCB gas exchange with other studies.

Location	Flux (ng/m ² ·d)	Wind Speed (m/s)	Temperature (°C)	Reference
Lake Superior	19 - 141	calm - 5	0 - 2.4	Baker and Eisenreich, 1990
Green Bay	13 - 1300	1 - 6.5	6 - 15.3	Achman et al., 1993
Bering Sea	-120 - 1.3	5 - 7	0 - 10	Iwata et al., 1993
Chukchi Sea	-50 - -25	7	0	Iwata et al., 1993
Gulf of Alaska	-49 - 2.7	5	10	Iwata et al., 1993
North Pacific	-100 - 8.5	5	10 - 20	Iwata et al., 1993
Lake Superior	55 - 80 ('88)	4.1 - 6.5	14.7	Hornbuckle et al., 1994
	35 - 110 ('90)	3.3 - 4.9	15.1 - 21.7	
	-40 - -16 ('92)	3.5 - 5.7	1.8 - 2.3	
Lake Baikal	0.47 - 88	0 - 10	0 - 2.4	Iwata et al., 1995

Experimental Lakes

Area				
L110	11	1.4	1.4	
L227	6	1.4	1.4	
South Tobacco Creek	-14 - 108 (2-Film)	0.6 - 6.2	2.6 - 25.1	Present study
	-19 - 313 (Surface Renewal)			

*not reported

Wind speeds, however, were within the range of reported values. H values were corrected for temperature using linear regression of slopes previously reported (McConnell et al., 1996, Achman et al., 1993).

An additional confounding factor in this study is the sampling location of air samples. Ambient air sampled from an overland site may have resulted in an under-estimation of PCB loadings in the air immediately above the water surface. A comparison of PCB levels in ambient air between overland and over-water locations has shown that significantly lower PCB concentrations are observed in overland sample collections (Hornbuckle et al., 1993). An under estimation of PCB loadings in ambient air used in the gas exchange calculations will bias flux estimates toward greater PCB loss via volatilization from the water surface.

7.4.4 Mass Balance

To further evaluate the predicted volatilization losses, a mass balance determination for representative PCBs in the South Tobacco Creek Watershed was performed. Although sampling was limited to a six month period (spring - autumn) of both years, PCB loading via precipitation, dryfall and gas exchange were assumed to be representative of the entire year.

Deposition of PCBs via precipitation was calculated for the entire South Tobacco Creek Watershed using the relationship between concentrations and amount of precipitation collected. Precipitation samples collected at one location represented PCB flux via precipitation (N_{pptn}) to the entire watershed. A correction for surface area and duration of sample collection was included (Eisenreich and Strachan, 1992).

$$N_{pptn} = \frac{C_{TP} \cdot \text{Precipitation Volume (L)}}{[\text{S.A}] \cdot [\text{days over which sample was collected}]} \quad \text{ng/m}^2 \cdot \text{d.} \quad [8]$$

PCB concentration in precipitation (C_{TP}) was the sum of both particulate and dissolved phases. Surface area is indicated by S.A. (m^2).

PCB deposition associated with dryfall (N_{dry}) was estimated using the relationship (Eisenreich and Strachan, 1992):

$$N_{dry} = C_{TA} \cdot \phi \cdot V_d \cdot S.A. \quad \text{ng/m}^2\text{-d.} \quad [9]$$

Total PCB concentrations in ambient air (Σ vapour + particulate) were used to estimate dry deposition to the watershed. The PCB fraction associated with the particulate phase ϕ , was determined by using temperature corrected subcooled liquid vapour pressure (P°_L) (Murphy et al., 1987) in the Junge-Pankow relationship (Hinckley et al., 1990; Eisenreich and Strachan, 1992):

$$\phi = \frac{(c \cdot \theta)}{P^{\circ}_L + (c \cdot \theta)} \quad [10]$$

where $c = 17.2 \text{ Pa}\cdot\text{cm}$, θ is the surface area of particles per unit volume of air (cm^2/cm^3). θ was estimated to be 3.5×10^{-6} , representative of background plus local sources (Bidleman, 1988). Subcooled liquid vapour pressure values were temperature corrected (Hinckley et al., 1990).

Deposition of PCBs from atmospheric compartments directly to South Tobacco Creek water will occur in addition to deposition to the land surface of the watershed. The mass of PCBs deposited on soils and plants eventually could be transported to the stream via surface

runoff (Dolan et al., 1993) although revolatilization back into the atmosphere may be a much more important pathway. PCB deposition to the 70 km² land surface of the South Tobacco Creek Watershed via precipitation and dryfall is three orders of magnitude greater than the amount deposited directly to the water surface (Table 7.6). Of the three atmospheric pathways; precipitation, dryfall and gas exchange, gas exchange is dominant. Estimates of PCB export via discharge from the watershed via stream water flow are within an order of magnitude of gas exchange export (volatilization) during both 1994 and 1995 (Table 7.6).

Discharge estimates for 1995 were recalculated using both suspended sediment and dissolved water concentrations for congeners 8, 18, 28, 64, 99 and 138, where suspended sediment data were available. For CBs 8, 18, 28, 64 and 99, there was <1% difference in total discharge estimates. However, discharge estimates of CB 138 increased by 13% when suspended sediment contributions for June and July, 1995 were included. This implies that the hexachlorinated congeners were underestimated in discharge estimates based on dissolved phase alone.

Export of CBs 8, 18, 28, 64, 99 and 138 through stream discharge ranged from < 1% to 15 of the amount deposited to the entire watershed via precipitation, except for CB 99 during the 1995 field season where precipitation inputs were extremely low. Export of these congeners through volatilization from the water surface generally ranged from <1% to 10% of the amount entering the entire watershed during rain events.

Mass balance determinations for CB 8, 18, 28, 64, 99 and 138 were performed by including the contributions of precipitation and dry deposition to the entire watershed, gas exchange movement across the air-water interface and losses via discharge in South Tobacco

Creek. A net deposition of PCBs was determined for each congener during both field seasons (Table 7.6). Greater deposition of the lower chlorinated congeners occurred in the 1994 field year than in 1995, however, the reverse was observed for the higher chlorinated congeners. Combined export (volatilization + discharge) was estimated to represent <1% to 23% of the total precipitation inputs, with the exception of PCB 99 during 1995, where discharge estimates were high and precipitation contributions were low. Export via volatilization and discharge combined ranged from 1% to 22% of total precipitation and dryfall inputs to the watershed.

In addition to air-water gas exchange which was estimated in this study, air-plant gas exchange and dryfall contributions may have led to increased PCB levels in vegetation. Air-plant gas exchange has been shown to occur for plant species exposed to hydrophobic organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and PCBs (Tremolada et al., 1996; Bacci et al., 1990). In recent studies, accumulation of contaminants in vegetation, in addition to air-plant gas exchange has been shown to be an important pathway (McLachlan et al., 1995; Tolls and McLachlan, 1994). Elevated PCBs in plant tissue, especially tree leaves and pollen that have been washed into runoff may contribute to higher than expected contaminant loadings in the surface water draining a given watershed, based on surface water and atmospheric samples alone (Jeremiason et al., 1997). Jeremiason et al. (1997) found that watershed inputs are important for all surface waters. In situations where large watershed area to water surface ratios exist, such as found in river systems, the watershed inputs may be extremely important (Jeremiason et al., 1997).

Table 7.6 Seasonal flux estimates (mg) of representative PCBs to the South Tobacco Creek water; (Fluxes to land surface of watershed indicated in parentheses). Volatilization flux expressed as a negative.

Congener	Dry Deposition		Precipitation		Gas Exchange	
	1994	1995	1994	1995	1994	1995
8	0.0 (0.0)	0.0 (0.0)	4.5 (5900)	1.1 (2600)	-61	-180
18	0.02 (29)	0.04 (56)	5.9 (7700)	1.3 (2300)	-46	-230
28	0.03 (34)	0.09 (130)	5.1 (660)	1.4 (2800)	-15	-80
64	0.0 (0.0)	6.0 (8300)	5.4 (7000)	0.90 (1600)	-16	-22
99	4.8 (6300)	11 (15000)	2.0 (2600)	0.17 (140)	-1.7	-4.1
138	0.81 (1100)	9.4 (13000)	7.5 (9800)	0.60 (290)	0.3	8.9

Congener	Stream Discharge		Net Flux to Entire Watershed	
	1994	1995	1994	1995
8	27	320	5800	2100
18	33	290	7700	1800
28	51	400	630	2500
64	85	160	6900	9700
99	10	830	8900	14000
138	7.8	38	11000	13000

Elevated levels of PCBs in the water column of the South Tobacco Creek may additionally result from resuspension of contaminated sediments. Bottom sediment contributions of PCB loadings to South Tobacco Creek water were not determined in this study. However, suspended sediment contributions were shown to affect discharge estimates for hexachlorinated congeners, based on a limited number of samples. This process of PCB movement from plant detritus and soil, to the stream, would, in part, explain why net volatilization of PCBs was relatively high compared to lakes for the majority of PCBs from the water surface despite the fact that there was no local source of these compounds. Jeremiason et al. (1997) have reported that the potential exists for evaporation and evapotranspiration to occur, which would result in increased PCB concentrations in runoff relative to precipitation inputs. In the present study, evaporation losses directly from the creek may have lead to the high Σ PCB concentrations in stream water samples.

Wind speed is an important factor in the estimation of gas exchange across the air-water interface. Hoff et al. (1996) have reported that the error associated with mass transfer of organic chemicals due to wind speed is 50%. Wind speed differences had similar effects on PCB gas exchange estimates for both the two-film and surface renewal model. Additionally, both models are highly temperature dependent through the effect of temperature on H. The error associated with H values for PCBs has been reported to be 30% (Hoff et al., 1996). Changes to water flow and depth, parameters which are used in the surface renewal model, affected gas exchange estimates to a lesser degree than wind speed and H differences.

7.5 Conclusions

PCB concentrations in stream water were not correlated with water flow, however, air concentrations were correlated with temperature via Clausius-Clapeyron type relationships. The surface renewal model over predicted volatilization of PCBs from the South Tobacco Creek relative to the two-film model, although the surface renewal model is generally thought to under-predict gas exchange movement. Based on these results, the two-film model dramatically under predicts gas exchange of PCBs in shallow flowing waters. Higher fluxes were observed from the South Tobacco Creek than for large lakes, however, this may be explained by resuspension of sediment and detritus in the water contributing to elevated PCB levels in the water column or by evaporation/evapotranspiration from the water. Additionally higher temperatures in the stream water than observed in large lakes may have contributed to these elevated fluxes.

Overall deposition of PCBs to the South Tobacco Creek occurred during both years of this study based on PCB contributions via precipitation and dryfall to the entire watershed. Of the three atmospheric pathways considered; precipitation, dryfall and gas exchange, the most important pathway was gas exchange if fluxes directly to the water column alone were considered. The watershed is exporting PCBs via volatilization at a similar rate to that of stream discharge losses.

8. GENERAL DISCUSSION

8.1 Surface Water

8.1.1 Temporal Trends

Pesticides were found in southern Manitoba surface waters throughout the duration of the four-year study. In general, maximum pesticide concentrations were observed during regional application periods (May - July). Maximum concentrations of MCPA, dichlorprop and bromoxynil, three of the most frequently applied herbicides in southern Manitoba, were detected in July in both the South Tobacco Creek and in the larger river systems. Elevated pesticide levels also were observed in creek water during the spring melt and runoff period in the small South Tobacco Creek Watershed, where detailed studies were performed. In contrast, pesticide concentrations in the Red River and its major tributaries did not show increased pesticide concentrations during the spring thaw period. A spring flush of pesticides during snow melt and runoff has been shown to occur in the midwestern US states, similar to observations in the South Tobacco Creek watershed (Thurman et al., 1991).

Observed differences in temporal trends between the South Tobacco Creek Watershed and the Red River system may be due to differences in water discharge levels or to timing of sample collection. The potential exists for the dilution of pesticide residues during major flow periods. The river systems had larger water discharge during the spring melt than did the

South Tobacco Creek, which may have resulted in dilution of pesticide levels to below method detection limits. Additionally, for logistical reasons, sampling of the South Tobacco Creek commenced earlier in the field season than sample collection in the Red River and its tributaries, each year of the study. Initial water samples were collected from the river systems between late April and early May, seasonally, which may have resulted in missing the detection of the pesticides lost during the earlier spring flush period. At the South Tobacco Creek station, however, water samples were collected during the first water movement in the spring, generally in early March.

Pesticides are generally present at maximum concentrations in surface waters during and extending beyond regional application times. Atrazine was present at maximum seasonal concentrations in the Minnesota River during the first major discharge event after herbicide application was completed (Schottler et al., 1994). Similarly, Thurman et al. (1992) observed that cyanazine was present in US midwest reservoirs during the postplanting period. Both alachlor and metolachlor concentrations have been shown to decrease between summer and autumn sampling events (Pereira and Hostettler, 1993). Phenoxyacid and phenolic herbicides also show seasonality, with elevated concentrations in surface waters corresponding to post application periods (Morgensen and Spliid, 1995).

Although atrazine was not used within the South Tobacco Creek Watershed throughout the duration of this study, it was used to a minor extent in the rest of southern Manitoba. Atrazine was detected, however, in water from all of the sampling locations in this study. In South Tobacco Creek, a strong seasonal variation in atrazine levels was observed at low concentrations during the preplanting period, with maximum concentrations occurring

in June. In the larger river systems, a similar seasonality in atrazine levels was found. These results are consistent with observations from studies elsewhere in North America, where atrazine concentrations in surface waters correspond to regional use periods (Senseman et al., 1997; Larson et al., 1995; Schottler et al., 1994; Thurman et al., 1992).

During the four-year study, pesticide levels were not correlated to water flow in the South Tobacco Creek, in the Red River or its tributaries. Water flow, however, was correlated with the nutrients total nitrogen and total phosphorus ($r^2=0.42$ and 0.47 , respectively) in the South Tobacco Creek. This correlation suggests that surface runoff is an important source of nutrient loadings to creek water. Similar correlations between nutrient levels and water flow were not observed for the Red River or its tributaries, however, there were few nutrient data for the river systems, limiting our ability to determine accurate correlations. Similar to the pesticides, there was no correlation between PCB levels and water flow in South Tobacco Creek. The lack of correlation between pesticides and water flow indicated that there were sources other than surface runoff from treated fields contributing to pesticide levels in creek water. Although surface runoff from treated fields has traditionally been considered the major loss mechanism for pesticides, this study indicated that there were other possible routes of contamination, such as atmospheric deposition. In this respect, the results differ from studies in the US midwest, although other studies may not have had an atmospheric component.

PCBs were measured in water samples collected from the South Tobacco Creek as a means of comparing current use products with chemicals that are solely present due to atmospheric transport and deposition. There is no known source of PCBs in the South

Tobacco Creek Watershed, but they were detected in creek water. No seasonal trend was observed for PCBs in creek water, in contrast to the observed seasonality established for pesticides in the rivers and creek under investigation. Maximum PCB concentrations did, however, occur during the high flow period in 1995, indicating that runoff contributions from within the watershed may be an important source of PCBs to South Tobacco Creek. The lower chlorinated congeners were the largest contributing groups to Σ PCB levels in surface water samples collected. Surface water samples collected in the Great Lakes region have shown that the lower chlorinated congeners (tri- and tetrachlorinated) are large contributors to dissolved phase PCB loadings of lake water (Hornbuckle et al., 1995; Achman et al., 1993; Baker and Eisenreich, 1990). The high proportion of lower chlorinated congeners in South Tobacco Creek is consistent with inputs derived solely from long range transport and deposition.

8.1.2 Riverine Inputs from Other Regions

Alachlor was frequently detected in the Red River at each sampling station during each year of the study, although it is not registered for use in Canada. Maximum alachlor concentrations (50.9, 21.8, 121.9 ng/L, 1993, 1994 and 1995, respectively) were found at the Emerson site, where the Red River enters Canada. Alachlor, however, was not routinely observed in the tributaries of the Red River or the South Tobacco Creek. With no Canadian tributary input of alachlor, its presence in the Red River can be explained by inputs from the neighbouring states prior to the Red River reaching the Canada-US border. Although it was not used in southern Manitoba, the discharge of alachlor in the Red River at Selkirk was higher than discharge loads of the phenoxyacid herbicides, or bromoxynil. The high rate of

alachlor discharge compared to the rate for local high use herbicides may be due to its greater persistence, making it available for riverine transfer as was observed in the Mississippi River and its tributaries (Pereira et al., 1992).

Although chlorpyrifos use was low in southern Manitoba during the period of study, it was detected in both South Tobacco Creek and Red River water. Maximum chlorpyrifos concentrations were observed later in the field season (late July - August) than the herbicides, corresponding to late season insect control. Despite its long term use, chlorpyrifos has not been previously reported in southern Manitoba river waters, which may be due to high detection limits in previous monitoring programs, compared to the present study (Currie and Williamson, 1995). Chlorpyrifos has, however, been reported in rivers from other Canadian regions (Berryman and Giroux, 1994; Maguire and Tkacz, 1993). Chlorpyrifos levels were elevated in the Red River at Selkirk, downstream of the inputs from the City of Winnipeg. Municipal insect control programs in Winnipeg and in the rural towns along the Red River (e.g., Emerson, Morris, Ste. Agathe) may have contributed to chlorpyrifos loadings in the Red River.

8.1.3 Water Quality Guidelines

Although herbicides were present in rivers and streams in southern Manitoba throughout the study, they were present at concentrations well below Canadian water quality guidelines for the protection of freshwater aquatic life, where such guidelines exist. Chlorpyrifos was present infrequently in Manitoba surface waters, however, it was detected at concentrations exceeding draft water quality guidelines for the protection of freshwater aquatic life.

8.2 Atmospheric Compartments

8.2.1 Temporal Trends

Locally applied pesticides were detected in both the air and precipitation samples collected in the South Tobacco Creek Watershed. Although there was only one sampling site, it was located centrally within the watershed and assumed to be representative of atmospheric contributions via wet and dry processes to the entire watershed. Results from IADN shows that air and precipitation levels of persistent organochlorine compounds are relatively uniform over large areas (Hillery et al., 1997). Prior to application periods, pesticide concentrations were below detection limits. Pesticide concentrations increased to maximum seasonal levels during periods of local use in both rainfall and air samples. Pesticide concentrations rapidly decreased in both atmospheric compartments once regional applications ceased each year. Elevated levels of pesticides in atmospheric compartments during periods of use have been reported in the literature (Chevreuil and Garmouma, 1993; Nations and Hallberg, 1992; Woodrow et al., 1990; Richards et al., 1987).

Due to its extremely minor use relative to the phenoxyacid or dinitroaniline herbicides, concentrations of atrazine observed in rainfall and air samples were lower than observed for locally used products. Air and precipitation levels of atrazine increased in South Tobacco Creek with maximum concentrations occurring in June of each year. A reduction in atrazine levels were observed following use periods. Atrazine was not applied within the South Tobacco Creek Watershed during any year of this study, however, it was present in both precipitation and air samples collected within this watershed. Regional atrazine application,

however, is known to occur in southern Manitoba.

Similarly PCBs, which have no known source in the South Tobacco Creek Watershed, were observed in air and precipitation samples. Maximum PCB concentrations in precipitation were observed in August 1994, however, air concentrations were highest during August 1995. The lower chlorinated tri- and tetrachlorinated congeners contributed the largest percentage of the homolog groups, similar to surface water congeners.

8.2.2 Long Range Transport

Long range transport of chemicals into the South Tobacco Creek Watershed from distant locations has been shown in this study. Maximum atrazine concentrations were observed in air samples during June sampling events. Air mass back-trajectories were performed for these periods of elevated atrazine concentration. Air mass movements into the South Tobacco Creek Watershed from the south, passing over the US midwest, corresponded to maximum atrazine levels in air. Atrazine is widely used in the midwestern region of the US, during June, for weed control on corn. This movement of atrazine from the US midwest into southern Manitoba indicates the large airshed for this chemical.

Air mass movements originating in the south were also found to correspond to increased PCB levels in South Tobacco Creek air. Air masses originating north and west of the South Tobacco Creek Watershed did not result in elevated PCB levels. These data indicate that a source of PCBs is present in the southern or midwestern US. Hoff et al. (1992*b*) similarly observed increased air concentrations of PCBs corresponding to air masses originating in the southern US or to air passing over urban areas in the north.

8.2.3 Correlations

Although no seasonal correlation was observed for PCBs in precipitation, relationships between air temperature and PCB concentration were established which may reflect the sources of PCBs. Good correlations were found for the lower chlorinated compounds. In general, slope and intercept values were similar to those reported by Hoff et al. (1992*b*) for di- tri- and tetrachlorinated biphenyls in the Great Lakes region, however, as chlorination increased, compatibility with previous work was reduced.

Clausius-Clapeyron type plots for atrazine were developed to assess correlations between air temperature and atrazine concentration. No significant relationships were established with this herbicide although it is present in air due to transport into the South Tobacco Creek Watershed from other regions of use.

The above trends can be explained by volatilization of a chemical from local surfaces (Hoff et al., 1992*b*). Thus, PCBs are present in the South Tobacco Creek watershed, associated with plant, soil or other surfaces and volatilize during periods of elevated temperature. The poor correlation of atrazine with temperature can be explained by assuming that current uses of the product dominate airborne concentrations, rather than volatilization from local surfaces.

Although atrazine is a persistent current use herbicide, it is much less persistent than the PCBs (Mackay et al., 1992; Wauchope et al., 1992). In the South Tobacco Creek Watershed, PCB concentrations in the air were more consistent throughout the field season relative to those of current use products, which, by contrast, were present in the atmosphere at elevated levels during a brief period of the agricultural season. Vapour pressures and H

values of the lower chlorinated PCBs (Hoff et al., 1996; Eisenreich and Strachan, 1992) are higher than values for atrazine, indicating greater volatility (Wauchope et al., 1992). These data are consistent with fugacity ratios observed in this study for the lower chlorinated PCBs (e.g., CB 18: 1.3 - 84), which indicate a volatilization flux. Conversely, atrazine ratios indicated a depositional flux (1.1×10^{-5} - 0.04). The air and water fugacity ratios of PCBs indicated that PCBs are nearer to equilibrium than atrazine in this study. Because PCBs were nearer to equilibrium, this indicates that volatilization off of local surfaces is a dominant process. In comparison, atrazine is further from equilibrium which indicates that another process is dominant.

8.2.4 Flux

Atmospheric deposition flux estimates to terrestrial and aquatic systems have not generally been reported for current use pesticides, research emphasis has been placed on the older organochlorine insecticides and PCBs. Atrazine fluxes via wetfall in the South Tobacco Creek Watershed were similar to observed values in Germany and Switzerland, but lower than deposition rates in the Great Lakes region (Trevisan et al., 1993; Capel et al., 1991; Buser, 1990). Gas absorption estimates of atrazine in the present study were similar to results reported for a lake in a remote region of northwestern Ontario (Muir and Grift, 1995). Atrazine deposition estimates via gas exchange in the Great Lakes region were higher than observed in the South Tobacco Creek Watershed (Schottler and Eisenreich, 1997).

Many gas exchange estimates have been performed in the Great Lakes with PCBs. In general, volatilization fluxes of PCBs have been observed (Hornbuckle et al., 1994; Achman et al., 1993; Baker and Eisenreich, 1990), similar to observations in the South

Tobacco Creek. Fluxes across the air-water interface of the South Tobacco Creek were within the range of values reported by other researchers, however, maximum fluxes were higher in the present study. These results may reflect the higher water temperatures observed in the South Tobacco Creek than reported for large cool lakes. Greater losses via volatilization were estimated for the lower chlorinated PCBs using the surface renewal model, than by using the two film model.

Gas exchange estimates for the phenoxyacid herbicides were not possible in this study due to the lack of accurate physical property data for these chemicals. For example, the phenoxyacid herbicides may be present in their protonated or ionized form, in addition to ion pairs (salt) and each form of these products will have different vapour pressures resulting in differences to gas exchange estimates. This lack of knowledge on the specific forms of the products in the environment needs to be addressed to enable further examination of the movement of these chemicals through the atmosphere.

There are a number of errors associated with the estimation of gas exchange across the air-water interface. For example, large errors are associated with estimates of temperature related H values (Hoff et al., 1996) (Table 8.1) and with wind speed differences over a 24 h period, which are used in the estimation of the air side mass transfer. Error estimates of H for atrazine are larger than for PCBs because there are no data available on the temperature dependence of atrazine. The largest estimated source of error used in dry deposition calculations is for particle depositional velocity (v_d) (Hoff et al., 1996) (Table 8.1).

Table 8.1 Uncertainty in predicting atmospheric inputs into surface waters for PCBs and atrazine (Hoff et al., 1996).

Process	Parameter	Estimated Error (%)
Gas exchange	v_{tot}	50
	- H	30 ^a
	- T	10
	v_w - water velocity	10
	- water depth	10
	v_a - wind speed	30
	C_a	20
	C_w	10
Dry deposition	ϕ	40
	V_d	100
	C_a	20

^a no data were available for temperature dependence of atrazine, therefore H was based on average temperature dependence of chlorpyrifos, trifluralin and α and γ HCH (Chernyak et al., 1996)

9. CONCLUSIONS

Although surface runoff has traditionally been considered the major route of pesticide entry into surface waters, this study has established that atmospheric sources also are important in the prairie region of Canada. Less persistent, current use herbicides, such as the phenoxyacids, were present in surface waters at elevated concentrations during periods when maximum concentrations were observed in air and precipitation and no runoff events occurred. Accurate values of the physical properties of the phenoxyacid and phenolic herbicides are needed in order to develop atmospheric deposition flux estimates for these compounds.

Each year of the study, pesticides were found to be present in surface water systems in southern Manitoba on a cycle reflecting annual agricultural activities. Maximum pesticide concentrations in rivers and streams were generally observed during, and extending beyond, regional application times. Elevated concentrations of pesticides were observed during the spring melt and runoff period for a short duration. Therefore, the definition of pesticide temporal trends requires intensive sampling of surface waters, particularly during application periods and surface runoff events.

The presence of persistent herbicides detected in southern Manitoba was partially explained by long range transport and deposition. Atrazine was detected in air, precipitation and creek water in the South Tobacco Creek Watershed throughout the program of study,

although it was not applied within the watershed. Maximum atrazine concentrations were observed during sampling events corresponding to air masses that originated in the southern US and passed over the US midwest states, where atrazine is used extensively for weed control in corn.

Most of the 16 current use pesticides monitored in this study were present in surface waters in southern Manitoba throughout the open water season. Herbicides, however, are present at concentrations well below the Canadian water quality guideline values for the protection of freshwater aquatic life. During regional application periods the insecticide chlorpyrifos has been observed in Manitoba surface waters at concentrations exceeding draft guideline values. Water quality guidelines are generally lower for insecticides than herbicides, however, chlorpyrifos was the only insecticide under investigation in this study. Insecticide concentrations consistently above water quality guideline values may adversely effect non-target aquatic organisms. There have been no detailed studies of current use insecticides in Manitoba surface waters and this should be the subject of future studies.

Discharge losses of pesticides were much lower than would be anticipated based on chemical deposition to the entire watershed. Discharge loadings of the persistent herbicides, atrazine and alachlor, in the Red River are greater than observed for the high use phenoxyacid herbicides, despite minor uses of atrazine and no alachlor use in southern Manitoba. Movement of these chemicals into Canada results from uses in the neighbouring US states.

Elevated levels of pesticides are present in the Red River at Ste. Agathe and downstream of the City of Winnipeg. Urban pesticide uses may contribute significant amounts of these chemicals to the river systems in Manitoba.

PCBs were present in atmospheric compartments of the South Tobacco Creek Watershed, despite no known uses of these chemicals. The correlation between concentrations of the lower chlorinated PCBs with temperature suggests that the presence of these chemicals was in part a result of volatilization of PCBs from surfaces, such as soil and plants. Direct inputs of precipitation and gas exchange could explain some of the presence of PCBs in South Tobacco Creek water. Concentrations of PCBs in low volume flowing waters, i.e., South Tobacco Creek are higher than observed in large lakes. These elevated concentrations in streams and rivers may be a function of large watershed inputs and resuspension of bottom sediments. PCBs deposited on plant material, detritus and soil surfaces may be washed into streams and rivers during runoff periods, contributing to water loadings. Rivers are more prone to watershed impacts than lakes because of their large watershed area to water surface ratios.

Highly volatile pesticides, i.e., those with high H values, and PCBs are subject to loss from river and stream systems via volatilization. Chemicals deposited to the water can be removed through this mechanism during periods of elevated temperatures and low chemical concentration in air.

10. CONTRIBUTION TO KNOWLEDGE

This thesis has advanced the scientific knowledge concerning the transport and deposition of current use pesticides and PCBs to surface waters by:

- establishing the first high resolution dataset of current use pesticides in southern Manitoba over a period of several years;
- determining that herbicides in Manitoba river systems remain below Canadian water quality guideline values for the protection of freshwater aquatic life;
- detecting the first record of chlorpyrifos in southern Manitoba surface waters and establishing that its maximum concentrations exceed draft guideline values;
- establishing that influx of pesticides from the US occurs via riverine transport along the Red River;
- determining flux estimates for pesticides and PCBs in flowing water systems and establishing that pesticides are both volatilized from and deposited to the water surface throughout an agricultural season. PCBs, however, are volatilized from the water surface throughout the open water season; and
- determining that both PCBs and several herbicides in Manitoba surface water result from atmospheric inputs (either direct or via contribution from the

watershed) rather than point sources and that long range transport and deposition of these chemicals occurs.

11. REFERENCES

- Achman, D.R., K.C. Hornbuckle and S.J. Eisenreich. 1993.** Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. *Environ. Sci. Technol.* **27**: 75-87.
- Adams, C.D. and E.M. Thurman. 1991.** Formation and transport of deethylatrazine in the soil and vadose zone. *J. Environ. Qual.* **20**: 540-547.
- Agriculture Canada. 1996.** Addendum No. 7 to PFRA hydrology division hydrology report #104 (May 1983). The determination of gross and effective drainage areas in the prairie provinces.
- Agriculture Canada. 1980.** Report on determination of river distances for the Saskatchewan-Nelson River Basin. Hydrology Report # 95.
- Ahlborg, U.G., G.C. Becking, L.S. Birnbaum, A. Brouwer, H.J.G.M. Derks, M. Feeley, G. Color, A. Nhanberg, J.C. Larsen, A.K.D. Liem, S.H. Safe, C. Schlatter, F. Wærn, M. Younes, and E. Yrjänheikki. 1994.** Toxic-equivalency factors for dioxin-like PCBs. *Chemosphere* **28**: 1049-1067.
- Alberta Agriculture Food and Rural Development. 1998.** Agricultural impacts on water quality in Alberta - an initial assessment-. Canada - Alberta Environmentally Sustainable Agriculture.
- Alcock, R.E., A.E. Johnston, S.P. McGrath, M.L Berrow and K.C. Jones. 1994.** Long-term changes in the polychlorinated biphenyl content of United Kingdom soils. *Environ. Sci. Technol.* **27**: 1918-1923.
- Anonymous. 1996.** 1996 Crop protection guide. Conex/Land O'Lakes.
- Aulerich, R.J. and R.K. Ringer. 1977.** Current status of PCB toxicity to mink, and effect on their reproduction. *Arch. Environ. Contam. Toxicol.*, **6**: 279-292.
- Bacci, E., M.J. Cerejeira, C.Gaggi, G. Chemello, D.Calamari and M. Vighi. 1990.** Bioconcentration of organic chemical vapours in plant leaves: the azalea model. *Chemosphere.* **21**: 525-535.

- Baker, L.W., D.L. Fitzell, J.N. Seiber, T.R. Parker, T. Shibamoto, M.W. Poore, K.E. Longley, R.P. Tomlin, R. Propper and D.W. Duncan. 1996.** Ambient air concentrations of pesticides in California. *Environ. Sci. Technol.* **30**: 1365-1368.
- Baker, J.E., S.J. Eisenreich and B.J. Eadie. 1991.** Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior. *Environ. Sci. Technol.* **25**: 500-509.
- Baker, J.E. and S.J. Eisenreich. 1990.** Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior. *Environ. Sci. Technol.* **24**: 342-352.
- Baker, J.E. and S.J. Eisenreich. 1986.** Influence of colloids on sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. *Environ. Sci. Technol.* **20**: 1136-1143.
- Barron, M.G., H. Galbraith, and D. Beltman. 1995.** Comparative reproductive and developmental toxicology of PCBs in birds. *Comp. Biochem. Physiol.* **112C**: 1-14.
- Beck, A.E., V. Chacko, W. Tibbatts and D.J. Green. 1992.** Herbicide contamination of the Stephenfield reservoir, Manitoba, Canada. Environmental management division, Manitoba environment, Water quality management report 92-2.
- Bernhoft, A., H. Hektoen, J.U. Skaare, and K. Ingebrigtsen. 1994.** Tissue distribution and effects on hepatic xenobiotic metabolising enzymes of 2,3,3',4,4'-pentachlorobiphenyl (PCB-105) in cod (*Gadus morhua*) and rainbow trout (*Oncorhynchus mykiss*). *Environ. Pollut.* **85**: 351-359.
- Berryman, D. and L. Giroux. 1994.** La contamination des cours d'eau par les pesticides dans les regions de culture intensive de maïs au Quebec. Campagnes d'échantillonnage de 1992 et 1993.
- Bester, K., H. Huhnerfuss, B. Neudorf and W. Thiemann. 1995.** Atmospheric deposition of triazine herbicides in Northern Germany and the German Bight (North Sea). *Chemosphere.* **30**: 1639-1653.
- Bidleman, T.F. and L.L. McConnell. 1995.** A review of field experiments to determine air-water gas exchange of persistent organic pollutants. *Sci. Total Environ.* **159**: 101-117.
- Bidleman, T.F. 1988.** Atmospheric processes. Wet and dry deposition of organic compounds are controlled by their vapour-particle partitioning. *Environ. Sci. Technol.* **22**: 361-367.

- Bidleman, T.F. and W.T. Foreman. 1987.** Vapor-particle partitioning of semivolatile organic compounds. *in Sources and Fates of Aquatic Pollutants*. R.A. Hites and S.J. Eisenreich Eds. American Chemical Society. Washington. D.C. 27-56.
- Bleavins, M.R., R.J. Aulerich, and R.K. Ringer. 1980.** Polychlorinated biphenyls (Arochlor 1016 and 1242): Effects on survival and reproduction in mink and ferrets. *Arch. Environ. Contam. Toxicol.* **9**: 627-635.
- Bosveld, A.T.C. and M. Van den Berg. 1994.** Effects of polychlorinated biphenyls, dibenzo-p-dioxins and dibenzofurans on fish-eating birds. *Environ. Rev.* **2**: 147-166.
- Burkhardt, M.R. and W. Werner. 1994.** Methods of analysis by the national water quality laboratory: determination of pesticides in water by solid-phase extraction and high performance liquid chromatography. (Schedule 2050/2051).
- Buser, H.R. 1990.** Atrazine and other s-triazine herbicides in lakes and in rain in Switzerland. *Environ. Sci. Technol.* **24**: 1049-1058.
- Buttle, J.M. and B.J. Harris. 1991.** Hydrological pathways of metolachlor export from an agricultural watershed. *Water, Air and Soil Pollution.* **60**: 315-335.
- Capel, P.D. 1991.** Wet atmospheric deposition of herbicides in Minnesota. *in: Proceedings of the technical meeting. US Geological Survey toxic substances hydrology program.* 334.
- Capel, P.D., C. Leuenberger and W. Giger. 1991.** Hydrophobic organic chemicals in urban fog. *Atmos. Environ.* **25A**: 1335-1346.
- Capel, P.D. and S.J. Eisenreich. 1985.** PCBs in Lake Superior, 1978-1980. *J. Great Lakes Res.* **11**: 447-461.
- Carignan, R., S. Lorrain and K. Lum. 1994.** A 50-yr record of pollution by nutrients, trace metals and organic chemicals in the St. Lawrence River. *Can. J. Fish. Aquat. Sci.* **51**: 1088-1100.
- CCME (Canadian Council of Ministers of the Environment). 1998.** Canadian water quality guidelines fact sheet on chlorpyrifos. Ottawa, Ontario.
- CCREM. 1987.** Canadian water quality guidelines. Canadian Council of Resource and Environment Ministers. Environment Canada. Ottawa, Ontario.

- Cessna, A.J., J.A. Elliott, K.B. Best, R. Grover and W. Nicholaichuk. 1997.** Transport of nutrients and postemergence-applied herbicides in runoff from corrugation irrigation of wheat. *in* Herbicide Metabolites in surface and groundwater. M.T. Meyer and E.M. Thurman Eds. American Chemical Society Books. ACS Symposium series 630.
- Chacko, V.T., H.H. Vaughan, D.J. Munro and R.N. Woychuk. 1991.** Results of multimedia analyses, large volume extraction and biotoxicity tests in nine prairie rivers of western Canada; and their role in routine water quality monitoring. Water Quality Branch. Inland Waters Directorate, Conservation and Protection Service, Environment Canada, Regina, Saskatchewan.
- Chernyak, S.M., C.P. Rice and L.L. McConnell. 1996.** Evidence of currently-used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi Sea. *Marine. Poll. Bull.* 32: 410-419.
- Chevreuil, M., M. Garmouma, M.J. Teil and A. Cheterikoff. 1996.** Occurrence of organochlorines (PCBs, pesticides) and herbicides (triazines, phenylureas) in the atmosphere and in the fallout from urban and rural stations of the Paris area. *Sci. Total Environ.* 182: 25-37.
- Chevreuil, M. and M. Garmouma. 1993.** Occurrence of triazines in the atmospheric fallout on the catchment of the River Marne. *Chemosphere.* 27: 1605-1608.
- Clendening, L.D., W.A. Jury and F.F. Ernst. 1990.** A field mass balance study of pesticide volatilization, leaching and persistence. *in* Long range transport of pesticides. D.A. Kurtz Ed. Lewis Publishers, Chelsea, Michigan. 47-60.
- Cotham, W.E. and T.F. Bidleman. 1995.** Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in air at an urban and a rural site near Lake Michigan. *Environ. Sci. Technol.* 29: 2782-2789.
- Couillard, D. 1982.** Evaluation des teneurs en composés organochlorés dans le fleuve, l'estuaire et le golfe Saint-Laurent, Canada. *Environ. Pollut. (Series B).* 3: 219-270.
- Coulston, F. And A.C. Kolbye. (Ed.) 1994.** Interpretive review of the potential adverse effects of chlorinated organic chemicals on human health and the environment: report of an expert panel. Chapter 5: Polychlorinated Biphenyls. *Regulatory Toxicology and Pharmacol.* 20: 187-307.
- Currie, R.S. and D.A. Williamson. 1995.** An assessment of pesticide residues in surface waters of Manitoba, Canada. Manitoba Environment Report No. 95-08.

- Delzell, E., J. Doull, J. Giesy, D. Mackay, I. Munro, and G. Williams. 1994.** Interpretive review of the potential adverse effects of chlorinated organic chemicals on human health and the environment: Report of an expert panel. Chapter 5: Polychlorinated biphenyls. *Regulatory Toxicol. Pharmacol.* **20**: S187-S307.
- Dolan, D.M., K.P. McGunagle, S. Perry and E. Voldner. 1993.** Source investigation for Lake Superior. International Joint Commission. Windsor, Ontario.
- Donald, D.B. and J. Syrgiannis. 1995.** Occurrence of pesticides in prairie lakes in Saskatchewan in relation to drought and salinity. *J. Environ. Qual.* **24**: 266-270.
- Eisenreich, S.J., K.C Hornbuckle and D.R. Achman. 1997.** Air-water exchange of semivolatile organic chemicals in the Great Lakes. *in Atmospheric Deposition of Contaminants to the Great Lakes and coastal waters.* J.E. Baker Ed. SETAC Press, Pensacola, FL. USA.
- Eisenreich, S.J. and W.M.J. Strachan. 1992.** Estimating atmospheric deposition of toxic substances to the Great Lakes - an update. National Water Research Institute. Environment Canada. Burlington, ON. 59 pp.
- Environment Canada. 1997.** Methods Manual. Water quality laboratory. Environment Canada. Environmental Protection Branch. Prairie and Northern Region, Saskatoon, SK.
- Environment Canada. 1990.** Unpublished data.
- Falconer, R.L., T.F. Bidleman and D.J. Gregor. 1995.** Air-water gas exchange and evidence for metabolism of hexachlorocyclohexanes in Resolute Bay, N.W.T. *Sci. Tot. Environ.* **160/161**: 65-74.
- Fischer, J.D., B.E. Apedaile and L.K. Vanclief. 1995.** Seasonal loadings of atrazine and metolachlor to a southeastern Ontario river from surface runoff and groundwater discharge. *Water Qual. Res. J. Canada.* **30**: 533-553.
- Foster, G.D. and K.A. Lippa. 1996.** Fluvial loadings of selected organonitrogen and organophosphorus pesticides to Chesapeake Bay. *J. Agric. Food Chem.* **44**: 2447-2454.
- Fox, M.E., R.M. Khan and P.A. Thiessen. 1996.** Loadings of PCBs and PAHs from Hamilton Harbour to Lake Ontario. *Water Qual. Res. J. Canada.* **31**: 593-608.

- Frank, R. and L. Logan. 1988.** Pesticide and industrial chemical residues at the mouth of the Grand, Saugeen and Thames Rivers, Ontario, Canada, 1981-95. *Arch. Environ. Contam. Toxicol.* **17**: 741-754.
- Franz, T.P. and S.J. Eisenreich. 1993.** Wet deposition of polychlorinated biphenyls to Green Bay, Lake Michigan. *Chemosphere.* **26**: 1767-1788.
- Gaynor, J.D., C.S. Tan, C.F. Drury, I.J. van Wesenbeeck and T.W. Welacky. 1995.** Atrazine in surface and subsurface runoff as affected by cultural practices. *Water Qual. Res. J. Canada.* **30**: 513-531.
- Gaynor, J.D. and I.J. van Wesenbeeck. 1995.** Effects of band widths on atrazine, metribuzin and metolachlor runoff. *Weed Technol.* **9**: 107-112.
- Gianessi, L.P. and J.E. Anderson. 1995a.** Pesticide use in Minnesota. Crop production. National Center for Food and Agricultural Policy. Washington, D.C.
- Gianessi, L.P. and J.E. Anderson. 1995b.** Pesticide use in North Dakota. Crop production. National Center for Food and Agricultural Policy. Washington, D.C.
- Glotfelty, D.E., G.H. Williams, H.P. Freeman and M.M. Leech. 1990.** Regional atmospheric transport and deposition of pesticides in Maryland. *in Long Range Transport of Pesticides*. David A. Kurtz Ed. Lewis Publishers. Chelsea, Michigan. 199-221.
- Glotfelty, D.E., M.M. Leech, J. Jersey and A.W. Taylor. 1989.** Volatilization and wind erosion of soil surface applied atrazine, simazine, alachlor, and toxaphene. *J. Agric. Food Chem.* **1989**. 546-551.
- Glotfelty, D.E., J.N. Seiber and L.A. Liljedahl. 1987.** Pesticides in fog. *Nature.* **325**: 602-605.
- Goolsby, D.A., E.M. Thurman, M.L. Pomes, M.T. Meyer and W.A. Battaglin. 1997.** Herbicides and their metabolites in rainfall: origin, transport, and deposition patterns across the midwestern and northeastern United States, 1990-1991. *Environ. Sci. Technol.* **31**: 1325-1333.
- Goolsby, D.A., E.A. Scribner, E.M. Thurman, M.L. Pomes and M.T. Meyer. 1995.** Data on selected herbicides and two triazine metabolites in precipitation of the midwestern and northeastern United States, 1990-91. U.S. Geological Survey Open-File Report 95-469.

- Goolsby, D.A., E.M. Thurman, M.L. Pomes and W.A. Battaglin. 1994.** Temporal and geographic distribution of herbicides in precipitation in the midwest and northeast United States, 1990-1991. *in* New directions in pesticide research, development, management, and policy. Proceedings of the fourth national conference on pesticides. D.L. Weigmann Ed. 696-710.
- Goolsby, D.A., E.M. Thurman, M.L. Pomes and W.A. Battaglin. 1993.** Temporal and geographic distribution of herbicides in precipitation in the midwest and northeast United States, 1990-1991. Proceedings of the fourth national conference on pesticides. Blacksburg, Virginia.
- Goolsby, D.A., R.C. Coupe and D.J. Markovchick. 1991.** Distribution of selected herbicides and nitrate in the Mississippi River and its major tributaries. April through June 1991. US Geological Survey. Water-Resources Investigations Report 91-4163.
- Gregor, D., C. Teixeira and R. Rowsell. 1996.** Deposition of atmospherically transported polychlorinated biphenyls in the Canadian Arctic. *Chemosphere*. **33**: 227-244.
- Gregor, D.J. and W.D. Gummer. 1989.** Evidence of atmospheric transport and deposition of organochlorine pesticides and polychlorinated biphenyls in Canadian Arctic snow. *Environ. Sci. Technol.* **23**: 561-565.
- Grover, R., D.T. Waite, A.J. Cessna, W. Nicholaichuk, D.G. Irvin, L.A. Kerr and K. Best. 1997.** Magnitude and persistence of herbicide residues in farm dugouts and ponds in the Canadian prairies. *Environ. Toxicol. Chem.* **16**: 638-643.
- Grover, R., S.R. Shewchuk, A.J. Cessna, A.E. Smith and J.H. Hunter. 1985.** Fate of 2,4-D *iso*-octyl ester after application to a wheat field. *J. Environ. Qual.* **14**: 203-210.
- Gruessner, B. And M.C. Watzin. 1995.** Patterns of herbicide contamination in selected Vermont streams detected by enzyme immunoassay and gas chromatography/mass spectrometry. *Environ. Sci. Technol.* **29**: 2806-2813.
- Hall, J.C., T.D. Van Deynze, J. Struger and C.H. Chan. 1993.** Enzyme immunoassay based survey of precipitation and surface water for the presence of atrazine, metolachlor and 2,4-D. *J. Environ. Sci. Health.* **B28**: 577-598.
- Halsall, C.J., R.G.M. Lee, P.J. Coleman, V. Burnett, P. Harding-Jones and K.C. Jones 1995.** PCBs in U.K. urban air. *Environ. Sci. Technol.* **29**: 2368-2376.
- Haraguchi, K., E. Kitamura, T. Yamashita and A. Kido. 1995.** Simultaneous determination of trace pesticides in urban precipitation. *Atmos. Environ.* **29**: 247-253.

- Haraguchi, K., E. Kitamura, T. Yamashita and A. Kido. 1994.** Simultaneous determination of trace pesticides in urban air. *Atmos. Environ.* **28**: 1319-1325.
- Harker, D.B., K. Bolton, L. Townley-Smith and B. Bristol. 1997.** A prairie-wide perspective of nonpoint agricultural effects on water quality. A review of documented evidence and expert opinion. PFRA Prairie Resources division. Regina, Saskatchewan.
- Harner, T. And T.F. Bidleman. 1996.** Measurements of octanol-air partition coefficients for polychlorinated biphenyls. *J. Chem. Eng. Data.* **41**: 895-899.
- Harner, T. and D. Mackay. 1995.** Measurements of octanol-air partition coefficients for chlorobenzenes, PCBs and DDT. *Environ. Sci. Technol.* **29**: 1599-1606.
- Hawthorne, S.B., D.J. Miller, P.K.K. Louie, R.D. Butler and G.G. Mayer. 1996.** Atmospheric pollutants and trace gases. *J. Environ. Qual.* **25**: 594-600.
- Helle, E., M. Olsson, and S. Jensen. 1976a.** PCB levels correlated with pathological changes in seal uteri. *Ambio* **5**: 261-263.
- Helle, E., M. Olsson, and S. Jensen. 1976b.** DDT and PCB levels and reproduction in ringed seal from the Bothnian Bay. *Ambio* **5**: 188-189.
- Henriksen, E.O., G.W. Gabrielsen, and J.U. Skaare. 1996.** Levels and congener pattern of polychlorinated biphenyls in kittiwakes (*Rissa tridactyla*), in relation to mobilization of body-lipids associated with reproduction. *Environ. Pollut.* **92**: 27-37.
- Hillel, D. 1982.** Introduction to Soil Physics. Academic Press, Inc. San Diego, California.
- Hillery, B.R., I. Basu, C.W. Sweet and R.A. Hites. 1997.** Temporal and spatial trends in a long-term study of gas-phase PCB concentrations near the Great Lakes. *Environ. Sci. Technol.* **31**: 1811-1816.
- Hinckley, D.A., T.F. Bidleman, W.T. Foreman and J.R. Tuschall. 1990.** Determination of vapour pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data. *J. Chem. Eng. Data.* **35**: 232-237.
- Hippe, D.J., D.J. Wangness, E.A. Frick and J.W. Garrett. 1994.** Water quality of the Apalachicola-Chattahoochee-Flint and Ocmulgee River basins related to flooding from Tropical Storm Alberto; pesticides in urban and agricultural watersheds; and nitrate and pesticides in groundwater. Georgia, Alabama and Florida. US Geological Survey. Water Resources Investigations Report 94-4183.

- Hoff, R.M., W.J.M. Strachan, C.W. Sweet, C.H. Chan, M. Shackleton, T.F. Bidleman, K.A. Brice, D.A. Burniston, S. Cussion, D.F. Gatz, K. Harlin and W.H. Schroeder. 1996.** Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. *Atmos. Environ.* **30**: 3505-3527.
- Hoff, J.T., F. Wania, D. Mackay and R. Gillham. 1995.** Sorption of non-polar organic vapors by ice and snow. *Environ. Sci. Technol.* **29**: 1982-1989.
- Hoff, R.M., D.C.G. Muir and N.P. Grift. 1992a.** Annual cycle of polychlorinated biphenyls and organohalogen pesticides in air in southern Ontario. 1. Air concentration data. *Environ. Sci. Technol.* **26**: 266-275.
- Hoff, R.M., D.C.G. Muir and N.P. Grift. 1992b.** Annual cycle of polychlorinated biphenyls and organohalogen pesticides in air in southern Ontario. 2. Atmospheric transport and sources. *Environ. Sci. Technol.* **26**: 276-283.
- Holsen, T.M., X. Zhu, N.R. Khalili, J.J. Lin, P. Lestari, C-S. Lu and K.E. Noll. 1997.** Atmospheric particle size distribution and dry deposition measured around Lake Michigan. *in Atmospheric Deposition of Contaminants to the Great Lakes and coastal waters*. J.E. Baker Ed. SETAC Press, Pensacola, FL. USA.
- Holsen, T.M., K.E. Noll, G-C. Fang, W-J. Lee, J-M. Lin and G.J. Keeler. 1993.** Dry deposition and particle size distribution measured during the Lake Michigan urban air toxics study. *Environ. Sci. Technol.* **27**: 1327-1333.
- Holsen, T.M. and K.E. Noll. 1992.** Dry deposition of atmospheric particles: application of current models to ambient data. *Environ. Sci. Technol.* **26**: 1807-1815.
- Holsen, T.M., K.E. Noll, S-P. Liu and W-J. Lee. 1991.** Dry deposition of polychlorinated biphenyls in urban areas. *Environ. Sci. Technol.* **25**: 1075-1081.
- Honrath, R.E., C.I. Sweet and C.J. Plouff. 1997.** Surface exchange and transport processes governing atmospheric PCB levels over Lake Superior. *Environ. Sci. Technol.* **31**: 842-852.
- Hornbuckle, K.C., C.W. Sweet, R.F. Pearson, D.L. Swakhamer and S.J. Eisenreich. 1995.** Assessing annual water-air fluxes of polychlorinated biphenyls in Lake Michigan. *Environ. Sci. Technol.* **29**: 869-877.
- Hornbuckle, K.C., J.D. Jeremiason, C.W. Sweet and S.J. Eisenreich. 1994.** Seasonal variations in air-water exchange of polychlorinated biphenyls in Lake Superior. *Environ. Sci. Technol.* **28**: 1491-1501.

- Hornbuckle, K.C., D.R. Achman and S.J. Eisenreich. 1993.** Over-water and over-land polychlorinated biphenyls in Green Bay, Lake Michigan. *Environ. Sci. Technol.* **27**: 87-98.
- Hutzinger, O., S. Safe and V. Zitko. 1983.** The chemistry of PCBs. CRC Press, Inc. Cleveland, OH.
- Iwata, H., S. Tanabe, K. Ueda and R. Tatsukawa. 1995.** Persistent organochlorine residues in air, water, sediments, and soils from the Lake Baikal region, Russia. *Environ. Sci. Technol.* **29**: 792-801.
- Iwata, H., S. Tanabe, N. Sakai and R. Tatsukawa. 1993.** Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci. Technol.* **27**: 1080-1098.
- Jantunen, L.M. and T.F. Bidleman. 1995.** Reversal of the air-water gas exchange direction of hexachlorocyclohexanes in the Bering and Chukchi Seas: 1993 versus 1988. *Environ. Sci. Technol.* **29**: 1081-1089
- Jayachandran, K., T.R. Steinheimer, L. Somasundaram, T.B. Moorman, R.S. Kanwar and J.R. Coats. 1994.** Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow groundwater. *J. Environ. Qual.* **23**: 311-319.
- Jeremiason, J.D., S.J. Eisenreich, M.J. Paterson, D.L. Findlay, H.J. Kling, K.G. Beaty, R. Hecky and J.J. Elser. 1997.** Biogeochemical cycling of atmospherically-derived PCBs in lakes of variable trophic status: A paired-lake experiment. Manuscript in preparation.
- Jeremiason, J.D., K.C. Hornbuckle and S.J. Eisenreich. 1994.** PCBs in Lake Superior, 1978-1992: Decreases in water concentrations reflect loss by volatilization. *Environ. Sci. Technol.* **28**: 903-914.
- Jury, W.A., W.F. Spencer and W.J. Farmer. 1984.** Behaviour assessment model for trace organics in soil: III Application of screening model. *J. Environ. Qual.* **13**: 573-579.
- Jury, W.A., W.F. Spencer and W.J. Farmer. 1983.** Behaviour assessment model for trace organics in soil. I. Model description. *J. Environ. Qual.* **12**: 558-564.
- Keith, L.H. 1991.** Environmental sampling and analysis: A practical guide. Lewis Publishers. CRC Press Inc. Boca Raton, Florida.
- Kimbrough, R.A. and D.W. Litke. 1996.** Pesticides in streams draining agricultural and urban areas in Colorado. *Environ. Sci. Technol.* **30**: 908-916.

- Knisel, W.G. (Ed).** 1980. CREAMS. A field scale model for chemicals, runoff and erosion from agricultural management systems. Science and education admin. USDA, Conservation research report No. 26.
- Koester, C.J. and R.A. Hites.** 1992. Wet and dry deposition of chlorinated dioxins and furans. *Environ. Sci. Technol.* **26**: 1375-1382.
- Kolpin, D.A., E.M. Thurman and D.A. Goolsby.** 1996. Occurrence of selected pesticides and their metabolites in near-surface aquifers of the midwestern United States. *Environ. Sci. Technol.* **30**: 335-340.
- Kolpin, D.W. and S.J. Kalkhoff.** 1993. Atrazine degradation in a small stream in Iowa. *Environ. Sci. Technol.* **27**: 134-139.
- Larson, S.J., P.D. Capel, D.A. Goolsby, S.D. Zaugg and M.W. Sandstrom.** 1995. Relations between pesticide use and riverine flux in the Mississippi River basin. *Chemosphere.* **31**: 3305-3321.
- Leonard, R.A.** 1988. Herbicides in surface waters. *in* Environmental Chemistry of herbicides Volume I. CRC Press. Boca Raton.
- Lode, O., O.M. Eklo, B. Holen, A. Svensen and A.M. Johnsen.** 1995. Pesticides in precipitation in Norway. *Sci. Total Environ.* **160/161**: 421-431.
- Mackay, D., W.Y. Shiu and K.C. Ma.** 1992. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Volume I. Monoaromatic hydrocarbons, chlorobenzenes and PCBs. Lewis Publishers, Chelsea, MI.
- Maguire, R.J. and R.J. Tkacz.** 1993. Occurrence of pesticides in the Yamaska River, Quebec. *Arch. Environ. Contam. Toxicol.* **25**: 220-226.
- Maguire, R.J., R.J. Tkacz and S.P. Batchelor.** 1993. Extraction efficiencies of hydrocarbons from Niagara River water. *Environ Toxicol. Chem.* **12**: 805-811.
- Majewski, M.J. and P.D. Capel.** 1995. Pesticides in the Atmosphere. R.J. Gilliom Ed. Pesticides in the hydrologic system. Volume 1. Ann Arbor Press. Chelsea, Michigan.
- Majewski, M., R. Desjardins, P. Rochette, E. Pattey, J. Seiber and D. Glotfelty.** 1993. Field comparison of an eddy accumulation and an aerodynamic-gradient system for measuring pesticide volatilization fluxes. *Environ. Sci. Technol.* **27**: 121-128.

- Manchester-Neesvig, J.B. and A.W. Andren. 1989.** Seasonal variation in the atmospheric concentration of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* **23**: 1138-1148.
- Manitoba Natural Resources. 1967.** Province of Manitoba map showing municipality or L.G.D. boundaries; provincial waterway watershed boundaries. Winnipeg, Manitoba.
- Marti, E.A. and D.E. Armstrong. 1990.** Polychlorinated biphenyls in Lake Michigan tributaries. *J. Great Lakes Res.* **16**: 396-405.
- McConnell, L.L., E. Nelson, C.P. Rice, J.E. Baker, W.E. Johnson, J.A. Harman and K. Bialek. 1997.** Chlorpyrifos in the air and surface water of Chesapeake Bay: predictions of atmospheric fluxes. *Environ. Sci. Technol.* **31**: 1390-1398.
- McConnell, L.L., J.R. Kucklick, T.F. Bidleman, G.P. Ivanov and S.M. Chernyak. 1996.** Air-water gas exchange of organochlorine compounds in Lake Baikal, Russia. *Environ. Sci. Technol.* **30**: 2975-2983.
- McConnell, L.L., W.E. Cotham and T.F. Bidleman. 1993.** Gas exchange of hexachlorocyclohexane in the Great Lakes. *Environ. Sci. Technol.* **27**: 1304-1311.
- McLachlan, M.S., K. Welsch-Pausch and J. Tolls. 1995.** Field validation of a model of the uptake of gaseous SOC in *Lolium multiflorum* (rye grass). *Environ. Sci. Technol.* **29**: 1988-2204.
- McMillin, D.J. and J.C. Means. 1996.** Spatial and temporal trends of pesticide residues in water and particulates in the Mississippi River plume and the northwestern Gulf of Mexico. *J. Chromatogr.* **754**: 169-185.
- McVeety, B.D. and R.A. Hites. 1988.** Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. *Atmos. Environ.* **22**: 511-536.
- Miles, C.J. and R.J. Pfeuffer. 1997.** Pesticides in canals of south Florida. *Arch. Environ. Contam. Toxicol.* **32**: 337-345.
- Miller, G.T. 1995.** Rainfall runoff analysis for the October 16-18, 1994 storm in the South Tobacco Creek basin near Miami, Manitoba. Prairie Farm Rehabilitation Administration. Hydrology Memorandum #43.
- Miller, G.T. 1994.** Rainfall runoff analysis for the May 8-9, June 7, July 25-25 and July 27, 1993 storms in the South Tobacco Creek basin near Miami, Manitoba. Prairie Farm Rehabilitation Administration. Hydrology Memorandum #42.

- Monosmith, C.L. and M.H. Hermanson. 1996.** Spatial and temporal trends of atmospheric organochlorine vapors in the central and upper Great Lakes. *Environ. Sci. Technol.* 1996. **30**: 3464-3472.
- Moody, J.A. and D.A. Goolsby. 1993.** Spatial variability of triazine herbicides in the Lower Mississippi River. *Environ. Sci. Technol.* **27**: 2120-2126.
- Morgensen, B.B. and N.H. Spliid. 1995.** Pesticides in Danish watercourses: occurrence and effects. *Chemosphere.* **31**: 3977-3990.
- Muir, D.C.G. and N.P. Grift. 1995.** Fate of herbicides and organochlorine insecticides in lake waters. *in Eighth International Congress of pesticide Chemistry: Options 2000.* N. Ragsdale, P.C. Kearney and J.R. Plimmer Eds. American Chemical Society. 141-156.
- Muir, D.C.G. 1991.** Dissipation and transformation in water and sediment. *in Environmental chemistry of herbicides. Volume II.* R. Grover and A.J. Cessna Eds. CRC Press, Boca Raton.
- Muir, D.C.G. and N.P. Grift. 1987.** Herbicide levels in rivers draining two prairie watersheds (1984). *J. Environ. Sci. Health.* **B22**: 259-284.
- Murphy, T.J., M.D. Mullin and J.A. Meyer. 1987.** Equilibration of polychlorinated biphenyls and toxaphene with air and water. *Environ. Sci. Technol.* **21**: 155-162.
- Nations, B.K. and G.R. Hallberg. 1992.** Pesticides in Iowa precipitation. *J. Environ. Qual.* **21**: 486-492.
- Nikolaidis, E., B. Brunnström, and L. Dencker. 1988a.** Effects of the TCDD congeners 3,3',4,4'-tetrachlorobiphenyl and 3,3',4,4'-tetrachloroazoxybenzene on lymphoid development in the bursa of Fabricius of the chick embryo. *Toxicol. Appl. Pharmacol.* **92**: 315-323.
- Nikolaidis, E., B. Brunnström, and L. Dencker. 1988b.** Effects of the TCDD and its congeners 3,3',4,4'-tetrachloroazoxybenzene and 3,3',4,4'-tetrachlorobiphenyl on lymphoid development in the thymus of avian embryos. *Pharmacol. Toxicol.* **63**: 333-336.
- Noll, K.E., P-F. Yuen and K. Y-P. Fang. 1990.** Atmospheric coarse particulate concentrations and dry deposition fluxes for ten metals in two urban environments. *Atmos. Environ.* **24A**: 903-908.

- Noll, K.E., K. Y-P Fang and L.A. Watkins. 1988.** Characterization of the deposition of particles from the atmosphere to a flat plate. *Atmos. Environ.* **22**: 1461-1468.
- Noll, K.E., A. Pontius, R. Frey and M. Gould. 1985.** Comparison of atmospheric coarse particles at an urban and non-urban site. *Atmos. Environ.* **19**: 1931-1943.
- O'Connor, D.J. and W.E. Dobbins. 1958.** Mechanism of reaeration in natural streams. *Trans. ASCE.* **123**: 641-684.
- Oehme, M., J-E. Haugen and M. Schlabach. 1996.** Seasonal changes and relations between levels of organochlorines in Arctic ambient air: First results of an all-year-round monitoring program at Ny-Alesund, Svalbard, Norway. *Environ. Sci. Technol.* **30**: 2294-2304.
- Offenberg, J.H. and J.E Baker. 1997.** Polychlorinated biphenyls in Chicago precipitation: Enhanced wet deposition to near-shore lake Michigan. *Environ. Sci. Technol.* **31**: 1534-1538.
- Olsson, M., Ö. Andersson, Å. Bergman, G. Blomkvist, A. Frank, and C. Rappe. 1992.** Contaminants and diseases in seals from Swedish waters. *Ambio* **21**: 561-562.
- Pearson, R.F., K.C. Hornbuckle, S.J. Eisenreich and D.L. Swakhamer. 1996.** PCBs in Lake Michigan water revisited. *Environ. Sci. Technol.* **30**: 1429-1436.
- Pankow, J.F. 1987.** Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.* **21**: 2275-2283.
- Pereira, W.E. and F.D. Hostettler. 1993.** Nonpoint source contamination of the Mississippi River and its tributaries by herbicides. *Environ. Sci. Technol.* **27**: 1542-1552.
- Pereira, W.E., C.E. Rostad and T.J. Leiker. 1992.** Synthetic organic agrochemicals in the lower Mississippi River and its major tributaries: distribution, transport and fate. *J. Contam. Hydrol.* **9**: 175-188.
- Pereira, W.E. and C.E. Rostad. 1990.** Occurrence, distributions, and transport of herbicides and their degradation products in the lower Mississippi River and its tributaries. *Environ. Sci. Technol.* **24**: 1400-1406.
- Pirrone, N., G.J. Keeler and T.M. Holsen. 1995.** Dry deposition of semivolatilie organic compounds to Lake Michigan. *Environ. Sci. Technol.* **29**: 2123-2132.

- Poster, D.L. and J.E. Baker. 1997.** Mechanisms of atmospheric wet deposition of chemical contaminants. *in Atmospheric deposition of contaminants to the Great Lakes and coastal waters*. J.E. Baker Ed. SETAC Press, Pensacola, Florida.
- Poster, D.L. and J.E. Baker. 1996.** Influence of submicron particles on hydrophobic organic contaminants in precipitation. 1. Concentrations and distributions of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environ. Sci. Technol.* **30**: 341-348.
- Rao, P.S.C., R.E. Jessup and J.M. Davidson. 1988.** Mass flow and dispersion. *in Environmental chemistry of herbicides. Volume I*. R. Grover Ed. CRC Press. Boca Raton, Florida.
- Rawn, D.F.K. 1998.** The transport and deposition of current use pesticides and PCBs to surface waters in the Red River drainage basin. Ph.D. thesis. University of Manitoba.
- Rawn, D.F.K., T.H.J. Halldorson and D.C.G. Muir. 1998a.** A multi-year study of four herbicides in air and precipitation from a small prairie watershed. Submitted to *J. Environ. Qual.*
- Rawn, D.F.K., T.H.J. Halldorson and D.C.G. Muir. 1998b.** Atmospheric transport and deposition, an additional input pathway for atrazine to surface waters. *in Triazine herbicides: risk assessment*. L. Balantine, J. McFarland and D. Hackett Eds. American Chemical Society. Washington D.C.
- Rawn, D.F.K., T.H.J. Halldorson, W.N. Turner, R.N. Woychuk, J-G. Zakrevsky and D.C.G. Muir. 1998c.** A multi-year study of four herbicides in surface water of a small prairie watershed. Submitted to *J. Environ. Qual.*
- Rawn, D.F.K., T.H.J. Halldorson, B.D. Lawson and D.C.G. Muir. 1998d.** Polychlorinated biphenyls in a rural watershed in the southern prairie region of Canada. Accepted by *Environmental Pollution*.
- Richards, R.P., J.W. Kramer, D.B. Baker and K.A. Krieger. 1987.** Pesticides in rainwater in the northeastern United States. *Nature.* **327**: 129-131.
- Ridal, J.J., B. Kerman, L. Durham and M.E. Fox. 1996.** Seasonality of air-water fluxes of hexachlorocyclohexanes in Lake Ontario. *Environ. Sci. Technol.* **30**: 852-858.
- Ross, L.J., S. Nicosia, M.M. McChesney, K.L. Hefner, D.A. Gonzalez and J.N. Seiber. 1990.** Volatilization, off-site deposition, and dissipation of DCPA in the field. *J. Environ. Qual.* **19**: 715-722.

- Safe, S.** 1990. Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). *Crit. Rev. Toxicol.* **21**: 51-88.
- Sandmann, R.L.C., P.R. de Beer and L.P. van Dyk.** 1991. Atmospheric pollution by auxin-type herbicides in Tala Valley, Natal. *Chemosphere.* **22**: 137-145.
- Schomburg, C.J., D.E. Glotfelty and J.N. Seiber.** 1991. Pesticide occurrence and distribution in fog collected near Monterey, California. *Environ. Sci. Technol.* **25**: 155-160.
- Schottler, S.P. and S.J. Eisenreich.** 1997. Mass balance model to quantify atrazine sources, transformation rates, and trends in the Great Lakes. *Environ. Sci. Technol.* **31**: 2616-2625.
- Schottler, S.P., S.J. Eisenreich and P.D. Capel.** 1994. Atrazine, alachlor and cyanazine in a large agricultural river system. *Environ. Sci. Technol.* **28**: 1079-1089.
- Schwarzenbach, R.P., P.M. Gschwend and D.M. Imboden.** 1993. Environmental Organic Chemistry. John Wiley and Sons. New York., NY.
- Scribner, E.A., D.A. Goolsby, E.M. Thurman, M.T. Meyer and W.A. Battaglin.** 1996. Concentrations of selected herbicides, herbicide metabolites, and nutrients in outflow from selected Midwestern reservoirs, April 1992 through September 1993.
- Seibers, J., D. Gottschild and H.-G. Nolting.** 1994. Pesticides in precipitation in northern Germany. *Chemosphere.* **28**: 1559-1570.
- Senseman, S.A., T.L. Lavy, J.D. Mattice, E.E. Gbur and B.W. Skulman.** 1997. Trace level pesticide detections in Arkansas surface waters. *Environ. Sci. Technol.* **31**: 395-401.
- Simik, M.F., T.P. Franz, H. Zhang and S.J. Eisenreich.** 1998. Gas-particle partitioning of PCBs and PAHs in the Chicago urban and adjacent coastal atmosphere: states of equilibrium. *Environ. Sci. Technol.* **32**: 251-257.
- Shiu, W.Y., K.C. Ma, D. Mackay, J.N. Seiber, R.D. Wauchope.** 1990. Solubilities of pesticide chemicals in water. *Rev. Environ. Contam. Toxicol.* **116**: 1-187.
- Spalding, R.F., D.D. Snow, D.A. Cassada and M.E. Burbach.** 1994. Study of pesticide occurrence in two closely spaced lakes in northeastern Nebraska. *J. Environ. Qual.* **23**: 571-578.

- Squillace, P.J. and E.M. Thurman. 1992.** Herbicide transport in rivers: importance of hydrology and geochemistry in nonpoint-source contamination. *Environ. Sci. Technol.* **26:** 538-545.
- Statistics Canada. 1996.** Census of agriculture, Manitoba. Winnipeg, Manitoba.
- Stern, G.A., C.J. Halsall, L.A. Barrie, D.C.G. Muir, P. Fellin, B. Rosenberg, F. Rovinski, E. Konovov and B. Postoukov. 1997.** Polychlorinated biphenyls in Arctic air. 1. Temporal trends and spatial trends: 1992-1994. *Environ. Sci. Technol.* **31:** 3619-3628.
- Swackhamer, D.L., B.D. McVeety and R.A. Hites. 1988.** Deposition and evaporation of polychlorobiphenyl congeners to and from Siskiwit Lake, Isle Royale, Lake Superior. *Environ. Sci. Technol.* **22:** 664-672.
- SWRRB Manual. 1985.** Pesticide Runoff Simulation. US EPA Simulator for Water Resources in Rural Basins. Second Edition. US Environmental Protection Agency. Office of Pesticide Programs. Washington. D.C.
- Tanabe, S., H. Iwata and R. Tatsukawa. 1994.** Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *Sci. Tot. Environ.* **154:**163-178.
- Thurman, E.M., D.A. Goolsby, M.T. Meyer, M.S. Mills, ML. Pomes and D.W. Kolpin. 1992.** A reconnaissance study of herbicides and their metabolites in surface water of the midwestern United States using immunoassay and gas chromatography/mass spectrometry. *Environ. Sci. Technol.* **26:** 2440-2447.
- Thurman, E.M., D.A. Goolsby, M.T. Meyer and D.W. Kolpin. 1991.** Herbicides in surface waters of the midwestern United States: The effect of spring flush. *Environ. Sci. Technol.* **25:** 1794-1796.
- Tolls, J. and M.S. McLachlan. 1994.** Partitioning of semivolatile organic compounds between air and *Lolium multiflorum* (Welsh rye grass). *Environ. Sci. Technol.* **28:** 159-166.
- Tornes, L.H. and M.E. Brigham. 1994.** Nutrients, suspended sediment and pesticides in waters of the Red River of the North basin, Minnesota, North Dakota and South Dakota. 1970-90. US Geological Survey. Water Resources Investigations Report. 93-4231. MoundsView, Minnesota.

- Tremolada, P., V. Burnett, D.E. Calamari and K.C. Jones. 1996.** Spatial distribution of PAHs in the UK atmosphere using pine needles. *Environ. Sci. Technol.* **30**: 3570-3577.
- Trevisan, M., C. Montepianni, L. Ragozza, C. Bartletti, E. Ioannilli and A.A.M. Del Re. 1993.** Pesticides in rainfall and air in Italy. *Environ. Poll.* **80**: 31-39.
- Tronczynski, J., C. Munschy, G. Durand and D. Barcelo. 1993.** Monitoring of trace-levels of herbicides and their degradation products in the river Rhone, France, by gas chromatography-mass spectrometry. *Sci. Total Environ.* **132**: 327-337.
- Velleux, M., D. Endicott, J. Steuer, S. Jaeger and D. Patterson. 1995.** Long-term simulation of PCB export from the Fox River to Green Bay. *J. Great Lakes Res.* **21**: 359-372.
- Velleux, M. and D. Endicott. 1994.** Development of a mass balance model for estimating PCB export from the Lower Fox River to Green Bay. *J. Great Lakes Res.* **20**: 416-434.
- Vos, J.G., H. Van Loveren, P.W. Wester, and A.D. Vethaak. 1988.** The effects of environmental pollutants on the immune system. *Eur. Environ. Rev.* **2**: 2-7.
- Waite, D.T., R. Grover, N.D. Westcott, D.G. Irvine, L.A. Kerr and H. Sommerstad. 1995.** Atmospheric deposition of pesticides in a small southern Saskatchewan watershed. *Environ. Toxicol Chem.* **14**: 1171-1175.
- Waite, D.T., R. Grover, N.D. Westcott, H. Sommerstad and L. Kerr. 1992.** Pesticides in ground water, surface water and spring runoff in a small Saskatchewan watershed. *Environ. Toxicol. Chem.* **11**: 741-748.
- Wania, F. and D. Mackay. 1996.** Tracking the distribution of persistent organic pollutants. Control strategies for these contaminants will require a better understanding of how they move around the globe. *Environ. Sci. Technol.* **30**: 390A-396A.
- Water Survey of Canada. 1994-1996.** Water flow and depth data stored under Federal-Provincial arrangements. Winnipeg, Manitoba.
- Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers and J.P. Burt. 1992.** The SCS/ARS/CES Pesticide Properties Database for Environmental Decision Making. *Rev. Environ. Contam. Toxicol.* **123**: 1-155.
- Wauchope, R.D. and R.A. Leonard. 1980.** Maximum pesticide concentrations in agricultural runoff: a semiempirical prediction formula. *J. Environ. Qual.* **9**: 665-672.

- Wauchope, R.D. 1978.** The pesticide content of surface water draining from agricultural fields - a review. *J. Environ. Qual.* 7: 459-472.
- Whang, J.M., C.J. Schomburg, D.E. Glotfelty and A.W. Taylor. 1993.** Volatilization of fonofos, chlorpyrifos, and atrazine from conventional and no-till surface soils in the field. *J. Environ. Qual.* 22: 173-180.
- Worthing, C.R. and R.J. Hance. 1991.** The pesticide manual. A world compendium. British Crop Protection Council Farnham, Surrey, UK.
- Woodrow, J.E., M.M. McChesney and J.N Seiber. 1990.** Modelling the volatilization of pesticides and their distribution in the atmosphere. *in Long range transport of pesticides.* D.A. Kurtz Ed. Lewis Publishers. Chelsea Michigan.
- Yarotski, J.B. 1996.** Canada-Manitoba Soil Conservation Agreement Program 6 Spouth Tobacco Creek pilot project effect of headwater storage on runoff peaks. Prairie Farm Rehabilitation Administration. Hydrology report #142.
- Zabik, J.M. and J.N. Seiber. 1993.** Atmospheric transport of organophosphate pesticides from California's central valley to the Sierra Nevada Mountains. *J. Environ. Qual.* 22: 80-90.
- Zaugg, S.D., M.W. Sandstrom, S.G. Smith and K.M Fehlberg. 1995.** Methods of analysis by the US Geological Survey national water quality laboratory - determination of pesticides in water by Carbopack-B solid phase extraction and capillary column gas chromatography/mass spectrometry with select ion monitoring. Open File Report 95-182.

12. APPENDICES

I. Pesticide Method Detection Limits

Pesticide	Water and precipitation (ng/L)	Air (ng/m ³)
Alachlor	0.06	0.006
Atrazine	0.042	0.005
Bromoxynil	0.015	0.003
Chlorpyrifos	0.082	0.007
Chlorthal dimethyl (Dacthal)	0.013	0.003
Cyanazine	0.19	0.002
2,4-D	0.011	0.003
Dichlorprop	0.007	0.002
Diclofop methyl	0.023	0.004
Ethalfuralin	0.28	0.036
MCPA	0.01	0.002
Metolachlor	0.023	0.004
Terbuthylazine	0.041	0.006
Triallate	0.04	0.013
Triclopyr	0.033	0.004
Trifluralin	0.023	0.005

II. Pesticide Concentrations in South Tobacco Creek Water (ng/L)

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
6/7/93	0.172	0.213	0.300	3.444	<MDL	<MDL	<MDL	1.682	0.078	<MDL
9/7/93	0.154	0.835	0.296	3.670	<MDL	<MDL	<MDL	2.232	<MDL	<MDL
12/7/93	3.052	3.716	0.594	6.745	<MDL	0.170	<MDL	0.922	<MDL	<MDL
15/7/93	<MDL	<MDL	<MDL	0.320	<MDL	0.204	<MDL	2.516	<MDL	<MDL
21/7/93	0.127	0.051	1.262	11.965	0.085	<MDL	<MDL	1.338	<MDL	<MDL
25/7/93	3.168	0.887	0.406	1.329	<MDL	<MDL	<MDL	0.545	<MDL	<MDL
27/7/93	0.042	0.092	0.501	10.047	<MDL	<MDL	<MDL	1.943	0.263	<MDL
2/8/93	0.194	0.411	0.315	4.468	<MDL	0.110	<MDL	0.662	0.490	<MDL
9/8/93	0.046	<MDL	0.523	1.140	<MDL	<MDL	<MDL	0.529	0.336	<MDL
18/8/93	0.046	0.172	0.386	1.062	<MDL	<MDL	<MDL	0.591	0.451	<MDL
26/8/93	0.098	0.251	0.400	0.490	<MDL	<MDL	<MDL	0.394	0.116	<MDL
7/9/93	1.238	0.739	0.408	0.979	<MDL	<MDL	0.947	0.944	<MDL	<MDL
18/10/93	2.268	1.348	0.738	1.482	<MDL	<MDL	1.909	1.181	0.456	<MDL
05/03/94	4.872	4.816	7.427	2.049	<MDL	0.143	<MDL	0.716	<MDL	<MDL
14/03/94	2.318	0.484	<MDL	1.141	<MDL	<MDL	<MDL	0.861	<MDL	<MDL
31/03/94	0.264	<MDL	0.588	0.357	<MDL	0.139	<MDL	0.453	<MDL	0.208
03/05/94	<MDL	<MDL	<MDL	0.181	15.533	0.190	<MDL	0.472	<MDL	<MDL
11/05/94	<MDL	<MDL	<MDL	0.198	<MDL	0.162	<MDL	1.331	<MDL	<MDL
16/05/94	0.294	<MDL	<MDL	0.213	<MDL	0.359	<MDL	0.774	<MDL	0.147
26/05/94	0.379	<MDL	<MDL	0.824	<MDL	0.392	<MDL	4.094	<MDL	<MDL
30/05/94	<MDL	<MDL	<MDL	<MDL	0.298	0.316	<MDL	1.446	<MDL	<MDL
07/06/94	0.699	<MDL	<MDL	2.563	0.550	0.448	<MDL	2.091	<MDL	<MDL
14/06/94	0.697	0.933	<MDL	5.361	<MDL	0.208	<MDL	5.315	<MDL	<MDL
27/06/94	3.668	7.647	2.605	5.765	0.439	0.775	<MDL	<MDL	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
07/07/94	<MDL	4.796	0.471	5.877	<MDL	0.306	<MDL	2.215	<MDL	<MDL
11/07/94	4.949	9.308	4.536	3.869	<MDL	0.155	<MDL	<MDL	<MDL	<MDL
19/07/94	2.355	3.810	1.756	1.929	0.269	0.421	<MDL	<MDL	<MDL	<MDL
25/07/94	0.988	3.265	1.914	0.637	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
07/10/94	<MDL	<MDL	<MDL	3.063	<MDL	0.319	<MDL	0.446	<MDL	<MDL
08/10/94	1.166	2.292	1.360	1.962	<MDL	0.228	<MDL	0.457	<MDL	<MDL
13/10/94	<MDL	<MDL	<MDL	3.005	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/10/94	0.501	1.820	0.825	0.562	<MDL	0.144	<MDL	0.301	<MDL	<MDL
18/10/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.754	<MDL	<MDL
19/10/94	<MDL	<MDL	<MDL	<MDL	<MDL	0.926	<MDL	<MDL	<MDL	<MDL
10/11/94	<MDL	<MDL	<MDL	0.159	<MDL	<MDL	<MDL	1.417	<MDL	<MDL
17/3/95	<MDL	2.860	0.744	0.634	0.403	0.457	<MDL	<MDL	<MDL	<MDL
4/3/95	<MDL	3.698	<MDL	0.659	0.305	1.316	<MDL	<MDL	<MDL	<MDL
11/4/95	<MDL	0.643	<MDL	0.339	0.552	0.479	<MDL	<MDL	<MDL	<MDL
13/4/95	<MDL	<MDL	<MDL	0.254	2.259	1.878	<MDL	0.914	0.722	<MDL
24/4/95	<MDL	<MDL	<MDL	0.178	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95	0.001	<MDL	<MDL	0.365	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/5/95	<MDL	<MDL	<MDL	0.290	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95	0.106	<MDL	0.134	0.291	<MDL	<MDL	<MDL	<MDL	0.394	<MDL
23/5/95	0.363	0.425	6.002	0.379	0.285	0.435	<MDL	0.759	0.213	<MDL
27/5/95	0.217	<MDL	1.041	0.504	<MDL	<MDL	<MDL	0.659	<MDL	<MDL
2/6/95	<MDL	<MDL	<MDL	0.329	0.261	0.472	<MDL	0.572	0.397	<MDL
5/6/95	<MDL	<MDL	<MDL	14.713	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95	1.879	<MDL	<MDL	1.010	<MDL	<MDL	<MDL	0.469	<MDL	<MDL
19/6/95	<MDL	<MDL	<MDL	4.609	<MDL	1.395	<MDL	4.429	<MDL	0.463
26/6/95	1.977	1.842	0.555	2.186	<MDL	0.679	<MDL	2.507	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
4/7/95	<MDL	<MDL	<MDL	2.018	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/7/95	3.955	18.285	0.240	41.607	<MDL	0.839	<MDL	2.349	<MDL	<MDL
14/7/95	1.141	3.800	0.329	4.426	<MDL	0.718	<MDL	<MDL	<MDL	<MDL
17/7/95	44.224	2.730	<MDL	11.694	<MDL	0.514	<MDL	3.363	<MDL	<MDL
27/7/95	<MDL	<MDL	<MDL	0.497	0.229	0.602	<MDL	0.824	0.720	<MDL
19/8/95	<MDL	<MDL	<MDL	5.796	<MDL	3.885	<MDL	<MDL	<MDL	<MDL
21/8/95	6.683	3.941	9.639	3.952	<MDL	0.387	<MDL	<MDL	<MDL	<MDL
25/8/95	1.948	1.667	1.755	1.250	0.161	0.582	<MDL	2.379	<MDL	<MDL
31/8/95	0.665	<MDL	1.921	0.557	<MDL	0.207	<MDL	3.865	<MDL	<MDL
6/9/95	<MDL	<MDL	<MDL	0.730	<MDL	<MDL	<MDL	1.860	<MDL	<MDL
11/9/95	0.263	0.446	0.190	0.362	0.119	0.515	<MDL	2.457	<MDL	<MDL
18/10/95	1.539	4.388	2.436	0.477	0.319	0.490	<MDL	<MDL	<MDL	<MDL
30/10/95	0.203	1.154	0.504	0.424	0.440	0.693	0.265	2.514	<MDL	<MDL
16/3/96	8.384	8.845	4.705	5.510	<MDL	3.753	<MDL	7.458	<MDL	<MDL
10/4/96	3.533	3.266	3.161	1.863	5.495	4.777	<MDL	4.183	<MDL	<MDL
3/5/96	<MDL	<MDL	0.959	<MDL	6.185	5.385	<MDL	17.306	<MDL	<MDL
17/5/96	9.041	<MDL	10.367	<MDL	<MDL	4.780	<MDL	6.831	<MDL	<MDL
21/5/96	<MDL	3.408	<MDL	4.295	<MDL	3.681	<MDL	4.106	<MDL	<MDL
29/5/96	<MDL	<MDL	3.992	0.916	<MDL	4.184	<MDL	2.889	<MDL	<MDL
31/5/96	1.303	<MDL	1.056	0.925	5.748	4.492	<MDL	3.373	<MDL	<MDL
2/6/96	<MDL	<MDL	<MDL	0.912	5.236	4.286	<MDL	3.155	<MDL	<MDL
3/6/96	0.957	<MDL	<MDL	1.351	5.137	4.147	<MDL	2.720	<MDL	<MDL
4/6/96	<MDL	<MDL	<MDL	3.976	7.232	6.042	<MDL	6.856	<MDL	<MDL
6/6/96	2.063	<MDL	1.542	1.302	5.222	4.198	<MDL	3.225	<MDL	<MDL
8/6/96	<MDL	<MDL	1.415	0.773	5.112	4.193	<MDL	2.827	<MDL	<MDL
10/6/96	<MDL	<MDL	1.272	1.518	<MDL	8.187	<MDL	5.230	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
12/6/96	1.852	0.417	1.263	0.988	5.435	4.301	<MDL	2.904	<MDL	<MDL
14/6/96	1.625	<MDL	37.243	0.873	<MDL	4.219	<MDL	3.007	<MDL	<MDL
16/6/96	4.159	2.261	2.775	3.459	2.683	2.174	<MDL	5.946	<MDL	<MDL
17/6/96	4.705	<MDL	5.104	1.242	<MDL	4.188	<MDL	3.924	<MDL	<MDL
18/6/96	4.884	1.381	3.488	1.908	<MDL	4.362	<MDL	3.607	<MDL	<MDL
20/6/96	1.582	2.745	<MDL	3.780	<MDL	0.932	<MDL	7.524	3.385	<MDL
22/6/96	1.628	2.480	5.840	1.821	<MDL	7.801	<MDL	7.661	<MDL	<MDL
24/6/96	1.260	5.852	7.597	1.260	5.787	<MDL	7.590	<MDL	7.393	<MDL
26/6/96	1.150	7.441	<MDL	3.197	<MDL	<MDL	<MDL	7.710	<MDL	<MDL
28/6/96	0.864	3.315	0.359	2.102	<MDL	8.928	<MDL	8.352	<MDL	<MDL
30/6/96	9.659	16.013	20.802	4.344	<MDL	<MDL	<MDL	8.018	<MDL	<MDL
2/7/96	1.460	5.391	0.533	1.807	<MDL	7.559	<MDL	7.942	1.186	<MDL
4/7/96	8.907	3.427	2.255	1.870	<MDL	7.602	<MDL	8.652	<MDL	<MDL
6/7/96	3.800	5.276	<MDL	3.752	<MDL	<MDL	<MDL	8.176	<MDL	<MDL
8/7/96	0.923	5.824	<MDL	1.376	<MDL	7.586	<MDL	7.173	<MDL	<MDL
12/7/96	12.154	14.602	4.815	2.082	6.680	7.557	<MDL	7.752	<MDL	<MDL
14/7/96	24.320	13.908	7.724	1.391	<MDL	7.558	<MDL	10.535	<MDL	<MDL
16/7/96	10.031	3.057	2.386	1.406	<MDL	7.575	<MDL	7.363	<MDL	<MDL
18/7/96	4.184	2.653	0.914	1.461	<MDL	7.691	<MDL	8.070	<MDL	<MDL
22/7/96	39.479	8.226	680.468	4.920	<MDL	7.540	<MDL	7.582	<MDL	<MDL
24/7/96	15.708	7.431	42.369	3.052	<MDL	3.758	<MDL	7.483	<MDL	<MDL
26/7/96	4.983	2.462	25.158	1.735	<MDL	7.540	<MDL	7.657	<MDL	<MDL
28/7/96	4.118	3.221	7.716	2.578	<MDL	4.865	<MDL	5.299	<MDL	<MDL
29/7/96	<MDL	2.920	11.721	2.534	<MDL	4.835	<MDL	<MDL	<MDL	<MDL
30/7/96	1.635	2.175	4.031	1.196	<MDL	7.686	<MDL	7.134	<MDL	<MDL
1/8/96	<MDL	2.534	14.242	2.365	<MDL	4.727	<MDL	5.197	<MDL	<MDL

5/8/96	DATE	
12/8/96		
<MDL 3.952	MCPA	
2.361 3.087	DICHLORPROP	
<MDL 6.752	2,4-D	
2.534 2.377	BROMOXYNIL	
<MDL <MDL	ETHALFLURALIN	
5.133 4.925	TRIFLURALIN	
<MDL <MDL	TRICLOPYR	
9.420 5.370	ATRAZINE	
<MDL <MDL	TERBUTHYLAZINE	
<MDL <MDL	CYANAZINE	

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
6/7/93	0.600	0.401	0.404	<MDL	0.087	0.400
9/7/93	0.339	0.157	0.366	<MDL	0.065	0.492
12/7/93	0.904	0.505	0.648	<MDL	0.061	<MDL
15/7/93	0.510	<MDL	0.363	<MDL	0.063	<MDL
21/7/93	0.548	0.443	0.645	<MDL	0.102	0.516
25/7/93	0.173	<MDL	0.419	<MDL	0.039	<MDL
27/7/93	0.776	0.437	0.498	0.268	0.113	1.903
2/8/93	0.673	1.099	0.710	<MDL	0.087	0.869
9/8/93	0.315	0.504	0.251	<MDL	0.066	2.473
18/8/93	0.316	0.413	0.331	<MDL	0.061	2.599
26/8/93	0.108	<MDL	0.081	<MDL	0.019	0.126
7/9/93	<MDL	<MDL	0.747	0.157	0.032	0.414
18/10/93	<MDL	<MDL	1.450	0.448	0.059	0.710
05/03/94	0.331	<MDL	<MDL	<MDL	0.346	0.774
14/03/94	0.912	<MDL	<MDL	2.399	0.100	0.601
31/03/94	0.534	<MDL	<MDL	<MDL	<MDL	0.395
03/05/94	0.652	<MDL	<MDL	<MDL	0.037	0.069
11/05/94	0.749	<MDL	<MDL	<MDL	0.027	0.245
16/05/94	0.770	<MDL	<MDL	<MDL	0.091	0.175
26/05/94	0.554	0.612	<MDL	<MDL	0.068	0.194
30/05/94	0.556	<MDL	<MDL	<MDL	0.126	<MDL
07/06/94	<MDL	<MDL	<MDL	<MDL	0.202	0.401
14/06/94	0.713	<MDL	<MDL	<MDL	0.163	0.425
27/06/94	<MDL	<MDL	<MDL	<MDL	0.291	0.700

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
07/07/94	0.523	<MDL	<MDL	<MDL	0.192	<MDL
11/07/94	0.451	<MDL	<MDL	<MDL	0.052	0.428
19/07/94	<MDL	<MDL	<MDL	<MDL	0.144	0.515
25/07/94	<MDL	<MDL	<MDL	<MDL	0.139	0.342
07/10/94	0.618	<MDL	<MDL	<MDL	<MDL	0.428
08/10/94	0.488	<MDL	<MDL	<MDL	0.165	0.415
13/10/94	<MDL	<MDL	<MDL	<MDL	0.161	<MDL
17/10/94	0.636	<MDL	<MDL	0.948	0.184	0.497
18/10/94	0.822	<MDL	<MDL	<MDL	0.297	<MDL
19/10/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
10/11/94	0.959	<MDL	<MDL	<MDL	0.087	<MDL
17/3/95	<MDL	2.209	<MDL	<MDL	0.151	0.607
4/3/95	30.992	<MDL	16.157	<MDL	0.113	0.963
11/4/95	0.559	<MDL	<MDL	<MDL	0.035	0.195
13/4/95	0.966	<MDL	<MDL	<MDL	<MDL	<MDL
24/4/95	0.370	<MDL	0.257	<MDL	0.037	<MDL
2/5/95	0.374	<MDL	<MDL	0.969	0.098	0.041
8/5/95	0.493	0.464	0.624	<MDL	0.055	<MDL
15/5/95	0.508	<MDL	0.297	<MDL	0.043	<MDL
23/5/95	0.235	0.174	0.775	<MDL	0.054	0.165
27/5/95	<MDL	0.007	0.712	<MDL	0.055	0.080
2/6/95	0.289	<MDL	0.332	<MDL	0.035	<MDL
5/6/95	0.801	<MDL	3.734	<MDL	0.053	<MDL
14/6/95	0.276	<MDL	<MDL	<MDL	0.030	0.185
19/6/95	0.724	<MDL	0.474	<MDL	0.051	<MDL
26/6/95	0.398	<MDL	<MDL	<MDL	0.044	0.384

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
4/7/95	<MDL	<MDL	<MDL	<MDL	0.033	<MDL
8/7/95	0.415	<MDL	<MDL	<MDL	0.058	2.326
14/7/95	0.580	<MDL	<MDL	<MDL	0.049	0.431
17/7/95	0.371	<MDL	<MDL	<MDL	0.079	0.653
27/7/95	0.726	<MDL	<MDL	3.641	0.062	0.119
19/8/95	<MDL	<MDL	<MDL	25.019	0.252	0.861
21/8/95	<MDL	<MDL	<MDL	5.824	0.217	1.160
25/8/95	0.813	<MDL	<MDL	8.776	0.101	0.498
31/8/95	0.506	<MDL	<MDL	4.314	0.134	0.266
6/9/95	0.746	<MDL	<MDL	11.587	0.203	<MDL
11/9/95	0.473	<MDL	0.137	1.904	0.090	0.176
18/10/95	0.028	<MDL	<MDL	<MDL	0.130	<MDL
30/10/95	0.190	<MDL	<MDL	1.469	0.115	0.060
16/3/96	<MDL	<MDL	<MDL	<MDL	0.594	<MDL
10/4/96	<MDL	<MDL	<MDL	<MDL	0.408	4.339
3/5/96	18.195	<MDL	15.504	<MDL	0.085	3.043
17/5/96	1.662	2.747	3.110	<MDL	0.466	<MDL
21/5/96	2.515	<MDL	<MDL	<MDL	0.424	<MDL
29/5/96	<MDL	<MDL	<MDL	<MDL	0.051	<MDL
31/5/96	1.801	<MDL	<MDL	<MDL	0.025	<MDL
2/6/96	1.763	<MDL	1.893	<MDL	<MDL	<MDL
3/6/96	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
4/6/96	<MDL	<MDL	<MDL	<MDL	0.339	<MDL
6/6/96	<MDL	<MDL	<MDL	<MDL	0.026	<MDL
8/6/96	1.457	<MDL	<MDL	<MDL	0.000	<MDL
10/6/96	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
12/6/96	1.260	<MDL	<MDL	<MDL	<MDL	1.455
14/6/96	<MDL	<MDL	<MDL	<MDL	0.032	<MDL
16/6/96	0.704	<MDL	<MDL	<MDL	0.436	1.508
17/6/96	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/6/96	1.319	<MDL	<MDL	<MDL	<MDL	<MDL
20/6/96	<MDL	<MDL	<MDL	<MDL	0.811	<MDL
22/6/96	<MDL	<MDL	<MDL	9.664	0.793	<MDL
24/6/96	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/6/96	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
28/6/96	<MDL	<MDL	<MDL	11.172	0.882	<MDL
30/6/96	<MDL	<MDL	<MDL	<MDL	0.796	<MDL
2/7/96	6.611	<MDL	1.929	<MDL	0.872	<MDL
4/7/96	<MDL	<MDL	<MDL	<MDL	0.758	1.813
6/7/96	<MDL	<MDL	<MDL	<MDL	0.822	<MDL
8/7/96	6.714	<MDL	<MDL	<MDL	0.743	<MDL
12/7/96	<MDL	<MDL	<MDL	85.327	0.756	<MDL
14/7/96	6.641	<MDL	<MDL	21.947	0.884	<MDL
16/7/96	3.325	<MDL	<MDL	14.116	0.849	<MDL
18/7/96	3.342	<MDL	<MDL	64.912	0.776	<MDL
22/7/96	<MDL	<MDL	<MDL	10.711	0.841	<MDL
24/7/96	3.607	<MDL	2.908	104.621	1.251	<MDL
26/7/96	<MDL	<MDL	5.730	<MDL	0.782	<MDL
28/7/96	<MDL	<MDL	<MDL	10.180	0.757	<MDL
29/7/96	<MDL	<MDL	<MDL	11.952	0.744	<MDL
30/7/96	<MDL	<MDL	<MDL	11.184	0.749	<MDL
1/8/96	5.124	<MDL	<MDL	9.920	0.727	<MDL

5/8/96	DATE
12/8/96	
<MDL 5.554	TRIALATE
<MDL 1.413	ALACHLOR
<MDL <MDL	METOLACHLOR
<MDL 9.356	CHLORPYRIFOS
0.872	DACTHAL
<MDL	DICLOFOP-METHYL

III. Pesticide Concentrations in Precipitation in the South Tobacco Creek Watershed (ng/L)

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
22/6/93	0.843	3.342	1.183	59.766	0.131	4.310	<MDL	12.551	<MDL	0.456
15/7/93	4.396	1.753	3.284	28.750	<MDL	0.346	<MDL	6.865	<MDL	<MDL
27/7/93	<MDL	0.184	0.974	0.585	<MDL	0.303	<MDL	0.417	<MDL	<MDL
18/8/93	<MDL	0.398	<MDL	<MDL	<MDL	0.639	<MDL	0.698	<MDL	<MDL
20/10/93	<MDL	<MDL	1.321	0.318	<MDL	1.253	<MDL	8.382	<MDL	<MDL
20/05/94	<MDL	<MDL	<MDL	0.811	<MDL	<MDL	<MDL	57.072	<MDL	<MDL
26/05/94	<MDL	<MDL	<MDL	3.674	<MDL	<MDL	<MDL	33.679	<MDL	<MDL
13/06/94	261.848	136.999	62.441	209.937	<MDL	<MDL	<MDL	33.096	<MDL	<MDL
25/06/94	112.319	84.252	48.189	112.719	<MDL	<MDL	<MDL	3.202	<MDL	<MDL
07/07/94	3.780	7.930	<MDL	20.510	<MDL	1.712	<MDL	4.074	<MDL	<MDL
19/07/94	3.829	5.558	<MDL	5.502	<MDL	0.435	0.796	1.583	<MDL	<MDL
12/08/94	<MDL	<MDL	<MDL	1.378	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/08/94	<MDL	<MDL	<MDL	1.238	<MDL	0.895	<MDL	<MDL	<MDL	<MDL
05/09/94	<MDL	<MDL	<MDL	0.709	<MDL	0.317	<MDL	3.794	<MDL	<MDL
11/10/94	<MDL	2.093	<MDL	0.525	0.434	5.097	<MDL	1.278	<MDL	<MDL
24/10/94	<MDL	<MDL	<MDL	0.505	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95	<MDL	0.868	<MDL	1.004	<MDL	<MDL	<MDL	0.366	<MDL	<MDL
8/6/95	37.531	12.439	22.440	37.899	<MDL	0.962	0.371	0.765	<MDL	<MDL
2/7/95	287.390	220.259	428.907	99.183	<MDL	2.025	<MDL	<MDL	<MDL	<MDL
20/7/95	<MDL	27.482	0.498	184.818	<MDL	2.814	<MDL	3.466	3.671	<MDL
7/8/95	<MDL	<MDL	3.218	4.329	<MDL	0.370	<MDL	1.629	<MDL	<MDL
19/8/95	<MDL	<MDL	<MDL	0.551	<MDL	0.846	<MDL	9.681	<MDL	<MDL
6/9/95	<MDL	<MDL	<MDL	0.532	0.462	2.013	<MDL	1.481	0.914	<MDL
18/10/95	<MDL	<MDL	<MDL	0.705	<MDL	0.681	<MDL	<MDL	<MDL	<MDL
30/10/95	<MDL	<MDL	<MDL	1.116	2.922	6.264	<MDL	<MDL	4.093	<MDL

DATE		MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
2/6/96		2.724	<MDL	11.164	1.674	7.130	8.428	<MDL	13.999	<MDL	<MDL
6/6/96		46.592	5.615	59.819	7.946	11.190	9.700	<MDL	23.606	<MDL	<MDL
16/6/96		160.714	37.943	64.677	25.745	11.089	11.836	<MDL	180.454	<MDL	54.364
20/6/96		188.720	64.150	128.960	45.106	1.966	5.774	<MDL	8.435	<MDL	<MDL
24/6/96		939.741	259.323	212.392	38.577	<MDL	<MDL	<MDL	19.403	<MDL	<MDL
26/6/96		14.837	10.984	0.158	14.647	<MDL	5.448	<MDL	5.491	<MDL	<MDL
8/7/96		407.659	128.395	219.888	92.436	<MDL	<MDL	<MDL	8.844	<MDL	<MDL
12/7/96		101.362	22.274	178.855	12.551	<MDL	10.914	<MDL	14.239	<MDL	<MDL
14/7/96		32.567	11.012	11.955	3.255	1.810	2.287	<MDL	<MDL	<MDL	<MDL
20/7/96		47.295	15.992	17.361	4.728	2.629	3.322	<MDL	<MDL	<MDL	<MDL
22/7/96		7.728	18.827	18.066	2.425	<MDL	11.363	<MDL	<MDL	<MDL	<MDL
28/7/96		5.223	3.077	62.156	1.432	<MDL	<MDL	<MDL	5.746	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
22/6/93	3.829	4.669	0.990	0.599	1.942	10.064
15/7/93	3.529	1.198	1.051	<MDL	1.645	0.833
27/7/93	1.093	<MDL	0.322	<MDL	1.852	0.678
18/8/93	<MDL	<MDL	<MDL	1.288	4.070	6.503
20/10/93	0.765	<MDL	<MDL	3.416	1.344	0.858
20/05/94	3.456	<MDL	4.037	<MDL	2.291	<MDL
26/05/94	5.406	3.780	119.975	<MDL	2.744	0.351
13/06/94	5.232	2.441	0.932	<MDL	3.791	12.027
25/06/94	2.956	<MDL	<MDL	<MDL	1.848	<MDL
07/07/94	3.257	<MDL	0.254	<MDL	2.526	0.349
19/07/94	<MDL	<MDL	<MDL	<MDL	0.804	0.809
12/08/94	<MDL	<MDL	<MDL	23.876	1.040	<MDL
24/08/94	<MDL	<MDL	<MDL	37.528	1.726	<MDL
05/09/94	<MDL	<MDL	<MDL	8.736	2.958	<MDL
11/10/94	1.781	0.388	<MDL	0.646	4.373	<MDL
24/10/94	<MDL	<MDL	<MDL	<MDL	2.351	<MDL
15/5/95	5.976	2.004	2.717	1.458	2.230	<MDL
8/6/95	4.759	2.634	2.776	<MDL	1.028	8.399
2/7/95	18.170	5.397	2.409	<MDL	1.388	38.250
20/7/95	2.784	<MDL	<MDL	<MDL	0.697	8.471
7/8/95	<MDL	<MDL	<MDL	2.882	0.283	<MDL
19/8/95	1.265	<MDL	0.423	16.042	<MDL	<MDL
6/9/95	1.120	<MDL	<MDL	12.197	1.717	<MDL
18/10/95	0.988	<MDL	<MDL	<MDL	1.460	<MDL

DATE		TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
30/10/95		6.259	<MDL	<MDL	<MDL	1.521	<MDL
2/6/96		13.042	3.041	7.307	<MDL	2.187	<MDL
6/6/96		9.818	<MDL	3.984	<MDL	<MDL	8.283
16/6/96		<MDL	<MDL	<MDL	<MDL	2.070	33.314
20/6/96		10.573	<MDL	<MDL	<MDL	1.981	6.999
24/6/96		10.480	<MDL	<MDL	16.403	2.390	4.810
26/6/96		6.754	<MDL	<MDL	<MDL	1.865	1.843
8/7/96		6.251	<MDL	<MDL	<MDL	1.856	4.131
12/7/96		<MDL	<MDL	<MDL	24.059	1.678	3.646
14/7/96		<MDL	<MDL	<MDL	20.123	0.682	0.891
20/7/96		<MDL	<MDL	<MDL	29.224	0.991	1.294
22/7/96		10.226	<MDL	<MDL	31.762	4.175	<MDL
28/7/96		<MDL	<MDL	<MDL	8.854	0.617	<MDL

IV. Pesticide Concentrations in Air (total of vapour and particle phases) in the South Tobacco Creek Watershed (ng/m³)

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
15/6/93	0.012	0.033	0.016	0.315	0.750	5.968	<MDL	0.099	0.025	<MDL
21/6/93	0.965	0.039	0.061	0.535	1.225	11.243	<MDL	0.002	<MDL	0.017
27/6/93	0.001	<MDL	0.013	0.066	0.366	0.499	<MDL	0.079	<MDL	<MDL
3/7/93	<MDL	0.029	0.015	0.095	0.900	2.744	<MDL	0.134	0.021	<MDL
7/9/93	0.005	0.017	0.005	0.095	0.382	1.654	<MDL	0.053	<MDL	0.037
15/7/93	0.011	0.017	0.021	0.061	0.952	4.070	<MDL	0.066	0.080	<MDL
21/7/93	0.007	0.016	0.022	0.056	0.668	1.605	<MDL	0.044	0.013	<MDL
27/7/93	<MDL	<MDL	0.019	0.046	0.140	0.737	<MDL	0.079	0.013	<MDL
2/8/93	0.002	<MDL	0.014	<MDL	0.126	0.568	<MDL	0.011	<MDL	<MDL
9/8/93	0.007	0.018	0.025	0.049	0.164	3.040	<MDL	0.100	<MDL	<MDL
26/8/93	<MDL	0.021	0.002	0.041	0.136	2.553	<MDL	0.086	<MDL	<MDL
7/9/93	0.004	<MDL	0.017	0.036	<MDL	0.356	<MDL	0.047	<MDL	<MDL
19/9/93	0.038	<MDL	0.014	0.013	<MDL	0.483	<MDL	0.037	<MDL	<MDL
4/10/93	<MDL	0.037	0.023	0.038	<MDL	0.048	<MDL	0.013	0.014	<MDL
26/4/94	0.003	<MDL	0.011	0.026	0.032	0.050	<MDL	0.018	<MDL	<MDL
2/5/94	<MDL	<MDL	0.024	0.059	0.078	0.194	<MDL	0.043	<MDL	<MDL
8/5/94	<MDL	0.007	<MDL	0.045	<MDL	0.202	<MDL	0.054	<MDL	<MDL
14/5/94	0.009	0.010	0.022	<MDL	<MDL	0.202	<MDL	0.056	<MDL	<MDL
20/5/94	0.011	0.013	0.008	<MDL	<MDL	<MDL	<MDL	0.019	<MDL	<MDL
26/5/94	<MDL	<MDL	<MDL	0.054	0.159	<MDL	<MDL	0.050	0.026	<MDL
1/6/94	0.014	0.011	<MDL	0.352	0.136	2.015	<MDL	0.083	0.026	0.029
7/6/94	0.004	0.002	0.003	0.248	<MDL	0.105	<MDL	0.099	<MDL	0.008
13/6/94	0.038	0.304	0.021	0.277	5.359	17.557	<MDL	0.104	<MDL	<MDL
19/6/94	0.052	0.281	0.023	0.330	0.903	9.862	<MDL	0.087	<MDL	<MDL
25/6/94	0.002	0.003	<MDL	0.061	0.163	2.501	<MDL	0.045	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
1/7/94	0.007	0.004	0.029	0.118	<MDL	1.334	<MDL	0.033	0.016	<MDL
7/7/94	<MDL	0.001	0.008	0.030	0.073	0.666	<MDL	0.032	<MDL	0.005
17/7/94	<MDL	<MDL	<MDL	<MDL	0.113	1.204	<MDL	0.034	0.008	<MDL
25/7/94	0.006	<MDL	0.020	0.031	0.100	0.309	<MDL	0.068	0.010	0.010
31/7/94	0.004	0.037	0.026	<MDL	0.134	1.992	<MDL	0.011	0.026	<MDL
6/8/94	0.001	0.002	0.020	0.034	0.078	0.768	<MDL	0.059	<MDL	<MDL
12/8/94	0.004	<MDL	0.019	0.042	0.110	1.138	<MDL	0.077	0.012	<MDL
18/8/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.030	0.045	<MDL
24/8/94	<MDL	<MDL	0.020	<MDL	0.135	2.515	<MDL	0.051	0.065	<MDL
30/8/94	<MDL	0.018	0.022	0.004	<MDL	0.309	<MDL	0.026	<MDL	<MDL
5/9/94	<MDL	0.137	0.014	0.035	<MDL	5.453	<MDL	0.011	0.007	<MDL
17/9/94	0.014	0.007	0.012	0.028	0.025	3.770	<MDL	0.054	<MDL	<MDL
29/9/94	0.008	0.002	0.023	0.038	0.199	1.533	<MDL	0.027	<MDL	<MDL
11/10/94	0.008	0.017	0.019	0.069	0.510	1.301	<MDL	0.074	0.040	<MDL
23/10/94	<MDL	<MDL	0.014	0.045	0.094	<MDL	<MDL	0.102	0.459	<MDL
3/5/95	<MDL	0.013	0.013	0.011	0.074	0.380	<MDL	0.007	<MDL	<MDL
9/5/95	<MDL	0.008	<MDL	0.013	0.091	0.210	<MDL	0.016	0.010	<MDL
15/5/95	<MDL	<MDL	<MDL	<MDL	0.124	0.438	<MDL	0.008	0.008	<MDL
21/5/95	<MDL	<MDL	<MDL	<MDL	0.263	1.215	<MDL	0.011	<MDL	<MDL
27/5/95	<MDL	0.032	0.013	0.014	0.093	1.357	<MDL	0.014	<MDL	<MDL
2/6/95	<MDL	<MDL	<MDL	0.045	0.643	7.184	<MDL	0.018	<MDL	<MDL
8/6/95	<MDL	<MDL	0.008	0.019	0.118	1.007	<MDL	0.007	<MDL	<MDL
14/6/95	0.008	<MDL	<MDL	0.059	0.082	0.212	<MDL	0.240	<MDL	0.173
20/6/95	0.008	<MDL	<MDL	0.040	0.758	13.469	<MDL	0.050	<MDL	0.022
26/6/95	0.009	0.015	<MDL	0.157	0.120	3.872	<MDL	0.025	<MDL	0.018
2/7/95	0.016	<MDL	<MDL	0.118	0.194	1.180	<MDL	0.012	<MDL	<MDL
8/7/95	0.008	0.011	0.018	0.074	0.111	0.928	<MDL	0.020	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
14/7/95	<MDL	<MDL	<MDL	0.041	0.118	0.825	<MDL	0.025	0.012	<MDL
20/7/95	<MDL	<MDL	<MDL	0.036	0.077	0.605	<MDL	0.016	<MDL	<MDL
26/7/95	<MDL	<MDL	<MDL	0.034	0.058	0.477	<MDL	0.010	<MDL	<MDL
1/8/95	<MDL	<MDL	0.020	0.028	0.092	0.155	0.002	0.011	<MDL	<MDL
7/8/95	<MDL	0.161	0.018	0.033	0.165	1.107	<MDL	0.013	<MDL	<MDL
13/8/95	<MDL	<MDL	<MDL	0.022	0.073	0.925	<MDL	0.016	<MDL	<MDL
19/8/95	<MDL	0.003	<MDL	0.008	0.028	0.297	<MDL	0.005	<MDL	<MDL
25/8/95	<MDL	0.006	<MDL	0.013	0.045	0.587	<MDL	0.011	<MDL	<MDL
31/8/95	<MDL	0.007	<MDL	0.013	0.050	0.256	<MDL	0.010	<MDL	<MDL
6/9/95	<MDL	<MDL	<MDL	0.007	<MDL	0.125	<MDL	0.006	<MDL	<MDL
12/9/95	<MDL	<MDL	0.009	0.009	0.059	0.467	<MDL	0.013	<MDL	<MDL
24/9/95	<MDL	<MDL	<MDL	0.004	0.027	0.290	<MDL	0.025	<MDL	<MDL
6/10/95	<MDL	<MDL	<MDL	0.003	0.064	0.597	<MDL	0.004	<MDL	<MDL
12/10/95	<MDL	<MDL	<MDL	0.006	0.177	0.475	<MDL	0.004	<MDL	<MDL
30/10/95	<MDL	0.107	<MDL	0.006	0.047	0.239	<MDL	0.006	<MDL	<MDL
29/5/96	0.038	0.828	0.107	0.044	0.173	5.919	<MDL	0.106	<MDL	<MDL
31/5/96	<MDL	0.145	0.034	0.047	1.347	9.239	<MDL	<MDL	<MDL	<MDL
2/6/96	0.012	0.160	<MDL	0.011	0.117	2.413	<MDL	0.045	<MDL	<MDL
4/6/96	<MDL	0.178	<MDL	0.089	0.464	3.608	<MDL	0.153	<MDL	<MDL
6/6/96	<MDL	0.706	<MDL	0.044	1.509	7.169	<MDL	0.148	<MDL	<MDL
8/6/96	0.004	0.021	<MDL	0.160	<MDL	0.077	<MDL	0.104	<MDL	<MDL
10/6/96	0.031	0.120	0.082	0.116	0.113	1.325	<MDL	0.214	<MDL	<MDL
12/6/96	<MDL	0.021	0.030	0.086	0.121	1.001	<MDL	<MDL	<MDL	<MDL
14/6/96	<MDL	0.017	0.078	0.158	0.307	4.989	<MDL	0.185	<MDL	0.046
16/6/96	<MDL	0.039	0.037	0.201	0.070	1.498	<MDL	0.385	<MDL	0.080
18/6/96	0.026	0.022	0.077	0.117	0.398	8.229	<MDL	0.045	<MDL	<MDL
20/6/96	0.032	0.027	0.040	0.136	0.882	10.462	<MDL	<MDL	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
22/6/96	0.040	0.212	0.030	0.220	0.209	1.771	<MDL	0.044	<MDL	<MDL
24/6/96	<MDL	0.113	<MDL	0.565	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/6/96	2.824	0.190	0.644	0.332	0.811	5.290	<MDL	0.165	<MDL	<MDL
28/6/96	13.110	0.959	3.511	2.079	0.129	1.465	<MDL	0.036	<MDL	<MDL
30/6/96	0.036	0.063	0.028	0.327	0.105	1.371	<MDL	0.040	<MDL	<MDL
2/7/96	7.092	0.555	2.178	0.896	0.051	0.633	<MDL	0.136	<MDL	<MDL
4/7/96	0.037	0.128	0.025	0.288	0.100	1.057	<MDL	0.075	<MDL	<MDL
6/7/96	0.014	0.198	0.085	0.084	0.118	1.383	<MDL	<MDL	<MDL	<MDL
8/7/96	0.029	0.307	<MDL	0.078	0.107	1.536	<MDL	0.047	<MDL	<MDL
10/7/96	0.030	0.558	0.044	0.148	0.366	3.897	<MDL	0.173	<MDL	<MDL
12/7/96	0.012	0.135	0.021	0.048	0.083	2.199	<MDL	<MDL	<MDL	<MDL
14/7/96	<MDL	0.307	0.016	0.014	0.064	1.882	<MDL	0.025	<MDL	<MDL
16/7/96	0.008	0.663	0.029	0.029	0.177	1.442	<MDL	0.031	<MDL	<MDL
18/7/96	<MDL	0.129	0.039	0.003	0.079	1.368	<MDL	0.027	<MDL	<MDL
20/7/96	<MDL	<MDL	0.013	0.026	0.060	0.117	0.053	<MDL	<MDL	<MDL
24/7/96	0.010	<MDL	0.019	<MDL	0.060	0.123	<MDL	<MDL	<MDL	<MDL
26/7/96	<MDL	<MDL	0.050	<MDL	0.187	1.005	<MDL	<MDL	<MDL	<MDL
28/7/96	<MDL	<MDL	<MDL	0.044	0.083	0.558	<MDL	<MDL	<MDL	<MDL
30/7/96	<MDL	<MDL	<MDL	0.038	0.067	0.951	<MDL	<MDL	<MDL	<MDL
1/8/96	<MDL	0.027	0.051	0.062	0.114	0.401	<MDL	<MDL	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
15/6/93	0.841	0.076	0.047	0.339	0.026	0.071
21/6/93	0.391	<MDL	<MDL	0.063	0.025	1.613
27/6/93	0.044	0.007	0.012	0.031	0.005	0.049
3/7/93	0.390	<MDL	<MDL	0.076	<MDL	<MDL
7/9/93	0.595	0.119	0.029	0.045	0.005	<MDL
15/7/93	0.288	0.035	0.014	0.042	0.025	0.007
21/7/93	0.322	0.047	0.028	0.052	<MDL	0.008
27/7/93	0.041	0.018	0.013	0.071	0.013	<MDL
2/8/93	0.043	<MDL	0.012	0.032	0.006	<MDL
9/8/93	0.295	<MDL	<MDL	0.092	0.022	<MDL
26/8/93	0.194	0.109	0.028	0.057	0.014	<MDL
7/9/93	0.077	0.042	0.016	0.041	0.002	0.012
19/9/93	0.070	<MDL	<MDL	0.057	0.005	<MDL
4/10/93	0.004	0.182	0.017	0.038	0.001	<MDL
26/4/94	0.003	0.007	0.007	0.015	<MDL	0.005
2/5/94	0.142	0.013	<MDL	0.033	0.084	<MDL
8/5/94	0.017	0.026	0.013	0.028	0.069	<MDL
14/5/94	0.126	0.015	0.020	0.041	0.074	<MDL
20/5/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94	0.492	0.045	0.016	0.044	<MDL	0.018
1/6/94	0.162	0.048	0.016	0.041	<MDL	0.018
7/6/94	0.026	0.011	0.016	0.048	<MDL	0.016
13/6/94	<MDL	0.060	<MDL	1.430	0.081	0.047
19/6/94	1.911	0.111	<MDL	0.082	<MDL	0.038
25/6/94	0.233	0.038	0.014	0.037	<MDL	0.014

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
1/7/94	0.154	0.014	<MDL	0.460	0.018	0.014
7/7/94	<MDL	0.018	0.008	0.045	<MDL	0.006
17/7/94	0.256	0.040	0.014	0.135	<MDL	0.017
25/7/94	0.065	0.043	0.010	0.027	<MDL	0.017
31/7/94	0.115	0.072	0.022	1.556	<MDL	0.303
6/8/94	0.067	<MDL	0.013	3.773	<MDL	0.009
12/8/94	0.120	0.042	0.014	9.809	<MDL	0.020
18/8/94	<MDL	<MDL	<MDL	0.011	0.015	0.087
24/8/94	0.186	0.057	0.024	<MDL	<MDL	0.021
30/8/94	0.034	0.015	0.013	0.102	0.074	<MDL
5/9/94	0.223	<MDL	0.012	<MDL	<MDL	0.008
17/9/94	0.181	0.105	0.011	0.065	<MDL	0.006
29/9/94	0.033	0.024	0.012	0.035	0.003	0.004
11/10/94	0.090	0.027	<MDL	0.053	0.025	<MDL
23/10/94	0.059	0.051	<MDL	0.019	0.015	0.011
3/5/95	0.079	<MDL	<MDL	0.020	0.005	<MDL
9/5/95	0.077	<MDL	<MDL	0.072	0.001	<MDL
15/5/95	0.089	<MDL	<MDL	0.015	0.004	<MDL
21/5/95	0.078	<MDL	<MDL	<MDL	0.004	<MDL
27/5/95	<MDL	<MDL	<MDL	0.029	0.006	<MDL
2/6/95	0.546	<MDL	<MDL	0.043	0.006	<MDL
8/6/95	0.453	0.015	<MDL	<MDL	0.003	<MDL
14/6/95	0.142	0.018	0.009	0.023	0.007	0.027
20/6/95	7.853	0.027	<MDL	0.067	0.008	0.021
26/6/95	2.351	<MDL	<MDL	0.069	0.001	0.001
27/95	0.263	0.012	<MDL	0.025	0.007	0.013

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACHTAL	DICLOFOP-METHYL
8/7/95	0.518	<MDL	<MDL	<MDL	0.001	0.011
14/7/95	0.124	<MDL	<MDL	<MDL	0.002	<MDL
20/7/95	0.463	<MDL	<MDL	0.110	0.005	<MDL
26/7/95	0.350	<MDL	<MDL	0.040	0.003	<MDL
1/8/95	0.055	<MDL	0.002	23.543	0.001	<MDL
7/8/95	0.389	<MDL	<MDL	16.790	0.016	<MDL
13/8/95	0.370	<MDL	<MDL	4.903	0.011	<MDL
19/8/95	0.320	0.021	<MDL	1.146	0.005	0.003
25/8/95	0.308	<MDL	<MDL	0.549	0.008	<MDL
31/8/95	0.209	0.022	<MDL	0.201	0.004	<MDL
6/9/95	<MDL	<MDL	<MDL	0.093	0.003	<MDL
12/9/95	0.056	<MDL	<MDL	0.128	0.004	<MDL
24/9/95	0.073	<MDL	<MDL	<MDL	0.002	<MDL
6/10/95	0.160	<MDL	<MDL	0.027	0.002	<MDL
12/10/95	0.099	<MDL	<MDL	0.019	0.006	<MDL
30/10/95	0.109	<MDL	<MDL	<MDL	0.002	<MDL
29/5/96	12.270	0.275	0.063	0.111	0.026	<MDL
31/5/96	8.824	0.012	<MDL	<MDL	0.032	0.008
2/6/96	0.452	0.016	<MDL	0.116	0.014	<MDL
4/6/96	1.602	<MDL	<MDL	<MDL	0.021	0.027
6/6/96	4.091	<MDL	<MDL	<MDL	0.017	<MDL
8/6/96	<MDL	<MDL	<MDL	<MDL	0.007	0.027
10/6/96	1.029	0.013	<MDL	<MDL	0.030	0.133
12/6/96	0.077	0.015	<MDL	<MDL	0.007	0.072
14/6/96	5.518	<MDL	<MDL	<MDL	0.031	0.285
16/6/96	0.524	0.023	<MDL	2.027	0.032	0.082

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
18/6/96	3.394	0.010	0.100	<MDL	0.083	0.133
20/6/96	1.493	0.027	<MDL	<MDL	0.016	0.019
22/6/96	0.297	0.022	0.057	<MDL	0.303	0.014
24/6/96	<MDL	0.034	<MDL	<MDL	<MDL	<MDL
26/6/96	4.103	0.024	<MDL	<MDL	0.011	0.048
28/6/96	0.583	<MDL	<MDL	<MDL	0.019	0.019
30/6/96	0.433	0.016	<MDL	<MDL	0.015	0.013
2/7/96	0.902	<MDL	<MDL	<MDL	0.013	0.022
4/7/96	0.793	<MDL	<MDL	0.166	0.017	0.043
6/7/96	0.336	<MDL	<MDL	<MDL	0.010	<MDL
8/7/96	0.333	0.013	<MDL	<MDL	0.011	<MDL
10/7/96	1.720	<MDL	<MDL	12.072	0.026	0.080
12/7/96	0.392	<MDL	<MDL	8.142	0.008	<MDL
14/7/96	0.589	0.008	<MDL	9.908	0.003	0.017
16/7/96	0.721	0.010	<MDL	102.544	0.013	0.033
18/7/96	0.123	0.013	<MDL	25.063	0.008	<MDL
20/7/96	0.237	0.030	<MDL	4.341	0.019	<MDL
24/7/96	0.097	0.005	<MDL	3.411	0.006	0.031
26/7/96	0.152	0.012	<MDL	21.639	0.010	0.035
28/7/96	0.148	0.012	<MDL	13.984	0.016	<MDL
30/7/96	0.153	0.042	<MDL	1.988	0.010	<MDL
1/8/96	0.536	0.015	<MDL	11.639	0.014	<MDL

V. Pesticide Concentrations in the Red River and Tributaries (ng/L)

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
Assiniboine River										
18/6/93	3.920	3.414	4.528	3.829	<MDL	<MDL	0.086	1.256	0.442	<MDL
5/7/93	7.435	2.774	5.944	2.803	<MDL	0.097	0.130	5.872	0.477	<MDL
26/7/93	0.183	0.135	1.135	14.041	1.831	1.181	<MDL	0.237	2.337	<MDL
16/8/93	8.872	14.275	6.492	7.724	<MDL	<MDL	0.187	0.793	0.833	<MDL
6/9/93	2.347	6.155	2.012	0.511	<MDL	<MDL	9.920	0.967	2.494	1.554
20/10/93	0.744	1.938	1.929	0.205	<MDL	<MDL	0.178	5.991	2.314	<MDL
5/5/94	<MDL	<MDL	<MDL	0.859	<MDL	<MDL	<MDL	3.330	<MDL	<MDL
17/5/94	0.921	<MDL	1.043	1.066	2.970	2.433	<MDL	4.889	<MDL	<MDL
31/5/94	0.614	0.815	0.774	0.789	2.066	1.709	<MDL	6.928	<MDL	<MDL
16/6/94	1.810	1.037	1.022	2.887	<MDL	<MDL	<MDL	0.906	<MDL	<MDL
28/6/94	4.311	1.805	3.192	1.700	<MDL	<MDL	<MDL	4.867	<MDL	<MDL
12/7/94	5.920	2.920	4.301	10.178	<MDL	0.485	<MDL	2.628	<MDL	<MDL
26/7/94	1.412	0.956	1.123	0.975	<MDL	<MDL	<MDL	4.559	<MDL	<MDL
9/8/94	0.377	<MDL	0.433	0.204	<MDL	<MDL	<MDL	0.863	<MDL	<MDL
23/8/94	0.261	<MDL	0.687	0.619	<MDL	0.453	<MDL	0.700	<MDL	<MDL
7/9/94	0.303	<MDL	<MDL	0.226	<MDL	<MDL	<MDL	1.470	<MDL	<MDL
27/9/94	0.157	<MDL	<MDL	0.189	0.428	0.393	<MDL	1.417	<MDL	<MDL
18/10/94	0.324	0.202	<MDL	0.185	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
28/3/95	<MDL	<MDL	<MDL	0.864	0.768	0.600	<MDL	1.401	<MDL	<MDL
11/4/95	<MDL	<MDL	<MDL	0.107	<MDL	<MDL	<MDL	0.418	<MDL	<MDL
25/4/95	0.646	0.581	1.105	0.254	0.285	0.301	0.098	0.776	<MDL	<MDL
9/5/95	<MDL	<MDL	<MDL	0.065	0.244	0.260	<MDL	0.449	<MDL	<MDL
24/5/95	<MDL	<MDL	<MDL	0.247	0.391	0.293	<MDL	0.927	<MDL	<MDL
6/6/95	0.024	<MDL	0.025	0.023	<MDL	0.088	<MDL	0.140	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
20/6/95	<MDL	<MDL	<MDL	0.349	<MDL	0.258	<MDL	1.066	<MDL	<MDL
5/7/95	<MDL	<MDL	<MDL	1.473	<MDL	0.263	<MDL	0.504	<MDL	<MDL
18/7/95	<MDL	<MDL	<MDL	0.226	0.355	0.305	<MDL	0.549	<MDL	<MDL
1/8/95	0.100	<MDL	<MDL	0.108	<MDL	0.271	0.258	0.956	<MDL	<MDL
22/8/95	<MDL	<MDL	<MDL	0.033	<MDL	0.160	<MDL	0.491	<MDL	<MDL
13/9/95	<MDL	<MDL	0.040	0.008	<MDL	0.052	<MDL	0.118	<MDL	<MDL
3/10/95	<MDL	<MDL	<MDL	0.031	0.340	0.251	<MDL	0.635	<MDL	<MDL
31/10/95	0.135	<MDL	<MDL	0.037	0.441	0.336	0.055	0.654	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Assiniboine River

18/6/93	0.718	<MDL	1.986	2.331	0.094	0.272
5/7/93	0.689	<MDL	0.831	0.587	0.130	1.459
26/7/93	4.607	0.083	0.653	13.216	0.197	0.377
16/8/93	1.507	0.424	0.148	0.691	0.333	1.205
6/9/93	<MDL	<MDL	0.050	<MDL	0.113	1.229
20/10/93	0.715	<MDL	0.339	<MDL	0.053	<MDL
5/5/94	1.711	<MDL	<MDL	<MDL	0.083	0.298
17/5/94	1.486	<MDL	1.436	<MDL	0.032	0.551
31/5/94	1.114	<MDL	0.759	<MDL	0.058	0.518
16/6/94	1.156	<MDL	0.657	<MDL	0.056	0.722
28/6/94	1.412	<MDL	2.148	<MDL	0.100	0.976
12/7/94	0.139	<MDL	<MDL	<MDL	0.076	<MDL
26/7/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
9/8/94	<MDL	<MDL	<MDL	<MDL	0.038	<MDL
23/8/94	<MDL	<MDL	<MDL	1.007	0.062	<MDL
7/9/94	0.158	<MDL	<MDL	<MDL	0.062	<MDL
27/9/94	<MDL	<MDL	<MDL	<MDL	0.029	<MDL
18/10/94	<MDL	<MDL	<MDL	<MDL	0.024	0.074
28/3/95	<MDL	<MDL	<MDL	<MDL	0.081	<MDL
11/4/95	2.133	<MDL	0.395	<MDL	0.044	<MDL
25/4/95	3.176	<MDL	0.352	<MDL	0.047	0.312
9/5/95	0.804	<MDL	0.195	<MDL	0.022	<MDL
24/5/95	0.823	<MDL	0.462	<MDL	0.049	<MDL
6/6/95	0.058	<MDL	<MDL	<MDL	0.007	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
20/6/95	0.289	<MDL	<MDL	<MDL	0.046	<MDL
5/7/95	<MDL	<MDL	<MDL	<MDL	0.028	0.241
18/7/95	0.239	<MDL	<MDL	0.515	0.044	0.172
1/8/95	0.160	<MDL	0.308	2.145	0.023	<MDL
22/8/95	<MDL	<MDL	<MDL	<MDL	0.022	<MDL
13/9/95	<MDL	<MDL	<MDL	<MDL	0.004	<MDL
3/10/95	<MDL	<MDL	<MDL	<MDL	0.018	<MDL
31/10/95	0.233	<MDL	<MDL	<MDL	0.025	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	------	-------------	-------	-----------	---------------	-------------	-----------	----------	----------------	-----------

LaSalle River

14/6/93	12.589	4.367	16.113	5.610	<MDL	<MDL	5.357	0.793	<MDL	<MDL
7/7/93	0.939	0.344	1.502	1.884	<MDL	0.092	0.415	7.046	2.391	<MDL
26/7/93	0.116	0.106	1.930	22.887	0.201	2.770	<MDL	0.427	<MDL	0.134
16/8/93	4.703	5.211	13.364	5.356	<MDL	0.709	0.226	0.734	0.473	<MDL
6/9/93	1.216	12.110	6.367	3.499	<MDL	<MDL	58.740	5.597	2.414	<MDL
8/9/93	14.953	10.322	2.248	2.653	<MDL	0.093	54.258	5.911	0.608	1.451
19/10/93	2.111	2.916	1.208	0.449	<MDL	0.098	9.769	5.562	2.433	<MDL
4/5/94	<MDL	<MDL	<MDL	1.123	<MDL	<MDL	1.790	3.686	<MDL	<MDL
17/5/94	<MDL	<MDL	<MDL	0.088	<MDL	<MDL	<MDL	3.062	<MDL	<MDL
31/5/94	<MDL	<MDL	<MDL	1.975	<MDL	<MDL	<MDL	15.717	0.141	1.369
16/6/94	0.519	0.369	<MDL	3.344	<MDL	<MDL	0.298	8.704	<MDL	<MDL
28/6/94	14.568	2.459	3.841	1.726	<MDL	<MDL	2.389	3.519	<MDL	<MDL
12/7/94	134.239	9.785	11.740	42.386	<MDL	0.431	7.883	3.968	0.396	<MDL
26/7/94	256.684	6.682	7.455	43.174	<MDL	<MDL	7.354	2.254	<MDL	<MDL
9/8/94	23.259	3.458	8.674	1.270	<MDL	0.225	2.366	2.740	<MDL	<MDL
23/8/94	5.895	3.492	5.390	0.255	<MDL	0.171	1.260	4.273	<MDL	<MDL
7/9/94	2.513	<MDL	0.830	0.778	<MDL	<MDL	<MDL	0.917	<MDL	<MDL
27/9/94	1.198	0.915	3.233	0.524	<MDL	0.317	<MDL	2.475	<MDL	<MDL
18/10/94	0.067	0.138	<MDL	0.150	0.364	0.342	<MDL	0.942	<MDL	<MDL
28/3/95	<MDL	<MDL	<MDL	0.268	0.472	0.662	<MDL	0.973	<MDL	<MDL
11/4/95	<MDL	0.513	<MDL	0.424	0.973	1.086	<MDL	2.260	<MDL	<MDL
25/4/95	<MDL	<MDL	<MDL	0.201	<MDL	0.251	<MDL	1.307	<MDL	<MDL
9/5/95	<MDL	<MDL	<MDL	0.208	0.352	0.290	<MDL	1.583	<MDL	<MDL
24/5/95	<MDL	<MDL	<MDL	0.007	0.103	0.077	<MDL	0.531	<MDL	0.216

DATE		MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
6/6/95		2.442	<MDL	<MDL	1.501	<MDL	0.500	1.013	7.049	<MDL	<MDL
20/6/95		2.273	<MDL	0.587	1.347	<MDL	0.313	1.110	5.129	<MDL	<MDL
5/7/95		0.407	0.558	0.230	0.951	<MDL	0.321	0.083	3.302	<MDL	<MDL
18/7/95		<MDL	<MDL	0.052	0.130	<MDL	0.047	<MDL	0.336	<MDL	<MDL
1/8/95		<MDL	<MDL	<MDL	0.121	<MDL	0.164	<MDL	1.675	<MDL	<MDL
22/8/95		<MDL	<MDL	<MDL	0.111	<MDL	0.244	0.086	1.005	<MDL	<MDL
13/9/95		<MDL	<MDL	<MDL	0.043	<MDL	0.052	<MDL	1.036	<MDL	<MDL
3/10/95		0.164	<MDL	<MDL	1.343	<MDL	0.202	<MDL	0.897	<MDL	<MDL
31/10/95		<MDL	<MDL	<MDL	0.065	<MDL	0.411	<MDL	0.710	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

LaSalle River

14/6/93	1.945	0.561	1.002	1.702	0.117	1.041
7/7/93	2.354	0.974	1.414	0.086	0.151	0.592
26/7/93	10.167	<MDL	0.095	0.623	0.280	0.132
16/8/93	2.433	0.374	0.340	1.028	0.313	0.822
6/9/93	3.493	1.857	<MDL	2.910	0.116	1.022
8/9/93	0.637	<MDL	0.058	0.275	0.122	1.388
19/10/93	1.508	<MDL	<MDL	0.150	0.045	0.694
4/5/94	1.712	<MDL	<MDL	<MDL	0.096	0.406
17/5/94	0.661	<MDL	0.698	<MDL	0.110	<MDL
31/5/94	4.297	<MDL	0.437	<MDL	<MDL	0.698
16/6/94	1.088	<MDL	0.928	<MDL	0.179	
28/6/94	1.566	<MDL	0.541	<MDL	0.114	2.088
12/7/94	0.642	<MDL	<MDL	<MDL	0.097	<MDL
26/7/94	0.596	<MDL	<MDL	<MDL	0.056	1.358
9/8/94	0.356	<MDL	<MDL	<MDL	0.023	0.776
23/8/94	0.668	<MDL	<MDL	1.265	0.045	0.721
7/9/94	4.316	<MDL	<MDL	1.041	0.076	0.330
27/9/94	0.467	<MDL	<MDL	<MDL	0.074	0.516
18/10/94	0.504	<MDL	<MDL	<MDL	0.093	<MDL
28/3/95	1.252	<MDL	0.299	<MDL	0.067	<MDL
11/4/95	1.356	<MDL	0.559	<MDL	0.089	<MDL
25/4/95	<MDL	<MDL	<MDL	<MDL	0.055	<MDL
9/5/95	0.419	<MDL	0.335	<MDL	0.060	<MDL
24/5/95	0.058	0.050	0.111	0.094	0.009	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
6/6/95	<MDL	<MDL	0.862	<MDL	0.082	0.569
20/6/95	<MDL	<MDL	<MDL	<MDL	0.075	0.802
5/7/95	<MDL	<MDL	0.226	<MDL	0.043	0.136
18/7/95	0.045	<MDL	<MDL	<MDL	0.003	<MDL
1/8/95	0.230	<MDL	0.196	4.175	0.014	<MDL
22/8/95	0.194	<MDL	<MDL	0.973	0.037	<MDL
13/9/95	<MDL	<MDL	<MDL	<MDL	0.006	<MDL
3/10/95	0.366	<MDL	<MDL	<MDL	0.058	<MDL
31/10/95	0.271	<MDL	<MDL	<MDL	0.036	<MDL

DATE		MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	--	------	-------------	-------	------------	---------------	-------------	-----------	----------	----------------	-----------

Morris River

18/6/93	109.931	20.073	26.272	18.285	<MDL	0.373	0.520	1.687	1.141	<MDL
7/7/93	17.426	1.180	3.099	114.177	<MDL	0.368	<MDL	32.529	0.326	<MDL
28/7/93	<MDL	0.647	10.059	25.083	<MDL	8.172	<MDL	12.968	0.065	<MDL
17/8/93	1.762	2.077	1.894	4.261	<MDL	1.050	<MDL	13.391	0.129	<MDL
8/9/93	0.594	0.737	1.180	0.868	<MDL	0.467	0.160	9.254	2.201	0.279
19/10/93	0.401	3.011	7.628	0.381	<MDL	0.157	4.780	18.092	3.173	<MDL
5/5/94	1.346	1.551	2.139	0.212	<MDL	<MDL	3.789	5.016	<MDL	<MDL
17/5/94	<MDL	<MDL	0.539	0.174	<MDL	3.395	<MDL	11.300	<MDL	<MDL
31/5/94	1.198	0.825	2.996	1.143	<MDL	3.228	5.752	39.313	<MDL	<MDL
16/6/94	24.241	4.593	2.608	5.389	<MDL	<MDL	3.356	8.507	<MDL	<MDL
28/6/94	8.246	1.195	1.000	56.153	<MDL	<MDL	<MDL	15.513	<MDL	0.274
12/7/94	13.631	3.244	6.687	4.275	<MDL	0.711	1.188	9.690	<MDL	1.188
26/7/94	7.294	2.260	4.313	0.553	<MDL	0.758	0.516	8.211	<MDL	<MDL
9/8/94	0.809	0.838	0.696	0.684	<MDL	0.846	<MDL	2.944	<MDL	<MDL
23/8/94	9.525	1.811	7.487	0.662	<MDL	<MDL	2.049	26.343	<MDL	0.964
7/9/94	10.749	0.347	0.287	2.696	<MDL	0.286	<MDL	1.835	<MDL	1.170
18/10/94	0.523	<MDL	<MDL	0.827	<MDL	0.745	<MDL	3.082	<MDL	<MDL
28/3/95	0.694	0.732	0.364	0.644	0.596	1.316	<MDL	8.988	<MDL	<MDL
11/4/95	0.420	<MDL	<MDL	0.583	0.842	0.957	<MDL	5.752	<MDL	<MDL
25/4/95	<MDL	<MDL	<MDL	0.358	0.344	0.270	<MDL	3.458	<MDL	<MDL
9/5/95	<MDL	<MDL	<MDL	0.206	0.313	0.274	<MDL	6.204	<MDL	<MDL
24/5/95	<MDL	<MDL	<MDL	<MDL	0.611	0.400	<MDL	3.804	<MDL	<MDL
6/6/95	0.471	<MDL	<MDL	2.166	0.354	0.789	<MDL	4.507	<MDL	<MDL
20/6/95	<MDL	<MDL	<MDL	0.883	<MDL	0.198	<MDL	3.940	<MDL	<MDL

DATE		MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
5/7/95		0.611	<MDL	<MDL	2.739	<MDL	0.540	<MDL	32.402	<MDL	<MDL
18/7/95		0.676	0.339	0.219	3.242	0.265	0.228	<MDL	3.701	<MDL	<MDL
1/8/95		0.074	<MDL	<MDL	0.117	<MDL	0.306	<MDL	2.890	<MDL	<MDL
22/8/95		0.027	<MDL	0.070	0.990	<MDL	<MDL	<MDL	0.937	<MDL	0.907
13/9/95		<MDL	<MDL	<MDL	1.332	<MDL	0.324	<MDL	2.703	<MDL	<MDL
3/10/95		0.388	1.059	<MDL	0.473	0.197	0.382	<MDL	26.544	<MDL	<MDL
31/10/95		0.081	0.079	0.218	0.054	0.280	0.248	<MDL	5.191	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Morris River

18/6/93	0.844	<MDL	1.693	1.225	0.120	0.696
7/7/93	0.934	0.058	1.406	2.064	0.240	0.724
28/7/93	4.681	2.403	6.280	7.449	0.421	0.687
17/8/93	1.413	0.940	1.045	0.653	0.295	5.051
8/9/93	<MDL	<MDL	0.173	1.706	0.126	1.446
19/10/93	1.312	<MDL	<MDL	3.904	0.111	1.046
5/5/94	<MDL	<MDL	<MDL	<MDL	0.175	
17/5/94	<MDL	<MDL	<MDL	<MDL	0.183	<MDL
31/5/94	1.472	<MDL	4.773	<MDL	0.139	0.484
16/6/94	1.681	<MDL	1.553	<MDL	0.161	1.129
28/6/94	1.739	<MDL	1.073	<MDL	0.382	0.921
12/7/94	<MDL	0.009	<MDL	<MDL	0.082	0.478
26/7/94	<MDL	0.005	<MDL	<MDL	0.049	0.425
9/8/94	0.923	<MDL	<MDL	<MDL	0.055	<MDL
23/8/94	0.007	<MDL	4.078	<MDL	0.049	0.448
7/9/94	0.129	<MDL	0.220	1.086	0.088	<MDL
18/10/94	<MDL	0.045	<MDL	<MDL	0.117	<MDL
28/3/95	1.001	<MDL	0.488	<MDL	0.074	0.273
11/4/95	1.264	<MDL	<MDL	<MDL	0.078	<MDL
25/4/95	1.083	<MDL	0.308	<MDL	0.039	0.198
9/5/95	0.536	<MDL	0.346	<MDL	0.051	<MDL
24/5/95	0.412	0.219	0.691	<MDL	0.055	<MDL
6/6/95	0.513	<MDL	0.368	<MDL	0.065	0.324
20/6/95	0.299	<MDL	0.315	<MDL	0.034	0.157

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
5/7/95	0.443	<MDL	0.968	<MDL	0.071	<MDL
18/7/95	0.271	<MDL	<MDL	<MDL	0.020	<MDL
1/8/95	0.260	<MDL	<MDL	17.760	0.022	<MDL
22/8/95	0.045	<MDL	<MDL	0.735	0.017	0.081
13/9/95	0.260	<MDL	0.268	2.214	0.042	<MDL
3/10/95	0.360	<MDL	1.041	<MDL	0.081	0.243
31/10/95	0.315	<MDL	0.306	0.441	0.038	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	------	-------------	-------	------------	---------------	-------------	-----------	----------	----------------	-----------

Pembina River

17/6/93	37.486	3.692	112.602	6.122	<MDL	0.085	0.095	2.517	0.363	<MDL
6/7/93	0.151	0.178	2.195	5.064	<MDL	0.055	<MDL	1.595	<MDL	<MDL
27/7/93	0.964	0.598	0.987	11.499	<MDL	0.728	0.110	2.823	4.202	<MDL
18/8/93	1.499	0.728	1.753	0.537	<MDL	<MDL	0.608	1.671	<MDL	<MDL
7/9/93	0.901	<MDL	1.177	0.137	<MDL	<MDL	<MDL	0.464	3.188	<MDL
18/10/93	1.031	1.453	3.351	0.200	<MDL	<MDL	0.165	0.767	<MDL	<MDL
3/5/94	<MDL	<MDL	<MDL	0.639	<MDL	<MDL	<MDL	3.344	<MDL	<MDL
16/5/94	1.757	0.987	1.295	0.882	2.447	<MDL	<MDL	1.238	<MDL	<MDL
30/5/94	<MDL	<MDL	<MDL	0.836	<MDL	<MDL	<MDL	2.704	<MDL	<MDL
14/6/94	3.057	0.546	0.457	4.604	<MDL	0.812	<MDL	2.461	<MDL	<MDL
27/6/94	0.801	0.925	0.916	1.709	<MDL	2.267	<MDL	1.093	<MDL	<MDL
11/7/94	0.773	0.320	0.167	0.368	0.492	0.456	<MDL	1.321	<MDL	<MDL
25/7/94	2.177	1.233	2.424	0.680	<MDL	<MDL	0.939	1.035	<MDL	<MDL
10/8/94	0.964	0.566	1.329	0.254	<MDL	<MDL	<MDL	0.622	<MDL	<MDL
22/8/94	0.293	0.628	0.602	0.273	<MDL	<MDL	<MDL	0.818	<MDL	<MDL
6/9/94	0.364	<MDL	<MDL	0.863	<MDL	<MDL	<MDL	0.649	<MDL	<MDL
26/9/94	0.159	<MDL	<MDL	0.148	<MDL	<MDL	0.117	<MDL	<MDL	<MDL
17/10/94	<MDL	<MDL	<MDL	0.231	<MDL	0.329	<MDL	0.632	<MDL	<MDL
3/4/95	0.347	<MDL	0.577	0.259	<MDL	0.239	0.150	0.834	<MDL	<MDL
10/4/95	<MDL	<MDL	<MDL	0.377	<MDL	0.320	<MDL	0.635	<MDL	<MDL
24/4/95	0.152	<MDL	<MDL	0.169	<MDL	0.387	<MDL	0.426	<MDL	<MDL
8/5/95	<MDL	<MDL	<MDL	0.359	0.378	0.432	<MDL	0.895	<MDL	<MDL
23/5/95	<MDL	<MDL	<MDL	0.167	<MDL	0.232	<MDL	0.489	<MDL	<MDL
5/6/95	0.254	<MDL	0.107	0.195	<MDL	0.196	<MDL	0.402	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
19/6/95	0.096	<MDL	<MDL	0.280	<MDL	0.235	<MDL	0.920	<MDL	<MDL
17/7/95	<MDL	<MDL	<MDL	0.623	<MDL	0.321	<MDL	1.772	<MDL	<MDL
31/7/95	0.165	<MDL	<MDL	0.506	0.142	0.192	<MDL	0.913	<MDL	<MDL
21/8/95	<MDL	<MDL	<MDL	3.819	<MDL	0.208	<MDL	0.905	<MDL	<MDL
11/9/95	0.109	<MDL	<MDL	0.100	<MDL	0.185	<MDL	0.681	<MDL	<MDL
2/10/95	<MDL	<MDL	<MDL	0.042	<MDL	0.185	<MDL	0.410	<MDL	<MDL
30/10/95	0.109	0.059	0.140	0.039	0.333	0.264	<MDL	0.424	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Pembina River

17/6/93	6.999	1.661	0.880	0.213	0.147	1.180
6/7/93	5.219	0.326	0.228	0.430	0.170	2.171
27/7/93	16.861	0.262	0.571	0.789	0.149	1.149
18/8/93	1.202	0.126	0.186	<MDL	0.090	1.534
7/9/93	<MDL	<MDL	7.861	1.736	<MDL	0.912
18/10/93	1.824	<MDL	<MDL	<MDL	0.062	0.926
3/5/94	5.435	<MDL	<MDL	<MDL	0.077	0.984
16/5/94	2.855	<MDL	<MDL	<MDL	0.111	0.867
30/5/94	2.182	<MDL	0.260	<MDL	0.053	<MDL
14/6/94	1.876	<MDL	<MDL	<MDL	0.122	6.185
27/6/94	1.753	<MDL	<MDL	<MDL	0.100	0.485
11/7/94	0.312	<MDL	<MDL	<MDL	0.059	<MDL
25/7/94	0.222	<MDL	<MDL	0.599	0.041	<MDL
10/8/94	<MDL	<MDL	<MDL	1.614	0.046	0.651
22/8/94	0.286	<MDL	<MDL	<MDL	0.057	<MDL
6/9/94	2.341	<MDL	<MDL	<MDL	0.115	1.931
26/9/94	<MDL	<MDL	<MDL	<MDL	0.043	<MDL
17/10/94	1.492	<MDL	<MDL	<MDL	0.141	<MDL
3/4/95	0.445	<MDL	<MDL	<MDL	0.045	<MDL
10/4/95	2.491	<MDL	<MDL	<MDL	<MDL	0.292
24/4/95	2.361	<MDL	<MDL	<MDL	0.039	0.329
8/5/95	1.717	0.075	0.498	<MDL	0.070	<MDL
23/5/95	0.400	<MDL	0.233	<MDL	0.038	<MDL
5/6/95	0.241	0.056	14.444	<MDL	0.032	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
19/6/95	0.384	<MDL	<MDL	<MDL	0.044	<MDL
17/7/95	0.444	<MDL	<MDL	<MDL	0.041	<MDL
31/7/95	0.278	<MDL	<MDL	1.242	0.024	0.049
21/8/95	<MDL	<MDL	<MDL	0.440	0.032	<MDL
11/9/95	0.292	0.374	<MDL	<MDL	0.015	0.382
2/10/95	0.181	<MDL	<MDL	<MDL	0.015	<MDL
30/10/95	0.284	<MDL	<MDL	<MDL	0.017	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BRONIXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	------	-------------	-------	------------	---------------	-------------	-----------	----------	----------------	-----------

Rat River

18/6/93	6.291	3.318	18.084	6.424	<MDL	<MDL	0.061	5.191	1.983	<MDL
7/7/93	1.190	0.651	18.316	2.368	<MDL	0.091	0.084	0.703	<MDL	<MDL
28/7/93	1.053	1.198	0.862	25.400	<MDL	1.001	<MDL	<MDL	<MDL	<MDL
17/8/93	1.493	0.631	4.616	0.536	<MDL	0.540	4.499	1.261	0.522	<MDL
9/9/93	0.430	0.328	3.154	0.272	<MDL	<MDL	2.494	3.382	<MDL	<MDL
19/10/93	<MDL	0.560	1.171	0.208	<MDL	0.190	0.161	0.504	<MDL	<MDL
5/5/94	<MDL	<MDL	0.770	0.329	<MDL	<MDL	<MDL	7.772	2.398	<MDL
17/5/94	<MDL	<MDL	<MDL	0.279	<MDL	<MDL	<MDL	4.312	<MDL	<MDL
31/5/94	1.015	<MDL	1.275	1.094	<MDL	2.116	<MDL	6.845	<MDL	<MDL
16/6/94	1.019	<MDL	0.786	1.970	<MDL	1.717	<MDL	10.050	<MDL	<MDL
28/6/94	18.188	1.945	3.546	11.718	<MDL	<MDL	<MDL	11.013	<MDL	<MDL
12/7/94	2.311	0.482	0.610	4.929	<MDL	0.390	0.138	14.398	<MDL	1.072
26/7/94	1.541	0.770	3.206	0.939	<MDL	<MDL	0.427	7.659	<MDL	3.789
9/8/94	14.846	0.696	2.776	9.636	<MDL	<MDL	0.474	3.624	<MDL	<MDL
23/8/94	10.776	<MDL	2.318	8.927	<MDL	0.867	0.265	2.890	<MDL	<MDL
7/9/94	10.753	<MDL	1.085	7.053	<MDL	<MDL	<MDL	3.011	<MDL	1.791
27/9/94	4.932	<MDL	0.274	2.976	<MDL	0.395	<MDL	2.703	<MDL	<MDL
18/10/94	0.795	<MDL	<MDL	0.964	1.243	1.004	0.144	2.194	<MDL	<MDL
28/3/95	0.228	<MDL	<MDL	0.156	0.283	0.219	<MDL	1.963	<MDL	<MDL
11/4/95	<MDL	<MDL	<MDL	0.312	<MDL	0.289	<MDL	1.004	<MDL	<MDL
25/4/95	<MDL	<MDL	<MDL	0.030	<MDL	0.348	<MDL	0.887	<MDL	<MDL
9/5/95	<MDL	<MDL	<MDL	0.130	0.232	0.193	<MDL	0.941	<MDL	<MDL
24/5/95	<MDL	<MDL	<MDL	0.099	0.318	0.293	<MDL	2.514	<MDL	<MDL
6/6/95	<MDL	<MDL	0.425	0.332	0.107	0.202	<MDL	1.952	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
20/6/95	0.143	<MDL	<MDL	1.436	<MDL	0.250	<MDL	2.735	<MDL	<MDL
5/7/95	3.644	2.313	1.203	3.093	<MDL	0.354	<MDL	4.961	<MDL	<MDL
18/7/95	<MDL	<MDL	<MDL	1.306	0.243	0.202	<MDL	14.800	<MDL	<MDL
1/8/95	0.033	<MDL	0.108	0.176	0.098	0.136	<MDL	1.400	<MDL	0.574
22/8/95	0.084	<MDL	<MDL	2.484	0.428	0.328	<MDL	4.932	<MDL	<MDL
13/9/95	0.173	0.173	0.238	0.239	0.253	0.205	0.133	3.306	<MDL	<MDL
3/10/95	0.174	<MDL	<MDL	0.176	0.247	0.189	<MDL	2.198	<MDL	<MDL
31/10/95	0.067	<MDL	<MDL	0.029	0.217	0.167	0.177	0.735	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Rat River

18/6/93	0.674	<MDL	3.090	1.016	0.099	1.702
7/7/93	<MDL	0.617	1.351	0.252	0.096	0.447
28/7/93	4.823	<MDL	30.828	<MDL	0.288	0.775
17/8/93	0.181	0.401	0.334	0.942	0.054	4.254
9/9/93	<MDL	<MDL	0.702	<MDL	0.046	0.255
19/10/93	<MDL	<MDL	<MDL	0.507	0.094	0.427
5/5/94	9.520	<MDL	<MDL	1.006	0.301	<MDL
17/5/94	<MDL	<MDL	<MDL	<MDL	0.013	<MDL
31/5/94	<MDL	<MDL	0.511	<MDL	<MDL	0.594
16/6/94	<MDL	<MDL	<MDL	<MDL	0.075	0.743
28/6/94	0.901	<MDL	7.780	<MDL	0.196	0.729
12/7/94	0.512	<MDL	0.361	<MDL	0.077	<MDL
26/7/94	<MDL	0.346	1.833	<MDL	0.226	0.275
9/8/94	0.397	0.354	0.380	<MDL	0.036	0.272
23/8/94	<MDL	0.003	<MDL	<MDL	0.032	<MDL
7/9/94	0.466	<MDL	<MDL	<MDL	0.072	<MDL
27/9/94	<MDL	<MDL	<MDL	<MDL	0.039	<MDL
18/10/94	<MDL	<MDL	<MDL	<MDL	0.058	<MDL
28/3/95	0.290	<MDL	0.708	<MDL	0.047	<MDL
11/4/95	<MDL	<MDL	<MDL	<MDL	0.039	0.106
25/4/95	0.197	<MDL	<MDL	<MDL	0.030	<MDL
9/5/95	<MDL	0.155	0.510	<MDL	0.041	<MDL
24/5/95	<MDL	0.692	1.715	<MDL	0.036	<MDL
6/6/95	0.086	<MDL	0.526	<MDL	0.033	<MDL

DATE		TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
20/6/95		<MDL	<MDL	0.439	<MDL	0.042	<MDL
5/7/95		<MDL	<MDL	0.625	<MDL	0.077	<MDL
18/7/95		<MDL	<MDL	0.402	<MDL	0.034	<MDL
1/8/95		0.035	<MDL	0.841	3.677	0.012	<MDL
22/8/95		0.417	<MDL	0.470	1.090	0.085	<MDL
13/9/95		0.170	<MDL	1.170	0.522	0.028	0.075
3/10/95		0.206	<MDL	0.401	<MDL	0.053	<MDL
31/10/95		0.138	<MDL	0.243	<MDL	0.018	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	------	-------------	-------	-----------	---------------	-------------	-----------	----------	----------------	-----------

Roseau River

17/6/93	56.363	0.610	23.837	11.762	<MDL	<MDL	0.427	8.330	<MDL	<MDL
6/7/93	0.184	0.100	0.332	2.660	<MDL	0.037	0.080	1.448	<MDL	0.204
27/7/93	0.083	0.101	2.661	5.573	<MDL	<MDL	0.067	2.106	<MDL	<MDL
18/8/93	2.251	0.432	27.920	0.552	<MDL	<MDL	7.531	6.383	2.183	<MDL
7/9/93	0.512	<MDL	3.114	0.309	<MDL	<MDL	0.369	16.406	0.178	<MDL
18/10/93	0.252	<MDL	0.622	0.259	<MDL	<MDL	<MDL	0.488	0.413	<MDL
3/5/94	<MDL	<MDL	<MDL	1.020	<MDL	2.388	0.958	1.401	<MDL	<MDL
16/5/94	<MDL	<MDL	0.363	0.446	<MDL	1.076	2.166	1.382	<MDL	<MDL
30/5/94	3.075	<MDL	1.470	2.973	<MDL	2.586	0.966	5.718	0.415	<MDL
13/6/94	0.641	<MDL	<MDL	2.882	<MDL	<MDL	<MDL	1.682	<MDL	<MDL
27/6/94	0.801	0.587	0.489	1.626	<MDL	1.063	0.256	3.524	<MDL	<MDL
11/7/94	1.812	<MDL	2.987	1.005	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/7/94	0.305	<MDL	20.033	0.200	<MDL	<MDL	1.793	1.399	<MDL	<MDL
10/8/94	0.263	<MDL	3.641	0.106	<MDL	<MDL	7.160	0.209	<MDL	<MDL
22/8/94	<MDL	<MDL	<MDL	0.126	<MDL	<MDL	1.240	0.567	<MDL	<MDL
6/9/94	0.129	<MDL	<MDL	0.155	<MDL	<MDL	1.089	0.573	<MDL	<MDL
26/9/94	0.222	<MDL	3.588	0.112	<MDL	0.226	1.983	1.036	<MDL	<MDL
17/10/94	0.152	<MDL	0.241	0.122	<MDL	<MDL	0.595	0.529	<MDL	<MDL
3/4/95	<MDL	<MDL	0.646	0.450	0.548	0.484	<MDL	<MDL	<MDL	<MDL
10/4/95	0.334	<MDL	0.396	0.288	<MDL	0.269	0.114	0.854	<MDL	<MDL
24/4/95	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.491	<MDL	<MDL
8/5/95	0.140	<MDL	<MDL	0.130	<MDL	0.194	<MDL	0.467	<MDL	<MDL
23/5/95	<MDL	<MDL	<MDL	0.287	<MDL	0.246	<MDL	<MDL	<MDL	<MDL
5/6/95	1.100	<MDL	2.331	0.616	<MDL	0.416	0.651	1.664	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
19/6/95	<MDL	<MDL	<MDL	0.444	<MDL	0.221	<MDL	1.689	<MDL	<MDL
4/7/95	1.118	<MDL	<MDL	8.594	<MDL	0.157	<MDL	13.051	<MDL	<MDL
17/7/95	<MDL	<MDL	<MDL	0.946	<MDL	0.447	<MDL	5.139	<MDL	<MDL
31/7/95	<MDL	<MDL	<MDL	0.071	0.233	0.180	<MDL	1.182	<MDL	<MDL
21/8/95	<MDL	<MDL	<MDL	0.051	<MDL	0.231	<MDL	1.180	<MDL	<MDL
11/9/95	0.103	<MDL	0.255	0.045	<MDL	0.424	<MDL	0.842	<MDL	<MDL
2/10/95	<MDL	<MDL	<MDL	0.024	<MDL	0.165	0.159	1.900	<MDL	<MDL
30/10/95	0.410	<MDL	0.461	0.340	<MDL	0.307	1.236	0.919	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Roseau River

17/6/93	0.506	1.209	0.990	0.311	0.127	0.651
6/7/93	0.240	<MDL	0.245	0.629	0.168	0.283
27/7/93	<MDL	<MDL	0.361	1.783	0.146	0.358
18/8/93	0.279	0.162	0.265	<MDL	0.116	0.385
7/9/93	<MDL	<MDL	1.050	0.172	0.142	<MDL
18/10/93	<MDL	<MDL	<MDL	<MDL	0.134	0.350
3/5/94	1.409	<MDL	<MDL	<MDL	0.038	<MDL
16/5/94	0.634	<MDL	0.415	<MDL	0.019	<MDL
30/5/94	<MDL	<MDL	<MDL	<MDL	0.054	0.724
13/6/94	1.109	<MDL	<MDL	<MDL	0.169	0.604
27/6/94	<MDL	<MDL	<MDL	<MDL	0.214	0.276
11/7/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/7/94	<MDL	<MDL	<MDL	<MDL	0.039	<MDL
10/8/94	<MDL	<MDL	<MDL	<MDL	0.041	<MDL
22/8/94	<MDL	<MDL	<MDL	<MDL	0.043	<MDL
6/9/94	<MDL	<MDL	<MDL	<MDL	0.120	<MDL
26/9/94	<MDL	<MDL	<MDL	<MDL	0.030	<MDL
17/10/94	<MDL	<MDL	<MDL	0.523	0.044	<MDL
3/4/95	2.934	<MDL	<MDL	<MDL	0.064	<MDL
10/4/95	<MDL	<MDL	<MDL	<MDL	0.042	<MDL
24/4/95	0.289	<MDL	0.352	<MDL	0.043	<MDL
8/5/95	0.311	0.195	<MDL	0.227	0.041	<MDL
23/5/95	<MDL	0.786	0.687	<MDL	<MDL	<MDL
5/6/95	<MDL	<MDL	<MDL	<MDL	0.098	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
19/6/95	<MDL	<MDL	<MDL	<MDL	0.163	<MDL
4/7/95	0.161	<MDL	<MDL	<MDL	0.037	<MDL
17/7/95	<MDL	<MDL	<MDL	<MDL	0.222	<MDL
31/7/95	<MDL	<MDL	<MDL	0.466	0.016	0.183
21/8/95	0.132	<MDL	<MDL	<MDL	0.051	<MDL
11/9/95	<MDL	<MDL	<MDL	<MDL	0.049	<MDL
2/10/95	<MDL	<MDL	<MDL	<MDL	0.036	<MDL
30/10/95	<MDL	<MDL	<MDL	<MDL	0.048	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	------	-------------	-------	-----------	---------------	-------------	-----------	----------	----------------	-----------

Seine River

18/6/93	7.696	4.813	15.984	6.024	<MDL	<MDL	1.105	0.268	<MDL	<MDL
5/7/93	1.618	1.532	2.277	3.801	<MDL	0.128	0.049	7.242	0.746	<MDL
28/7/93	3.778	22.481	64.328	49.913	<MDL	0.517	0.072	1.083	0.262	<MDL
16/8/93	<MDL	<MDL	148.826	5.426	<MDL	0.160	<MDL	1.908	<MDL	<MDL
8/9/93	1.095	2.018	5.055	0.442	<MDL	<MDL	0.101	1.187	1.817	12.933
19/10/93	0.622	<MDL	14.489	1.062	<MDL	1.022	<MDL	1.191	2.221	<MDL
5/5/94	<MDL	<MDL	<MDL	0.132	<MDL	<MDL	<MDL	5.108	<MDL	<MDL
17/5/94	<MDL	<MDL	<MDL	0.160	<MDL	<MDL	<MDL	4.493	<MDL	<MDL
31/5/94	<MDL	<MDL	<MDL	1.029	2.084	1.710	<MDL	14.252	<MDL	<MDL
16/6/94	11.698	3.110	4.409	3.323	<MDL	1.563	<MDL	4.230	<MDL	<MDL
28/6/94	8.983	2.601	3.981	2.808	<MDL	2.148	<MDL	16.304	<MDL	<MDL
12/7/94	36.155	10.458	5.393	120.771	0.519	0.400	<MDL	57.283	<MDL	<MDL
26/7/94	0.708	<MDL	1.423	0.942	<MDL	<MDL	<MDL	4.065	<MDL	<MDL
9/8/94	0.504	0.563	1.247	2.539	<MDL	<MDL	<MDL	1.633	<MDL	<MDL
23/8/94	0.417	0.607	3.351	0.215	<MDL	0.386	1.363	2.130	<MDL	<MDL
7/9/94	0.093	<MDL	<MDL	0.058	<MDL	<MDL	0.710	0.456	<MDL	<MDL
27/9/94	0.215	0.142	1.131	0.141	<MDL	<MDL	2.376	3.589	<MDL	<MDL
18/10/94	0.164	0.137	0.293	0.211	0.415	<MDL	0.141	0.993	<MDL	<MDL
28/3/95	0.438	<MDL	<MDL	0.324	<MDL	0.264	<MDL	1.377	<MDL	<MDL
11/4/95	0.938	<MDL	0.664	0.510	<MDL	0.460	<MDL	2.012	<MDL	<MDL
25/4/95	<MDL	<MDL	0.189	0.185	<MDL	<MDL	<MDL	0.899	<MDL	<MDL
9/5/95	<MDL	<MDL	<MDL	0.299	<MDL	<MDL	<MDL	1.119	<MDL	<MDL
24/5/95	<MDL	<MDL	<MDL	0.420	0.644	0.397	<MDL	1.436	<MDL	<MDL
6/6/95	0.245	<MDL	<MDL	0.255	<MDL	<MDL	<MDL	1.386	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
20/6/95	<MDL	<MDL	<MDL	0.252	<MDL	0.234	<MDL	0.991	<MDL	<MDL
5/7/95	3.584	1.456	3.571	1.653	<MDL	0.101	0.123	5.205	<MDL	<MDL
18/7/95	<MDL	<MDL	<MDL	3.907	0.283	0.220	<MDL	96.432	<MDL	<MDL
1/8/95	<MDL	<MDL	<MDL	0.120	<MDL	0.157	<MDL	54.758	<MDL	<MDL
22/8/95	0.361	1.899	10.156	0.753	<MDL	0.309	<MDL	11.871	<MDL	<MDL
13/9/95	<MDL	0.169	0.057	0.618	<MDL	0.489	<MDL	9.189	<MDL	<MDL
3/10/95	<MDL	0.903	<MDL	0.083	0.603	0.456	<MDL	29.904	<MDL	<MDL
31/10/95	0.185	0.184	0.144	0.037	0.404	0.299	<MDL	2.173	<MDL	<MDL

DATE	TRIALATE	ALACILOR	METOLACILOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Seine River

18/6/93	1.195	1.307	1.183	1.711	0.085	0.528
5/7/93	1.167	0.047	<MDL	0.113	0.114	0.945
28/7/93	4.381	0.541	2.404	<MDL	0.293	0.283
16/8/93	8.998	1.303	5.446	1.497	0.364	0.401
8/9/93	5.046	<MDL	0.190	0.066	0.092	0.546
19/10/93	2.777	<MDL	0.587	0.928	0.075	0.373
5/5/94	1.370	<MDL	1.615	<MDL	0.171	<MDL
17/5/94	<MDL	<MDL	<MDL	<MDL	0.140	<MDL
31/5/94	1.368	<MDL	<MDL	<MDL	0.056	0.405
16/6/94	<MDL	<MDL	<MDL	<MDL	0.060	0.519
28/6/94	<MDL	<MDL	<MDL	<MDL	0.069	0.443
12/7/94	0.464	<MDL	0.774	<MDL	0.123	0.310
26/7/94	<MDL	<MDL	<MDL	<MDL	0.047	0.272
9/8/94	<MDL	<MDL	<MDL	<MDL	0.077	0.287
23/8/94	<MDL	<MDL	<MDL	<MDL	0.050	<MDL
7/9/94	<MDL	<MDL	<MDL	<MDL	0.031	<MDL
27/9/94	0.056	<MDL	<MDL	<MDL	0.020	<MDL
18/10/94	0.053	<MDL	<MDL	<MDL	0.044	<MDL
28/3/95	0.586	<MDL	<MDL	<MDL	0.053	<MDL
11/4/95	<MDL	<MDL	0.869	<MDL	0.072	<MDL
25/4/95	<MDL	<MDL	<MDL	<MDL	0.044	<MDL
9/5/95	<MDL	<MDL	0.534	<MDL	0.040	<MDL
24/5/95	<MDL	<MDL	<MDL	<MDL	0.062	<MDL
6/6/95	<MDL	<MDL	0.311	<MDL	0.039	0.469

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
20/6/95	0.174	<MDL	<MDL	<MDL	0.030	<MDL
5/7/95	<MDL	<MDL	<MDL	<MDL	0.017	<MDL
18/7/95	<MDL	<MDL	<MDL	<MDL	0.020	<MDL
1/8/95	<MDL	<MDL	<MDL	4.159	0.013	<MDL
22/8/95	0.729	<MDL	<MDL	<MDL	0.099	<MDL
13/9/95	0.136	<MDL	<MDL	1.626	0.070	0.014
3/10/95	<MDL	<MDL	<MDL	<MDL	0.045	<MDL
31/10/95	0.181	<MDL	<MDL	<MDL	0.028	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	------	-------------	-------	-----------	---------------	-------------	-----------	----------	----------------	-----------

Red River @ Emerson

17/6/93	36.228	0.721	9.152	26.969	<MDL	0.398	0.330	26.127	2.103	<MDL
6/7/93	6.856	2.885	15.543	25.243	<MDL	0.391	0.214	52.417	<MDL	<MDL
27/7/93	0.223	0.465	0.189	17.401	<MDL	1.182	<MDL	3.451	0.281	<MDL
18/8/93	7.843	1.037	29.514	0.747	<MDL	0.450	<MDL	9.471	0.572	<MDL
7/9/93	1.600	<MDL	3.594	0.788	<MDL	0.095	0.151	2.040	0.746	<MDL
18/10/93	0.423	<MDL	1.187	0.279	<MDL	0.263	<MDL	7.260	0.422	<MDL
3/5/94	<MDL	<MDL	<MDL	0.359	<MDL	0.472	<MDL	23.320	<MDL	<MDL
13/6/94	11.434	<MDL	2.119	12.414	<MDL	1.009	<MDL	24.956	<MDL	<MDL
11/7/94	24.016	<MDL	12.449	13.200	<MDL	<MDL	<MDL	8.775	<MDL	<MDL
16/5/94	1.951	0.316	3.282	0.394	0.727	0.919	<MDL	16.990	<MDL	<MDL
27/6/94	173.428	0.898	28.544	171.568	<MDL	1.165	0.461	64.741	<MDL	10.947
30/5/94	1.146	<MDL	<MDL	1.740	<MDL	0.061	<MDL	16.151	<MDL	<MDL
25/7/94	6.846	<MDL	4.726	4.956	<MDL	0.590	<MDL	115.834	<MDL	14.192
10/8/94	2.422	0.538	5.101	1.216	<MDL	<MDL	0.248	50.735	<MDL	14.556
22/8/94	4.833	0.534	12.981	1.138	<MDL	0.299	0.723	44.847	3.746	15.225
6/9/94	1.567	<MDL	0.247	0.622	<MDL	1.220	<MDL	1.458	<MDL	0.337
26/9/94	0.597	4.386	1.643	0.796	<MDL	0.303	0.432	12.038	<MDL	<MDL
17/10/94	<MDL	<MDL	<MDL	0.459	<MDL	<MDL	<MDL	5.798	<MDL	<MDL
3/4/95	0.528	0.845	0.412	0.437	0.652	0.541	<MDL	0.997	0.059	<MDL
10/4/95	<MDL	<MDL	<MDL	0.433	0.650	0.627	<MDL	8.007	<MDL	<MDL
24/4/95	<MDL	<MDL	<MDL	0.642	<MDL	<MDL	<MDL	6.559	<MDL	0.789
8/5/95	<MDL	<MDL	<MDL	0.612	1.150	1.082	<MDL	11.198	1.721	3.452
23/5/95	0.307	<MDL	<MDL	0.320	0.587	0.489	<MDL	3.746	<MDL	<MDL
5/6/95	0.559	<MDL	<MDL	0.983	<MDL	0.880	<MDL	2.594	<MDL	<MDL

330

DATE		MCFA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
19/6/95		<MDL	<MDL	<MDL	1.866	<MDL	1.064	<MDL	9.035	<MDL	<MDL
4/7/95		<MDL	<MDL	<MDL	6.919	<MDL	0.540	<MDL	16.213	<MDL	1.477
17/7/95		0.329	<MDL	<MDL	51.443	0.767	0.571	<MDL	144.806	<MDL	1.123
31/7/95		<MDL	<MDL	<MDL	2.201	<MDL	1.685	<MDL	77.649	<MDL	11.548
21/8/95		<MDL	<MDL	<MDL	0.265	<MDL	0.420	<MDL	0.834	<MDL	<MDL
11/9/95		<MDL	<MDL	<MDL	0.655	<MDL	<MDL	<MDL	9.582	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	0.461	<MDL	0.656	<MDL	5.136	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Red River @ Emerson

17/6/93	1.627	50.927	34.807	<MDL	<MDL	1.756
6/7/93	3.008	19.157	205.270	2.062	0.134	1.247
27/7/93	3.733	8.674	31.411	0.766	0.245	0.641
18/8/93	3.032	0.953	13.169	0.730	0.172	6.671
7/9/93	0.881	<MDL	2.469	0.434	0.182	0.744
18/10/93	0.337	<MDL	2.063	<MDL	0.144	0.186
3/5/94	7.914	<MDL	8.157	<MDL	0.271	<MDL
13/6/94	1.371	3.396	27.458	<MDL	0.081	5.757
11/7/94	3.183	3.274	37.168	<MDL	0.182	17.519
16/5/94	3.807	<MDL	6.536	<MDL	0.103	0.407
27/6/94	4.238	21.766	73.351	1.838	0.346	106.367
30/5/94	1.111	2.480	17.218	<MDL	0.134	5.715
25/7/94	1.960	11.913	57.921	1.385	0.193	1.559
10/8/94	0.754	1.441	19.603	<MDL	0.202	0.627
22/8/94	0.787	<MDL	10.922	<MDL	0.182	1.185
6/9/94	0.232	<MDL	1.057	<MDL	0.336	0.016
26/9/94	<MDL	1.051	3.764	<MDL	0.203	1.040
17/10/94	0.836	0.067	1.693	<MDL	0.168	<MDL
3/4/95	0.495	<MDL	<MDL	<MDL	0.021	0.363
10/4/95	21.189	1.232	9.527	<MDL	0.075	<MDL
24/4/95	5.014	0.505	32.304	<MDL	0.084	<MDL
8/5/95	<MDL	0.236	19.865	<MDL	0.066	<MDL
23/5/95	1.497	1.936	8.840	<MDL	0.049	<MDL
5/6/95	<MDL	1.263	9.174	<MDL	0.051	<MDL

DATE	TRIALATE	ALACILOR	METOLACHILOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
19/6/95	1.024	0.791	8.202	<MDL	0.045	<MDL
4/7/95	0.818	1.026	7.659	<MDL	0.047	0.325
17/7/95	1.598	121.900	37.946	1.122	0.075	<MDL
31/7/95	1.323	4.094	16.625	<MDL	0.066	<MDL
21/8/95	0.362	<MDL	<MDL	0.872	0.009	<MDL
11/9/95	<MDL	0.008	<MDL	<MDL	0.050	<MDL
30/10/95	0.824	0.302	1.326	<MDL	0.045	<MDL

DATE		MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	--	------	-------------	-------	-----------	---------------	-------------	-----------	----------	----------------	-----------

Red River @ Ste. Agathe

18/6/93	30.663	2.532	6.662	48.975	<MDL	<MDL	0.396	11.667	1.142	<MDL
7/7/93	3.853	1.631	24.457	31.155	<MDL	0.384	0.767	6.690	0.842	<MDL
27/7/93	<MDL	0.261	0.456	30.058	<MDL	2.080	<MDL	41.835	3.143	<MDL
17/8/93	11.425	2.421	24.730	3.245	<MDL	0.762	1.188	7.177	0.521	<MDL
8/9/93	0.739	<MDL	2.518	0.610	<MDL	0.183	0.087	8.711	0.611	<MDL
19/10/93	0.401	<MDL	2.512	0.162	<MDL	<MDL	<MDL	9.866	1.026	<MDL
4/5/94	<MDL	<MDL	<MDL	0.265	<MDL	<MDL	<MDL	4.604	<MDL	<MDL
17/5/94	0.983	<MDL	1.105	0.210	0.529	0.380	<MDL	19.819	<MDL	<MDL
31/5/94	0.200	<MDL	<MDL	2.256	<MDL	0.848	<MDL	19.371	<MDL	<MDL
16/6/94	2.906	<MDL	0.415	8.278	<MDL	<MDL	<MDL	9.902	<MDL	<MDL
28/6/94	0.098	<MDL	<MDL	90.428	<MDL	1.762	<MDL	59.358	<MDL	14.668
12/7/94	6.730	<MDL	1.031	9.337	<MDL	0.492	0.285	34.972	<MDL	3.725
19/7/94	38.358	0.897	34.175	15.372	<MDL	1.851	0.936	36.720	<MDL	<MDL
26/7/94	9.034	0.624	9.860	6.703	<MDL	0.336	1.018	58.742	<MDL	5.155
9/8/94	2.841	<MDL	3.735	1.459	<MDL	0.280	0.277	97.065	<MDL	49.067
23/8/94	0.088	0.449	<MDL	0.609	<MDL	<MDL	<MDL	21.919	<MDL	5.589
7/9/94	0.135	<MDL	<MDL	0.729	<MDL	0.465	0.219	22.093	<MDL	<MDL
27/9/94	1.173	0.931	3.011	1.008	<MDL	0.398	1.196	10.804	<MDL	<MDL
18/10/94	0.122	<MDL	<MDL	1.109	0.440	0.953	<MDL	10.187	<MDL	<MDL
28/3/95	1.104	0.734	0.844	0.656	0.836	0.776	<MDL	2.823	0.090	<MDL
11/4/95	0.832	0.926	0.663	0.844	1.156	1.321	<MDL	11.495	<MDL	2.154
25/4/95	<MDL	<MDL	<MDL	0.324	<MDL	0.478	<MDL	1.774	<MDL	<MDL
9/5/95	<MDL	<MDL	<MDL	0.574	1.140	0.959	<MDL	5.422	0.897	<MDL
24/5/95	0.317	<MDL	<MDL	0.381	0.625	0.519	<MDL	5.718	<MDL	<MDL

DATE		ALCPA	DICHLORPROP	D-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
6/6/95		<MDL	<MDL	<MDL	3.094	<MDL	<MDL	<MDL	9.048	<MDL	<MDL
20/6/95		<MDL	<MDL	<MDL	2.018	<MDL	<MDL	<MDL	13.568	2.163	5.484
5/7/95		0.557	<MDL	<MDL	7.279	<MDL	1.532	<MDL	18.511	<MDL	8.525
18/7/95		0.457	<MDL	0.699	21.786	2.510	3.231	<MDL	188.145	<MDL	24.881
1/8/95		0.312	<MDL	<MDL	4.926	1.731	1.531	<MDL	34.607	<MDL	4.984
22/8/95		<MDL	<MDL	<MDL	3.638	<MDL	1.072	<MDL	68.743	<MDL	3.728
3/10/95		<MDL	<MDL	<MDL	0.515	<MDL	0.733	<MDL	7.565	<MDL	<MDL
31/10/95		0.830	<MDL	1.180	0.935	<MDL	<MDL	1.157	132.334	<MDL	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	----------	----------	-------------	--------------	---------	-----------------

Red River @ Ste. Agathe

18/6/93	1.909	114.187	79.470	0.412	0.155	1.805
7/7/93	1.306	8.805	113.394	2.462	0.130	1.932
27/7/93	5.153	6.834	27.976	0.632	0.335	1.105
17/8/93	1.843	0.823	10.293	2.389	0.076	0.413
8/9/93	1.648	<MDL	4.244	0.235	0.156	1.287
19/10/93	1.535	<MDL	4.079	<MDL	0.082	0.732
4/5/94	5.068	<MDL	4.958	<MDL	0.204	0.336
17/5/94	4.051	1.929	7.186	<MDL	0.167	<MDL
31/5/94	1.180	4.649	49.385	<MDL	0.166	1.712
16/6/94	2.270	4.500	33.682	<MDL	0.121	4.521
28/6/94	<MDL	13.051	55.591	<MDL	0.228	2.464
12/7/94	1.512	<MDL	24.294	<MDL	0.240	3.912
19/7/94	4.121	6.904	72.727	3.006	0.185	9.332
26/7/94	1.461	11.483	53.768	<MDL	0.192	3.149
9/8/94	<MDL	3.495	26.605	1.489	0.153	0.835
23/8/94	<MDL	0.297	7.512	<MDL	0.151	0.732
7/9/94	0.566	<MDL	3.549	<MDL	0.222	0.452
27/9/94	1.664	<MDL	2.163	<MDL	0.224	1.300
18/10/94	0.935	1.226	1.715	<MDL	0.249	0.220
28/3/95	<MDL	0.428	<MDL	<MDL	0.061	0.640
11/4/95	25.595	1.478	10.185	<MDL	0.136	0.637
25/4/95	3.049	<MDL	8.982	<MDL	0.038	<MDL
9/5/95	16.412	<MDL	11.655	<MDL	0.044	<MDL
24/5/95	<MDL	1.886	8.279	<MDL	0.046	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTIAL	DICLOFOP-METHYL
6/6/95	4.893	1.416	32.894	<MDL	0.144	<MDL
20/6/95	0.961	1.277	11.598	<MDL	0.051	0.770
5/7/95	1.193	1.336	17.295	<MDL	0.035	1.266
18/7/95	2.601	116.733	81.150	3.197	0.462	2.240
1/8/95	1.264	0.418	4.487	3.002	0.206	<MDL
22/8/95	1.039	2.594	7.989	2.894	0.051	<MDL
3/10/95	<MDL	0.007	<MDL	<MDL	0.054	<MDL
31/10/95	1.457	1.713	5.506	<MDL	<MDL	0.273

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXYNIL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERBUTHYLAZINE	CYANAZINE
------	------	-------------	-------	------------	---------------	-------------	-----------	----------	----------------	-----------

Red @ Selkirk

21/6/93	20.043	1.425	19.621	62.897	<MDL	0.141	0.346	3.408	<MDL	<MDL
5/7/93	0.136	0.064	0.259	4.581	<MDL	<MDL	<MDL	33.146	<MDL	<MDL
29/7/93	2.416	0.378	2.441	14.854	<MDL	1.205	0.285	10.808	<MDL	<MDL
16/8/93	5.191	2.769	13.927	3.731	<MDL	0.557	0.560	7.257	<MDL	<MDL
6/9/93	0.776	<MDL	0.807	1.222	<MDL	0.299	0.113	4.782	1.571	1.663
20/10/93	0.076	0.076	0.076	0.076	0.076	0.076	0.076	0.076	0.076	0.076
5/5/94	2.301	1.672	<MDL	0.554	<MDL	0.316	<MDL	<MDL	<MDL	<MDL
17/5/94	<MDL	<MDL	<MDL	0.207	0.196	0.261	<MDL	7.924	<MDL	<MDL
31/5/94	10.752	0.824	6.510	6.642	<MDL	0.556	<MDL	16.513	<MDL	<MDL
16/6/94	0.755	0.289	<MDL	4.684	<MDL	0.454	<MDL	16.987	<MDL	<MDL
28/6/94	83.840	3.426	46.945	180.045	<MDL	2.240	0.116	1.124	<MDL	<MDL
12/7/94	58.664	18.504	88.310	28.376	<MDL	<MDL	0.600	47.869	<MDL	<MDL
19/7/94	15.256	1.188	12.412	24.062	<MDL	0.821	0.457	53.364	1.549	11.531
26/7/94	7.155	0.770	4.105	12.076	<MDL	0.408	0.651	145.053	<MDL	51.827
9/8/94	2.555	<MDL	5.060	2.210	<MDL	<MDL	0.281	71.899	<MDL	<MDL
23/8/94	3.140	<MDL	5.379	0.832	0.411	0.316	1.286	58.804	0.825	<MDL
7/9/94	6.622	<MDL	24.679	0.983	0.396	0.145	2.188	37.147	<MDL	<MDL
27/9/94	1.177	0.690	2.324	1.314	0.408	0.420	1.206	12.474	<MDL	<MDL
18/10/94	1.894	<MDL	1.637	0.979	0.443	0.507	0.193	7.923	<MDL	<MDL
28/3/95	1.456	<MDL	<MDL	1.044	2.041	1.783	<MDL	4.650	<MDL	<MDL
11/4/95	1.711	1.281	2.649	0.740	0.380	0.909	0.145	7.613	0.365	<MDL
25/4/95	0.955	0.976	<MDL	0.921	1.454	1.268	<MDL	4.756	<MDL	<MDL
9/5/95	0.990	0.535	0.720	0.559	<MDL	0.863	<MDL	2.949	<MDL	<MDL
24/5/95	<MDL	<MDL	<MDL	0.616	0.770	0.683	<MDL	7.541	<MDL	<MDL

DATE	MCPA	DICHLORPROP	2,4-D	BROMOXNYL	ETHALFLURALIN	TRIFLURALIN	TRICLOPYR	ATRAZINE	TERRBUTHYLAZINE	CYANAZINE
6/6/95	0.160	<MDL	<MDL	0.739	<MDL	1.112	<MDL	6.988	<MDL	0.932
20/6/95	0.843	<MDL	<MDL	1.941	<MDL	0.470	<MDL	3.715	<MDL	<MDL
5/7/95	1.456	0.612	0.460	6.626	<MDL	0.538	<MDL	12.554	<MDL	2.110
18/7/95	<MDL	<MDL	<MDL	8.885	<MDL	0.733	<MDL	21.379	<MDL	<MDL
1/8/95	<MDL	<MDL	<MDL	4.627	<MDL	1.095	<MDL	65.294	<MDL	5.084
22/8/95	0.508	<MDL	<MDL	0.633	<MDL	<MDL	<MDL	9.341	<MDL	<MDL
13/9/95	<MDL	<MDL	0.762	5.057	<MDL	1.152	<MDL	5.238	<MDL	<MDL
3/10/95	0.155	<MDL	<MDL	0.654	0.660	0.535	<MDL	5.302	<MDL	<MDL
31/10/95	0.762	<MDL	0.674	0.716	1.019	0.854	0.310	7.721	<MDL	<MDL

DATE		TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
------	--	----------	----------	-------------	--------------	---------	-----------------

Red @ Selkirk

21/6/93	3.568	149.889	125.645	2.590	0.155	0.148
5/7/93	1.770	10.251	15.755	1.644	0.132	0.551
29/7/93	4.879	0.658	17.117	8.533	0.285	0.310
16/8/93	1.701	1.034	5.823	2.313	0.166	1.128
6/9/93	0.282	0.044	1.032	0.492	0.199	0.251
20/10/93	0.076	0.076	0.076	0.076	0.076	0.076
5/5/94	<MDL	<MDL	3.729	<MDL	0.150	1.669
17/5/94	<MDL	<MDL	3.199	<MDL	0.155	<MDL
31/5/94	<MDL	2.281	22.377	<MDL	0.096	1.686
16/6/94	1.035	<MDL	20.316	<MDL	0.072	3.143
28/6/94	0.105	1.251	0.491	0.167	0.377	103.434
12/7/94	1.732	1.019	9.131	13.960	0.411	5.107
19/7/94	5.626	3.575	23.811	2.404	0.286	12.423
26/7/94	2.093	32.857	82.428	1.984	0.187	3.149
9/8/94	<MDL	7.459	28.602	3.103	0.213	0.897
23/8/94	<MDL	<MDL	12.807	1.733	0.175	1.194
7/9/94	0.478	1.264	4.553	4.352	0.583	0.428
27/9/94	1.920	<MDL	1.746	<MDL	0.223	1.376
18/10/94	0.784	<MDL	1.721	<MDL	0.197	0.736
28/3/95	11.498	0.906	4.035	1.531	0.515	0.878
11/4/95	8.571	1.125	6.700	<MDL	0.088	1.273
25/4/95	<MDL	0.589	8.430	<MDL	0.063	0.715
9/5/95	1.597	<MDL	4.486	<MDL	0.038	0.159
24/5/95	1.600	1.405	7.224	<MDL	0.062	<MDL

DATE	TRIALATE	ALACHLOR	METOLACHLOR	CHLORPYRIFOS	DACTHAL	DICLOFOP-METHYL
6/6/95	1.331	0.220	8.030	<MDL	0.047	0.058
20/6/95	0.699	5.238	6.049	<MDL	0.036	1.276
5/7/95	0.804	<MDL	5.313	<MDL	0.039	0.645
18/7/95	<MDL	4.949	4.874	<MDL	0.032	<MDL
1/8/95	1.024	3.315	6.639	3.593	0.073	<MDL
22/8/95	0.539	<MDL	1.096	1.679	0.081	<MDL
13/9/95	1.074	0.026	<MDL	<MDL	0.109	<MDL
3/10/95	<MDL	0.016	<MDL	1.550	0.044	0.135
31/10/95	0.856	<MDL	3.699	<MDL	0.050	<MDL

VI. PCB Concentrations in South Tobacco Creek Water (pg/L)

DATE	Congener	3	4/10	7	8	9	19	18	2724	16	
5/3/94		<MDL	7.883	0.312	<MDL	0.188	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94		<MDL	1.318	<MDL	<MDL	15.811	<MDL	<MDL	20.881	<MDL	16.384
31/3/94		<MDL	7.959	<MDL	<MDL	1.603	<MDL	<MDL	0.928	<MDL	4.587
3/5/94		<MDL	3.851	<MDL	0.495	4.455	<MDL	<MDL	7.276	<MDL	9.423
11/5/94		73.733	24.520	<MDL	5.558	19.225	<MDL	3.378	22.367	<MDL	11.775
16/5/94		<MDL	6.866	10.519	2.860	16.174	<MDL	<MDL	17.574	6.657	21.495
26/5/94		78.757	22.367	<MDL	<MDL	18.185	<MDL	<MDL	28.892	<MDL	24.213
30/5/94		<MDL	<MDL	<MDL	<MDL	1.031	<MDL	<MDL	<MDL	<MDL	<MDL
7/6/94		47.075	15.137	<MDL	1.822	8.241	<MDL	3.169	<MDL	<MDL	15.068
14/6/94		<MDL	<MDL	<MDL	<MDL	0.149	<MDL	<MDL	2.317	<MDL	<MDL
27/6/94		<MDL	2.165	13.563	<MDL	<MDL	<MDL	<MDL	6.099	1.712	9.906
7/7/94		38.814	31.735	<MDL	6.542	28.490	<MDL	5.696	31.685	<MDL	34.662
11/7/94		<MDL	<MDL	<MDL	<MDL	7.950	<MDL	<MDL	9.659	<MDL	13.790
19/7/94		58.689	25.433	4.065	3.208	13.886	<MDL	<MDL	13.557	<MDL	12.758
25/7/94		<MDL	4.724	1.809	0.119	2.464	<MDL	<MDL	4.542	<MDL	6.107
7/10/94		<MDL	14.279	<MDL	<MDL	16.764	<MDL	<MDL	12.251	<MDL	14.296
8/10/94		<MDL	13.956	4.719	<MDL	13.864	<MDL	<MDL	8.465	<MDL	13.909
13/10/94		11.781	10.922	<MDL	2.338	8.970	<MDL	<MDL	17.612	<MDL	20.625
17/10/94		<MDL	7.747	4.647	<MDL	6.232	<MDL	<MDL	7.497	<MDL	7.526
19/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	20.028
10/11/94		<MDL	<MDL	<MDL	<MDL	0.394	<MDL	<MDL	<MDL	<MDL	<MDL
17/3/95		<MDL	7.679	2.110	0.247	3.479	<MDL	<MDL	5.342	<MDL	11.393
3/4/95		<MDL	12.305	4.121	1.259	1.537	<MDL	<MDL	9.392	<MDL	7.422
11/4/95		<MDL	11.466	<MDL	0.249	<MDL	<MDL	0.942	<MDL	<MDL	<MDL
13/4/95		24.448	35.405	11.838	25.843	145.057	<MDL	9.676	118.803	10.551	111.241
24/4/95		<MDL	5.046	2.095	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95		13.206	54.847	3.762	2.937	14.863	<MDL	<MDL	12.807	<MDL	13.932

DATE	Congener	3	4/10	7	6	8	9	19	18	2724	16
8/5/95		<MDL	19.776	<MDL	2.834	<MDL	<MDL	<MDL	3.351	<MDL	<MDL
15/5/95		2.346	27.083	<MDL	0.684	<MDL	<MDL	<MDL	7.760	4.758	2.185
23/5/95		0.711	23.327	3.538	<MDL	<MDL	<MDL	<MDL	2.710	0.837	1.743
27/5/95		13.542	59.115	1.276	2.441	11.098	<MDL	2.257	15.625	2.650	9.481
2/6/95		14.444	26.221	2.407	0.543	1.046	<MDL	<MDL	5.869	<MDL	5.291
5/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.000	<MDL	1.858
14/6/95		11.050	18.130	4.058	0.712	3.395	<MDL	2.591	7.279	<MDL	5.412
19/6/95		<MDL	2.713	2.001	<MDL	<MDL	<MDL	<MDL	0.344	<MDL	2.301
26/6/95		20.720	13.664	4.940	2.474	11.709	<MDL	2.127	8.755	<MDL	6.461
8/7/95		14.291	23.191	<MDL	1.560	6.621	<MDL	<MDL	11.905	5.032	9.108
14/7/95		11.188	20.081	3.996	2.542	6.194	<MDL	2.451	10.578	1.971	7.573
17/7/95		<MDL	16.237	1.897	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/7/95		19.726	51.084	11.142	17.077	75.012	<MDL	13.394	146.337	15.403	204.779
19/8/95		8.317	22.658	4.055	1.797	6.877	<MDL	3.327	13.138	3.743	10.276
21/8/95		1.818	24.123	5.636	0.131	2.216	<MDL	<MDL	4.552	2.779	1.849
25/8/95		1.698	13.528	0.970	<MDL	1.784	<MDL	<MDL	8.778	<MDL	5.784
31/8/95		<MDL	16.805	<MDL	<MDL	<MDL	<MDL	<MDL	2.312	<MDL	3.455
11/9/95		0.806	15.731	1.330	<MDL	1.332	<MDL	<MDL	7.723	<MDL	2.823
18/10/95		4.087	14.521	2.531	<MDL	0.483	<MDL	<MDL	7.432	1.982	2.820
30/10/95		1.085	11.573	2.039	<MDL	<MDL	<MDL	<MDL	4.095	2.127	3.163

DATE	Congener	26	25	31	28	33	22	51	49	52	59
5/3/94		0.879	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94		0.848	<MDL	27.542	24.413	33.106	8.666	0.489	<MDL	82.172	7.439
31/3/94		3.885	<MDL	1.667	3.175	8.425	1.229	<MDL	<MDL	19.700	1.719
3/5/94		<MDL	<MDL	8.432	8.050	6.681	4.994	<MDL	<MDL	14.915	3.503
11/5/94		<MDL	<MDL	17.707	4.724	9.744	2.225	7.179	<MDL	578.705	71.104
16/5/94		<MDL	<MDL	22.382	17.710	33.578	<MDL	<MDL	<MDL	84.684	13.880
26/5/94		10.807	<MDL	21.497	12.571	20.832	8.792	<MDL	<MDL	491.066	56.049
30/5/94		<MDL	<MDL	2.046	9.889	6.911	<MDL	<MDL	6.536	37.208	<MDL
7/6/94		5.407	<MDL	12.519	6.408	12.385	<MDL	<MDL	<MDL	389.232	54.779
14/6/94		<MDL	<MDL	<MDL	<MDL	2.205	<MDL	<MDL	<MDL	6.663	<MDL
27/6/94		14.202	<MDL	<MDL	14.789	21.926	<MDL	<MDL	<MDL	<MDL	7.715
7/7/94		15.897	<MDL	33.944	23.068	27.134	8.681	<MDL	<MDL	426.796	64.979
11/7/94		<MDL	<MDL	6.191	12.856	18.569	12.371	<MDL	<MDL	69.600	15.978
19/7/94		5.589	<MDL	14.393	6.288	8.780	4.274	3.896	<MDL	423.991	64.792
25/7/94		6.785	<MDL	5.159	5.079	16.871	2.044	<MDL	<MDL	9.512	1.339
7/10/94		<MDL	<MDL	7.782	11.032	15.850	3.774	<MDL	<MDL	54.322	3.906
8/10/94		6.006	<MDL	4.154	2.865	6.445	2.378	<MDL	<MDL	9.449	6.778
13/10/94		5.376	<MDL	9.985	10.641	9.215	1.261	<MDL	<MDL	135.891	17.928
17/10/94		1.791	1.065	5.304	5.940	7.986	2.350	<MDL	<MDL	20.966	2.078
19/10/94		<MDL	<MDL	13.399	25.209	35.344	6.308	<MDL	10.549	44.323	7.504
10/11/94		<MDL	<MDL	<MDL	3.371	3.360	<MDL	<MDL	<MDL	14.716	<MDL
17/3/95		5.627	<MDL	8.413	11.584	5.242	2.459	<MDL	<MDL	18.847	0.238
3/4/95		<MDL	<MDL	0.650	1.139	1.191	0.508	<MDL	<MDL	6.954	0.803
11/4/95		3.546	<MDL	<MDL	0.642	<MDL	1.991	<MDL	<MDL	3.112	<MDL
13/4/95		28.103	12.198	208.197	179.692	147.607	98.963	13.537	<MDL	661.205	160.723
24/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95		7.323	<MDL	17.519	10.691	10.981	6.233	<MDL	<MDL	84.811	14.717

344

DATE	Congener	26	25	31	28	33	22	45	46	52	49
8/5/95		<MDL	<MDL	1.518	<MDL	44.064	<MDL	<MDL	<MDL	4.058	<MDL
15/5/95		3.150	1.876	3.964	0.602	1.763	<MDL	<MDL	<MDL	35.314	2.955
23/5/95		3.104	0.506	1.032	<MDL	<MDL	1.190	<MDL	<MDL	7.740	1.237
27/5/95		2.650	<MDL	14.468	8.828	10.100	6.729	<MDL	<MDL	165.343	25.408
2/6/95		3.511	<MDL	5.372	<MDL	<MDL	0.241	<MDL	<MDL	156.946	20.388
5/6/95		<MDL	<MDL	<MDL	3.104	3.683	3.941	<MDL	<MDL	2.448	<MDL
14/6/95		3.863	<MDL	4.166	<MDL	1.573	1.118	<MDL	<MDL	144.308	19.088
19/6/95		4.464	<MDL	<MDL	<MDL	0.193	1.155	<MDL	<MDL	3.270	<MDL
26/6/95		4.254	<MDL	7.441	5.650	2.304	1.580	2.264	<MDL	207.656	26.565
8/7/95		<MDL	<MDL	12.065	7.190	4.561	3.173	<MDL	<MDL	255.724	37.789
14/7/95		2.557	<MDL	8.168	2.216	1.707	0.278	<MDL	<MDL	337.951	44.841
17/7/95		2.673	<MDL	<MDL	<MDL	<MDL	0.324	<MDL	<MDL	0.996	<MDL
27/7/95		36.591	4.323	177.824	164.650	192.459	73.002	25.997	<MDL	418.310	106.054
19/8/95		3.223	<MDL	12.987	5.876	3.619	0.907	<MDL	<MDL	311.635	51.763
21/8/95		5.454	2.701	5.958	1.605	4.831	1.137	<MDL	<MDL	10.094	<MDL
25/8/95		4.609	<MDL	11.371	4.999	17.015	<MDL	<MDL	<MDL	13.799	1.509
31/8/95		<MDL	<MDL	1.863	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/9/95		<MDL	<MDL	2.267	2.240	0.056	1.364	<MDL	<MDL	6.171	<MDL
18/10/95		4.392	<MDL	6.012	2.695	2.070	<MDL	3.721	2.165	166.887	22.547
30/10/95		3.403	<MDL	5.944	2.939	3.992	1.817	<MDL	<MDL	14.957	0.479

DATE	Congener	47	48	44	42	64	40	74	70	95	66
5/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94		7.764	<MDL	17.369	19.443	37.488	<MDL	<MDL	3.567	<MDL	2.162
31/3/94		30.270	3.069	2.682	<MDL	16.118	<MDL	<MDL	<MDL	4.563	0.498
3/5/94		<MDL	<MDL	5.755	<MDL	9.029	<MDL	5.659	0.632	2.511	<MDL
11/5/94		1.759	<MDL	188.021	16.554	39.575	<MDL	31.937	148.382	364.439	30.135
16/5/94		22.767	<MDL	34.441	<MDL	33.115	<MDL	<MDL	16.695	36.418	8.038
26/5/94		<MDL	<MDL	158.589	28.909	41.264	<MDL	36.516	113.286	316.269	17.204
30/5/94		<MDL	<MDL	7.713	<MDL	15.187	<MDL	18.528	52.895	3.143	<MDL
7/6/94		<MDL	<MDL	125.323	5.593	27.621	<MDL	20.526	109.121	229.043	17.988
14/6/94		3.808	<MDL	<MDL	<MDL	3.179	<MDL	11.092	50.688	<MDL	<MDL
27/6/94		105.566	<MDL	7.525	2.091	20.830	<MDL	<MDL	31.270	<MDL	<MDL
7/7/94		12.079	<MDL	141.508	26.958	46.954	<MDL	33.814	146.992	229.566	20.999
11/7/94		49.133	<MDL	11.437	25.475	25.323	<MDL	10.025	<MDL	10.478	<MDL
19/7/94		<MDL	<MDL	140.460	10.840	29.030	6.521	25.606	130.208	260.285	18.301
25/7/94		<MDL	<MDL	4.131	<MDL	2.149	<MDL	0.372	4.813	1.942	<MDL
7/10/94		18.476	<MDL	7.536	20.374	9.261	<MDL	<MDL	<MDL	0.470	<MDL
8/10/94		13.184	<MDL	1.119	<MDL	4.191	<MDL	5.760	<MDL	<MDL	<MDL
13/10/94		<MDL	<MDL	45.410	11.438	15.456	<MDL	5.901	32.620	82.076	6.989
17/10/94		4.846	<MDL	1.673	<MDL	7.372	<MDL	1.123	<MDL	2.528	<MDL
19/10/94		52.121	<MDL	16.469	<MDL	28.902	<MDL	6.578	2.989	6.425	3.754
10/11/94		4.816	<MDL	0.894	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/3/95		0.318	3.316	0.465	<MDL	4.895	<MDL	1.992	<MDL	1.104	1.211
3/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/4/95		<MDL	1.053	2.732	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1.665
13/4/95		38.406	32.426	314.633	29.441	67.772	19.919	108.658	437.015	436.379	162.978
24/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95		<MDL	<MDL	25.203	4.922	6.083	<MDL	2.112	14.123	36.448	3.708

DATE	Congener	47	48	44	42	64	40	74	70	95	66
8/5/95		<MDL	2.022	<MDL	<MDL	9.867	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	3.284	11.092	2.413	3.090	<MDL	0.052	2.199	15.920	<MDL
23/5/95		<MDL	2.456	2.280	1.519	<MDL	<MDL	3.127	<MDL	1.234	<MDL
27/5/95		<MDL	4.023	58.367	<MDL	7.463	<MDL	15.906	33.912	81.185	5.876
2/6/95		<MDL	3.059	51.698	5.316	7.732	<MDL	7.693	31.254	83.624	4.553
5/6/95		<MDL	8.002	<MDL	6.363	2.003	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95		<MDL	<MDL	44.431	<MDL	7.119	<MDL	<MDL	24.334	66.864	1.472
19/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	4.062	<MDL	<MDL	<MDL
26/6/95		2.648	<MDL	63.849	5.969	12.248	<MDL	18.270	47.470	108.188	9.592
8/7/95		<MDL	4.630	88.045	<MDL	15.582	<MDL	6.536	66.907	138.409	10.890
14/7/95		<MDL	1.811	106.649	<MDL	17.599	<MDL	12.087	96.066	168.007	12.066
17/7/95		<MDL	2.155	<MDL	2.802	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/7/95		10.446	21.857	197.969	42.070	81.196	<MDL	54.117	168.406	144.137	64.834
19/8/95		<MDL	5.250	112.862	6.602	22.251	<MDL	16.607	104.668	208.822	18.048
21/8/95		<MDL	6.727	<MDL	6.623	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	0.721	<MDL	3.954	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	3.089	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/9/95		<MDL	<MDL	0.258	<MDL	<MDL	<MDL	1.906	<MDL	<MDL	<MDL
18/10/95		<MDL	4.941	53.619	<MDL	6.610	<MDL	8.851	52.198	104.702	9.040
30/10/95		<MDL	3.711	0.103	<MDL	1.075	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener												
5/3/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94	<MDL	0.453	<MDL	<MDL	<MDL	5.148	<MDL	<MDL	0.707	<MDL	0.809	<MDL	6.697
31/3/94	<MDL	0.603	<MDL	<MDL	<MDL	0.592	<MDL	<MDL	1.436	<MDL	<MDL	<MDL	1.729
3/5/94	<MDL	0.505	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	5.212
11/5/94	12.586	77.574	277.394	64.995	76.977	127.214	17.305	277.816	<MDL	<MDL	<MDL	<MDL	13.089
16/5/94	<MDL	10.428	35.861	7.467	10.045	15.020	6.241	44.767	<MDL	<MDL	<MDL	<MDL	11.470
26/5/94	14.553	68.056	203.837	48.084	52.447	94.102	19.239	214.321	<MDL	<MDL	<MDL	<MDL	23.506
30/5/94	<MDL	3.637	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/6/94	7.060	50.834	150.530	34.996	42.567	70.996	7.601	153.645	<MDL	<MDL	<MDL	<MDL	15.847
14/6/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/6/94	<MDL	0.214	<MDL	<MDL	<MDL	<MDL	2.586	11.337	11.337	<MDL	11.337	<MDL	<MDL
7/7/94	8.998	47.246	147.564	33.486	40.623	67.981	10.555	140.295	<MDL	<MDL	<MDL	<MDL	22.057
11/7/94	<MDL	1.702	<MDL	0.220	1.935	<MDL	<MDL	0.185	<MDL	<MDL	0.185	<MDL	0.143
19/7/94	7.064	59.503	174.043	37.330	46.972	80.601	8.135	165.423	<MDL	<MDL	<MDL	<MDL	16.768
25/7/94	<MDL	0.495	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.455
7/10/94	<MDL	2.817	<MDL	<MDL	2.412	<MDL	<MDL	5.570	<MDL	<MDL	5.570	<MDL	11.130
8/10/94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/10/94	0.367	20.698	54.561	16.499	16.165	21.667	4.302	59.556	<MDL	<MDL	<MDL	<MDL	8.922
17/10/94	<MDL	0.847	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.274
19/10/94	<MDL	4.556	<MDL	<MDL	<MDL	<MDL	6.409	2.591	<MDL	<MDL	<MDL	<MDL	<MDL
10/11/94	<MDL	0.312	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/3/95	5.657	<MDL	<MDL	<MDL	1.545	4.867	4.570	<MDL	<MDL	<MDL	<MDL	<MDL	8.943
3/4/95	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/4/95	2.408	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/4/95	81.501	95.140	485.767	113.286	64.712	195.521	44.695	386.242	<MDL	<MDL	<MDL	<MDL	32.478
24/4/95	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95	<MDL	5.333	26.234	4.588	7.489	7.155	7.289	11.038	<MDL	<MDL	<MDL	<MDL	3.208

348

DATE	Congener	60	84	101/89	99	97	87	136	110	82	151
8/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	2.819	5.765	<MDL	<MDL	<MDL	<MDL	0.366	<MDL	<MDL
23/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1.278	<MDL	<MDL	<MDL
27/5/95		2.194	12.527	60.309	10.176	4.476	10.057	4.344	48.239	<MDL	<MDL
2/6/95		<MDL	16.863	48.380	9.023	4.839	22.031	4.352	46.572	5.918	<MDL
5/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95		<MDL	14.228	37.768	3.561	1.159	12.409	2.208	21.366	6.210	<MDL
19/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	3.310	<MDL
26/6/95		<MDL	20.142	60.942	12.673	15.106	32.862	4.322	50.840	8.713	<MDL
8/7/95		0.955	20.910	93.260	18.089	10.919	38.718	7.202	74.812	<MDL	<MDL
14/7/95		-3.166	35.021	101.574	18.395	12.262	44.467	4.780	94.422	9.963	<MDL
17/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/7/95		81.734	26.516	112.589	28.795	37.473	48.182	12.823	108.047	<MDL	12.063
19/8/95		10.750	43.628	169.687	34.491	22.804	77.239	11.037	166.186	16.738	5.185
21/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.018	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		0.297	29.229	103.853	20.936	27.311	50.503	8.008	98.828	10.797	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	135 (144)	149	118	134	114	131	153	132	105	141
5/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/5/94		17.386	50.719	101.676	10.220	<MDL	<MDL	29.672	33.036	20.083	6.520
16/5/94		10.468	19.839	18.678	<MDL	<MDL	<MDL	12.979	12.122	<MDL	7.628
26/5/94		21.396	40.372	62.034	<MDL	<MDL	<MDL	21.290	27.752	17.892	4.926
30/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/6/94		8.273	18.477	42.136	8.203	<MDL	<MDL	6.502	11.327	14.402	4.316
14/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/6/94		0.851	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/7/94		13.426	22.870	33.415	3.378	<MDL	<MDL	0.268	13.253	<MDL	6.674
11/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/7/94		6.104	11.065	40.880	6.775	<MDL	<MDL	<MDL	13.005	7.564	<MDL
25/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/10/94		<MDL	2.748	19.656	<MDL	<MDL	<MDL	<MDL	2.646	3.648	<MDL
17/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/10/94		<MDL	0.182	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
10/11/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/3/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/4/95		41.789	176.940	215.454	3.449	<MDL	<MDL	164.283	58.994	60.431	40.437
24/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95		5.258	6.816	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	135 (144)	149	118	134	114	131	153	132	105	141
8/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/5/95		1.135	7.985	8.595	<MDL	<MDL	<MDL	<MDL	1.319	<MDL	<MDL
2/6/95		3.374	0.175	8.633	2.558	<MDL	<MDL	<MDL	0.832	<MDL	<MDL
5/6/95		0.123	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95		0.911	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/6/95		2.429	<MDL	8.963	2.676	<MDL	<MDL	<MDL	1.704	<MDL	<MDL
8/7/95		4.466	<MDL	19.272	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/7/95		3.495	<MDL	21.358	<MDL	<MDL	<MDL	<MDL	5.791	<MDL	<MDL
17/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/7/95		6.713	15.458	25.478	<MDL	<MDL	<MDL	<MDL	19.115	<MDL	<MDL
19/8/95		8.695	24.928	58.853	<MDL	<MDL	<MDL	11.390	24.309	14.103	6.327
21/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		5.031	9.182	47.173	5.917	<MDL	<MDL	8.973	11.307	7.909	3.059
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	137	130	138	158	178	129	187	183	128	185
5/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.546	<MDL
3/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/5/94		<MDL	<MDL	64.656	8.980	<MDL	<MDL	<MDL	<MDL	18.497	<MDL
16/5/94		<MDL	<MDL	18.812	<MDL	18.645	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	43.390	6.966	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/6/94		<MDL	<MDL	6.000	4.069	<MDL	<MDL	<MDL	<MDL	9.881	<MDL
14/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/7/94		<MDL	<MDL	8.438	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/7/94		<MDL	<MDL	1.463	1.226	<MDL	<MDL	<MDL	<MDL	9.400	<MDL
25/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
10/11/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/3/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.774	1.110
11/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/4/95		3.654	8.853	180.122	14.051	8.441	6.073	34.761	15.633	33.816	12.404
24/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	12.712	<MDL	<MDL

DATE	Congener	137	130	138	158	178	129	187	183	128	185
8/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/5/95		<MDL	<MDL	<MDL	2.377	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	5.416	<MDL
5/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	5.619	<MDL
26/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	8.302	<MDL
8/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/7/95		<MDL	<MDL	15.513	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	37.790	5.714	0.448	<MDL	<MDL	<MDL	<MDL	<MDL
21/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	23.608	4.211	<MDL	<MDL	<MDL	<MDL	14.335	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	174	171	156	201	157	172	180	193	191	200
5/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/3/94		<MDL	1.848	1.578	<MDL	<MDL	<MDL	<MDL	<MDL	1.126	<MDL
3/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	22.901	<MDL
26/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/5/94		24.713	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/7/94		<MDL	10.465	<MDL	<MDL	<MDL	3.775	<MDL	<MDL	<MDL	<MDL
11/7/94		1.101	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/7/94		<MDL	9.047	3.037	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	9.055	<MDL	<MDL	<MDL	<MDL
8/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.833
19/10/94		<MDL	31.177	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
10/11/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/3/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/4/95		29.899	9.728	10.963	<MDL	<MDL	2.265	34.064	<MDL	<MDL	<MDL
24/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95		4.649	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	174	171	156	201	157	172	180	193	191	200
8/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	2.413	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23/5/95		<MDL	1.695	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/5/95	14.426	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/6/95		<MDL	4.391	<MDL	<MDL	<MDL	<MDL	<MDL	3.225	<MDL	<MDL
8/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
21/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/9/95		<MDL	4.501	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	170	190	198	199	196	189	208	195	207	194
5/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/3/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	4.288	<MDL	<MDL	<MDL	<MDL
14/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	45.007	<MDL	<MDL
10/11/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/3/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/4/95		2.868	3.140	<MDL	7.140	1.207	<MDL	<MDL	<MDL	<MDL	<MDL
24/4/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	170	190	198	199	196	189	208	195	207	194
8/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23/5/95		<MDL	0.704	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
27/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
21/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	205	206	209
------	----------	-----	-----	-----

5/3/94		<MDL	<MDL	<MDL
14/3/94		<MDL	<MDL	<MDL
31/3/94		<MDL	<MDL	<MDL
3/5/94		<MDL	<MDL	<MDL
11/5/94		<MDL	<MDL	<MDL
16/5/94		<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	<MDL
30/5/94		<MDL	<MDL	<MDL
7/6/94		<MDL	<MDL	<MDL
14/6/94		<MDL	<MDL	<MDL
27/6/94		<MDL	<MDL	<MDL
7/7/94		<MDL	<MDL	<MDL
11/7/94		<MDL	<MDL	<MDL
19/7/94		<MDL	<MDL	<MDL
25/7/94		<MDL	<MDL	<MDL
7/10/94		<MDL	<MDL	<MDL
8/10/94		<MDL	<MDL	<MDL
13/10/94		<MDL	<MDL	<MDL
17/10/94		<MDL	<MDL	<MDL
19/10/94		<MDL	<MDL	<MDL
10/11/94		<MDL	<MDL	<MDL
17/3/95		<MDL	<MDL	<MDL
3/4/95		<MDL	<MDL	<MDL
11/4/95		<MDL	<MDL	<MDL
13/4/95		<MDL	<MDL	<MDL
24/4/95		<MDL	<MDL	<MDL
2/5/95		<MDL	<MDL	<MDL

DATE	Congener	205	206	209
8/5/95		<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL
23/5/95		<MDL	<MDL	<MDL
27/5/95		<MDL	<MDL	<MDL
2/6/95		<MDL	<MDL	<MDL
5/6/95		<MDL	<MDL	<MDL
14/6/95		<MDL	<MDL	<MDL
19/6/95		<MDL	<MDL	<MDL
26/6/95		<MDL	<MDL	<MDL
8/7/95		<MDL	<MDL	<MDL
14/7/95		<MDL	<MDL	<MDL
17/7/95		<MDL	<MDL	<MDL
27/7/95		<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL
21/8/95		<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL
11/9/95		<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL

VII. PCB Concentrations in Precipitation in the South Tobacco Creek Watershed (pg/L)

DATE	Congener	3	4/10	7	6	8	5	19	18	2724	16
20/5/94		<MDL	122.973	<MDL	<MDL	178.830	<MDL	<MDL	161.148	<MDL	114.312
26/5/94		11.991	18.474	18.168	4.983	25.203	<MDL	<MDL	23.308	<MDL	28.031
13/6/94		1.691	7.647	4.698	2.796	15.910	<MDL	<MDL	8.979	<MDL	12.524
25/6/94		17.419	52.845	<MDL	29.792	122.959	<MDL	<MDL	125.748	<MDL	141.312
7/7/94		<MDL	9.728	<MDL	6.123	24.439	<MDL	<MDL	26.317	<MDL	27.969
19/7/94		<MDL	<MDL	19.053	14.855	52.198	<MDL	<MDL	62.458	<MDL	52.358
12/8/94		<MDL	10.152	<MDL	7.880	30.252	<MDL	<MDL	29.450	<MDL	33.715
24/8/94		70.348	105.876	<MDL	61.754	330.899	<MDL	33.819	253.943	70.112	262.446
5/9/94		<MDL	15.287	1.821	2.736	25.042	<MDL	<MDL	19.706	<MDL	15.490
11/10/94		<MDL	<MDL	<MDL	<MDL	8.042	<MDL	<MDL	5.304	<MDL	5.925
24/10/94		<MDL	<MDL	<MDL	22.519	<MDL	<MDL	<MDL	132.811	200.053	<MDL
15/5/95		8.875	18.998	7.918	2.668	15.950	<MDL	<MDL	27.988	<MDL	23.318
8/6/95		2.912	61.103	<MDL	29.571	107.976	<MDL	7.610	115.327	<MDL	98.014
2/7/95		<MDL	11.973	<MDL	8.037	30.278	<MDL	<MDL	35.418	<MDL	13.227
20/7/95		2.334	6.406	<MDL	0.946	5.393	<MDL	<MDL	3.190	<MDL	3.197
7/8/95		18.587	23.996	8.200	12.841	68.679	<MDL	<MDL	62.944	<MDL	59.843
19/8/95		12.723	10.475	1.528	2.450	12.336	<MDL	<MDL	9.391	<MDL	13.751
6/9/95		1.051	7.885	4.205	0.104	2.143	<MDL	2.102	5.193	<MDL	3.582
18/10/95		<MDL	5.446	1.436	<MDL	9.751	<MDL	<MDL	9.824	<MDL	15.096
30/10/95		4.937	20.561	58.952	4.504	37.908	<MDL	<MDL	61.138	<MDL	46.182

DATE	Congener	26	25	31	28	33	22	45	46	52	49
20/5/94		102.554	<MDL	114.614	180.526	210.046	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	16.952	23.166	18.187	9.128	<MDL	<MDL	52.146	10.623
13/6/94		9.209	<MDL	14.483	15.465	23.837	9.384	<MDL	<MDL	51.228	5.372
25/6/94		48.710	<MDL	158.814	182.217	231.217	70.100	<MDL	<MDL	410.563	56.488
7/7/94		12.420	3.736	35.359	28.255	31.138	<MDL	<MDL	<MDL	75.978	23.029
19/7/94		28.146	<MDL	42.388	75.152	75.875	33.468	<MDL	<MDL	155.067	34.611
12/8/94		18.514	<MDL	33.854	33.845	30.868	12.020	<MDL	<MDL	81.984	21.543
24/8/94		162.377	<MDL	357.838	371.362	415.015	106.876	27.456	<MDL	914.056	219.445
5/9/94		11.964	<MDL	19.036	23.572	31.405	15.475	<MDL	<MDL	53.646	<MDL
11/10/94		3.851	<MDL	3.021	5.270	3.582	<MDL	<MDL	<MDL	13.766	1.194
24/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		10.529	<MDL	16.269	3.507	8.583	<MDL	<MDL	<MDL	52.436	0.782
8/6/95		66.704	<MDL	125.996	129.609	130.181	57.860	<MDL	<MDL	215.907	45.204
2/7/95		19.288	11.267	37.022	38.214	37.549	12.270	<MDL	<MDL	57.905	16.633
20/7/95		3.053	<MDL	6.049	5.006	7.092	2.514	<MDL	<MDL	15.040	3.784
7/8/95		20.227	<MDL	64.774	78.296	67.106	42.149	<MDL	<MDL	88.804	21.788
19/8/95		4.379	<MDL	17.317	21.923	27.748	<MDL	<MDL	2.891	59.253	<MDL
6/9/95		<MDL	<MDL	11.451	4.298	6.574	3.587	<MDL	<MDL	18.525	6.056
18/10/95		<MDL	<MDL	11.245	6.553	33.405	7.715	<MDL	<MDL	77.955	13.290
30/10/95		25.846	17.715	85.679	69.997	83.065	18.444	<MDL	<MDL	187.330	50.682

DATE	Congener	47	48	44	42	64	40	74	70	95	66
20/5/94		<MDL	<MDL	119.229	163.821	192.860	<MDL	<MDL	149.975	61.581	<MDL
26/5/94		24.035	36.518	10.453	<MDL	34.098	<MDL	6.374	14.431	27.320	11.755
13/6/94		<MDL	<MDL	16.672	<MDL	20.289	<MDL	16.616	31.419	67.317	12.663
25/6/94		120.909	<MDL	149.073	77.742	114.005	<MDL	55.651	215.354	221.076	70.862
7/7/94		19.236	1.433	25.824	11.148	20.238	<MDL	5.374	23.365	51.348	11.009
19/7/94		37.343	<MDL	59.553	<MDL	38.504	<MDL	20.460	54.026	87.248	21.606
12/8/94		<MDL	<MDL	22.412	<MDL	24.893	<MDL	9.356	17.938	32.816	4.611
24/8/94		342.674	<MDL	353.867	126.438	233.069	<MDL	119.067	397.510	384.912	199.784
5/9/94		<MDL	<MDL	13.854	<MDL	17.485	41.353	14.334	21.941	35.080	9.328
11/10/94		12.590	<MDL	0.908	<MDL	3.030	<MDL	<MDL	<MDL	11.166	<MDL
24/10/94		<MDL	<MDL	86.636	105.393	102.301	178.763	<MDL	221.300	29.491	-9.138
15/5/95		<MDL	<MDL	9.859	<MDL	<MDL	<MDL	<MDL	5.564	10.119	13.485
8/6/95		23.914	14.468	91.920	90.286	61.433	<MDL	16.986	49.446	27.277	27.032
2/7/95		21.286	10.312	27.636	<MDL	30.276	<MDL	4.396	3.609	28.356	23.899
20/7/95		<MDL	3.412	4.267	8.619	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/8/95		24.131	<MDL	50.426	18.587	27.478	<MDL	23.908	71.388	64.985	41.702
19/8/95		1.956	5.411	7.726	<MDL	18.854	<MDL	<MDL	8.999	2.221	2.014
6/9/95		<MDL	2.453	10.299	<MDL	2.382	<MDL	<MDL	<MDL	0.276	<MDL
18/10/95		4.559	7.897	16.581	<MDL	19.838	<MDL	19.787	3.716	21.236	4.980
30/10/95		101.649	96.123	126.918	18.731	73.044	<MDL	17.867	108.777	85.104	67.528

DATE	Congener	60	84	101/89	99	97	87	136	110	82	151
20/5/94		<MDL	22.401	60.599	23.564	41.980	87.008	12.263	152.517	<MDL	<MDL
26/5/94		<MDL	7.458	31.080	9.100	11.134	22.708	7.459	62.379	15.080	1.265
13/6/94		19.432	21.772	79.766	21.528	34.513	54.693	18.791	149.960	18.418	20.033
25/6/94		<MDL	64.681	237.502	85.893	130.667	175.722	48.794	409.216	<MDL	93.704
7/7/94		8.811	15.813	44.574	14.351	20.785	36.645	10.630	89.687	19.453	6.882
19/7/94		38.766	25.959	87.929	36.622	42.399	62.705	16.574	161.363	58.890	15.951
12/8/94		<MDL	9.262	35.430	11.081	19.421	37.101	7.311	75.044	14.430	7.149
24/8/94		220.631	94.630	394.528	121.170	172.891	214.893	62.679	476.467	70.230	<MDL
5/9/94		20.181	12.554	26.407	13.349	17.830	26.898	7.927	73.832	<MDL	<MDL
11/10/94		1.618	7.514	8.165	3.471	7.278	4.697	3.666	25.849	<MDL	<MDL
24/10/94		<MDL	17.818	25.653	12.960	23.041	28.858	10.582	55.753	53.136	<MDL
15/5/95		<MDL	4.698	4.665	1.419	0.259	<MDL	2.232	8.608	<MDL	<MDL
8/6/95		21.774	4.855	<MDL	1.699	<MDL	7.797	9.767	13.413	<MDL	4.430
2/7/95		7.722	4.242	25.099	7.490	<MDL	17.647	10.773	20.527	<MDL	7.983
20/7/95		0.599	4.268	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/8/95		34.138	12.595	71.879	20.449	24.856	45.785	22.257	87.620	<MDL	39.760
19/8/95		0.600	2.216	4.259	<MDL	0.822	<MDL	0.252	0.230	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.880	<MDL	<MDL	<MDL
18/10/95		<MDL	2.109	12.344	2.072	19.882	15.768	6.648	10.936	<MDL	5.979
30/10/95		93.813	21.930	122.284	34.276	62.444	69.714	27.593	152.493	<MDL	50.980

DATE	Congener	135 (144)	149	118	134	114	131	153	132	105	141
20/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	31.844	<MDL	<MDL
26/5/94		<MDL	36.627	36.101	<MDL	<MDL	<MDL	9.815	21.610	<MDL	<MDL
13/6/94		22.023	74.073	94.847	<MDL	<MDL	<MDL	62.962	51.741	35.797	22.198
25/6/94		<MDL	258.833	251.585	<MDL	<MDL	<MDL	207.657	122.252	112.529	61.702
7/7/94		<MDL	29.786	65.806	<MDL	<MDL	<MDL	23.572	32.029	24.029	13.257
19/7/94		19.739	65.209	119.666	13.423	<MDL	21.218	68.805	66.332	62.848	30.690
12/8/94		8.820	29.934	<MDL	<MDL	<MDL	<MDL	20.117	21.941	<MDL	10.903
24/8/94		<MDL	599.451	261.219	<MDL	<MDL	<MDL	235.819	84.540	<MDL	<MDL
5/9/94		<MDL	68.090	54.281	<MDL	<MDL	<MDL	14.908	17.000	<MDL	<MDL
11/10/94		<MDL	62.885	31.579	3.539	<MDL	<MDL	<MDL	13.111	<MDL	<MDL
24/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	27.206	<MDL	<MDL
15/5/95		2.986	<MDL	1.154	<MDL	<MDL	<MDL	<MDL	4.667	<MDL	<MDL
8/6/95		7.830	3.400	<MDL	<MDL	<MDL	<MDL	<MDL	8.793	<MDL	<MDL
2/7/95		8.552	14.350	11.068	<MDL	<MDL	<MDL	9.020	0.267	<MDL	15.283
20/7/95		1.332	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1.276	<MDL	<MDL
7/8/95		25.693	86.225	64.716	<MDL	<MDL	<MDL	70.639	27.544	32.374	23.015
19/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.463
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		2.703	4.039	12.837	<MDL	<MDL	<MDL	<MDL	7.669	<MDL	<MDL
30/10/95		23.240	120.263	129.838	<MDL	<MDL	<MDL	124.186	58.094	30.364	33.843

DATE	Congener	137	130	138	158	178	129	187	183	128	185
20/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	40.878	<MDL	<MDL
26/5/94		<MDL	<MDL	60.502	3.934	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/6/94		<MDL	<MDL	159.189	14.759	<MDL	20.861	9.889	1.410	45.481	11.840
25/6/94		<MDL	<MDL	410.476	26.504	<MDL	<MDL	40.309	21.511	135.806	<MDL
7/7/94		<MDL	<MDL	72.722	1.902	<MDL	<MDL	<MDL	<MDL	15.301	<MDL
19/7/94		<MDL	<MDL	152.295	<MDL	<MDL	<MDL	<MDL	15.803	46.332	<MDL
12/8/94		<MDL	<MDL	68.517	<MDL	<MDL	<MDL	<MDL	2.621	<MDL	<MDL
24/8/94		<MDL	<MDL	426.909	<MDL	<MDL	<MDL	32.391	31.251	115.361	<MDL
5/9/94		<MDL	<MDL	47.007	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/10/94		2.082	<MDL	7.557	<MDL	<MDL	<MDL	<MDL	<MDL	15.717	<MDL
24/10/94		<MDL	<MDL	<MDL	<MDL	34.638	<MDL	11.657	20.953	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/7/95		<MDL	<MDL	0.695	3.234	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/8/95		<MDL	<MDL	78.156	11.067	<MDL	<MDL	25.021	17.860	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	187.221	16.413	<MDL	<MDL	58.543	<MDL	<MDL	<MDL

DATE	Congener	174	171	156	201	157	172	180	193	191	200
20/5/94		45.908	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94		<MDL	45.239	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/6/94		18.463	<MDL	<MDL	<MDL	<MDL	<MDL	12.115	<MDL	<MDL	<MDL
25/6/94		62.996	<MDL	<MDL	<MDL	<MDL	<MDL	38.539	<MDL	<MDL	<MDL
7/7/94		<MDL	10.670	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/7/94		15.362	29.878	23.383	<MDL	<MDL	<MDL	19.192	<MDL	<MDL	<MDL
12/8/94		6.326	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/8/94		39.526	118.307	<MDL	<MDL	<MDL	<MDL	9.186	<MDL	<MDL	<MDL
5/9/94		24.152	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/10/94		54.402	37.477	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/6/95		2.860	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/7/95		6.808	<MDL	<MDL	<MDL	<MDL	<MDL	0.002	<MDL	<MDL	<MDL
20/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/8/95		23.226	<MDL	<MDL	<MDL	<MDL	<MDL	21.216	<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	96.009	<MDL	<MDL	<MDL

DATE	Congener	170	190	1-8	199	196	189	208	195	207	194
20/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/6/94		3.665	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/7/94		3.563	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/7/94		23.165	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/9/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/6/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/8/95		3.646	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		139.264	48.643	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	205	206	209
------	----------	-----	-----	-----

20/5/94		<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	<MDL
13/6/94		<MDL	<MDL	<MDL
25/6/94		<MDL	<MDL	<MDL
7/7/94		<MDL	<MDL	<MDL
19/7/94		<MDL	<MDL	<MDL
12/8/94		<MDL	<MDL	<MDL
24/8/94		<MDL	<MDL	<MDL
5/9/94		<MDL	<MDL	<MDL
11/10/94		<MDL	<MDL	<MDL
24/10/94		<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL
8/6/95		<MDL	<MDL	<MDL
2/7/95		<MDL	<MDL	<MDL
20/7/95		<MDL	<MDL	<MDL
7/8/95		<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL

VIII. PCB Concentration in Air (total of vapour and particle phase) in the South Tobacco Creek Watershed (pg/m³)

DATE	Congener	3	4/10	7	8	8	9	19	18	2724	16
26/4/94		<MDL	<MDL	<MDL	0.263	<MDL	<MDL	<MDL	0.157	<MDL	0.021
2/5/94		0.188	<MDL	0.006	1.458	0.975	<MDL	<MDL	0.689	<MDL	0.352
8/5/94		<MDL	0.096	0.892	1.892	4.090	<MDL	<MDL	5.049	1.073	2.399
14/5/94		0.782	<MDL	0.007	0.849	0.725	<MDL	<MDL	1.057	<MDL	0.011
20/5/94		<MDL	<MDL	0.031	0.761	1.563	<MDL	<MDL	3.353	<MDL	1.299
26/5/94		<MDL	<MDL	0.651	1.915	3.614	<MDL	<MDL	4.850	<MDL	1.613
1/6/94		<MDL	<MDL	0.190	0.888	2.193	<MDL	<MDL	3.038	<MDL	0.908
7/6/94		<MDL	<MDL	0.108	0.515	0.531	<MDL	<MDL	1.192	0.341	0.349
13/6/94		<MDL	0.004	0.115	0.664	0.940	<MDL	<MDL	1.062	<MDL	0.482
19/6/94		0.069	<MDL	0.211	0.803	1.234	<MDL	0.618	2.291	0.237	0.508
25/6/94		<MDL	<MDL	0.031	0.463	0.361	<MDL	<MDL	1.569	0.103	0.382
1/7/94		0.066	<MDL	0.098	0.732	1.117	<MDL	<MDL	1.570	<MDL	<MDL
7/7/94		0.066	<MDL	0.098	0.732	1.117	<MDL	<MDL	1.570	<MDL	<MDL
17/7/94		<MDL	<MDL	<MDL	0.045	<MDL	<MDL	<MDL	0.753	<MDL	<MDL
25/7/94		<MDL	0.009	0.051	0.500	0.729	<MDL	<MDL	1.228	<MDL	0.068
31/7/94		<MDL	<MDL	0.231	0.852	1.443	<MDL	<MDL	1.807	0.297	<MDL
6/8/94		0.086	0.082	0.141	1.259	1.202	<MDL	<MDL	2.652	<MDL	<MDL
12/8/94		0.081	<MDL	0.004	0.419	0.659	<MDL	0.202	1.623	0.293	0.865
18/8/94		0.049	<MDL	0.227	0.753	1.385	<MDL	<MDL	1.472	0.124	0.484
24/8/94		<MDL	<MDL	0.021	0.445	0.866	<MDL	<MDL	1.444	0.092	0.104
30/8/94		<MDL	<MDL	0.130	1.029	2.350	<MDL	<MDL	3.235	0.679	2.026
5/9/94		<MDL	<MDL	<MDL	0.528	1.392	<MDL	<MDL	0.574	<MDL	0.517
17/9/94		<MDL	0.049	0.038	0.962	1.059	<MDL	<MDL	1.285	<MDL	0.288
29/9/94		<MDL	<MDL	<MDL	0.688	0.812	<MDL	<MDL	1.381	0.274	<MDL
11/10/94		<MDL	0.084	0.103	0.499	0.706	<MDL	<MDL	0.823	<MDL	0.044
23/10/94		<MDL	<MDL	0.138	0.608	0.939	<MDL	<MDL	0.610	<MDL	0.353
3/5/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	<MDL	0.040

DATE	Congener	3	4/10	7	6	8	5	19	18	2724	16
9/5/95		<MDL	<MDL	0.054	0.628	0.361	<MDL	<MDL	1.850	<MDL	3.089
15/5/95		0.556	1.141	0.261	2.109	3.687	<MDL	<MDL	2.675	<MDL	1.698
21/5/95		0.259	0.347	0.108	0.232	1.013	<MDL	0.217	0.640	<MDL	0.406
27/5/95		0.482	0.542	0.220	0.599	1.526	<MDL	0.283	0.829	<MDL	0.715
2/6/95		<MDL	0.083	<MDL	0.128	0.150	<MDL	<MDL	0.267	<MDL	0.207
8/6/95		0.431	0.214	0.569	1.462	2.737	<MDL	0.454	2.712	<MDL	3.927
14/6/95		<MDL	1.535	0.798	2.102	5.520	<MDL	0.637	4.897	<MDL	3.431
20/6/95		0.242	<MDL	0.035	0.694	1.524	<MDL	0.204	3.671	0.462	3.804
26/6/95		0.086	0.182	0.337	1.336	3.860	<MDL	0.453	6.255	1.045	4.342
2/7/95		0.282	0.408	0.276	1.016	3.992	<MDL	0.824	5.296	0.765	3.386
8/7/95		<MDL	<MDL	<MDL	0.497	1.458	<MDL	0.440	3.452	<MDL	1.982
14/7/95		0.303	0.533	0.412	1.865	6.140	<MDL	0.838	8.412	1.016	5.319
20/7/95		0.335	0.478	0.330	1.027	4.439	<MDL	0.722	6.477	0.908	5.010
26/7/95		0.171	0.368	0.263	1.144	3.979	<MDL	0.441	4.828	1.190	4.097
1/8/95		<MDL	0.057	0.097	0.344	1.563	<MDL	0.258	4.282	0.717	4.209
7/8/95		<MDL	0.036	0.050	0.510	1.024	<MDL	0.164	0.901	0.244	0.882
13/8/95		0.141	0.255	0.215	0.596	3.401	<MDL	0.636	11.134	1.258	15.655
19/8/95		0.191	0.929	0.475	1.201	4.872	<MDL	0.707	7.258	1.169	0.079
25/8/95		0.024	<MDL	0.058	0.121	0.598	<MDL	0.146	4.388	1.471	7.440
31/8/95		0.102	<MDL	0.122	0.602	2.179	<MDL	0.250	3.063	<MDL	3.292
6/9/95		0.202	0.569	0.377	1.730	4.920	<MDL	0.429	4.228	0.693	3.227
12/9/95		0.060	0.390	0.297	0.464	1.995	<MDL	0.094	1.821	0.459	1.438
24/9/95		0.156	0.480	0.178	0.968	2.923	<MDL	0.301	2.237	0.354	7.447
6/10/95		0.032	0.015	0.149	0.470	2.162	<MDL	0.255	2.831	0.450	3.137
18/10/95		0.006	<MDL	<MDL	0.021	0.132	<MDL	0.032	0.094	0.087	3.178
30/10/95		0.092	0.196	0.111	0.252	0.458	<MDL	0.096	0.292	0.208	0.176
29/5/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/5/96		<MDL	<MDL	<MDL	<MDL	0.111	<MDL	0.117	0.070	<MDL	0.017
2/6/96		0.434	<MDL	0.474	1.032	4.756	<MDL	0.741	2.757	4.056	7.574

DATE	Congener	3	4/10	7	6	8	6	19	18	2724	16
4/6/96		0.710	2.956	0.909	0.392	0.114	<MDL	<MDL	2.941	<MDL	4.734
6/6/96		<MDL	<MDL	<MDL	<MDL	0.203	<MDL	<MDL	0.378	0.027	0.102
8/6/96		0.264	0.341	0.794	1.660	10.930	<MDL	1.149	19.418	2.434	20.132
10/6/96		<MDL	0.291	<MDL	0.072	0.491	0.277	<MDL	0.618	<MDL	0.372
12/6/96		<MDL	0.153	<MDL	<MDL	0.463	0.184	0.059	8.519	1.412	14.245
14/6/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.110	<MDL	0.712	2.251
16/6/96		<MDL	0.184	<MDL	0.150	0.411	0.073	<MDL	0.375	<MDL	0.410
18/6/96		<MDL	0.349	<MDL	0.046	0.436	0.086	0.161	0.335	0.625	4.131
20/6/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.138	2.124	<MDL	5.278
22/6/96		<MDL	0.239	<MDL	0.186	1.589	<MDL	<MDL	6.117	<MDL	8.253
24/6/96		1.203	1.325	0.052	<MDL	0.330	<MDL	<MDL	0.883	<MDL	1.480
27/6/96		0.101	0.306	<MDL	<MDL	0.538	<MDL	0.164	0.747	<MDL	1.539
28/6/96		<MDL	0.144	0.023	0.074	0.370	<MDL	<MDL	0.176	<MDL	0.103
30/6/96		0.483	0.436	0.081	0.252	2.712	<MDL	<MDL	9.407	<MDL	10.338
2/7/96		<MDL	0.237	<MDL	0.125	0.563	<MDL	<MDL	0.651	0.102	0.513
4/7/96		<MDL	<MDL	<MDL	<MDL	0.119	<MDL	0.637	0.927	<MDL	6.394
6/7/96		<MDL	0.208	<MDL	10.921	0.416	0.025	0.375	3.789	1.017	7.947
8/7/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.268	5.523	0.738	12.494
10/7/96		<MDL	0.250	<MDL	0.049	0.613	<MDL	0.263	0.705	0.820	6.437
12/7/96		0.156	1.437	0.339	2.023	7.646	<MDL	1.262	14.456	<MDL	14.168
14/7/96		<MDL	<MDL	<MDL	<MDL	0.026	<MDL	<MDL	-8.503	<MDL	0.019
16/7/96		<MDL	<MDL	<MDL	<MDL	0.220	<MDL	0.129	0.573	0.402	0.468
18/7/96		<MDL	0.044	<MDL	<MDL	0.266	<MDL	<MDL	0.416	<MDL	0.545
20/7/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.127	<MDL	2.342
24/7/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.072	<MDL	<MDL
26/7/96		0.086	0.075	0.140	1.684	11.035	<MDL	2.243	24.839	<MDL	30.440
28/7/96		<MDL	0.030	<MDL	0.462	2.438	<MDL	1.015	7.773	<MDL	15.643
30/7/96		0.183	0.952	0.463	1.062	5.972	<MDL	1.503	9.224	0.869	17.245
1/8/96		<MDL	<MDL	<MDL	0.037	0.214	<MDL	<MDL	<MDL	<MDL	0.223

DATE	Congener	26	25	31	28	33	22	15	16	52	19
26/4/94		<MDL	<MDL	0.332	0.150	0.404	0.038	<MDL	<MDL	<MDL	<MDL
2/5/94		0.036	<MDL	0.689	0.062	0.712	<MDL	<MDL	<MDL	2.525	0.050
8/5/94		0.026	<MDL	4.182	4.581	3.019	1.524	<MDL	<MDL	15.471	0.403
14/5/94		0.033	<MDL	1.605	1.535	0.550	0.070	<MDL	<MDL	3.169	0.557
20/5/94		0.029	<MDL	3.040	2.371	2.323	1.907	<MDL	<MDL	11.120	0.585
26/5/94		0.783	<MDL	5.003	3.180	2.384	<MDL	<MDL	<MDL	12.781	0.399
1/6/94		0.009	<MDL	2.676	2.217	3.759	<MDL	<MDL	<MDL	9.802	0.488
7/6/94		0.008	<MDL	1.035	0.798	0.524	0.025	<MDL	<MDL	6.276	0.354
13/6/94		0.202	<MDL	0.955	1.120	0.901	0.021	<MDL	<MDL	0.963	0.037
19/6/94		0.012	<MDL	3.506	2.116	1.255	0.367	<MDL	<MDL	5.301	0.005
25/6/94		0.326	<MDL	2.196	1.792	0.978	0.021	<MDL	<MDL	3.971	0.065
1/7/94		<MDL	<MDL	2.337	1.109	<MDL	<MDL	<MDL	<MDL	13.228	1.254
7/7/94		<MDL	<MDL	2.337	1.109	<MDL	0.036	<MDL	<MDL	13.228	1.254
17/7/94		0.325	<MDL	1.445	0.922	0.444	0.316	<MDL	<MDL	8.243	0.907
25/7/94		0.297	<MDL	1.179	0.470	0.053	0.017	<MDL	<MDL	5.706	0.415
31/7/94		0.291	<MDL	1.412	0.918	1.335	<MDL	<MDL	<MDL	1.997	0.061
6/8/94		0.021	<MDL	3.552	2.397	3.354	0.078	<MDL	<MDL	10.851	0.838
12/8/94		1.209	<MDL	2.667	2.432	2.462	1.373	<MDL	<MDL	1.838	0.536
18/8/94		0.733	<MDL	1.578	1.002	2.045	2.306	<MDL	<MDL	4.160	0.476
24/8/94		0.047	<MDL	1.564	1.167	0.453	0.059	<MDL	<MDL	0.788	0.018
30/8/94		0.756	<MDL	2.586	2.606	1.585	2.545	<MDL	<MDL	4.976	0.412
5/9/94		0.255	<MDL	0.368	0.505	0.347	0.059	<MDL	<MDL	2.349	0.008
17/9/94		0.015	<MDL	0.704	0.566	0.425	<MDL	<MDL	<MDL	4.796	0.092
29/9/94		0.640	<MDL	1.659	1.632	0.483	<MDL	<MDL	<MDL	4.721	0.280
11/10/94		<MDL	<MDL	0.731	0.984	0.559	<MDL	<MDL	<MDL	2.791	0.031
23/10/94		0.171	<MDL	0.542	0.293	0.617	0.037	<MDL	<MDL	0.072	0.009
3/5/95		<MDL	<MDL	0.076	0.015	0.056	<MDL	<MDL	<MDL	0.748	0.178

DATE	Congener	26	25	31	28	33	22	27	29	25	29
9/5/95	<MDL	<MDL	<MDL	1.436	1.352	3.480	0.681	<MDL	<MDL	8.501	1.915
15/5/95	<MDL	<MDL	1.920	2.078	2.930	1.157	0.319	<MDL	<MDL	7.399	1.169
21/5/95	0.751	<MDL	0.516	0.700	0.932	0.042	0.090	<MDL	<MDL	2.664	0.596
27/5/95	0.674	<MDL	0.350	0.666	1.163	0.197	<MDL	<MDL	<MDL	2.093	0.342
2/6/95	0.727	<MDL	0.271	0.288	1.181	0.695	<MDL	<MDL	<MDL	3.828	0.865
8/6/95	3.657	<MDL	4.031	2.202	5.870	1.549	<MDL	<MDL	<MDL	12.577	1.722
14/6/95	1.227	<MDL	3.997	4.285	4.816	2.096	<MDL	<MDL	<MDL	12.345	0.212
20/6/95	2.161	<MDL	3.953	3.529	4.021	1.474	0.343	<MDL	<MDL	5.443	1.779
26/6/95	1.522	<MDL	5.746	4.740	6.606	2.676	0.490	<MDL	<MDL	10.815	2.284
27/95	4.247	<MDL	4.983	3.981	3.981	1.247	0.257	<MDL	<MDL	14.905	2.596
8/7/95	<MDL	<MDL	4.951	5.671	5.702	1.503	<MDL	<MDL	<MDL	12.449	1.744
14/7/95	2.752	0.048	5.171	5.623	6.304	1.385	0.740	<MDL	<MDL	9.904	1.318
20/7/95	3.654	<MDL	5.103	4.889	8.158	0.059	<MDL	<MDL	<MDL	12.717	2.143
26/7/95	1.743	<MDL	3.103	2.334	3.533	2.046	<MDL	<MDL	<MDL	3.227	0.707
1/8/95	2.225	<MDL	5.063	4.595	5.901	1.743	0.769	<MDL	<MDL	6.267	1.810
7/8/95	<MDL	<MDL	1.180	1.057	1.854	0.451	<MDL	<MDL	<MDL	2.618	0.536
13/8/95	9.704	4.373	66.785	58.377	64.165	35.981	8.663	4.767	81.523	49.040	26.839
19/8/95	9.530	5.693	1.085	23.464	21.792	24.713	13.229	3.686	0.356	26.839	26.839
25/8/95	7.600	2.020	40.528	31.113	36.816	25.001	4.827	2.462	45.270	23.958	23.958
31/8/95	2.441	<MDL	4.658	2.405	6.695	3.684	<MDL	<MDL	6.493	1.065	1.065
6/9/95	2.369	<MDL	3.026	3.302	4.329	2.835	<MDL	<MDL	4.185	1.288	1.288
12/9/95	0.616	<MDL	0.957	0.987	1.341	0.158	<MDL	<MDL	1.067	0.285	0.285
24/9/95	1.197	<MDL	1.049	0.657	2.057	0.737	<MDL	<MDL	2.502	0.706	0.706
6/10/95	0.907	<MDL	3.002	1.604	2.723	0.967	<MDL	<MDL	2.220	0.348	0.348
18/10/95	0.218	<MDL	0.066	0.071	0.095	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95	0.196	<MDL	0.079	0.097	0.123	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29/5/96	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/5/96	<MDL	0.179	0.092	0.063	0.008	0.279	0.064	0.268	6.754	1.734	1.734
2/6/96	5.927	<MDL	0.201	5.057	4.266	6.229	0.187	<MDL	14.331	2.179	2.179

DATE	Congener	29	25	31	28	33	22	9	9	22	9
4/6/96	<MDL	<MDL	12.133	1.677	8.517	<MDL	0.924	<MDL	9.325	0.852	
6/6/96	<MDL	<MDL	0.555	0.602	1.001	0.459	-0.301	<MDL	2.742	-0.071	
8/6/96	11.582	2.711	21.698	22.864	21.494	12.503	2.266	1.006	42.722	9.256	
10/6/96	0.176	<MDL	0.470	0.485	0.586	2.645	0.314	0.353	6.884	2.361	
12/6/96	7.611	2.578	21.405	26.486	29.985	15.551	2.595	0.713	41.623	15.550	
14/6/96	<MDL	0.379	<MDL	0.042	<MDL	2.492	0.345	<MDL	10.998	1.703	
16/6/96	<MDL	<MDL	16.533	8.102	0.333	<MDL	0.504	0.385	5.951	1.668	
18/6/96	0.616	1.484	0.029	5.616	3.847	2.623	0.569	<MDL	14.052	3.948	
20/6/96	<MDL	<MDL	3.521	7.534	9.276	<MDL	1.135	0.499	12.476	3.155	
22/6/96	<MDL	<MDL	24.557	10.313	17.319	0.106	0.755	<MDL	17.890	4.021	
24/6/96	0.811	<MDL	<MDL	<MDL	<MDL	2.866	0.598	<MDL	15.011	2.273	
27/6/96	<MDL	<MDL	0.455	0.468	0.419	0.660	-0.647	<MDL	8.595	1.895	
28/6/96	<MDL	<MDL	4.830	0.043	8.715	0.004	-0.325	<MDL	-2.660	0.005	
30/6/96	0.143	0.106	19.271	4.299	22.316	27.512	0.368	<MDL	27.810	4.102	
2/7/96	0.128	<MDL	0.619	0.389	0.511	0.363	-0.077	<MDL	2.253	0.078	
4/7/96	<MDL	<MDL	<MDL	6.597	9.988	3.377	-0.647	<MDL	28.364	1.927	
6/7/96	0.789	<MDL	0.125	7.433	5.401	1.970	0.585	<MDL	14.483	0.479	
8/7/96	<MDL	<MDL	2.369	5.212	10.792	8.758	1.217	0.450	17.584	6.749	
10/7/96	1.547	<MDL	0.647	4.107	4.554	2.293	0.026	<MDL	15.857	3.894	
12/7/96	<MDL	<MDL	68.664	14.479	<MDL	<MDL	-0.647	<MDL	22.707	2.316	
14/7/96	<MDL	<MDL	0.020	0.080	0.048	<MDL	-0.647	<MDL	0.548	0.114	
16/7/96	0.901	<MDL	0.607	0.672	0.778	0.137	-0.167	<MDL	3.906	1.246	
18/7/96	0.043	<MDL	0.741	0.869	0.680	0.197	-0.486	<MDL	1.512	0.508	
20/7/96	0.058	<MDL	0.128	0.181	0.190	7.878	0.447	0.137	3.910	0.331	
24/7/96	0.025	<MDL	0.079	0.088	0.163	10.276	0.122	<MDL	0.236	0.280	
26/7/96	3.897	2.200	12.973	21.022	17.687	11.778	2.721	0.974	16.956	6.657	
28/7/96	2.626	<MDL	1.958	11.259	12.703	9.480	1.916	<MDL	19.579	0.888	
30/7/96	3.580	0.035	3.232	14.828	13.122	7.379	1.370	0.774	18.809	4.906	
1/8/96	0.072	<MDL	0.163	0.243	0.253	0.957	-0.356	<MDL	1.636	0.641	

DATE	Congener	47	48	44	42	64	40	74	70	95	66
26/4/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/94		0.613	0.292	0.133	<MDL	0.680	<MDL	0.130	0.003	0.010	<MDL
8/5/94		0.029	0.002	3.261	<MDL	3.118	<MDL	<MDL	1.019	1.874	0.463
14/5/94		0.190	0.457	1.760	<MDL	1.261	<MDL	0.761	3.007	1.476	0.912
20/5/94		0.020	0.015	3.744	<MDL	2.672	<MDL	0.249	3.334	2.121	1.034
26/5/94		0.068	0.034	2.406	<MDL	3.426	<MDL	0.029	<MDL	<MDL	0.018
1/6/94		0.006	<MDL	1.601	<MDL	2.187	<MDL	0.272	<MDL	<MDL	0.849
7/6/94		0.225	0.425	0.977	<MDL	1.570	<MDL	0.073	0.033	<MDL	0.017
13/6/94		0.278	0.094	<MDL	<MDL	0.016	<MDL	<MDL	0.016	<MDL	0.037
19/6/94		0.488	0.204	0.618	<MDL	0.001	<MDL	0.196	<MDL	<MDL	<MDL
25/6/94		0.607	0.418	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/7/94		0.483	0.395	1.355	<MDL	<MDL	<MDL	0.042	0.492	7.882	0.194
7/7/94		0.483	0.395	1.355	<MDL	<MDL	<MDL	0.042	0.492	7.882	0.194
17/7/94		0.092	<MDL	0.860	<MDL	<MDL	<MDL	0.021	0.985	2.277	<MDL
25/7/94		0.245	0.104	1.071	<MDL	<MDL	<MDL	0.018	0.005	0.874	0.247
31/7/94		<MDL	0.023	0.101	<MDL	0.081	<MDL	<MDL	0.009	<MDL	<MDL
6/8/94		<MDL	<MDL	2.649	<MDL	<MDL	<MDL	1.256	1.214	<MDL	<MDL
12/8/94		0.346	0.211	1.419	<MDL	0.000	<MDL	0.005	0.733	0.033	<MDL
18/8/94		0.594	0.605	1.618	<MDL	1.526	<MDL	0.031	1.209	0.022	2.233
24/8/94		0.674	0.477	0.009	<MDL	0.023	<MDL	<MDL	<MDL	<MDL	<MDL
30/8/94		0.406	0.372	2.230	<MDL	2.100	<MDL	<MDL	0.032	<MDL	0.606
5/9/94		<MDL	<MDL	<MDL	<MDL	1.263	<MDL	0.012	0.946	<MDL	0.009
17/9/94		0.600	0.199	0.527	<MDL	0.039	<MDL	0.059	0.047	0.025	<MDL
29/9/94		0.500	0.447	0.950	<MDL	0.021	<MDL	0.017	<MDL	<MDL	<MDL
11/10/94		0.013	<MDL	<MDL	<MDL	0.829	<MDL	0.025	<MDL	<MDL	0.037
23/10/94		0.041	0.003	<MDL	<MDL	0.045	<MDL	0.031	<MDL	<MDL	<MDL
3/5/95		0.092	<MDL	0.451	<MDL	0.177	<MDL	0.219	1.314	2.625	0.530

DATE	Congener	47	48	44	42	64	30	74	70	95	66
9/5/95		0.111	<MDL	3.215	<MDL	4.710	<MDL	0.264	5.051	2.756	0.986
15/5/95		0.118	<MDL	1.972	<MDL	2.174	<MDL	0.274	2.569	3.109	0.656
21/5/95		0.454	<MDL	1.076	0.302	0.778	<MDL	0.376	2.375	4.490	0.834
27/5/95		0.225	<MDL	0.692	0.710	0.821	<MDL	0.094	0.754	1.444	0.454
2/6/95		0.570	<MDL	1.628	1.078	1.624	<MDL	0.453	3.086	4.396	1.085
8/6/95		0.150	<MDL	4.741	4.175	7.746	<MDL	0.181	8.505	4.476	1.462
14/6/95		0.129	<MDL	4.146	<MDL	7.310	<MDL	0.151	4.912	2.513	1.135
20/6/95		2.643	<MDL	2.893	1.253	3.770	<MDL	0.345	6.120	4.144	1.597
26/6/95		2.128	<MDL	4.319	4.097	4.350	<MDL	0.957	8.413	6.776	1.986
2/7/95		3.292	<MDL	4.738	5.737	2.994	<MDL	0.539	13.921	11.124	3.358
8/7/95		0.128	<MDL	5.787	<MDL	0.154	<MDL	0.439	11.589	8.071	2.363
14/7/95		1.967	<MDL	3.461	<MDL	5.785	<MDL	<MDL	7.276	3.408	1.612
20/7/95		0.101	<MDL	4.875	<MDL	<MDL	<MDL	<MDL	<MDL	1.071	1.090
26/7/95		1.188	<MDL	1.492	<MDL	3.427	<MDL	<MDL	2.403	<MDL	0.343
1/8/95		2.240	<MDL	3.327	1.895	3.024	<MDL	<MDL	3.317	0.424	0.830
7/8/95		0.801	<MDL	0.914	0.609	1.405	<MDL	<MDL	0.480	<MDL	0.373
13/8/95		34.885	<MDL	76.528	19.780	36.766	11.067	16.674	49.060	14.386	28.479
19/8/95		13.389	<MDL	21.282	8.119	11.000	5.152	3.033	10.419	4.318	5.679
25/8/95		15.478	<MDL	39.835	10.733	24.056	6.821	7.042	23.615	4.762	11.316
31/8/95		<MDL	<MDL	4.644	<MDL	9.591	<MDL	<MDL	8.868	<MDL	1.625
6/9/95		1.414	<MDL	3.691	<MDL	6.389	<MDL	<MDL	3.476	<MDL	0.804
12/9/95		0.241	<MDL	0.490	<MDL	0.649	<MDL	<MDL	<MDL	<MDL	<MDL
24/9/95		0.714	<MDL	1.176	<MDL	2.076	<MDL	<MDL	0.886	<MDL	0.221
6/10/95		0.632	<MDL	2.152	<MDL	3.367	<MDL	<MDL	1.570	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	0.321	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	0.010	<MDL	<MDL	<MDL	<MDL	<MDL
29/5/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.005	<MDL	<MDL	<MDL
31/5/96		0.681	0.714	3.918	<MDL	4.427	<MDL	0.536	3.587	0.011	1.522
2/6/96		1.955	0.126	8.102	<MDL	9.222	<MDL	0.467	11.473	2.080	3.520

DATE	Congener	47	48	49	52	64	69	71	70	95	96
4/6/96		0.484	1.061	3.033	<MDL	2.141	<MDL	0.773	4.596	5.602	2.015
6/6/96		0.306	0.307	0.361	<MDL	1.178	<MDL	0.089	0.538	0.207	0.226
8/6/96		4.901	4.148	19.052	2.499	13.271	<MDL	7.016	24.943	34.894	10.502
10/6/96		1.390	0.582	2.920	0.597	3.219	0.342	0.194	3.940	1.715	1.745
12/6/96		6.870	4.944	24.793	<MDL	22.569	<MDL	4.172	44.564	17.348	13.691
14/6/96		0.852	0.763	4.752	<MDL	5.905	<MDL	1.552	8.383	4.322	1.829
16/6/96		0.829	0.634	4.426	<MDL	3.612	<MDL	1.749	0.128	1.856	1.386
18/6/96		1.892	1.479	7.352	<MDL	7.379	<MDL	1.426	6.369	1.684	1.443
20/6/96		1.643	1.013	6.329	<MDL	5.251	<MDL	1.280	6.809	6.582	1.903
22/6/96		2.666	1.375	8.952	<MDL	8.744	<MDL	3.382	10.484	8.254	3.718
24/6/96		1.155	1.072	5.873	<MDL	4.776	<MDL	0.893	9.486	7.139	2.406
27/6/96		0.135	0.016	3.411	<MDL	2.985	<MDL	0.787	3.344	4.733	1.914
28/6/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/6/96		1.773	0.551	8.812	<MDL	15.078	<MDL	0.701	17.709	9.915	5.560
2/7/96		0.018	0.075	1.320	<MDL	3.980	<MDL	0.068	9.990	0.066	0.396
4/7/96		<MDL	<MDL	6.971	<MDL	19.893	<MDL	<MDL	20.774	6.780	5.220
6/7/96		1.939	0.837	7.654	<MDL	18.885	<MDL	0.014	17.458	0.725	1.997
8/7/96		2.499	1.844	9.199	0.987	6.925	<MDL	2.719	14.283	14.733	6.048
10/7/96		0.405	0.218	7.805	<MDL	9.246	<MDL	0.073	12.490	8.989	1.540
12/7/96		<MDL	0.153	6.888	<MDL	11.448	<MDL	2.040	10.618	12.556	3.614
14/7/96		0.334	<MDL	0.085	<MDL	1.297	<MDL	<MDL	0.053	0.115	0.039
16/7/96		0.437	0.280	2.235	0.158	3.502	<MDL	0.187	5.224	0.945	0.513
18/7/96		0.203	0.209	0.682	<MDL	3.077	<MDL	0.146	7.754	0.916	0.585
20/7/96		0.050	0.585	2.611	<MDL	2.802	<MDL	<MDL	5.691	0.088	0.160
24/7/96		0.340	0.078	0.229	<MDL	-0.292	<MDL	0.007	0.215	0.267	0.185
26/7/96		3.416	2.456	449.652	<MDL	8.409	<MDL	4.672	16.743	6.612	4.993
28/7/96		2.113	1.135	82.514	0.156	10.157	<MDL	1.603	18.251	1.672	3.052
30/7/96		2.883	2.346	11.049	<MDL	8.536	<MDL	2.716	15.238	6.013	4.531
1/8/96		0.402	0.272	2.106	<MDL	4.202	<MDL	0.088	3.374	0.219	0.130

DATE	Congener	60	84	101/89	99	97	87	136	110	82	151
26/4/94		0.061	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/94		0.140	0.016	<MDL	<MDL	<MDL	<MDL	<MDL	0.075	<MDL	0.008
8/5/94		0.487	0.833	2.083	1.162	1.121	1.772	0.155	3.517	<MDL	0.325
14/5/94		0.661	0.806	2.800	1.108	1.821	2.173	0.188	6.610	<MDL	0.207
20/5/94		<MDL	0.974	3.200	1.171	1.807	2.003	0.218	4.949	<MDL	0.401
26/5/94		<MDL	<MDL	<MDL	0.012	0.007	<MDL	<MDL	0.120	<MDL	0.050
1/6/94		0.172	0.265	<MDL	0.007	0.238	0.134	0.019	1.159	<MDL	0.022
7/6/94		0.727	0.092	0.323	0.438	0.209	0.341	0.038	0.389	<MDL	<MDL
13/6/94		0.005	<MDL	<MDL	0.024	0.045	0.011	<MDL	<MDL	<MDL	0.004
19/6/94		<MDL	<MDL	<MDL	0.003	<MDL	0.011	<MDL	<MDL	<MDL	0.023
25/6/94		0.012	<MDL	<MDL	0.021	0.006	<MDL	<MDL	<MDL	<MDL	<MDL
1/7/94		0.108	<MDL	10.848	2.808	1.141	1.702	0.586	0.844	<MDL	0.914
7/7/94		0.108	0.015	10.848	2.808	1.141	1.702	0.586	0.844	<MDL	0.914
17/7/94		<MDL	0.006	3.698	0.847	0.005	0.168	0.153	<MDL	<MDL	0.040
25/7/94		0.023	<MDL	1.659	0.523	0.024	0.002	0.018	<MDL	<MDL	0.030
31/7/94		0.174	<MDL	0.108	0.106	0.046	0.098	0.102	0.042	<MDL	0.146
6/8/94		<MDL	<MDL	0.282	0.077	<MDL	0.452	0.325	<MDL	<MDL	0.864
12/8/94		<MDL	<MDL	<MDL	0.007	0.011	<MDL	<MDL	0.031	<MDL	0.034
18/8/94		0.734	0.117	0.597	0.688	0.461	0.801	0.127	2.067	<MDL	0.236
24/8/94		<MDL	<MDL	<MDL	<MDL	0.010	0.021	0.024	<MDL	<MDL	0.018
30/8/94		0.027	0.311	0.934	0.711	0.874	1.449	0.124	4.500	<MDL	0.192
5/9/94		0.367	0.182	0.893	0.496	0.734	1.071	0.114	2.659	<MDL	0.244
17/9/94		<MDL	0.028	0.057	0.014	<MDL	0.022	0.011	0.091	<MDL	1.257
29/9/94		<MDL	<MDL	<MDL	<MDL	<MDL	0.014	0.165	0.005	<MDL	0.946
11/10/94		<MDL	<MDL	<MDL	0.016	0.038	<MDL	0.007	0.064	<MDL	0.096
23/10/94		0.008	<MDL	<MDL	<MDL	0.020	0.014	<MDL	<MDL	<MDL	0.137
3/5/95		0.327	0.862	4.055	1.226	1.690	3.801	0.706	8.818	0.713	0.587

DATE	Congener	60	84	101/89	99	97	87	136	110	82	151
9/5/95		0.425	1.032	4.534	1.378	2.070	4.369	0.906	10.121	0.803	0.856
15/5/95		0.310	1.050	5.162	1.500	2.157	4.368	0.899	10.707	0.794	0.746
21/5/95		0.700	1.504	5.368	1.902	2.823	5.210	0.968	13.030	1.293	0.926
27/5/95		0.350	0.483	1.848	0.688	0.955	1.944	0.420	4.367	0.274	0.383
2/6/95		0.818	1.532	5.778	1.612	2.896	5.038	1.171	12.024	1.402	0.698
8/6/95		2.087	1.474	5.650	1.893	2.891	5.703	1.265	12.638	1.750	0.851
14/6/95		0.340	0.653	3.026	0.963	1.344	2.584	0.561	6.134	0.409	0.914
20/6/95		1.914	1.347	5.799	1.869	2.490	5.262	1.098	12.781	1.038	1.102
26/6/95		1.788	1.849	8.300	2.590	3.819	7.111	2.183	16.055	2.566	2.293
2/7/95		3.460	3.236	15.838	4.734	7.473	13.791	3.430	32.371	3.590	3.371
8/7/95		0.551	2.728	12.326	3.621	5.565	10.945	2.906	24.047	3.438	3.230
14/7/95		2.252	0.906	3.827	1.486	1.286	3.236	1.085	10.527	<MDL	1.405
20/7/95		<MDL	0.185	0.651	0.125	0.260	0.123	1.161	<MDL	<MDL	1.183
26/7/95		<MDL	0.060	<MDL	<MDL	<MDL	<MDL	0.114	<MDL	<MDL	0.174
1/8/95		<MDL	0.003	<MDL	0.056	<MDL	<MDL	0.036	<MDL	<MDL	0.287
7/8/95		0.526	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/8/95		21.051	3.610	7.157	2.676	2.735	2.871	0.702	3.378	0.941	0.641
19/8/95		4.640	0.829	2.211	0.691	0.452	0.617	0.648	<MDL	0.616	0.978
25/8/95		8.728	1.052	1.683	0.754	0.079	0.260	<MDL	<MDL	<MDL	<MDL
31/8/95		2.630	0.087	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		1.572	0.018	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12/9/95		0.238	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/9/95		0.827	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/10/95		1.801	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		0.077	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29/5/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/5/96		0.879	0.186	0.024	0.310	0.222	0.922	<MDL	1.090	<MDL	<MDL
2/6/96		3.711	1.015	1.019	0.963	1.729	2.164	<MDL	4.243	<MDL	<MDL

DATE	Congener	60	84	101/89	99	97	87	136	110	82	151
4/6/96		3.485	1.298	10.215	0.781	0.993	2.118	2.613	5.066	1.391	5.352
6/6/96		0.129	0.036	0.399	0.066	0.370	0.192	0.131	0.146	0.060	0.238
8/6/96		11.784	2.922	42.813	5.384	5.941	11.525	18.057	22.148	3.728	40.485
10/6/96		3.517	0.373	0.780	0.541	0.662	1.416	0.235	2.535	<MDL	0.436
12/6/96		6.689	2.553	16.928	3.610	3.709	6.178	5.911	18.095	<MDL	10.497
14/6/96		3.510	0.534	4.063	0.723	1.257	1.097	1.461	3.285	0.799	2.567
16/6/96		0.170	0.882	3.015	0.388	0.864	<MDL	0.089	3.858	<MDL	0.027
18/6/96		0.507	0.711	0.501	0.567	1.346	2.169	<MDL	3.751	<MDL	<MDL
20/6/96		3.455	1.450	10.591	0.775	2.035	2.795	2.599	6.608	1.267	4.602
22/6/96		5.304	2.288	16.657	0.883	1.995	2.829	3.959	7.543	<MDL	6.719
24/6/96		1.411	1.309	11.495	2.897	4.192	7.268	2.220	16.392	2.567	2.117
27/6/96		0.712	0.190	5.571	0.681	0.771	1.887	3.223	4.026	0.084	6.159
28/6/96		<MDL	0.065	<MDL	0.300	0.644	0.916	<MDL	2.223	0.566	<MDL
30/6/96		6.545	2.438	14.019	3.583	4.068	8.093	2.549	20.071	<MDL	3.181
2/7/96		0.082	0.362	0.202	0.330	1.050	1.007	0.068	2.697	<MDL	0.198
4/7/96		<MDL	1.987	11.835	2.752	3.839	7.192	1.388	16.554	0.020	1.696
6/7/96		<MDL	0.821	0.229	0.590	1.581	0.947	0.054	1.198	<MDL	<MDL
8/7/96		2.478	2.201	15.671	2.649	2.556	5.346	7.518	12.876	0.940	15.364
10/7/96		0.206	1.250	10.247	1.821	1.892	2.566	4.638	8.844	<MDL	9.164
12/7/96		3.851	2.046	32.546	1.265	3.293	4.438	6.154	8.294	1.581	12.513
14/7/96		<MDL	<MDL	0.046	<MDL	0.026	<MDL	0.051	<MDL	<MDL	0.082
16/7/96		0.472	0.088	1.100	0.381	0.390	0.740	0.461	0.976	<MDL	0.875
18/7/96		0.221	0.113	1.182	0.248	0.368	0.590	0.537	0.857	<MDL	1.029
20/7/96		<MDL	0.340	0.820	0.189	0.558	0.052	0.050	0.052	<MDL	0.121
24/7/96		0.321	0.093	0.307	0.112	0.164	0.331	0.178	0.310	<MDL	0.333
26/7/96		8.828	1.254	6.798	0.875	3.586	4.925	2.116	6.303	<MDL	3.963
28/7/96		0.166	0.198	2.554	0.892	1.548	0.501	0.369	4.883	0.243	0.270
30/7/96		1.482	1.252	6.263	1.473	1.205	0.835	1.369	5.463	<MDL	1.643
1/8/96		0.152	0.039	0.287	0.085	0.139	0.166	0.121	0.590	<MDL	0.168

DATE	Congener	135 (144)	149	118	134	114	131	153	132	105	141
26/4/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/94		<MDL	0.042	0.027	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/5/94		0.393	0.670	1.966	<MDL	<MDL	<MDL	0.919	0.110	0.975	0.284
14/5/94		0.381	1.105	4.369	<MDL	<MDL	<MDL	0.910	0.415	1.963	0.470
20/5/94		0.452	1.312	3.179	<MDL	<MDL	<MDL	0.646	0.404	1.158	0.304
26/5/94		0.038	0.256	<MDL	<MDL	<MDL	<MDL	0.320	0.036	<MDL	0.468
1/6/94		0.038	0.470	0.568	0.214	<MDL	<MDL	0.259	0.108	-0.275	0.220
7/6/94		0.127	0.176	0.679	<MDL	<MDL	<MDL	0.101	0.024	<MDL	<MDL
13/6/94		0.026	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/6/94		<MDL	<MDL	0.007	<MDL	<MDL	<MDL	0.201	<MDL	<MDL	<MDL
25/6/94		0.015	<MDL	<MDL	<MDL	<MDL	<MDL	0.014	<MDL	<MDL	0.303
1/7/94		0.695	2.029	0.837	<MDL	<MDL	<MDL	0.968	0.081	<MDL	0.304
7/7/94		0.697	2.029	0.837	<MDL	<MDL	<MDL	0.968	0.081	0.001	0.304
17/7/94		0.314	0.433	0.265	<MDL	<MDL	<MDL	0.089	<MDL	0.002	0.004
25/7/94		0.195	0.014	<MDL	<MDL	<MDL	<MDL	<MDL	0.020	0.012	<MDL
31/7/94		0.004	0.685	<MDL	<MDL	<MDL	<MDL	0.009	0.072	0.065	<MDL
6/8/94		0.017	1.072	<MDL	<MDL	<MDL	<MDL	1.104	<MDL	0.010	<MDL
12/8/94		0.067	0.072	0.469	<MDL	<MDL	<MDL	0.034	0.012	<MDL	<MDL
18/8/94		0.256	-0.002	2.707	<MDL	<MDL	<MDL	0.854	0.189	0.868	0.208
24/8/94		0.144	0.905	<MDL	<MDL	<MDL	<MDL	0.526	<MDL	0.021	<MDL
30/8/94		0.690	0.935	5.001	<MDL	<MDL	<MDL	1.767	0.553	2.724	0.330
5/9/94		0.095	0.829	3.120	<MDL	<MDL	<MDL	0.923	0.441	1.444	0.292
17/9/94		0.601	1.133	<MDL	<MDL	<MDL	<MDL	1.635	0.005	0.219	0.403
29/9/94		0.206	1.224	<MDL	<MDL	<MDL	<MDL	0.943	0.018	0.004	<MDL
11/10/94		0.029	0.036	0.342	<MDL	<MDL	<MDL	0.862	<MDL	0.004	0.041
23/10/94		0.038	0.037	<MDL	<MDL	<MDL	<MDL	0.102	0.003	0.005	0.254
3/5/95		0.863	3.896	6.593	0.417	<MDL	<MDL	4.206	3.178	3.553	1.245

DATE	Congener	135 (144)	149	118	134	114	131	153	132	105	141
9/5/95		1.056	5.470	9.002	0.443	<MDL	<MDL	5.037	4.035	4.119	1.609
15/5/95		1.113	4.779	7.962	0.481	<MDL	0.270	5.328	3.811	4.014	1.532
21/5/95		1.254	5.983	10.430	0.421	<MDL	<MDL	6.337	5.068	5.160	1.936
27/5/95		0.539	2.146	4.159	0.158	<MDL	<MDL	2.458	1.910	1.759	0.766
2/6/95		1.229	5.250	9.360	0.677	<MDL	<MDL	5.151	4.131	4.604	1.842
8/6/95		1.561	5.691	10.000	0.568	<MDL	0.226	5.942	4.297	5.566	1.641
14/6/95		0.618	2.746	4.836	0.367	<MDL	<MDL	2.900	2.254	2.318	0.837
20/6/95		1.334	5.337	9.748	0.673	<MDL	<MDL	6.016	4.846	5.268	1.732
26/6/95		2.278	9.292	11.779	0.419	<MDL	<MDL	9.432	5.848	6.049	2.990
2/7/95		3.679	16.486	26.332	1.701	<MDL	<MDL	17.723	11.090	12.930	5.063
8/7/95		2.670	13.192	17.918	1.210	<MDL	<MDL	13.545	9.361	9.059	4.161
14/7/95		1.121	4.049	4.463	0.325	<MDL	<MDL	3.744	2.137	2.605	1.058
20/7/95		0.477	1.274	<MDL	<MDL	<MDL	<MDL	0.814	<MDL	<MDL	0.490
26/7/95		0.134	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/8/95		0.222	0.765	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/8/95		0.482	1.627	<MDL	<MDL	<MDL	<MDL	0.840	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29/5/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/5/96		0.017	<MDL	1.117	0.016	<MDL	<MDL	<MDL	<MDL	1.032	<MDL
2/6/96		<MDL	<MDL	3.048	<MDL	<MDL	<MDL	<MDL	0.134	1.352	<MDL

DATE	Congener	135 (144)	149	118	134	114	131	153	132	105	141
4/6/96		2.298	10.197	1.665	0.601	<MDL	0.869	7.692	1.640	0.602	1.847
6/6/96		0.122	0.724	0.096	<MDL	<MDL	0.379	0.573	<MDL	<MDL	0.202
8/6/96		16.188	81.571	11.450	1.749	<MDL	<MDL	59.355	10.959	3.030	13.992
10/6/96		0.415	1.014	1.800	<MDL	<MDL	<MDL	1.058	0.463	0.633	0.392
12/6/96		5.162	23.350	9.321	1.030	<MDL	<MDL	19.219	3.777	4.384	4.696
14/6/96		1.237	5.127	2.067	0.169	<MDL	<MDL	4.462	1.037	1.239	1.141
16/6/96		0.063	0.207	3.246	0.391	<MDL	<MDL	0.279	0.696	1.265	0.127
18/6/96		0.009	<MDL	2.760	0.430	<MDL	<MDL	<MDL	0.505	1.642	<MDL
20/6/96		2.150	10.602	5.178	0.534	<MDL	<MDL	10.035	3.178	2.410	2.654
22/6/96		2.899	14.590	4.434	0.559	<MDL	<MDL	10.847	3.195	1.382	2.703
24/6/96		2.088	9.890	14.512	0.777	<MDL	<MDL	11.692	4.113	6.223	2.717
27/6/96		2.904	12.801	3.240	0.715	<MDL	<MDL	10.832	2.466	0.576	0.248
28/6/96		<MDL	<MDL	2.674	0.135	<MDL	<MDL	<MDL	<MDL	0.884	<MDL
30/6/96		2.043	8.750	13.633	0.950	<MDL	<MDL	11.438	4.963	3.305	2.585
2/7/96		0.039	0.546	2.006	<MDL	<MDL	<MDL	0.918	0.347	1.583	0.203
4/7/96		1.707	7.499	13.388	<MDL	<MDL	<MDL	8.804	3.009	6.587	2.543
6/7/96		0.007	<MDL	2.129	<MDL	<MDL	<MDL	<MDL	0.020	0.083	0.013
8/7/96		6.697	31.273	6.545	1.531	<MDL	<MDL	21.829	3.501	1.854	5.333
10/7/96		4.164	19.028	4.451	0.428	<MDL	<MDL	15.325	3.677	1.563	3.829
12/7/96		4.766	24.533	3.994	<MDL	<MDL	0.018	16.687	3.015	1.481	4.406
14/7/96		<MDL	0.124	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.013
16/7/96		0.292	1.895	0.159	<MDL	<MDL	<MDL	1.509	0.423	<MDL	0.368
18/7/96		0.297	2.136	0.423	<MDL	<MDL	<MDL	1.640	0.162	<MDL	0.298
20/7/96		<MDL	0.160	0.588	0.166	<MDL	<MDL	0.235	0.121	0.583	0.001
24/7/96		0.154	0.635	<MDL	<MDL	<MDL	<MDL	0.394	0.012	<MDL	0.201
26/7/96		1.971	8.929	1.380	0.121	<MDL	<MDL	6.844	2.073	0.585	1.776
28/7/96		0.252	1.327	2.087	0.276	<MDL	0.276	3.205	1.901	1.573	0.521
30/7/96		1.128	4.001	1.479	<MDL	<MDL	<MDL	3.948	1.304	0.983	1.049
1/8/96		0.094	0.730	0.500	<MDL	<MDL	<MDL	0.941	0.558	0.093	0.208

DATE	Congener	137	130	138	158	178	129	187	183	128	185
26/4/94		<MDL	<MDL	<MDL	0.013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.056	<MDL	<MDL	<MDL
8/5/94		<MDL	<MDL	0.930	<MDL	<MDL	<MDL	0.095	0.165	<MDL	<MDL
14/5/94		<MDL	<MDL	2.513	0.054	<MDL	<MDL	0.122	<MDL	<MDL	<MDL
20/5/94		<MDL	<MDL	1.812	0.145	<MDL	<MDL	0.147	0.080	<MDL	<MDL
26/5/94		<MDL	<MDL	0.162	0.029	<MDL	<MDL	0.212	0.372	<MDL	<MDL
1/6/94		<MDL	<MDL	0.160	0.045	<MDL	<MDL	0.072	0.077	<MDL	<MDL
7/6/94		<MDL	<MDL	0.494	<MDL	<MDL	<MDL	0.046	0.035	<MDL	<MDL
13/6/94		<MDL	0.026	<MDL	<MDL	0.016	<MDL	0.080	0.113	<MDL	<MDL
19/6/94		<MDL	<MDL	0.144	0.131	<MDL	<MDL	0.304	0.166	<MDL	<MDL
25/6/94		<MDL	<MDL	<MDL	0.010	<MDL	<MDL	0.121	0.064	<MDL	<MDL
1/7/94		<MDL	<MDL	0.431	<MDL	<MDL	<MDL	0.235	<MDL	<MDL	<MDL
7/7/94		<MDL	<MDL	0.431	0.007	<MDL	<MDL	0.235	0.018	<MDL	<MDL
17/7/94		<MDL	<MDL	<MDL	0.014	<MDL	<MDL	0.037	0.050	<MDL	<MDL
25/7/94		<MDL	<MDL	<MDL	0.016	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/7/94		<MDL	<MDL	0.005	<MDL	<MDL	<MDL	0.089	<MDL	<MDL	<MDL
6/8/94		<MDL	<MDL	<MDL	0.017	<MDL	<MDL	0.193	0.024	<MDL	<MDL
12/8/94		<MDL	<MDL	0.337	0.012	<MDL	<MDL	0.059	<MDL	<MDL	<MDL
18/8/94		<MDL	<MDL	1.553	0.008	<MDL	<MDL	0.061	0.093	<MDL	<MDL
24/8/94		<MDL	<MDL	0.332	0.063	<MDL	<MDL	0.187	0.095	<MDL	<MDL
30/8/94		<MDL	<MDL	2.356	0.056	<MDL	<MDL	0.157	0.069	<MDL	<MDL
5/9/94		<MDL	<MDL	1.853	0.120	<MDL	<MDL	0.025	0.102	<MDL	<MDL
17/9/94		<MDL	<MDL	0.082	<MDL	<MDL	<MDL	1.167	0.666	<MDL	<MDL
29/9/94		<MDL	<MDL	1.459	0.007	<MDL	<MDL	1.004	0.525	<MDL	<MDL
11/10/94		<MDL	<MDL	<MDL	0.010	<MDL	<MDL	0.024	0.060	<MDL	<MDL
23/10/94		<MDL	<MDL	<MDL	0.028	<MDL	<MDL	0.386	0.267	<MDL	<MDL
3/5/95		0.637	0.477	11.247	0.717	0.075	0.653	0.302	0.359	2.894	<MDL

DATE	Congener	137	130	138	158	178	129	187	183	128	185
9/5/95		0.782	0.550	13.372	1.387	0.086	1.035	0.585	0.533	3.322	0.077
15/5/95		0.674	0.670	13.516	1.284	0.244	0.785	0.564	0.407	3.125	0.204
21/5/95		0.955	0.572	16.279	1.713	0.097	1.129	0.819	0.735	4.052	0.112
27/5/95		0.403	0.318	5.839	0.593	0.064	0.456	0.404	0.380	1.422	0.212
2/6/95		0.674	0.791	14.131	1.531	0.114	0.848	0.465	0.468	3.352	0.256
8/6/95		1.277	0.873	15.410	1.264	0.168	0.885	0.665	0.535	3.883	0.117
14/6/95		0.440	0.319	7.452	0.777	0.371	0.552	0.704	0.521	1.752	0.252
20/6/95		0.822	0.738	15.990	1.456	0.243	1.083	0.651	0.504	3.838	0.169
26/6/95		1.263	0.894	19.627	1.797	0.406	1.387	1.807	1.176	4.829	0.400
2/7/95		2.234	1.802	40.487	3.876	0.523	2.229	2.388	1.896	9.714	0.467
8/7/95		1.823	1.872	31.226	2.931	0.533	1.836	2.149	1.604	6.324	0.301
14/7/95		0.513	0.434	7.034	0.570	0.172	<MDL	0.976	0.604	1.199	0.205
20/7/95		<MDL	<MDL	<MDL	<MDL	0.244	<MDL	0.921	0.386	<MDL	0.197
26/7/95		<MDL	<MDL	<MDL	<MDL	0.007	<MDL	0.306	0.194	<MDL	<MDL
1/8/95		<MDL	<MDL	<MDL	<MDL	0.089	<MDL	0.219	0.364	<MDL	0.195
7/8/95		<MDL	<MDL	<MDL	<MDL	0.007	<MDL	0.012	<MDL	<MDL	0.087
13/8/95		<MDL	<MDL	<MDL	<MDL	0.052	<MDL	0.168	0.031	<MDL	0.101
19/8/95		<MDL	<MDL	<MDL	<MDL	0.144	<MDL	0.756	0.376	<MDL	0.208
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29/5/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/5/96		0.260	<MDL	<MDL	0.303	<MDL	0.157	<MDL	0.003	0.898	<MDL
2/6/96		<MDL	<MDL	2.753	0.426	<MDL	<MDL	<MDL	<MDL	0.753	<MDL

DATE	Congener	137	130	138	158	178	129	187	183	128	185
4/6/96		<MDL	<MDL	5.947	0.178	<MDL	<MDL	3.307	1.537	0.481	<MDL
6/6/96		<MDL	<MDL	0.442	0.011	0.107	<MDL	0.421	0.313	0.165	<MDL
8/6/96		<MDL	<MDL	41.719	2.200	4.229	<MDL	25.550	11.373	2.269	2.996
10/6/96		<MDL	<MDL	2.563	-0.028	0.189	<MDL	0.600	0.480	0.203	0.239
12/6/96		<MDL	<MDL	19.713	0.800	1.495	0.773	7.260	3.481	2.071	1.014
14/6/96		<MDL	<MDL	4.197	0.320	0.218	<MDL	1.433	0.881	0.293	0.243
16/6/96		<MDL	<MDL	4.006	0.062	<MDL	<MDL	0.144	0.223	1.779	0.589
18/6/96		<MDL	<MDL	0.651	0.178	<MDL	<MDL	<MDL	0.015	<MDL	<MDL
20/6/96		<MDL	<MDL	12.820	1.061	0.720	<MDL	3.259	1.525	2.509	0.519
22/6/96		<MDL	<MDL	9.790	0.386	1.132	<MDL	4.315	2.008	0.777	0.744
24/6/96		1.089	0.670	20.216	1.415	0.226	0.772	1.831	1.052	4.550	0.326
27/6/96		<MDL	<MDL	9.633	0.575	0.805	<MDL	4.531	2.380	1.002	0.778
28/6/96		<MDL	<MDL	<MDL	0.240	<MDL	<MDL	<MDL	<MDL	0.624	<MDL
30/6/96		0.271	0.273	18.130	1.405	0.234	<MDL	2.226	0.088	3.728	0.525
2/7/96		0.126	<MDL	1.822	0.180	<MDL	<MDL	0.060	0.178	0.799	0.132
4/7/96		0.766	0.474	14.078	1.023	0.232	1.198	1.444	0.866	2.041	0.299
6/7/96		<MDL	<MDL	<MDL	0.273	0.001	<MDL	<MDL	<MDL	<MDL	<MDL
8/7/96		<MDL	<MDL	16.859	0.830	1.576	<MDL	9.019	4.336	1.701	1.368
10/7/96		0.221	0.238	13.302	0.594	1.126	<MDL	5.714	2.810	1.360	0.745
12/7/96		<MDL	<MDL	11.731	0.399	1.561	<MDL	7.512	3.277	1.054	0.877
14/7/96		<MDL	<MDL	<MDL	<MDL	0.020	<MDL	0.004	0.022	0.123	0.061
16/7/96		<MDL	<MDL	1.167	0.059	0.165	<MDL	0.624	0.359	<MDL	0.173
18/7/96		<MDL	<MDL	1.260	0.050	0.220	<MDL	0.722	0.422	<MDL	0.183
20/7/96		<MDL	<MDL	0.493	0.100	<MDL	<MDL	<MDL	0.068	0.229	<MDL
24/7/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.058	0.280	<MDL	<MDL
26/7/96		<MDL	<MDL	6.349	0.529	0.410	<MDL	3.470	1.915	0.132	0.486
28/7/96		0.206	0.235	6.171	0.510	0.127	0.345	0.715	0.369	1.404	0.111
30/7/96		<MDL	<MDL	4.330	0.046	0.072	<MDL	1.373	0.640	0.903	0.069
1/8/96		0.102	0.055	1.518	0.159	0.145	<MDL	0.254	0.174	0.513	0.061

DATE	Congener	174	171	156	201	157	172	180	193	191	200
26/4/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.022	<MDL	<MDL	<MDL
8/5/94		0.022	<MDL	<MDL	<MDL	<MDL	<MDL	0.137	<MDL	<MDL	<MDL
14/5/94		0.038	<MDL	<MDL	<MDL	<MDL	<MDL	0.103	<MDL	<MDL	<MDL
20/5/94		0.001	0.068	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94		0.157	<MDL	<MDL	<MDL	<MDL	<MDL	0.112	<MDL	<MDL	<MDL
1/6/94		0.136	0.135	<MDL	<MDL	<MDL	<MDL	0.005	<MDL	<MDL	<MDL
7/6/94		0.135	0.145	<MDL	<MDL	<MDL	<MDL	0.017	<MDL	<MDL	<MDL
13/6/94		0.077	0.117	<MDL	<MDL	<MDL	<MDL	0.044	<MDL	<MDL	<MDL
19/6/94		0.080	<MDL	<MDL	<MDL	<MDL	<MDL	0.210	<MDL	<MDL	<MDL
25/6/94		0.013	<MDL	<MDL	<MDL	<MDL	<MDL	0.078	<MDL	<MDL	<MDL
1/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/7/94		0.016	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.005	<MDL	<MDL	<MDL
25/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.042	<MDL	<MDL	<MDL
31/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.048	<MDL	<MDL	<MDL
6/8/94		0.063	0.020	<MDL	<MDL	<MDL	<MDL	0.143	<MDL	<MDL	<MDL
12/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.025	<MDL	<MDL	<MDL
18/8/94		0.071	<MDL	<MDL	<MDL	<MDL	<MDL	0.014	<MDL	<MDL	<MDL
24/8/94		0.135	0.095	<MDL	<MDL	<MDL	<MDL	0.030	<MDL	<MDL	<MDL
30/8/94		0.013	<MDL	<MDL	<MDL	<MDL	<MDL	0.080	<MDL	<MDL	<MDL
5/9/94		0.046	<MDL	<MDL	<MDL	<MDL	<MDL	0.052	<MDL	<MDL	<MDL
17/9/94		0.546	0.456	<MDL	<MDL	<MDL	<MDL	0.335	<MDL	<MDL	<MDL
29/9/94		0.492	0.159	<MDL	<MDL	<MDL	<MDL	0.734	<MDL	<MDL	<MDL
11/10/94		0.153	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23/10/94		0.138	<MDL	<MDL	<MDL	<MDL	<MDL	0.227	<MDL	<MDL	<MDL
3/5/95		0.565	0.248	1.656	<MDL	0.219	<MDL	1.292	<MDL	<MDL	<MDL

DATE	Congener	174	171	156	201	157	172	180	193	191	200
9/5/95		0.628	0.303	1.891	<MDL	0.249	0.144	1.768	<MDL	<MDL	<MDL
15/5/95		0.772	0.333	1.660	<MDL	0.297	0.144	1.485	<MDL	<MDL	<MDL
21/5/95		0.939	0.449	2.172	0.113	0.400	0.177	2.067	<MDL	<MDL	<MDL
27/5/95		0.396	0.191	0.872	<MDL	0.180	0.087	0.804	<MDL	0.125	<MDL
2/6/95		0.717	0.454	1.937	<MDL	0.460	0.093	1.495	<MDL	<MDL	<MDL
8/6/95		0.869	0.394	2.333	<MDL	0.511	0.106	1.878	<MDL	<MDL	<MDL
14/6/95		0.569	0.142	0.990	<MDL	0.237	<MDL	0.884	<MDL	<MDL	<MDL
20/6/95		0.826	0.361	2.135	<MDL	0.362	0.148	1.790	<MDL	<MDL	<MDL
26/6/95		1.652	0.876	2.592	<MDL	0.579	0.280	3.040	<MDL	<MDL	<MDL
2/7/95		2.668	1.790	5.385	0.155	1.097	0.446	5.252	<MDL	<MDL	3.201
8/7/95		2.380	1.428	3.734	<MDL	1.014	0.391	4.032	<MDL	<MDL	<MDL
14/7/95		0.683	0.425	0.919	<MDL	<MDL	0.111	1.324	<MDL	<MDL	<MDL
20/7/95		0.486	0.017	<MDL	0.133	<MDL	<MDL	0.386	<MDL	<MDL	<MDL
26/7/95		0.226	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/8/95		0.082	<MDL	<MDL	0.099	<MDL	0.027	<MDL	<MDL	<MDL	<MDL
7/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/8/95		0.026	<MDL	<MDL	<MDL	<MDL	0.014	<MDL	<MDL	<MDL	<MDL
19/8/95		0.546	0.260	<MDL	<MDL	<MDL	<MDL	0.411	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29/5/96		0.035	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/5/96		<MDL	0.168	0.294	0.002	<MDL	0.126	0.024	0.060	<MDL	<MDL
2/6/96		<MDL	<MDL	0.569	0.128	<MDL	<MDL	<MDL	<MDL	<MDL	0.114

DATE	Congener	174	171	156	201	157	172	180	193	191	200
4/6/96		1.486	0.483	<MDL	0.248	<MDL	<MDL	4.203	<MDL	2.943	0.298
6/6/96		0.295	0.712	<MDL	<MDL	<MDL	<MDL	0.437	<MDL	<MDL	0.115
8/6/96		14.496	2.579	0.967	1.367	0.841	0.907	17.054	0.852	0.489	1.345
10/6/96		0.507	0.187	<MDL	0.115	<MDL	<MDL	0.767	0.145	<MDL	0.081
12/6/96		4.477	1.131	0.970	0.661	<MDL	0.302	5.707	0.269	<MDL	0.546
14/6/96		0.656	0.042	0.320	0.065	<MDL	0.108	1.064	0.148	<MDL	<MDL
16/6/96		0.074	0.735	0.894	<MDL	<MDL	<MDL	1.210	<MDL	<MDL	<MDL
18/6/96		-0.065	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20/6/96		2.105	0.722	1.180	0.310	<MDL	<MDL	3.925	<MDL	<MDL	0.196
22/6/96		2.572	2.114	0.312	0.273	<MDL	<MDL	4.038	<MDL	<MDL	0.451
24/6/96		1.491	0.463	2.381	0.091	0.339	0.249	2.658	0.327	<MDL	0.192
27/6/96		2.770	0.565	0.168	0.486	<MDL	0.351	3.796	<MDL	<MDL	1.023
28/6/96		<MDL	<MDL	0.370	-0.272	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/6/96		1.366	0.086	<MDL	0.150	<MDL	<MDL	2.900	<MDL	<MDL	0.329
2/7/96		0.101	0.111	0.321	<MDL	<MDL	<MDL	0.307	<MDL	<MDL	<MDL
4/7/96		1.033	0.189	1.597	0.137	<MDL	0.175	1.147	<MDL	<MDL	0.075
6/7/96		<MDL	0.004	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.159
8/7/96		5.206	1.019	0.737	0.445	<MDL	0.351	5.590	0.416	<MDL	0.435
10/7/96		3.223	0.661	0.910	0.294	<MDL	<MDL	4.231	<MDL	<MDL	0.828
12/7/96		3.635	0.329	0.069	0.374	<MDL	<MDL	7.017	<MDL	<MDL	0.526
14/7/96		<MDL	0.147	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16/7/96		0.429	0.113	<MDL	<MDL	<MDL	<MDL	0.336	<MDL	<MDL	<MDL
18/7/96		0.548	0.126	<MDL	<MDL	<MDL	<MDL	0.496	<MDL	<MDL	<MDL
20/7/96		0.034	0.051	<MDL	<MDL	<MDL	<MDL	0.088	<MDL	<MDL	<MDL
24/7/96		0.162	0.217	<MDL	<MDL	<MDL	<MDL	0.062	<MDL	<MDL	<MDL
26/7/96		0.457	0.186	<MDL	<MDL	<MDL	0.260	2.265	<MDL	<MDL	0.860
28/7/96		0.588	0.199	0.938	0.193	0.640	0.330	1.413	<MDL	<MDL	1.323
30/7/96		0.605	0.181	0.043	0.183	<MDL	0.192	0.805	<MDL	<MDL	0.166
1/8/96		0.232	0.099	<MDL	<MDL	<MDL	0.069	0.427	<MDL	<MDL	<MDL

DATE	Congener	170	190	198	199	196	189	208	195	207	194
26/4/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/6/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/7/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/8/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/9/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17/9/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29/9/94		0.216	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23/10/94		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/5/95		1.051	0.194	<MDL	0.194	0.233	<MDL	<MDL	<MDL	<MDL	0.361

DATE	Congener	170	190	198	199	196	189	208	195	207	194
9/5/95		1.268	0.329	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15/5/95		1.116	0.189	<MDL	0.182	0.246	<MDL	<MDL	<MDL	<MDL	<MDL
21/5/95		1.662	0.336	0.196	0.195	0.377	<MDL	<MDL	<MDL	<MDL	<MDL
27/5/95		0.658	0.113	<MDL	0.243	0.175	<MDL	<MDL	<MDL	<MDL	<MDL
2/6/95		1.452	0.167	<MDL	0.186	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/6/95		1.588	0.355	<MDL	0.323	0.345	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/95		0.713	0.149	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20/6/95		1.594	0.271	<MDL	0.299	0.369	<MDL	<MDL	<MDL	<MDL	0.383
26/6/95		2.003	0.381	<MDL	0.796	0.495	<MDL	<MDL	<MDL	<MDL	<MDL
2/7/95		1.490	0.232	<MDL	0.778	0.680	0.172	<MDL	<MDL	<MDL	0.902
8/7/95		2.963	0.884	<MDL	0.307	0.311	<MDL	<MDL	<MDL	<MDL	<MDL
14/7/95		0.773	<MDL	<MDL	0.310	0.296	<MDL	<MDL	<MDL	<MDL	<MDL
20/7/95		0.060	<MDL	<MDL	0.144	0.129	<MDL	<MDL	<MDL	<MDL	<MDL
26/7/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/8/95		<MDL	<MDL	<MDL	0.084	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
7/8/95		<MDL	<MDL	<MDL	0.096	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19/8/95		0.017	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/9/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29/5/96		0.057	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31/5/96		0.246	0.047	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/6/96		<MDL	0.143	<MDL	<MDL	0.126	<MDL	<MDL	<MDL	<MDL	<MDL

DATE	Congener	170	190	198	199	196	189	208	195	207	194
4/6/96		0.863	0.003	<MDL	<MDL	0.160	<MDL	<MDL	<MDL	<MDL	<MDL
6/6/96		0.376	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/6/96		3.838	1.081	<MDL	1.820	3.601	<MDL	<MDL	1.028	<MDL	1.265
10/6/96		0.390	0.064	<MDL	<MDL	0.233	<MDL	<MDL	<MDL	<MDL	<MDL
12/6/96		0.988	0.387	<MDL	0.366	1.529	<MDL	<MDL	<MDL	<MDL	<MDL
14/6/96		0.016	0.092	<MDL	<MDL	0.474	<MDL	<MDL	<MDL	<MDL	0.414
16/6/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/6/96		0.107	0.161	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20/6/96		1.762	<MDL	<MDL	<MDL	0.568	<MDL	<MDL	<MDL	<MDL	<MDL
22/6/96		1.864	<MDL	<MDL	<MDL	0.671	<MDL	<MDL	<MDL	<MDL	<MDL
24/6/96		6.736	1.001	0.883	<MDL	0.439	<MDL	<MDL	<MDL	<MDL	<MDL
27/6/96		1.445	0.184	<MDL	0.034	0.558	<MDL	<MDL	<MDL	<MDL	<MDL
28/6/96		0.023	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
30/6/96		2.778	<MDL	<MDL	<MDL	0.650	<MDL	<MDL	<MDL	<MDL	<MDL
2/7/96		0.363	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
4/7/96		0.481	0.219	<MDL	<MDL	0.377	<MDL	<MDL	<MDL	<MDL	<MDL
6/7/96		<MDL	0.042	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
8/7/96		1.262	0.418	<MDL	0.054	1.343	<MDL	<MDL	0.581	<MDL	0.324
10/7/96		0.521	0.259	<MDL	0.057	0.787	<MDL	<MDL	<MDL	<MDL	<MDL
12/7/96		0.077	<MDL	<MDL	<MDL	0.549	<MDL	<MDL	<MDL	<MDL	<MDL
14/7/96		0.071	0.042	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16/7/96		0.107	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18/7/96		0.169	0.055	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20/7/96		0.108	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24/7/96		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26/7/96		0.618	0.216	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
28/7/96		0.870	0.341	<MDL	<MDL	0.519	<MDL	<MDL	<MDL	<MDL	<MDL
30/7/96		0.555	0.094	<MDL	<MDL	0.132	<MDL	<MDL	<MDL	<MDL	<MDL
1/8/96		0.291	0.056	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

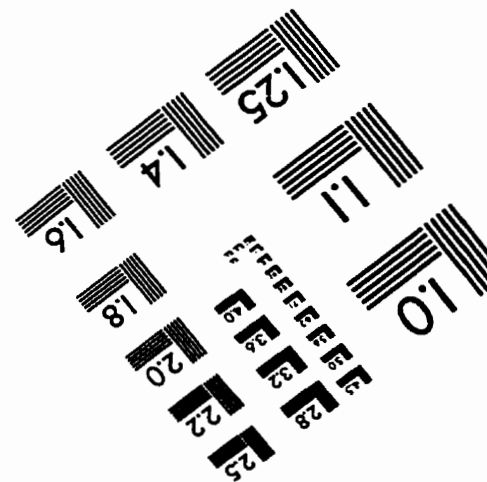
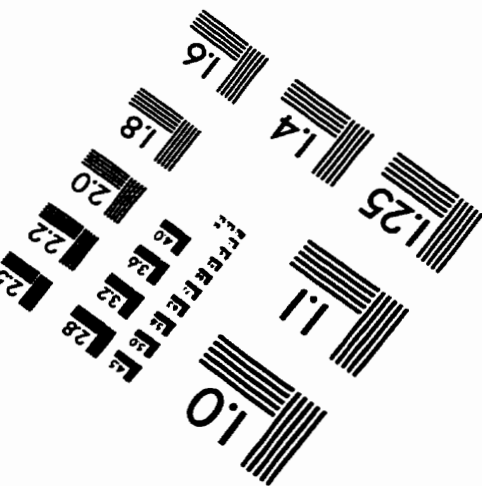
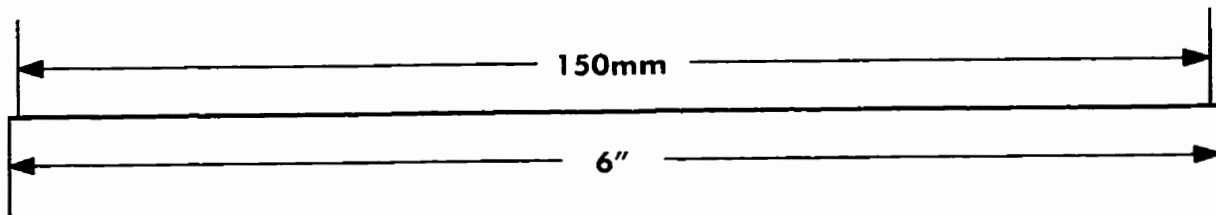
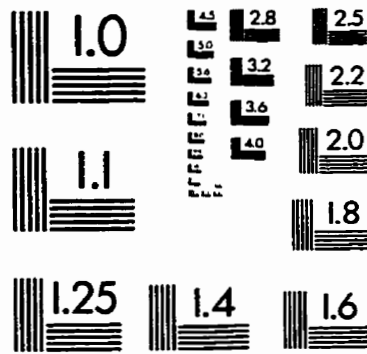
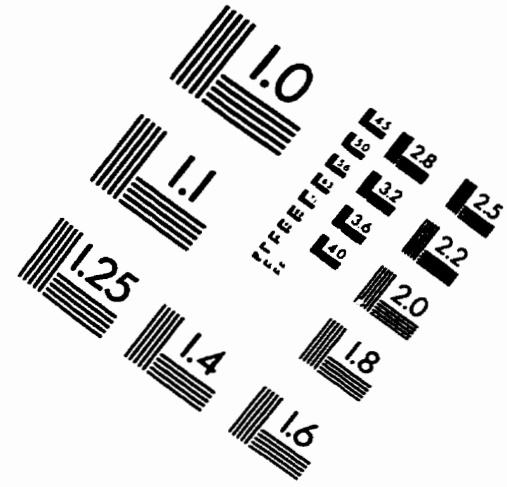
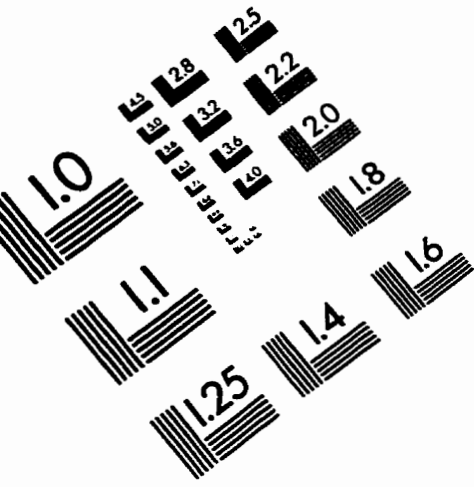
DATE	Congener	205	206	209
------	----------	-----	-----	-----

26/4/94		<MDL	<MDL	<MDL
2/5/94		<MDL	<MDL	<MDL
8/5/94		<MDL	<MDL	<MDL
14/5/94		<MDL	<MDL	<MDL
20/5/94		<MDL	<MDL	<MDL
26/5/94		<MDL	<MDL	<MDL
1/6/94		<MDL	<MDL	<MDL
7/6/94		<MDL	<MDL	<MDL
13/6/94		<MDL	<MDL	<MDL
19/6/94		<MDL	<MDL	<MDL
25/6/94		<MDL	<MDL	<MDL
1/7/94		<MDL	<MDL	<MDL
7/7/94		<MDL	<MDL	<MDL
17/7/94		<MDL	<MDL	<MDL
25/7/94		<MDL	<MDL	<MDL
31/7/94		<MDL	<MDL	<MDL
6/8/94		<MDL	<MDL	<MDL
12/8/94		<MDL	<MDL	<MDL
18/8/94		<MDL	<MDL	<MDL
24/8/94		<MDL	<MDL	<MDL
30/8/94		<MDL	<MDL	<MDL
5/9/94		<MDL	<MDL	<MDL
17/9/94		<MDL	<MDL	<MDL
29/9/94		<MDL	<MDL	<MDL
11/10/94		<MDL	<MDL	<MDL
23/10/94		<MDL	<MDL	<MDL
3/5/95		<MDL	<MDL	<MDL

DATE	Congener	205	206	209
9/5/95		<MDL	<MDL	<MDL
15/5/95		<MDL	<MDL	<MDL
21/5/95		<MDL	<MDL	<MDL
27/5/95		<MDL	<MDL	<MDL
2/6/95		<MDL	<MDL	<MDL
8/6/95		<MDL	<MDL	<MDL
14/6/95		<MDL	<MDL	<MDL
20/6/95		<MDL	<MDL	<MDL
26/6/95		<MDL	<MDL	<MDL
2/7/95		<MDL	<MDL	<MDL
8/7/95		<MDL	<MDL	<MDL
14/7/95		<MDL	<MDL	<MDL
20/7/95		<MDL	<MDL	<MDL
26/7/95		<MDL	<MDL	<MDL
1/8/95		<MDL	<MDL	<MDL
7/8/95		<MDL	<MDL	<MDL
13/8/95		<MDL	<MDL	<MDL
19/8/95		<MDL	<MDL	<MDL
25/8/95		<MDL	<MDL	<MDL
31/8/95		<MDL	<MDL	<MDL
6/9/95		<MDL	<MDL	<MDL
12/9/95		<MDL	<MDL	<MDL
24/9/95		<MDL	<MDL	<MDL
6/10/95		<MDL	<MDL	<MDL
18/10/95		<MDL	<MDL	<MDL
30/10/95		<MDL	<MDL	<MDL
29/5/96		<MDL	<MDL	<MDL
31/5/96		<MDL	<MDL	<MDL
2/6/96		<MDL	<MDL	<MDL

DATE	Congener	205	206	209
4/6/96		<MDL	<MDL	<MDL
6/6/96		<MDL	<MDL	<MDL
8/6/96		<MDL	<MDL	<MDL
10/6/96		<MDL	<MDL	<MDL
12/6/96		<MDL	<MDL	<MDL
14/6/96		<MDL	<MDL	<MDL
16/6/96		<MDL	<MDL	<MDL
18/6/96		<MDL	<MDL	<MDL
20/6/96		<MDL	<MDL	<MDL
22/6/96		<MDL	<MDL	<MDL
24/6/96		<MDL	<MDL	<MDL
27/6/96		<MDL	<MDL	<MDL
28/6/96		<MDL	<MDL	<MDL
30/6/96		<MDL	<MDL	<MDL
2/7/96		<MDL	<MDL	<MDL
4/7/96		<MDL	<MDL	<MDL
6/7/96		<MDL	<MDL	<MDL
8/7/96		<MDL	<MDL	<MDL
10/7/96		<MDL	<MDL	<MDL
12/7/96		<MDL	<MDL	<MDL
14/7/96		<MDL	0.890	0.733
16/7/96		<MDL	<MDL	<MDL
18/7/96		<MDL	6.816	6.597
20/7/96		<MDL	<MDL	<MDL
24/7/96		<MDL	<MDL	<MDL
26/7/96		<MDL	25.356	26.486
28/7/96		<MDL	<MDL	<MDL
30/7/96		<MDL	<MDL	<MDL
1/8/96		<MDL	<MDL	<MDL

IMAGE EVALUATION TEST TARGET (QA-3)




APPLIED IMAGE, Inc
 1653 East Main Street
 Rochester, NY 14609 USA
 Phone: 716/482-0300
 Fax: 716/288-5989

© 1993, Applied Image, Inc., All Rights Reserved