STREAM FLOW QUALITY - PESTICIDES IN ELEVEN AGRICULTURAL WATERSHEDS IN SOUTHERN ONTARIO, CANADA, 1974-77

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DISCLAIMER

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TABLE OF CONTENTS

3.0 RESULTS AND DISCUSSION

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

LIST OF APPENDICES

RECOMMENDATIONS

Feasible Remedial Measures

Insecticides and fungicides. The persistent organochlorine insecticides have virtually been elimated from use in agriculture and have been replaced by organophosphorus and carbamate insecticides. While many of these newer insecticides appear to be non-persistent and rarely contaminate stream water, over-use promoted by the appearance of insect resistance is leading to a build-up of residues in some muck soils which, in time, will contaminate water. This problem has not developed on mineral soils.

On January 1st, 1978 the major use of chlordane, rootworm control in corn, was deregistered leaving it available for minor uses on vegetables and major uses on turf and lawns. In October 1977 a major use of endosulfan, foliar insect control on tabacco, was also deregistered primarily because of residues in the cured tobacco leaf. These actions should greatly reduce the volume of use and the chance of entering water courses.

Usage of insecticides and fungicides is not confined to the agricultural sector, but is common to the domestic and industrial sectors and to the protection of forests. The Ontario Pesticide Act has gone far in removing the highly toxic insecticides and fungicides from the domestic sector and has made it mandatory that only trained personnel can apply such compounds to the industrial, forestry and aquatic environments.

Strict enforcement of regulations, adequate training of users and general education on new procedures and safeguards should contribute to lower the incidence of environmental contamination and allay future concerns.

Herbicides. The use of herbicides has grown dramatically over the last decade. These are employed by all facets of human society to control weeds in agriculture, on industrial and home properties, in forests and recreational areas.

Mammalian and avian toxicities are generally much lower than the insecticides and persistence is normally short termed; ranging from a few weeks to a season. A few herbicides can persist for longer periods, for example, simazine, atrazine and diuron. Although there is no evidence of any environmentally related problems, the rates at which atrazine (a corn production herbicide) is present in stream water may be cause for concern. This herbicide is readily removed from treated fields by storm runoff waters and can also be removed, but in less quantity, via tile drainage waters.

Other herbicides, such as cyanazine, can be substituted for atrazine under appropriate weed conditions and do not appear to either persist or be moved to stream water. Remedial measures that reduce soil erosion and storm water runoff could greatly reduce the loss of atrazine to water.

Some management practices like rotation, strip cropping, use of winter cover crop and grassed buffer strips will force a reduction in the use of atrazine and increase use of herbicides that neither persist nor turn up in stream water. Enforcement of current parts of the Pesticide Act could minimize spillage and/or carelessness around streams.

2,4-D type herbicides have been used in cereals and corn, but have not appeared at other than minimal levels in stream waters. These same materials are quite widely used for the control of weeds on roadsides, ditches, utility corridors and to control aquatic vegetation. While application personnel are generally aware of the dangers of spray drift damaging susceptible crops and garden plants, they have not been cognizant of the need to keep their sprays from contaminating water in ditches and streams around which weeds are being controlled.

The Pesticide Act of Ontario regulates the application of herbicides to water by permit and stipulates that application to public lands be done by licensed operators. However, education is needed to prevent the contamination of water when spraying such public properties.

Industrial organic toxicants. The problems associated with organic toxicants in Great Lakes water appear to be severe and reminiscent of the problems of the persistent organochlorine insecticides. Industrial organic toxicants like PBB, PCB, chlorinated naphthalenes and mirex are not used in agricultural production, but arrive on land through aerial fallout, misuse or disposal in rural areas e.g. dispersal of oil containing PCB on roadways.

Persistence, toxicology and use data are urgently required for currently used industrial organic toxicants. In addition, a system of collecting this data before new organics are introduced should be mandatory if future damage to the environment is to be averted. Continued monitoring and surveillance of industrial contaminants is paramount to safeguard food and water quality and alleviate the current chronic contamination of the Great Lakes basin.

SUMMARY

SUMMARY

The analytical procedures employed permitted the monitoring of 79 pesticides, their isomers and metabolites and two industrial chemicals. These 79 pesticides represented 74% of the insecticides, 10% of the fungicides and 47% of the herbicides used in the 11 agricultural watersheds. It did not cover nematocides, growth regulators or pesticide oils. Based on the actual volume of use in the 11 watersheds, the analytical procedures accounted for 93% of the insecticides, 0.2% of the fungicides and 81% of the herbicides applied (Table S-1).

Twenty six organic compounds were identified in stream water of which 18 were parent compounds and 8 were isomers and metabolites (Table S-1). The incidence of these contaminants in water varied from occasional to frequent.

Organochlorine Insecticides

Past Uses - ∑ DDT[1]: Four components of DDT namely p,p'-DDT, o,p'-DDT, p,p'-TDE and p,p'-DDE were identified in water; their incidence in water samples was respectively 10.5, 2.4, 23 and 93% over the two year period. The concentration of ∑DDT between the first and second year of the two year study showed a slight increase, however, the unit area loading showed a decline (Table S-2). The mean concentration of ∑DDT was above the 3 ng/L I.J.C. objective and 40.6% of the water samples exceeded this limit. All components were identified in sediment but only p,p'-DDE was found in rainwater.

The highest residues were found in AG-2 where larger quantities of DDT were used more recently than in other watersheds. ∑DDT entered streams largely with runoff events and in 1975-76 57.2% entered in the January to April period. In 1976-77 the amount entering during the same period was 83.4%.

Dieldrin: Aldrin was the insecticide widely used in Ontario, however. its metabolite dieldrin is the compound found in environmental samples. Dieldrin was present in one fifth of the water samples analysed (Table S-2) at a level of 1.6-1.7 ng/L. Sixteen percent of water samples exceeded the I.J.C. objective of 1 ng/L concentration level. Dieldrin was detected in the stream bed sediments of only one watershed (AG-13), the same watershed that had the highest levels of dieldrin in water (7-8 ng/L). The greatest losses occurred in the January to April period, with 49% and 90% of the annual total in 1975-76 and 1976-77, respectively.

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[1] ∑ DDT - Sum of DDE, TDE & DDT

TABLE S-1 Pesticides used past and present in Ontario agriculture and on roadsides with the frequency of their presence in water May, 1975 and April, 1977.

	Insecticides		Fungicides	Herbicides	Nematocides Growth Regulators	Others	Industrials
	Present	Past					
Project 5 -Survey (4)	27	0	10	34	4	2	0
Project 4B -Analysis (#)	20	8	1	16	0	0	2
-Volume (%)	93.1		0.1	74.8	0	0	0

Frequency in Water	Insecticides	Fungicides	Herbicides	Industrials
Frequent (40 - 100%)	p,p'-DDE	---	atrazine and desethyl atrazine	PCB
Infrequent (10 - 40%)	p,p'-TDE, p,p-'DDT, dieldrin β-endosulfan & endosulfan sulfate	----	---	---
Rarely (1 - 10%)	cis & trans chlordane o,p'-DDT, diazinon α-endosulfan, heptachlor epoxide	---	2,4-D, simazine, 2,4,5-T	
Occasionally (less than 1%)	chlorpyrifos ethion, malathion	---	alachlor, cyprazine dicamba, MCPA prometone	---

TABLE S-2 Amounts of pesticides lost per hectare from 11 agricultural watersheds and the quality of the water in relation to the I.J.C. objectives

	Unit Area Loadings		WaterQuality				I.J.C. Criteria	
	mg/ha/yr		1975-76		1976-77		Objective	Exceedence
	1975-76	1976-77	Mean (ng/L)	Presence (%)	Mean (ng/L)	Presence (%)	(ng/L)	(%)
<u>Organochlorine Insecticides</u>								
∑ DDT	32.1	25.5	6.7	92.5	7.7	93.6	3.0	40.6
dieldrin	3.91	2.80	1.6	20.9	1.7	20.4	1.0	16.0
chlordane	0.11	0.25	<9.4	0.0	<0.4	3.1	60.	0.0
∑ endosulfan	13.4	2.9	3.7	20.0	2.0	18.5	3.0	14.1
heptachlor epoxide	0.70	0.95	1.1	3.8	0.5	8.1	1.0	4.8
Organochlorine <u>Industrials</u>								
PCB	192	73	38	95.9	25.	92.9	10	78.2
			(µg/L)	(%)	(µg/L)	(%)	(µg/L)	(%)
<u>Organochlorine Herbicides</u>								
2,4,D	94	45	0.7	8.1	<0.1	5.8	100	0.1
2,4,5-T	25	5	0.1	1.0	<0.1	2.7	100	0.0
MCPA	8	0	0.1	0.9	<0.1	0.4	100	0.0
dicamba	1	0	<1.0	0.2	-	0.0	100	0.0
<u>Organophosphorus Insecticides</u>								
chlorpyrifos	0	1	<0.01	0.2	<0.01	0.4	0.13	0.0
diazinon	914[1]	110[1]	0.81	4.9	0.18	13.3	0.08	8.1
ethion	0	0	<0.01	0.4	-	0.0	0.035	0.1
malathion	0	31	-	0.0	< 0.01	0.8	5.1	0.0

Continued ......

TABLE S-2 Continued

	Unit Area Loadings		WaterQuality				I.J.C. Criteria	
	mg/ha/y/yr		1975-76		1976-77		Objective	Exceedence
	1975-76	1976-77	Mean (ng/L)	Presence (%)	Mean (ng/L)	Presence (%)	(ng/L)	(%)
Organonitrogen <u>Herbicides</u>								
alachlor	4	0	0.02	0.6	0.02	0.0	100	0.0
atrazine & desethyl	2190	1853	1.1	80.4	1.6	80.0	28	0.3
cyprazine	12	10	0.04	0.9	0.02	1.5	100	0.0
EPTC	-	0	-	-	0.1	5.7	100	0.0
metribuzin	4	9	0.02	1.7	0.02	1.3	100	0.0
prometone	1	3	0.02	0.2	0.02	1.5	100	0.0
simazine	24	58	0.02	6.2	0.06	12.3	100	0.0
Organonitrogen <u>Insecticides</u>								
carbofuran	-	1.5	-	-	0.5	23.0	6.0	0.0

[1] Point Source Losses

Present Uses: Chlordane - Heptachlor Epoxide. This insecticide was used on 4.5% of the corn hectarage in 11 watersheds for the control of root-worm, however the losses from watersheds using chlordane were negligible (Table S-2). Chlordane was not detected in stream bed sediments or rainwater. Since chlordane contains heptachlor, the presence of heptachlor epoxide (HE) in water was considered to originate from the use of chlordane. HE was present in 3.8 and 8.1% of waters respectively in the two year periods (Table S-2) and the unit area loadings were less than 1 mg/ha/yr and similar for the two periods. Both chlordane and HE were identified in watersheds where no commercial application appeared to have been made. Chlordane has been used for domestic purposes on lawns and shrubs (Table S-3). No water samples exceeded the 60 ng/L I.J.C. objective for chlordane, however 4.8% of water exceeded the 1 ng/L objective for HE (Table S-2).

∑ Endosulfan. Currently used to control foliar insects on tobacco, fruit and vegetables, endosulfan was present in water samples as the α (9.5%) and β (17.8%) isomers and as the sulfate metabolite (17.7%) over the two year period. Endosulfan was detected in watersheds where no commercial use was found and may have come from domestic applications to gardens. The major losses of endosulfan were in runoff waters (83.4% in 1975-76 and 66.9% in 1976-77). Spills and spray drift accounted for 14.8% in the first year and 21.1% in the second. Unit area loading was considerably lower in the second year of the study and may be linked to its removal as a recommendation for application on tobacco because of high product residues. Endosulfan exceeded the 3 ng/L I.J.C. objective in 14.4% of water samples. Endosulfan was detected in stream bed sediments of one watershed (AG-1). It was not detected in rainwater samples.

Organochlorine Herbicides

2,4-D. This herbicide was used to control weeds at 0.5 kg/ha in 40.9% of the cereals and only 8.4% of the corn in the 11 watersheds. Non agricultural land[s], especially rights-of-way, were sprayed with 2,4-D alone or in combination with 2,4,5-T. 2,4-D appeared in 8.1% and 5.8% of waters in the 1975-76 and 1976-77 periods respectively; annual losses amounted to 4.54 and 2.22 kg. Of the losses, 86.6% and 53.9% came from the spraying of rights of way and 13.4% and 47.2% came from agricultural use respectively in the two annual periods. In the case of spraying of rights of way 0.46% and 0.15% of that applied was lost to water in the first and second years respectively. In the case of spraying farm crops only 0.02% and 0.04% of that applied turned up in water. 2,4,D appeared in water to correspond with summer and fall spraying and was linked to actual use and not to residues in the soil. Unit area loadings in 1976-77 were half those in the first year (Table S-2). One water sample exceeded the I.J.C. objective and it came from right of way spraying where 2,4,D was directly sprayed into the water.

2,4,5-T. This herbicide was exclusively used in the spraying of rights of way. It was used in 9 of the 11 watersheds and was always used in conjunction with 2,4-D.

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[1] 3184 ha of non agricultural land, 490 (15%) was treated with herbicides

Losses of 2,4,5-T in 1975-76 were 1.36 kg and in 1976-77 0.32 kg, and represented 0.4% and 0.10% of the 2,4,5-T used. It's noteworthy that the percentage losses of 2,4-D/2,4,5-T are extremely close thus verifying that losses came from non-agricultural use. 2,4,5-T appeared in 1.0 and 2.7% of waters respectively in 1975-76 and 1976-77 (Table S-2). Unit area loadings were much lower in the second year of the study than the first (Table S-2). No water contained 2,4,5-T at or approaching the I.J.C. objective.

MCPA. The herbicide MCPA was used at 0.7 kg/ha on 11% of the cereal hectarage in the 11 agricultural watersheds to control weeds. Losses amounted to 0.32 kg in 1975-76 but none in 1976-77. This represented 0.046% of that applied. Losses were associated with spray drift or losses around water and not the result of runoff events. Concentrations in water were at or near the limit of detection of 0.1 µg/L. The unit area loading in 1975-76 was 8 mg/ ha/yr and zero for 1976-77. No water sample contained MCPA that even approached the I.J.C. objective.

Dicamba. This herbicide was used on 0.6 to 0.9% of the cereal hectarage in two watersheds only. It appeared in one water sample where it was suspected to have come from the treatment of a non-agricultural site. This water sample contained only 1 µg/L and did not approach the I.J.C. objective.

Organochlorine Industrials

PCB. No uses for PCB that involved agricultural production were known or discovered during the study. PCB were present in 95.9 and 92.9% of waters in the two yearly periods of the study respectively (Table S-2). Unit area loading declined from 192 mg/ha/yr in 1975-76 to 73 mg/ha/yr in 1976-77. The mean concentrations in water for the first year was 38 ng/L and for the second 25 ng/L. Taking 10 ng/L as the I.J.C. objective, 78.2% of waters exceeded this objective. PCB was shown to be present in rainwater between 2 and 100 ng/L in all six watersheds checked in 1975. PCB was also found in streambed sediments of all 11 agricultural watersheds at levels between 2 and 8 ng/g. No record was made of the number of transformers in each watershed, a possible source of contamination.

Organophosphorus Insecticides

Chlorpyrifos was used at 1 kg/ha on 58.7% of the tobacco hectarage in the 4 agricultural watersheds for cutworm control. A smaller percentage of vegetables were treated also. Chlorpyrifos appeared in 3 of 949 water samples resulting in a total loss of 51 g. Runoff from a tobacco field accounted for 35 g and the remainder was in two spills while spraying vegetables. The losses were 0.0035 and 0.0016% of that used in the two years of the study respectively. No water samples exceeded the I.J.C. objectives.

Diazinon was used at 0.7 kg/ha on only 11 ha vegetables. This use had little or no effect on water quality. However, an out-of-season spill and the use of diazinon in a series of mushroom houses that permitted its direct entry into stream water resulted in losses

TABLE S-3 Amounts applied to land in 11 agricultural watersheds and amounts lost in water through runoff events, tile drainage and carelessness in use.

Pesticides		1975 Application	Losses			
			1975 - 76		1976 - 77	
		(kg)	(g)	(%)	(g)	(%)
Organochlorine Insecticides						
Chlordane & HE	Agric.,	383	24	0.0063	62	0.016
	Non- Agric.1/	(?)	-	-	4	-
Endosulfan		682	494	0.072	82	0.012
Organochlorine Herbicides						
2,4-D	Agric.	2307	607	0.026	1023	0.044
	Non-Agric.	791	3932	0.497	1197	0.151
2,4,5-T	Agric.	2	-	-	-	-
	Non-Agric.	277	1360	0.491	320	0.116
MCPA	Agric.	697	318	0.046	-	-
Dicamba	Agric.	58	-	-	-	-
	Non- Agric.1/	(?)	25	-	-	-
Organophosphorus Insecticides						
Chlorpyrifos		1003	35	0.0035	16	0.0016
Diazinon	Field Use	8	2	0.0025	-	0.0000
	Indoor Use 2/	(?)	23434	HIGH	2408	HIGH
Ethion		(?)	5	-	-	-
Malathion	Field Use	19	-	-	-	-
	Indoor Use2/	(?)	-	-	72	-
Organonitrogen Herbicides						
Alachlor		2755	264	0.0096	-	-
Atrazine		10570	1101	0.955	-	-
Cyprazine 3/		14(?)	671	4.8	545	3.9
EPTC		540	-	0.0	0.1	0.00001

Continued ....

TABLE S-3 Continued

Pesticides	1975 Application (kg)	Losses 1975 - 76 (g)		Losses 1976- 77 (g)	
		(g)	(%)	(g)	(%)
Organonitrogen Herbicides (continued..)					
Metribuzin	239	127	0.054	274	0.115
Prometone [1/]	(?)	44	-	96	-
Simazine [3/]	389	973	0.250	2596	0.667
Organonitrogen Insecticides					
Carbofuran	1092	-	-	21	0.0019

[1/] Non-Agricultural Uses Unknown - chlordane, dicamba, prometone

[2/] Indoor Uses - diazinon, malathion

[3/] cyprazine and simazine - many uses missed in farm-to-farm survey

TABLE S-4 Stream flow, sediment and contaminant removal from agricultural watersheds between 1975-1977.

Item - Volume		1975-76 (10 Watersheds)				1976-77 (11 Watersheds)			
Weight (%)		May-Aug	Sep-Dec	Jan-Apr	TOTAL	May-Aug	Sep-Dec	Jan-Apr	TOTAL
Flow-x$10^3$$m^3$		28,768	43,439	137,908	210,115	40,100	26,956	90,178	157,234
	(%)	13.7	20.7	65.6		25.5	17.1	57.4	
Sediment(Mg)		3,944	817	9,373	14,134	2,091	265	6,207	8,563
	(%)	27.9	5.8	66.3		24.4	3.1	72.5	
∑ DDT(g)		317	393	949	1,659	199	40	1,242	1,481
	(%)	19.1	23.7	57.2		13.4	2.7	83.9	
Dieldrin(g)		59.1	26.4	65.9	151.4	5.2	2.7	94.5	102.4
	(%)	39.0	17.4	43.6		5.1	2.6	92.3	
Atrazine(kg)		44.23	16.79	39.64	100.66	32.80	10.55	45.48	88.83
	(%)	43.9	16.7	39.4		36.9	11.9	51.2	
Atrazine in runoff	(kg)	20.92	8.80	34.15	63.87	11.80	5.29	37.96	55.05
	(%)	32.7	13.8	53.5		21.4	9.6	69.0	
Atrazine in drainage	(kg)	7.11	5.99	5.49	18.59	5.59	4.07	7.52	17.18
	(%)	38.2	32.2	29.6		32.5	23.7	43.8	
Atrazine in spills	(kg)	16.20	2.00	0.00	18.20	15.41	1.19	0.00	16.60
	(%)	89.0	11.0	0.0		92.8	7.2	0.0	
PCB	(g)	1,658	2,066	5,405	9,129	806	693	2,213	3,712
	(%)	18.2	22.6	59.2		21.7	18.7	59.6	

of 21.03 kg in 1975-76 and 2.41 kg in 1976-77. The unit area loadings were all due to two point source losses (Table S-2). In 1975-76 and 1976-77 4.9 and 13.3% of water samples contained diazinon. The 80 ng/L I.J.C. objective was exceeded by 8.1% of waters all except one coming from the one point source in AG-13. The one came from the out-of-season spill in AG-2.

Ethion. No recorded uses for ethion were found, however it appeared in two waters in 1975-76 at concentrations close to the detection limit. Losses on these occasions amounted to 5 g. Ethion, being very toxic to fish, has a calculated I.J.C. criterion of 35 ng/L, a concentration close to the analytical detection limit. One of the two water samples contained ethion above the I.J.C. objective.

Leptophos. Leptophos was used to control cutworm on 36.2% of the tobacco hectarage in the 4 agricultural watersheds. Leptophos was not detected in water samples from the watersheds, but was detected in rainwater in AG-1 at 1.1 µg/L. No own use was found in AG-1 to explain this presence, suggesting it came from outside the watershed.

Malathion. Malathion was used in three watersheds to control insects in vegetables. No losses to water were associated with this use. The 72 g of malathion found in AG-13 was concluded to have come from an indoor use in the mushroom house mentioned under diazinon. Malathion was found in 0.8% of samples in 1976-77, all in the one watershed. None of these readings exceeded the I.J.C. objective of 500 ng/L.

Organonitrogen Herbicides

Alachlor. Alachlor was used in 4.4% of the soybean hectarage and 16.2% of the corn hectarage at an average rate of 1.9 kg/ha. In 1975 two spills occurred that contaminated water and resulted in the loss of 254 g, one occurring in a mixture with cyprazine. Only three waters were found where alachlor was present in the two year period (Table S-2). Losses represented 0.01% of that applied (Table S-3). No water exceeded or even approached the I.J.C. objective of 100 µg/L.

Atrazine. Atrazine was used to control weeds on 73% of the corn hectarage at a rate of 1.7 kg/ha. Atrazine appeared in 80.2% of water samples as both atrazine and desethyl atrazine (Table S-2). The ratio varied considerably but a mean average ratio was 3:1. The following were the inputs and outputs for the watersheds between 1975-77.

	1975-76 (10 watersheds)	1976-77 (11 watersheds)
Input g/ha/yr	230	225
Output g/ha/yr		
Storm runoff	1.36	1.05
Base Flow	0.45	0.39
Spills	0.38	0.42
Total	2.19	1.86
Loss/Application (%)	0.95	0.83

The losses based on unit area loading occurred in the following periods by percent.

	Loss (%)			
1975 - 76	May-Aug	Sep-Dec	Jan-Apr	Total
Storm Runoff	19.6	8.7	33.8	62.1
Base Flow	7.6	6.1	6.6	20.3
Spills	15.5	2.1	0.0	17.6
Total:	42.7	16.9	40.4	100.0
1976 - 77				
Storm Runoff	11.7	5. 0	40.1	56.8
Base Flow	6.3	4.6	9.9	20.8
Spills	20.2	2.2	0.0	22.4
Total:	38.2	11.8	50.0	100.0

The concentration of atrazine and its metabolite increased in water during the spray period from a level of less than 1 µg/L to a peak of 8-20 µg/L in the June-Aµgust period. The peak usually occurred in one month and then declined rapidly to the 1 µg/L. In some watersheds a second peak occurred in the fall to coincide with fall treatment of perennial weeds.

Losses of atrazine were greater from clay soils than lighter texture soils.

	Losses (kg/ha/yr)	
Soil Type	1975-76	1976-77
Clay & Clay Loam	4.47	2.75
Loam & Silt Loam	1.92	2.03
Sand & Sandy Loam	0.47	0.42

Only 0.3% of water samples exceeded the 28 µg/L I.J.C. objective for atrazine and desethyl atrazine.

<u>Cyprazine.</u> The actual quantity of cyprazine used to control weeds in corn was not known, probably because of confusion during the survey between cyprazine and cyanazine, two s-triazine herbicides of similar activity. This herbicide was being removed from the market during this period. Cyprazine was observed in 0.9 and 1.5% of water samples for the two years of the study (Table S-2). Losses occurred in watersheds where no record of use was available. In 1975-76 the 671g lost to water consisted of 130g in runoff waters and 541g in spills. The losses in 1976-77 amounted to 545g of which 540g was in runoff waters and 5g in spills. Unit area loading was 12 and 10 ng/ha/yr for the two years respectively. No water sample exceeded the 100 µg/L I.J.C. objective.

<u>EPTC.</u> EPTC was used to control weeds in beans and vegetables. In beans 23.6% of the hectarage was treated. EPTC was present in 5.7% of a limited number of samples collected during the spray season. Losses amounted to only 0.1 g. No samples exceeded the I.J.C. objective of 100 µg/L.

<u>Metribuzin.</u> Metribuzin was used to control weeds in soybeans, potatoes and tomatoes at 0.8 kg/ha. Over the two years, 1.5% of water samples contained residues of metribuzin. All occurred in the May to Aµgust period corresponding to the time of use. Unit area loadings were 4 and 9 mg/ha/yr respectively for the first and second years of the study (Table S-2). Losses amounted to 0.054 and 0.115% of that applied. In 1975, the total loss was 127 g of which 41 g was removed in a single runoff event while 86 g entered water directly from two events resulting from either spray drift or carelessness. In 1976 274 g were lost; 135 g were lost in one runoff event and 139 g entered a stream as a spill. No water samples violated the I.J.C. criterion of 100 µg/L.

<u>Prometone.</u> Prometone is not used in the production of food but is used for total vegetation control on industrial or non-agricultural lands. Prometone appeared in 0.2% of waters in 1975-76 and 1.5% in 1976-77. Losses in 1975-76 amounted to 44 g and occurred in a single runoff event. In 1976-77 96 g were lost; 94 g in runoff events and 2 g in a spill. No water samples exceeded the 100 µg/L I.J.C. objective.

<u>Simazine.</u> Simazine has many uses including weed control in corn, asparagus, tree and shrub nurseries, industrial sites, driveways, fence rows etc. as well as for aquatic vegetation control in streams. The survey only included its use on corn and asparagus, however, the enumeration failed to cover the total use in corn because simazine is used in an unrecognized mixture with atrazine. The survey indicated 3.3% of the corn hectarage was treated with 1.3 kg/ha however simazine was found in water of watersheds where none was recorded as being used. Simazine appeared in 6.2% of waters in the first year and 12.3% in the second year of the study (Table S-2). Unit area loadings were 24 and 58 mg/ha/yr and while use was recorded only in AG-1, 3, 5 and 13, residues were also found in AG-1,3,4,5,6,10,13 and 14.

The losses in 1975-76 were 973 g and in 1976-77 2596 g; these losses occurred in the following ways:

	Losses (%)	
	1975-76	1976-77
Storm runoff	66.9	33.7
Base Flow	2.6	0.7
Spills	30.5	65.6

No water samples exceeded the 100 µg/L I.J.C. objective.

Organonitrogen Insecticides

Carbofuran. Carbofuran was used at 1.3 kg/ha on 9.9% of the corn hectarage to control corn rootworm. In addition, a few hectares of vegetables were treated. Only a limited number of waters were analysed during the June-September period in watersheds where it was used and 23% contained traces of the insecticide. The total loss was 21 g or 0.0019% of that used (Table S-3).

No water samples exceeded the I.J.C. objective of 6 µg/L.

I. INTRODUCTION

1.1 Background

Article VI of the Great Lakes Water Quality Agreement, 1972, requested that the International Joint Commission inquire into and report on "pollution of the boundary waters of the Great Lakes System from agricultural, forestry and other land use activities, in accordance with the terms of reference attached to this agreement". The International Joint Commission (I.J.C.) established the International Reference Group on Great Lakes Pollution from Land Use Activities (PLUARG) to plan and implement the requested study.

In March, 1973, PLUARG submitted to the International Joint Commission a study plan to assess pollution of the Great Lakes from land use activities. This preliminary study plan outlined four main tasks including assessment of the problem (Task A), inventory of land use activities (Task B), watershed studies (Task C) and lake studies (Task D). A "Detailed Study Plan to Assess Great Lakes Pollution from Land Use Activities" was prepared (February 1974) and formed the basis for the PLUARG study.

Task C was described as "Intensive studies of a small number of representative watersheds, selected and conducted to permit some extrapolation of data to the entire Great Lakes Basin, and to relate contamination of water quality, which may be found at river mouths on the Great Lakes to specific land uses and practices".

Activity 1 (Canada) of Task C called for "Pilot Agricultural Watershed Surveys". The objective of this activity was "to obtain data on the inputs of pollutants into the Great Takes Drainage System which have their origins in the complex land use activities known as agriculture".

In February, 1974, the Agricultural subcommittee of the Task C Technical Committee, PLUARG, prepared a "Detailed Plan for the Study of Agricultural Watersheds in the Great Lakes Drainage Basin - Canada - 1974-1975". This plan called for a preliminary phase consisting of a monitoring program and additional studies for collection of background data. The second and intensive phase would consist of detailed studies of pollutants associated with agricultural land use.

The preliminary study phase, April 1974-1975, has been reported in detail in "Agricultural Watershed Studies, Great Lakes Drainage Basin, Canada Annual Report, 1974-1975". The requirements for continuation of the study were identified in that report and included a monitoring network, a detailed studies program, and a program for remedial

TABLE 1-1 Size of Major and Minor Watersheds

Great Lakes	Major Watershed			Minor Watershed		Distance [a/] from Lake (km)
	Name	Size (km^2)	AG-	Name	Size(km^2)	
Lake Huron	Ausable River	1562	3	Little Ausable River	62	121
	Maitland River	2686	6	Trib. of Upper Maitland River	55	110
	Saugeen River	3972	14	Mill Creek	45	36.7
Lake St. Clair	Thames River	5882	1	Big Creek	51	16.7
			5	Holiday Creek	30	253
Lake Erie	Big Creek	742	2	Venison Creek	79	19.6
	Grand River	6671	4	Canagagigue Creek	19	214
	Hillman Creek	162	13	Hillman Creek	20	7.4
Lake Ontario	Humber River	317	11	Salt Creek	24	34.9
	Shelter Valley Creek	944	7	Shelter Valley Creek	57	7.7
	Twenty Mile Creek	280	10	North Creek	30	26.5

[a/] Distance from flow gauging station and water sampling site to river mouth

TABLE 1-2 LAND USE, LIVESTOCK AND SOILS IN ELEVEN WATERSHEDS

Watershed	General Land Use	Livestock	Soils	County
AG-1	Cash crop, soybean, wheat, corn	few	clay	Essex
AG-2	Tobacco, cash crops	few	sand	Norfolk-Elgin
AG-3	Cash corn, beans, grains, pasture	beef, swine, dairy	clay loam	Huron-Perth
AG-4	Silage corn, mixed grain, pasture	dairy, beef	loam	Wellington
AG-5	Corn, pasture	dairy, beef	loam, silt loam	Oxford
AG-6	Mixed grain, pasture, corn	beef, dairy, swine	loam, silt loam	Huron-Wellington
AG-7	Forage, pasture, tobacco	general	sandy loam	Northumberland
AG-10	Pasture, mixed grains, corn	dairy, poultry, beef	clay	Niagara
AG-11	Pasture, mixed grains, corn	beef, dairy	clay loam	Peel
AG-13	Cash crops, fruit, vegetables	few	sandy loam, sand, clay	Essex
AG-14	Pasture, mixed grains	beef, dairy, swine	mixed loams	Bruce

measures or other future requirements.

The objective identified for the Phase I Monitoring Program was to measure the ambient concentrations and loading rates for various pollutants that occur with agricultural land use. The Phase II Detailed Studies would be directed towards the determination of the effects of soil, land use and associated practices on concentrations and loading rates of selected pollutants, the study of mechanisms of transport and storage of these pollutants in selected agricultural watersheds; and finally, the development of a predictive capability to allow extrapolation to other areas. The Phase II Future Requirement would allow for the development of remedial measures as significant problems were identified.

Projects to be included in Monitoring and Detailed Studies Programs were identified and an outline provided in the previously-mentioned "Annual Report, 1974-1975". The intensive phase of the Agricultural Watershed Studies Program was initiated in April 1975.

1.2 Project 4 - Stream Flow Quality (B) Pesticides

Project 4 was designed to measure concentrations of pesticides in stream water leaving each of the eleven agricultural watersheds and calculate actual amounts of pesticides leaving in stream waters. These findings would then be correlated with the detailed information on pesticide use in the watersheds collected under Project 5, Land Use Activities to determine unit area loadings.

Eleven watersheds (Table 1.2, Fig. 1) were chosen for examination of water quality, each being selected because it resembled a unique but larger area of the Province of Ontario where agriculture was practised. These agricultural watersheds include those where the use of pesticides ranged from intensive to extensive and included the use of specific pesticides or groups of pesticides.

Frank and Ripley (1977) collected and compiled detailed information on land use practices (Project 5) in eleven selected watersheds located in southern Ontario. The information on material inputs in the watersheds was intended to help in the interpretation of output parameters that were measured in the water leaving the mini-watershed on the way to the Great Lakes.

For this reason, tables showing the identity and amounts of those pesticides found in the survey of the eleven agricultural watersheds are reproduced in Appendix I, II, III and IV. Because the area of each watershed drained by the stream was slightly different from the one surveyed under Project 5, adjustments have been made on the data in the appendices.

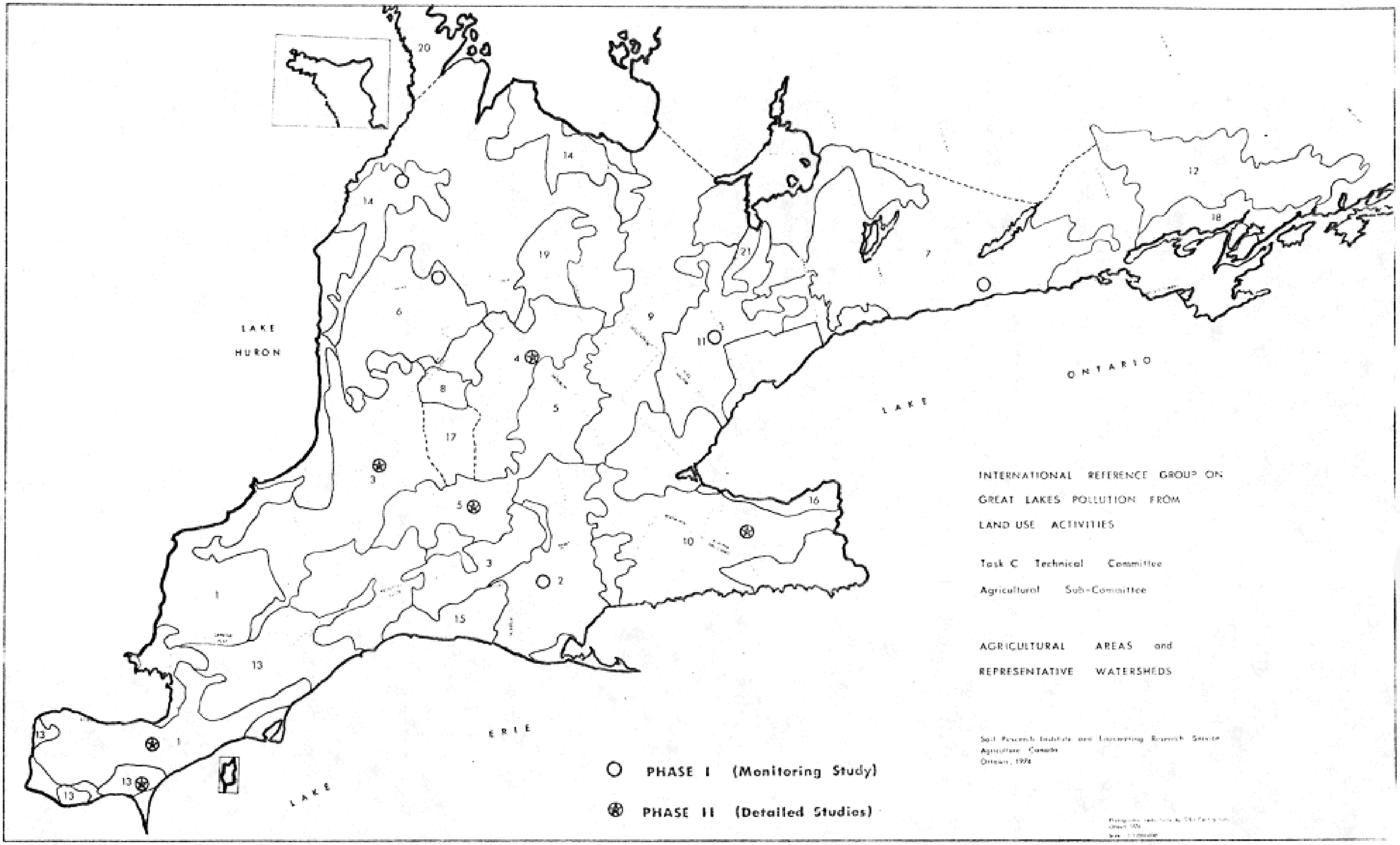

Fig. 1 Agricultural Watershed - Task C Study

1.3 Pesticides in Ontario

During the past decade the types of pesticides used in Ontario agriculture have shown considerable changes. DDT and other persistent organochlorine insecticides have been eliminated and replaced by organophosphorus and carbamate insecticides. Herbicides have increased in use and now account for more than half of the pesticide volume used in agriculture. Roller (1975) conducted a survey on pesticide use in the province during 1973 and showed that herbicides constitute 59% of the 4509 metric tons of pesticide now being used on field crops.

In comparison with organochlorine insecticide residues, little information has been generated on the replacement compounds in stream water and aquatic environment. Project 4 was intended to rectify this situation.

Frank *et al* (1974) have compared the concentrations of organochlorine insecticide r se dues in the bottom sediments of four study areas associated with four Ontario river and lake systems. The tobacco growing area drained by Big Creek reveals the highest levels of ΣDDT (DDT and metabolites) in the sediments of the four watersheds studied. This was to be expected due to the intensive use of DDT in this area. However, other areas showed only slightly lower concentrations of ΣDDT - Frequency and Content in Stream Water (ng/L) DDT in sediments despite the much smaller quantities used. This indicates the importance of such factors as the type of sediment sampled (sand or silt) and proximity of the application to the river, in addition to the soil type. In the Muskoka Takes drainage basin, insecticides were applied directly to the river and lake surfaces for biting fly control. Miles and Harris (1973) have reported also on the concentrations of organochlorine insecticides in the river water of this drainage basin. They concluded that the recreational use of insecticides was contributing a greater portion of these residues to the Great Lakes water system than was the use from agriculture. The authors did not attempt to draw any detailed relationships between pesticide use in the drainage areas and the concentrations in the water.

Harris and Miles (1974) have reported some results for organophosphate insecticide residues in the Bradford Marsh (a vegetable growing area of S. Ontario.) They found high levels of diazinon (up to 2.04 pph) in the drainage water. These high levels were associated with recent rainfall and application.

Project 4, Stream Flow Quality (B) Pesticides was inaugurated in 1974 and for one year a monitoring program was conducted on ambient concentrations of pesticides in streams. During the period 1975-1977 the monitoring program was expanded to cover a wider range of pesticides for both ambient concentrations in water and actual stream loadings in each of the eleven watersheds. This report summarizes the findings of pesticide losses in the agricultural watershed but does not infer that these materials will reach the Great Lakes.

TABLE 2-1 Pesticides and pollutants detectable in water by the prescribed screening procedures

A. ORGANOCHLORINE PESTICIDES AND POLLUTANTS

(i)	Diphenylethanes:	o,p' & p,p'-DDE, TDE and DDT, dicofol, methoxychlor (8 compounds)
(ii)	Cyclodienes:	aldrin, cis- and trans-chlordane, oxychlordane, dieldrin, α and β-endosulfan, endosulfan sulfate, endrin, heptachlor, heptachlor epoxide (11 compounds).
(iii)	Phenyloxy and Benzoic Acids:	2,4-D, 2,4-DB, chloramben, dicamba, dichlorprop, MCPA, MCPB, mecoprop, silvex, 2,4,5-T (10 compounds)
(iv)	Miscellaneous:	dichloran, lindane, mirex, PCB (4 compounds)

B. ORGANOPHOSPHORUS PESTICIDES

azinphos methyl, carbophenthion, chlorfenvinphos, chlorpyrifos demeton, diazinon and diazoxon, dichlofenthion, dimethoate, disulfoton, ethion & its oxon, fenchlorphos, fenthion, fenitrothion, fensulfothion and its sulfone, fonofos, leptophos, malathion & maloxon, parathion & paroxon, phonate & its sulfone and sulfoxide, phosalone, phosmet (28 compounds)

C. ORGANO NITROGEN PESTICIDES

(i)	s-triazines:	atrazine and desethylated atrazine, cyprazine, metribuzin, prometone, prometryne, simazine (7 compounds)
(ii)	N-methylcarbamates:	carbaryl, carbofuran and its 3-keto derivative, methiocarb, metalkamate(5 compounds)
(iii)	Thio-carbamates:	butylate, cycloate, diallate, EPTC, molinate, pebulate, vernolate (7 compounds)
(iv)	Others:	alachlor (1 compound)

TABLE 2-2 Limits of Detection in Screening Procedure (µg/L)

A. ORGANOCHLORINE INSECTICIDES

Aldrin	0.04	o,p’-DDT	0.002	Heptachlor	0.04
Chlordane	0.01	Dieldrin	0.001	Hept. Epoxide	0.002
p,p’-DDT	0.002	Endosulfan	0.005	Lindane	0.04
p,p’-DDE	0.001	Endrin	0.02	Methoxychlor	0.04

B. CHLORINATED POLLUTANTS

Mirex	0.04	PCB's	0.006

C. ORGANOPHOSPHORUS INSECTICIDES

Azinphosmethyl	5	Diazinon	0.05	Parathion	0.05
Chlorfenvinphos	1	Dimethoate	0.25	Phosalone	0.5
Chlorpyrifos	0.1	Leptophos	1	Phosmet	2
Demeton	1	Malathion	0.1	Ethion	0.1

D. CHLOROPHENOXY ALKANOIC AND CHLOROBENZOIC HERBICIDES

2,4-D	0.5	Dicamba	0.5
2,4,5-T	0.5	MCPA	0.5

E. s-TRIAZINE HERBICIDES

Atrazine	0.1	Metribuzin	0.1
Desethylated atrazine	0.1	Prometone	0.1
Cyprazine	0.1	Simazine	0.1

F. N-METHYLCARBAMATE INSECTICIDES

Carbaryl	1	Carbofuran	1

G. THIOCARBAMATE HERBICIDES

Butylate	1	Molinate	1
Cycloate	1	Pebulate	1
EPTC	1	Vernolate	1

2. METHODS AND MATERIALS

2.1 Field Collection

Over the three years of the study, a total of 1338 water samples and 11 sediment samples were collected (Appendix V) from eleven agricultural watersheds. Samples were collected from streams beside the gauging station, from ground water piezometers, rainfall gauges and stream bed. Stream water samples were taken to sample major high flow events with a few to cover basic flow rates. Samples were collected in all months of the year for the duration of the stream flow.

Depth integrated samples were collected at the centre of the flow. When the water depth was too great for wading, a weighted bucket was used to achieve a depth integrated sample. Under flood conditions 3 to 5 vertical samplings were taken depending on the cross sectional width of the stream. The temperature and pH of the stream water were recorded at the time of collection. When duplicates were collected these were obtained simultaneously. Water was placed in 1.5-L glass bottles and delivered to the Provincial Pesticide Residue Testing Laboratory as rapidly as possible, with transit time rarely longer than 5 days. After use, the bottles were washed and rinsed to remove pesticides and avoid cross contamination before being re-used.

Rain and groundwater samples were collected from volumes collected in rain collectors or from volumes drawn from piezometers. Stream bed sediments were taken from the top 5-10 cm of the stream bed which had been divided into 3-5 sections across the stream. The samples were collected using an aluminum coring device and cores were composited before subsampling. Temperature and pH of the sediments were determined prior to delivery to the laboratory. Sediments were air dried prior to analysis.

Between April 1974 and May 1977 a total of 1338 water samples and 11 sediment samples were analysed. This represented 7140 separate analyses (Appendix V). In 1974 water samples were analysed for herbicides only, and waters from watersheds AG-1,2,3,5,10 and 13 were analysed for s-triazines while water from AG-4,6,7,11 and 14 were analysed for phenoxyalkanoic and benzoic acids. Between 1975 and 1977 water samples were analysed for diphenylethanes, cyclodienes, organophosphates, PCB, triazines and chlorophenoxyalkanes. Between June and August water from AG-2,3,6,7 and 13 were analysed for N-methyl and/or thiocarbamates. Ground waters were analysed for s-triazines from six locations in AG-13 at depths between 2.4-7.8 m. Rain water samples collected May and December 1975 were analysed for diphenylethanes, cyclodienes, PCB and organophosphates. Special samples collected from AG-13 between October 1976 and May 1977 were analysed for organophosphates and especially diazinon.

Sediments were collected in 1976-1977 from the 11 watersheds and analysed for diphenylethanes, cyclodienes, PCB, organophosphates, triazines and chlorophenoxyalkanoic acids.

2.2 Analytical Procedures

Samples were analysed for each of the chemical groups listed in Table 2-1 in eight screening procedures designed to cover the detection of 79 pesticide compounds that included parent compounds, isomers and major metabolites. The minimum reportable values of each chemical appears in Table 2-2.

2.2.1 Organochlorine and Organophosphate Insecticides S Pollutants

Extraction: Water samples (ca 1.5L, accurately measured) were transferred to separatory funnels. Sample containers were rinsed with 50 ml dichloromethane and added to the sample. Saturated aqueous sodium chloride solution (50 ml) was added and the mixture was shaken vigorously for 60 seconds; phases were allowed to separate and the dichloromethane extract was drained through sodium sulfate. The extraction was repeated with a second 50 ml portion of dichloromethane, beginning with the sample container rinse. The combined extracts were evaporated just to dryness with rotary vacuum at 50C and re-dissolved in a measured aliquot of hexane to give a 500x concentrated factor. An aliquot of 0.50 mL was removed for analysis of organophosphorus insecticides and the remainder was cleaned up for organochlorine insecticide and pollutant analysis.

Cleanup and Fractionation: Extracts were cleaned up on activated Florisil, 60/100 mesh, 25g in a 22 mm i.d. column, pre-washed with hexane. Sample extracts were quantitatively introduced into the column with small hexane rinses and eluted successively with (A) 200 mL 20:80 dichloromethane: hexane and (B) 200 ml 0.35:50:50 acetonitrile:dichloromethane:hexane. Eluate fractions were concentrated just to dryness with rotary vacuum. Fraction A was re-dissolved in 5 mL acetone and Fraction B was re-dissolved in a measured amount of iso-octane to give a 500x concentration factor. (Mills *et al* , 1972.)

PCB Separation: Organochlorine insecticides were separated from PCB's on a 9 mm i.d. column containing 7.5cm charcoal (Fisher #5-690) sandwiched between two 1 cm layers of washed sand; the charcoal column was pre-washed with 1:3 acetone:ethyl ether. The acetone solution of Fraction A was introduced to the column using small acetone rinses to effect quantitative transfer and then eluted successively with (1) 180 mL 1:3 acetone:diethyl ether and (2) 80 ml benzene to give Fractions A-1 and A-2, respectively. Solvents were removed from each eluate fraction by rotary vacuum and re-dissolved in measured amounts of iso-octane for a concentration factor of 500x (Holdrinet, 1974).

GLC Determination

(a) Organophosphorus insecticides were determined by gas-liquid chromatography using the following parameters:

Column:	1.8 m x 2 mm i.d., 5% OV.1 on 80/100 mesh Gas Chrom Q
Column Temperature:	185 C isothermal
Carrier gas:	nitrogen at 60 mL/min.

Detector: flame photometric, phosphorus mode (526 nm filter)
Injector volume: 10 µL (5.0 ml sample equivalent)

(b) Organochlorine insecticides and PCB's were determined by gas-liquid chromatography with the following parameters:

Column: 1.8 m x 4 mm i.d., 1.5% OV-17 / 2.0 OV-210 on 100/120 mesh Gas Chrome Q Column
Temperature: 185 C isothermal
Carrier gas: electron capture, Ni-63 source
Injection volume: 5 µL (2.5 mL sample equivalent)

Insecticides Routinely Screened

Organophosphorus insecticides routinely screened included azinphosmethyl, chlorfenvinphos, chlorpyrifos, demeton, diazinon, dimethoate, ethion, leptophos, malathion, parathion, phosalone and phosmet. Additional organophosphorus compounds, if present in sufficient quantity, would also be detected.

Fraction A-1 organochlorine insecticides include chlordane, p,p’-DDT, o,p’-DDT, p,p’-DDD, p,p’-DDE and mirex; aldrin, heptachlor and lindane are also present in this fraction but positive confirmation is difficult.

Fraction A-2 contains PCB's. Quantitation of PCB's was based upon comparison with Aroclor 1254 as the reference standard.

Fraction B organochlorine insecticides include dieldrin, endrin, endosulfan, heptachlor epoxide and methoxychlor.

2.2.2 Chlorphenoxy Alkanoic and Chlorobenzoic Acid Herbicides

Extraction: The water sample (1.0L) was transferred to a reparatory funnel and the pH was adjusted to <1 by addition of 1 mL of 50% sulfuric acid. Extraction was effected by shaking twice for 60 seconds with 100 mL portions of diethyl ether and filtering the ether extracts through adsorbent cotton to remove excess dissolved water. Hexane (10 mL) was added to the combined extracts, evaporated to 1-2 mL with rotary vacuum, and transferred to a test tube using 5 mL iso-octane as a rinse. Diazomethane (4 mL, 4-6% in ethyl ether) was added and esterification was allowed to proceed for one hour at room temperature. The mixture was then evaporated to a fixed volume using a gentle stream of air (Yip, 1971.)

GLC Determination

Methyl esters of the phenoxy and benzoic acid herbicides were determined by gas-liquid chromatography with the following parameters:

Column: 1.8 m x 4 mm i.d., 5% Dexsil 400 GC on 80/100 mesh Varaport 30 Column
Temperature: 160C isothermal
Carrier gas: helium at 50 mL/min.
Detector: Coulson conductivity, halogen specific mode
Injection Volume: 2-50 µL (0.4-10 mL sample equivalent)

Herbicides Routinely Screened

The following compounds are routinely recovered, identified and measured: 2,4-D, 2,4,5-T, MCPA and dicamba.

2.2.3 s-Triazine Herbicides

Extraction: Water (1.0 L) was transferred to a separatory funnel and the pH was adjusted to 9 with dilute ammonia. Extraction was effected by shaking twice for 60 seconds with 100 mL portions of chloroform and passage of the chloroform extracts through dry adsorbent cotton. The combined extracts were evaporated to l-2 mL with rotary vacuum, 10 mL iso-octane were added, and re-evaporated just to dryness followed by re-solution in a measured amount of methanol (Ramsteiner *et al* , 1974, Sirons *et al*, 1973)

GLC Determination:

Triazine herbicides were measured by gas-liquid chromatography using the following parameters:

Column: 1.8 m x 4 mm i.d. 5% Carbowax 20 M on 80/100 mesh Varaport 30
Column Temperature: 210 C isothermal
Carrier gas: helium at 50 mL/min.
Detector: Coulson conductivity, nitrogen mode
Injection Volume: 2-50 µL (equivalent to 0.4-10 mL samples)

Herbicides Routinely Screened

The following s-Triazine herbicides are routinely measured by the described procedure: atrazine (including desethylated atrazine), cyprazine, metribuzin, prometone and simazine.

2.2.4 N-Methylcarbamate Insecticides

Extraction: Water (1.0 L) was transferred to a separatory funnel, adjusted to pH 2-4 with sulfuric acid, and 10 mL saturated aqueous sodium sulfate was added. The mixture was extracted sequentially with 150 mL and 100 mL dichloromethane, shaking 60 seconds each time. The combined extracts were washed by shaking once with 100 mL 0.114 potassium carbonate. (The carbonate wash may be retained and examined for the presence of hydrolytic carbamate phenols.) The dichloromethane extract was dried by filtration through sodium sulfate, 2 mL iso-octane were added, and the volume was reduced to 2 mL with rotary vacuum.

Hydrolysis and Derivatization: Methanolic potassium hydroxide (2 mL, 10%) was added to the concentrated extract and hydrolysis was carried out at 60C for 2 hours. The contents were transferred to a separatory funnel using a 50 mL water rinse, 50 mL dichloromethane were added, and after shaking briefly the organic phase was discarded. The aqueous phase was acidified to pH 2 and extracted twice with 50 mL benzene. Two mL iso-octane were added to the combined benzene extracts followed by concentration to 1-2 mL with rotary vacuum. Derivatization was carried out by adding 10 mL acetone, 25 µL 5% aqueous potassium carbonate, 100 µL pentafluorobenzyl bromide (1% in acetone), and allowing the reaction to proceed at 60C for 20 minutes.

Cleanup and Fractionation: Two mL iso-octane were added to the derivative solution and the volume was reduced to 1 mL with rotary vacuum; an additional 5 mL iso-octane were added and the volume was again reduced to 1 mL. Cleanup was carried out in a 10 mm i.d. chromatography column containing 5 g silica gel (grade 950) previously equilibrated with 1.5% water and pre-washed with 25 mL hexane. The concentrated iso-octane solution was quantitatively added to the column with small hexane rinses and eluted with 25 ml 5% benzene in hexane and all eluate collected to this point was discarded. The column was then eluted successively with 30 mL 1:3-benzene:hexane (Fraction *A)* followed by 40 mL 3:1-benzene:hexane (Fraction B). Both eluate fractions were concentrated to <5 mL, volume with rotary vacuum after the addition of 2 ml iso-octane and the volume was adjusted to 5.00 mL with benzene (Coburn *et al* , 1976.)

GLC Determination: Gas-liquid chromatographic parameters for the measurement of N-methylcarbamate insecticides were as follows:

Column:	1.8 m x 4 mm i.d., 3.6% OV-101/5.5% OV-210 on 80/100 mesh Chromosorb W, acid washed, DMCS treated
Column Temperature:	200C isothermal
Carrier gas:	5% methane in argon at 80 mL/min.
Detector:	electron capture, Ni-63 source, pulsed operation
Injection Volume:	5 µL (1 mL sample equivalent)

Insecticides Routinely Screened

N-methylcarbamates screened by the described procedure include carbaryl (Fraction A) and carbofuran plus propoxur (Fraction B).

2.2.5 Thiocarbamate Herbicides

Extraction: Water (1.0 L) was extracted twice with 100 mL portions of iso-octane, shaking 60 seconds each time. The extracts were dried and combined by filtration through sodium sulfate. The volume was reduced to ca 2 mL with rotary vacuum at 50C, transferred to a graduated tube with small iso-octane rinses and the final volume was adjusted to 5.0 mL.

GLC Determination: Thiocarb mate residues were determined by gas-liquid chromatography using the following parameters:

Column: 1.8 m x 4 mm i.d., 3.6% OV-101/5.5% OV-210 on 80/100 mesh Chromosorb W-AW, DMCS treated
Column temperature: 150C isothermal
Carrier gas: nitrogen at 80 mL/min
Detector: flame photometric, sulfur mode
Injection volume: 5 µL (1.0 mL sample equivalent)

Herbicides Routinely Screened

The following thiocarbamate herbicide residues in water are screened by the described procedure: butylate, cycloate, EPTC, molinate, pebulate and vernolate.

2.2.6 Confirmation Techniques

The low levels of pesticides and pollutants normally encountered in water makes confirmation by alternate means of analysis difficult. Semi-confirmation of pesticide identity was achieved by (a) the use of element-specific GLC detectors e.g., conductivity detection in the Cl- and N-specific modes, and flame photometric detection in the P- and S- specific modes; and (b) the use of alternate column GLC, i.e. use of a GLC column of different polarity so that characteristic retention times are significantly changed.

2.3 Quality Control

Duplicate water samples were picked up at random on 31 occasions to check the sampling technique and the analytical procedure (Appendix VI). On most occasions, good agreement was obtained where the contaminatory subtance was a general contaminant of the system. Poor agreement resulted on two occasions when, presumably, a slug of contaminant was passing down the system. This was verified in AG-13 on June 24, 1975, when an atrazine slug was passing downstream and again on September 27, 1976, when both atrazine and diazinon was passing downstream. On these occasions the duplicates contained marked differences in concentration of the contaminants.

Internal laboratory check samples were also injected at random throughout the program and good agreement was obtained in all cases.

2.4 Stream Loading

For purposes of tabulating concentrations in water the terms trace (TR) and not detected (ND) were retained for the monthly means and ranges. (Appendix VII). For purposes of loading calculations a number was assigned to trace levels (Appendix VII). In the cases of non-detection, compounds were divided into two groups. With the ubiquitously persistent organochlorine compounds e.g. DDT, dieldrin, PCB etc., a number was assigned for loading purposes on the assumption that the majority of samples contained some background level of the contaminant above zero but below trace amounts. With the non-persistent pesticides e.g. 2,4-D, MCPA, cyprazine etc., a figure of zero was assigned for loading purposes. This was based on the assumption that the majority of samples were in fact free of contaminant either because (a) none appeared to have been used in the watershed or (b) where applied, the rate of breakdown would suggest the level would more nearly approach zero than a level assigned to a trace level.

Flow data were obtained from Ontario Ministry of Environment (Appendix VIII).The daily flows were fed, along with the chemical analysis data, into the NAQUADAT computer in Ottawa and loadings were supplied through Agriculture Canada for each parameter in the agricultural watersheds for the period May 1975 to April 1977. This period was used as the main basis for the report. Unit area loading for all pesticides was based on the total area of the watershed and not just the treated area. Adjustments had to he made to the farm-to-farm survey (Frank S Ripley 1977) because the exact drainage area of each watershed was not finalized until the survey was complete. Corrections have been applied to data used from this survey.

3. RESULTS AND DISCUSSION

3.1 General

From the standpoint of permitted agricultural uses of pesticides in the 11 agricultural watersheds, the laboratory analytical screening procedures permitted detection of 20 of the 27 insecticides, 16 of the 34 herbicides and 1 of the 10 fungicides; none of the nematocides and growth regulators were measurable by the screening procedures (Table 3-1, Appendix I, II, III, IV). These procedures, however, accounted for 90.9% of the volume use of insecticides, 80.8% of the volume use of herbicides, but only 0.2% of the volume of fungicides applied in the 11 watersheds.

Several organochlorine insecticides used in previous years, but no longer permitted for use, were also identified and measured by the analytical procedures. These included the diphenylethanes DDT and TDE, and the cyclodiene dieldrin.

3.2 Organochlorine Insecticides - Diphenylethanes

The uses of DDT and TDE for agricultural purposes were restricted in 1970 and cancelled completely in 1972 (Frank *et al* , 1974, 1977; Harris and Miles 1975). Methoxychlor and dicofol are still permitted for use; in the 11 watersheds under study (Frank and Ripley, 1977), however, only dicofol was used in AG-13 (Appendix I).

3.2.1: Σ DDT

Presence in Water

Although no longer used in Ontario agriculture (the last official use was in 1972), DDT and its metabolites DDE and TDE were still detected in stream waters. The frequency of their occurrence in the water samples over the two-year study period was:

DDT	93%	p,p'-DDT	10.5%
p,p'-DDE	93%	o,p'-DDT	2.4%
p,p'-TDE	23%	o,p'-DDE and o,p'-TDE	not detected

The annual mean residues of : DDT for the 11 agricultural watersheds ranged from 3.1 to 21.0 ng/L with individual water samples containing from 40.4 to a high of 347 ng/L (Table 3-2, Appendix IX); the highest mean residues were found in AG-2,5,7 and 13 and were associated with tobacco and vegetable production where the use of DDT was either greater than that in the other watersheds, or where use was permitted until 1972 (Frank *et al* , 1977).

TABLE 3-1 Pesticides by group used in 11 agricultural watersheds and detected in the analytical screening procedure

		Used in Watershed		Included in Screening		
Pesticide Type	Chemical Group	Number	Volume (kg)	Number	Volume (kg)	Volume (%)
Insecticides	Organochlorine	4	1,113	4	1,113	100
	Organophosphorus	15	5,589	13	5,196	93.0
	Organonitrogen	8	2,055	3	1,828	89.0
	TOTAL	2.7	8,757	20	8,137	92.9
Fungicides	Organochlorine	4	2,348	1	11	0.5
	Organonitrogen	6	4,881	0	0	0
	TOTAL	10	7,229	1	11	0.2
Herbicides	Organochlorine	10	6,385	7	6,348	99.4
	Organonitrogen	24	21,706	9	16,351	75.3
	TOTAL	34	28,091	16	22,699	80.8
Pesticides[1]	TOTAL	71	44,077	37	30,841	70.0

[1] Does not include 2 nematocide -- 107,567 kg
2 growth regulators - 28,374 kg
2 petroleum products - 13,903 L

Ref: Frank 6 Ripley (1977)

The mean residue for all 11 watersheds over the two year period was 7.1 ng/L consisting of 4.1 ng/L DDE, 1.6 ng/L TDE and 1.4 ng/L DDT.

Monthly mean levels of DDE, TDE and DDT varied widely. The highest levels tended to occur between February and May, a period during which streams were being flushed by high flow rates; conversely, the lowest concentrations appeared to occur between August and October when the flow rates were low (Appendix VIII and IX).

Annual total losses of Σ DDT ranged from a low of 33 g in AG-4 to a high of 467 g in AG-2 in the May 1975 - April 1976 period, and from 7g in AG-11 to 698 g in AG-2 in the May 1976-April 1977 period (Appendix X). When calculated on the basis of unit area loadings, total losses ranged from 12.2 mg/ha/yr in AG-14 to 59.0 mg/ha/yr in AG-2 for 1975-76 and 2.94 mg/ha/yr to 88.2 mg/ha/yr in 1976-77 for AG-11 and AG-2, respectively (Table 3-3). Generally, for the 11 watersheds the highest losses occurred in the January to April period and represented 61% and 85% of the annual losses during 1975-76 and 1976-77, respectively.

DDE was the predominant component of ΣDDT; while present in 93% of the water samples, losses of DDE represented 68.5% and 46.1% respectively of the DDT amounts lost in 1975-76 and 1976-77 (Appendix IX and XI). DDE accounted for 61% to 100% of the ΣDDT concentrations found in individual water samples. TDE was present in 23% of the samples representing 21.1% and 23.4% of the DDT lost in the 1975-76 and 1976-77 periods, respectively (Appendix XI); TDE was found only as the p,p-isomer and its concentration represented 0 to 58% of the ΣDDT concentration in individual water samples. The o,p and p,p-isomers of DDT together represented 10.4% and 30.5% of the ΣDDT lost in the stream waters of the 11 watersheds in the two periods, respectively (Appendix XI). The incidence of o,p'-DDT and p,p'-DDT was highest during the high flow periods of March and April (especially in AG-2) and represented 0 to 85% of the ΣDDT concentration in individual water samples; at other times of the year, o,p- and p,p'-DDT were generally absent or present at only low levels. Frequency, mean concentrations, and amounts lost of DDE, TDE and DDT are briefly summarized as follows:

	Frequency	Mean Concentrations		Amount Lost	
	(%)	(ng/L)	(%)	(g)	(%)
DDE	93.0	4.1	57.7	1819	58.1
TDE	23.0	1.6	22.5	685	21.9
DDT	10.5	1.4	19.8	625	20.0

(Appendix IX,XI)

<u>Sources of ΣDDT</u>

Since DDT has had no official agricultural use in Ontario since 1972, its presence in stream water is the result of its long-term persistence. The main source of DDT and its analogs is largely derived from the soil which serves as a storage reservoir from past uses. Frank *et al* (1976,1977), Harris and Miles (1975) and Harris *et al* (1977) have reported on current levels of

ΣDDT in agricultural soils of Ontario. Soils used for the production of fruits, vegetables and tobacco are considerably higher in DDT content than those soils not involved in these practices, thus explaining why watersheds where these crops predominate have higher DDT levels in stream waters.

A second source of DDT is the stream bed sediments (Table 3-4). DDE residues were found to be present in the stream sediments of all watersheds at levels ranging from 0.5 to 5.0 ng/g. TDE and DDT were found in sediments of only four watersheds and ranged from 0.3 to 9.0 ng/g. The highest DDT residues were observed in AG-2 stream sediments, again reflecting the past uses of DDT as mentioned above. Frank *et al* (1974 a,b), Miles (1976), riles and Harris (1973) and Miles *et al* (1976) have documented ∑DDT residues in other stream sediments across the province.

A third source of DDT residues in water is the atmosphere. Measurable amounts of DDE were found in rainwater at concentrations ranging from 1.0 to 19 ng/L. DDT and TDE were not detected in these samples.

Entry into Stream Water

The entry of DDT into stream waters is largely the result of runoff events which mobilize soil particles carrying them into streams. In the 1975-76 and 1976-77 periods, DDT losses during the January to April months represented 61% and 85%, respectively, of the total annual losses and showed close correlation with runoff events, flow conditions and sediment mobility (Table 3-3, Appendix VIII a, b, X). High and low sediment losses can be correlated with the high and low losses of DDT but losses between these extremes were not readily correlated. This may be explained by the fact that all soils are not equally contaminated and that DDT residues can vary greatly from field to field and from farm to farm.

Stream flows, sediment losses and MDT losses are summarized as follows:

	Flow Volume m^3 x10^6 (%)	Sediment Loss x10^{3}kg (%)	ΣDDT Loss g(%)
1975-76 (10 watersheds)			
May-Aug.	28.8 (13.6)	3944 (27.9)	317 (19.1)
Sep-Dec.	43.4 (20.7)	817 (5.8)	393 (23.7)
Jan-Apr.	137.9 (65.7)	9373 (66.3)	949 (57.2)
Total	201.1	14134	1659
1976-77 (11 watersheds)			
May-Aug.	40.1 (25.9)	2091 (24.4)	199 (13.4)
Sep-Dec.	27.0 (17.4)	265 (3.1)	40 (2.7)
Jan-Apr.	87.8 (56.7)	6207 (72.5)	1242 (83.9)
Total	154.9	8563	1481

TABLE 3-2 The frequency and concentration of DDT found in stream water between May 1975 and April 1977 in 11 agricultural watersheds

		ΣDDT - Frequency and Content in Stream Water (ng/L)								
Watershed	Period May-Apr.	Analysis (#)	Not Det. (<0.4)	Trace (0.4-0.9)	Low (1.0-10.0)	Medium (11-100)	High (100+)	Mean	Range	SD
AG-1	1975-76	61	5	0	42	14	0	6.7	ND-39	14.0
	1976-77	58	4	2	49	3	0	3.1	ND-14	7.3
AG-2	1975-76	29	1	0	21	5	2	21.0	ND-347	139.0
	1976-77	34	1	2	21	8	2	17.0	ND-158	76.0
AG-3	1975-76	52	5	1	39	7	0	3.9	ND-46	17.0
	1976-77	57	4	5	43	4	1	7.1	ND-114	34.0
AG-4	1975-76	34	5	0	26	3	0	3.8	ND-14	8.2
	1976-77	43	2	3	33	5	0	6.5	ND-97	29.0
AG-5	1975-76	55	4	0	46	5	0	4.0	ND-17	7.7
	1976-77	56	4	5	38	8	1	11.0	ND-261	72.0
AG-6	1975-76	58	3	1	45	9	0	5.3	ND-55	16.0
	1976-77	41	3	3	29	6	0	4.5	ND-23	11.0
AG-7	1975-76	28	2	0	20	5	1	10.0	ND-120	45.0
	1976-77	19	1	2	13	3	0	3.5	ND-13	8.7
AG-10	1975-76	24	2	0	21	1	0	3.9	ND-13	6.4
	1976-77	37	2	1	28	5	1	8.9	ND-126	42.0

Continued ......

TABLE 3-2 Continued

ΣDDT - Frequency and Content in Stream Water (ng/L)

Watershed	Period	Analysis	Not Det. (<0.4)	Trace (0.4-0.9)	Low (1.0-10.0)	Medium (1-100)	High (100+)	Mean	Range	SD
AG-11	1975-76	18	0	0	15	3	0	5.6	1.0-17	9.2
	1976-77	5	0	1	3	1	0	4.7	0.7-12	1
AG-13	1975-76	62	2	0	48	12	0	7.9	ND-59	1
	1976-77	87	5	7	61	12	2	9.6	ND-211	5
AG-14	1975-76	48	6	0	35	7	0	5.3	ND-27	1
	1976-77	43	4	1	31	7	0	4.9	ND-24	11
TOTAL:	1975-76	469	35	2	358	71	3	6.7	ND-347	38
	1976-77	480	30	32	349	62	7	7.7	ND-211	1
GRAND TOTAL:	1975-77	949	65	34	707	133	10	7.1	ND-347	2

TABLE 3-3 Unit area loading of ΣDDT and dieldrin in 11 agricultural watersheds from May 1975 to April 1977

Watershed	ΣDDT(mg/ha)				Dieldrin (mg/ha)			
	May-Aug	Sep-Dec	Jan-Apr	Total	May-Aug	Sep-Dec	Jan-Apr	Total
1975-76 (May to April)								
AG-1	7.28	8.27	21.26	36.81	0.71	0.53	4.74	5.98
AG-2	24.14	12.89	21.99	59.02	4.76	0.81	1.09	6.66
AG-3	1.29	9.68	36.94	47.91	0.00	0.00	0.60	0.60
AG-4	0.00	3.76	13.98	17.74	0.00	0.00	0.00	0.00
AG-5	0.00	2.00	12.67	14.67	0.00	0.00	0.00	0.00
AG-6	4.75	10.23	28.87	43.85	0.09	0.49	0.00	0.58
AG-7	7.62	12.58	18.07	38.27	0.00	0.73	0.00	0.73
AG-10	1.32	4.96	13.22	19.50	0.00	0.00	0.00	0.00
AG-11	-	-	-	-	0.00	0.00	0.00	0.00
AG-13	3.52	4.02	23.12	30.66	8.69	4.57	14.82	28.08
AG-14	0.22	5.77	6.22	12.21	0.00	0.31	0.00	0.31
MEAN:	5.01	7.42	19.63	32.06	1.30	0.68	1.93	3.91

Continued ....

TABLE 3-3 Continued

Watershed	ΣDDT(mg/ha)				Dieldrin(mg/ha)			
	May-Aug	Sep-Dec	Jan-Apr	Total	May-Aug	Sep-Dec	Jan-Apr	Total
1976-77 (May- April)								
AG-1	0.98	0.00	14.17	15.15	0.20	0.00	2.07	2.27
AG-2	7.20	1.26	79.74	88.20	0.00	0.00	4.18	4.18
AG-3	5.16	1.94	27.26	34.36	0.00	0.00	1.26	1.26
AG-4	0.54	0.00	12.90	13.44	0.00	0.00	0.00	0.00
AG-5	2.33	0.33	16.33	18.99	0.00	0.00	0.17	0.17
AG-6	4.39	0.37	12.61	17.37	0.00	0.16	0.75	0.91
AG-7	9.39	0.71	7.44	17.54	0.00	0.00	0.00	0.00
AG-10	2.31	0.00	12.56	14.87	0.00	0.60	0.00	0.60
AG-11	0.00	0.00	2.94	2.94	0.00	0.00	0.00	0.00
AG-13	0.00	0.00	37.19	37.19	2.11	0.00	19.35	21.46
AG-14	2.89	2.44	14.88	20.21	0.00	0.00	0.00	0.00
MEAN:	3.20	0.64	21.64	25.48	0.21	0.07	2.52	2.80

TABLE 3-4 Residues of Pesticides and Pollutants found in stream bed sediment collected May 1976 - April 1977

Component	Content in Dried Sediment(ng/g)										
	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
DDE	3.0	4.0	1.0	0.8	0.5	0.9	0.5	0.9	0.5	5.0	0.3
TDE	0.3	2.0	0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	9.0	0.2
DDT	0.3	7.0	0.4	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	9.0	0.2
Σ DDT	3.6	13.0	1.7	1.0	0.7	1.1	0.7	1.1	0.7	23.0	0.5
Dieldrin	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	2.2	<0.2
Endosulfan	16.0 [3]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlordane	1.5	0.3	0.3	ND	ND	ND	ND	ND	ND	1.8	ND
Hept. Epoxide	ND	ND	ND	ND	ND	ND	ND	ND	0.4	ND	ND
PCB	4	4	8	6	4	6	<2	6	8	6	5
	Content in Dried Sediment(µg/g)										
2,4,5-T	ND	ND	ND	ND	3	4	14	ND	4	ND	6
Atrazine-April	ND	ND	ND	ND	ND	ND	ND	ND	15.8[1]	ND	ND
May-Oct	ND	ND	ND	20[2]	ND	72	ND	ND	ND	ND	72
Simazine	ND	ND	ND	ND	ND	ND	ND	ND	<1.0	ND	ND
2, 4-D	ND	ND	ND	ND	2	2	6	ND	4	ND	ND

[1] 15.8 - 7.6 µg/g atrazine and 8.2 µg/g desethylatrazine (April, 1977)

[2] Present as atrazine only (October)

[3] Endosulfan 16.0 ng/g (α-endosulfan 13 ng/g, β-endosulfan 2.2 ng/g, and endosulfan sulfate 0.8 ng/g)

TABLE 3-5 Contaminants found in rainwater collected between May to December 1975 in six agricultural watersheds

Component		Content in Rainwater(ng/L)						
		AG-1	AG-3	AG-4	AG-5	AG-10	AG-13	Mean
p,p'-DDT	May-June	4	ND	8	1	3	7	4
	June-July	3	2	11	2	7	4	5
	Aug-Sept	5	8	5	7	5	4	6
	Dec.	ND	13	4	NA[1]	19	16	10
Hept. Epox.	Dec.	<1	ND	7	NA[1]	ND	ND	1
PCB	May-June	60	40	10	50	20	30	35
	June-July	50	50	50	ND	80	60	48
	Aug-Sept	50	100	70	100	50	70	73
	Dec.	20	10	30	NA	80	90	46
Leptophos	May-June	1100	ND	ND	ND	ND	ND	

[1] NA - not analysed

To illustrate the effect of rainfall events on the mobility of DDT, on June 24, 1975, following a rainfall in AG-1, the stream flow increased from 0.09 to 16.75 m^3/sec, i.e. a rate increase of 186 times; the loss of ΣDDT, however, increased from 1 µg/hr to 965 µg/hr revealing a much greater increase in DDT mobilization than the rate increase on stream flow. While the DDE concentration in water rose from 3 ng/L to 8 ng/L during this flow event, both TDE and DDT were absent at the onset but increased with increasing flow rate to concentrations up to 3 ng/L TDE and 5 ng/L DDT at the crest of the event, suggesting that high stream flows increased both concentration and loading of EDDT (Appendix XII and Table 3-6). In three rainfall events in 1977, ΣDDT carried in stream water also increased as flow volume increased. During a declining high-flow event in AG-3 on December 15-16, 1975,Σ DDT losses were observed to decline also but wide fluctuations were noted (Table 3-6, Appendix XII.) During a high flow situation in AG-4 on September 11-12, 1975, DDT losses ranged from 2 ng/hr to 16 ng/hr (Table 3-6, Appendix XII.)

Water Quality

The I.J.C. (1977) has adopted a water quality criterion of 3 ng/L DDT for evaluation of the water quality of the Great Lakes boundary water. Applied to the 11 watersheds 40.6 of the water violated this criterion during the 2-year study period.

3.2.2 Methoxychlor and Dicofol

Neither methoxychlor nor dicofol were identified in water from the 11 watersheds over the 2-year period. The survey (Frank and Ripley, 1977) of agricultural uses of methoxychlor and dicofol revealed no use of methoxychlor in the 11 watersheds and only 36 kg dicofol used in AG-13 (Appendix I).

3.3 Organochloride Insecticides - Cyclodienes

The agricultural uses of aldrin, dieldrin and heptachlor were cancelled in 1969. Following these cancellations and the discontinuation of uses of DDT and TDE in 1972, an increase in the uses of the cyclodienes chlordane and endosulfan occurred. Recommendations for the use of endosulfan on tobacco were dropped in 1975 in order to reduce residues in cured tobacco (O.M.A.F. 1975-76). Chlordane uses were cancelled during the I.J.C. study period for all crops with the exception of corn and recommended uses on corn will be dropped in January, 1978. (Agriculture Canada, 1977)

3.3.1 Aldrin and Dieldrin

Presence in stream water: Aldrin was not identified in any of the 949 water samples analyzed, while dieldrin was found to be present in 20.7% of these samples. The annual mean residue of dieldrin ranged from non-detectable (<0.4 ng/L) in waters from AG-3,4,5,6,11 and 14, to a high mean residue of 8.0 ng/L in water from AG-13 during 1975-76 (Table 3-7, Appendix XIII); water samples from AG-13 also contained the highest single readings of dieldrin. Watershed AG-13 is associated with tobacco and vegetable production where aldrin found more extensive use for the control of soil insects.

The mean dieldrin residues for all 11 watersheds over the two-year period of May 1975 to April 1977 was 1.6 ng/L and showed little change between the first and second year of the study (Table

3-7); most water samples collected in 1976-77 showed slightly lower dieldrin residues than those collected in 1975-76 with the exception of AG-10, which exhibited an unexplainable increase. This increase was due, in large part, to a single sample with a level of 82 ng/L collected in September, 1976.

Annual losses of dieldrin by watershed ranged from 0 to 55.9 g in 1975-76 and 0 to 42.7 gin 1976-77 (Appendix XIV). Based on unit area loadings, these losses amounted to 0 to 28.08 mg/ha/yr in 1976-76 and 0 to 21.46 mg/ha/yr in 1976-77 (Table 3-3). The highest losses were observed in AG-13 where extensive past use of aldrin had occurred. The second highest losses of dieldrin were found in AG-2 where, again, aldrin had been used for the control of cutworm in tobacco (Harris et al, 1962).

Sources of Dieldrin

The source of dieldrin in water is largely from the soil which acts as a reservoir for storage of residues from past uses. Frank *et al* (1976, 1977), Harris and Miles (1975), and Harris *et al* (1977) have reported on current levels of dieldrin in Ontario agricultural soils; dieldrin residues are present in most soils of those watersheds producing tobacco and vegetables and are virtually absent from other soils, thus explaining the incidence of dieldrin in the stream waters of the 11 watersheds.

Dieldrin was also present in stream bed sediments which acts as another source of water contamination. Sediment analysis revealed that dieldrin was present only in AG-13 at a concentration of 2.2 ng/g (Table 3-4). Frank *et al* (1974 a,b) and Miles and Harris (1971,1973), Miles (1976) and Miles *et al* (1976) have documented dieldrin levels in sediments of streams, rivers and lakes in Ontario. Dieldrin was not identified in rainwater collected in six of the eleven watersheds in 1975 (Table 3-5).

Entry into Water

Dieldrin levels in water can also be correlated with runoff events which result in high soil particle mobility. During the January to April period of each year, a period when 55% and 68% of the total flow volume occurred, 49.4% and 90.0% of the total annual losses of dieldrin occurred (Appendix XIII and XIV).

In two rainfall events in 1977, dieldrin was carried in stream water. Dieldrin increased in both concentration and unit loading as the stream flow increased in volume (Table 3-6, Appendix XII). In the first event actual water concentrations in AG-13 were 7 ng/L but rose to 20-25 ng/L at the peak runoff. This was reflected in higher amounts of dieldrin carried downstream. In the second event, the concentrations remained constant over the runoff event and losses declined following the peak flow.

TABLE 3-6 Rates of loss of contaminants during the sampling of six stream flow events, 1975-1977.

Watershed Flow (m^3/sec)	Date & Time	Losses to Water (µg/hr)									
		Insecticides					Industrials	Herbicides			
		∑DDT	DLD	DIA	ENDO	HE	PCB	2,4-D	2,4,5-T	ATR	deA
AG-1	24 June '75										
0.09	1130	1	-	-	-	-	16	162	97	907	23
1.31	1600	28	-	-	-	-	471	3301	1414	193,828	330
16.75	1725	965	-	-	-	-	6030	253,260	42,210	560,790	102,510
AC-3	15-18 Dec.'75										
4.61	2330	763	-	-	-	-	498	-	-	29,873	26,554
4.44	0030	48	-	-	-	-	160	-	-	23,976	22,378
4.25	0130	61	-	-	-	-	459	-	-	19,890	18,360
3.96	0330	100	-	-	-	-	428	-	-	18,533	15,682
3.23	0930	290	-	-	-	-	1047	-	-	10,465	10,465
AG-4	11-12 Sep.'75										
0.00	1020	0	-	-	-	-	0	-	-	0	0
0.07	2330	2	-	-	-	-	8	-	-	25	50
0.08	0020	2	-	-	-	-	12	-	-	58	29
0.12	0120	4	-	-	-	-	22	-	-	43	43
0.18	0150	5	-	-	-	-	32	-	-	130	65
0.27	0250	16	-	-	-	-	39	-	-	486	292
0.25	0400	6	-	-	-	-	36	-	-	630	360
0.27	0530	16	-	-	-	-	47	-	-	1166	583
0.25	0700	10	-	-	-	-	36	-	-	1170	540
0.23	0830	13	-	-	-	-	38	-	-	580	497
0.21	1050	5	-	-	-	-	30	-	-	529	454
0.22	1300	12	-	-	3	-	32	-	-	396	475
0.22	1410	10	-	-	-	-	32	-	-	396	317

Continued .....

TABLE 3-6 Continued

Water Shed Flow (m^3/sec)	Date 8 Time	Losses to Water (µg/hr)									
		Insecticides					Industrials	Herbicides			
		∑ DDT	DID	DIA	ENDO	HE	PCB	2,4-D	2,4,5-T	ATR	deA
AG-6	Mar.21/77										
1.18	1200	29.7	-	-	-	-	84.9	-	-	290	290
1.18	1430	51.0	-	-	-	-	140.2	-	-	290	290
1.18	1630	63.7	-	-	-	-	68.0	-	-	290	290
AG-13	Feb.24/77										
2.54	0930	841	64	840	18.3	-	411	-	-	4572	640
4.39	1340	853	395	12,485	632	-	1580	-	-	7902	1106
6.08	1605	1094	438	13,571	394	-	2189	-	-	8755	1532
4.39	1900	1280	300	11,853	443	-	1422	-	-	6322	1106
	Feb.25/77										
1.81	1010	176	91.2	4,235	143	-	130	-	-	2606	456
AG-13	Mar.4/77										
2.17	1440	1687	297	2,890	391	-	547	-	-	LOST	
3.96	1805	3079	442	4,704	570	28.5	1996	-	-	7128	1426
7.08	2105	5811	790	11,215	1172	102.	3823	-	-	12,744	2549
	Mar.5/77										
0.65	1405	136	35.1	351	44.5	4.7	70.2	-	-	1170	164

DLD - dieldrin
DIA - diazinon
ENDO - endosulfan
HE - heptachlor epoxide
ATR - atrazine
deA - desethylatrazine

TABLE 3-7 The frequency and concentration of dieldrin in water collected from 11 agricultural watersheds between May 1975 and April 1977

Watershed	Period May-Apr.	Analysis (#)	Frequency and Content in Stream Water (ng/L) Not Det. (<0.4)	Trace (0.4-0.9)	Low (1.0-10.0)	Medium (11-100)	High (100+)	Mean	Range	SD
AG-1	1975-76	61	41	10	8	2	0	1.5	ND-32	11.
	1976-77	54	43	4	7	0	0	0.5	ND-4	1.6
AG-2	1975-76	29	19	3	6	1	0	2.7	ND-63	23.
	1976-77	34	29	1	4	0	0	0.5	ND-5	1.9
AG-3	1975-76	52	49	2	1	0	0	<0.4	ND-4	-
	1976-77	61	59	2	0	0	0	<0.4	ND-0.9	-
AG-4	1975-76	34	34	0	0	0	0	<0.4	ND	-
	1976-77	43	42	1	0	0	0	<0.4	ND-0.9	-
AG-5	1975-76	55	49	2	4	0	0	<0.4	ND-1	-
	1976-77	56	54	0	2	0	0	<0.4	ND-5	-
AG-6	1975-76	58	54	2	2	0	0	<0.4	ND-4	-
	1976-77	41	39	0	2	0	0	<0.4	ND-4	-
AG-7	1975-76	28	24	1	3	0	0	0.6	ND-9	3.4
	1976-77	19	18	0	1	0	0	<0.4	ND-1	-
AG-10	1975-76	24	22	2	0	0	0	<0.4	ND-0.9	-
	1976-77	37	34	1	0	2	0	2.7	ND-82	27.
AG-11	1975-76	18	18	0	0	0	0	<0.4	ND	-
	1976-77	5	5	0	0	0	0	<0.4	ND	-
AG-13	1975-76	62	16	3	28	14	1	8.0	ND-120	31.
	1976-77	87	18	2	43	24	0	6.8	ND-33	14.
AG-14	1975-76	48	45	2	1	0	0	<0.4	ND-1	-
	1976-77	43	41	1	1	0	0	<0.4	ND-1	-
TOTAL	1975-76	469	371	27	53	17	1	1.6	ND-120	14.
	1976-77	480	382	12	60	26	0	1.7	ND-82	11.
GRAND TOTAL: 1975-77		949	753	39	113	43	1	1.6	ND-120	12.

Water Quality

The I.J.C. (1977) has adopted a water quality objective for dieldrin of 1 ng/L. Of the water samples analysed over the two year period, 16.0% contained residues higher than the adopted objective with most of these samples originating from AG-13.

3.3.2 Chlordane and Heptachlor Epoxide

Chlordane consists of a mixture of insecticidally active components the cis and trans isomers constitute approximately 25-30% of technical chlordane, heptachlor is present to an extent of about 10-11%, and the remainder includes components such as chlordene and nonachlor (NRCC, 1974). Heptachlor *per se* was never widely used in Ontario (Frank *et al,* 1970) and its use was cancelled in 1969 by Order in Council in the Ontario legislature. Reported residues of heptachlor epoxide (HE), the major metabolite of heptachlor, are therefore assumed to originate from the heptachlor present in technical chlordane, rather than from past uses of heptachlor itself.

Presence in Water

The cis and trans isomers of chlordane were detected in 1.6% of the water samples from the 11 watersheds and heptachlor epoxide was detected in 5.2% of the samples (Table 3-8). Residues of cis and trans chlordane were low and, when found, were present in approximately equal concentrations. Chlordane was not detected in the 1975-76 sampling period but was found in the 1976-77 period in water collected in the months of June, July and August (Appendix XV and XVI). The mean residue of chlordane for all watersheds was below the level of detection (<0.4 ng/L) (Table 3-8). Only 1.3% of water samples had residues between 1 and 10 ng/L and only 0.2% contained above 10 ng/L. Oxychlordane was not detected in any samples.

Heptachlor epoxide (HE) was found in 5.2% of the samples with a mean residue for all 11 watersheds over the two-year period of 0.8 ng/L (Table 3-8, Appendix XV). HE was not detected in four of the watershed and only rarely in six other watersheds and all had mean residues below the detection limit of 0.4 ng/ L. Measurable mean residues of HE were found only in AG-13 at levels of 7.6 ng/L in 1975-76 and 2.9 ng/L in 1976-77. During the two-year period, HE was present in 25% of the samples from AG-13 indicating the past or present use of heptachlor and/or chlordane. According to Frank and Ripley (1977) neither chlordane nor heptachlor was used in AG-13 in 1975 and 1976. The highest level of HE found was 370 ng/L in a water sample collected on June 6, 1975, suggesting that heptachlor was being used at that time somewhere in the watershed. This was the only occasion on which the level of HE exceeded 100 ng/L in the two years of the study.

Total losses of chlordane per year ranged from 0 to 4g for individual watersheds in 1976-77 (Appendix XVI). Losses of HE ranged from 0 to 9 g/year in 1975-76 and 0 to 27 g/year in 1976-77. Unit area loadings for HE and chlordane ranged from 0 in AG-1,3,4,6,7,10,11 and 14 to 4.5 mg/ha/yr in AG-13 during 1975-76 and from 0 in AG-2,3,4,7,10 and 11 to 4.5 mg/ha/yr in AG-13 during 1976-77 (Table 3-9).

Source of Residues

Residues of chlordane and heptachlor epoxide in stream water are derived from past and/or present use of heptachlor and chlordane. According to the farm-to-farm survey (Frank and Ripley, 1977) chlordane was used for corn rootworm control only in AG-3 where 383 kg were applied on 256 ha of corn (Appendix I). No chlordane or HE, however, was detected in the stream waters of AG-3; in fact, no chlordane was detected in water from any watershed in 1975-76 which suggests that use may have been more widespread in 1976-77 than 1975-76. Chlordane is still used extensively for the control of white grubs on lawns and turf on residential properties, which may account for some of the presence of chlordane and HE in water. Frank *et al* (1976, 1977) and Harris *et al* (1975, 1977) have reported that current levels of chlordane and HE in agricultural soils in Ontario are well below 0.5 µg/g and hence the soil may act only as a minor reservoir or source of chlordane and HE in water.

Stream bed sediment may also act as a minor source of chlordane and HE. Chlordane was detected in the sediments of four watersheds (AG-1,2,3 and 13) at levels ranging from 0.3 to 1.8 µg/g (Table 3-4). HE was detected in the stream bed sediment of only AG-13 at a level of 0.4 µg/g. Low levels of chlordane have been detected in some Ontario streams by Harris and Miles (1975).

A third source of chlordane and HE may be the atmosphere. Although chlordane was not detected in any rainwater, HE was found in rain samples collected from two of five watersheds (Table 3-5). The highest concentration occurred in rainwater collected in AG-1, an area which has little or no use for chlordane on corn; furthermore, this sample was collected in December, 1975, during a period when no outside use would occur. HE was not detected in rainwater collected during the normal spray period of May to September.

Entry into Water

Chlordane was not detected in any of the six rainfall events while He was present in only one. This occurred in AG-13 on 4-5 March 1977. Heptachlor epoxide was absent in the early flow period but appeared as the flow volume peaked between 1805 and 2105 hr and reached the highest concentration during the highest flow (Table 3-6 and Appendix XII).

All chlordane entering water appeared to be lost in the May-August period and none was detected at other times, suggesting loss was closely associated with use. In the case of HE, however, losses occurred year round
in the following periods.

	Losses	g(%)
Hept.Epoxide	1975-76	1976-77
May-Aug.	8 (33)	3 (6)
Sep-Dec.	1 (4)	27 (50)
Jan-Apr.	15 (63)	24 (44)
Total:	24	54

(Appendix XVI)

TABLE 3-8: Frequency & concentration of chlordane and heptachlor epoxide in water collected from 11 agricultural watersheds between May 1975 and April 1977

Watershed	Period May-Apr.	Analysis (#)	Frequency & concentration in Stream Water (ng/L)							SD
			Not Det.	Trace (<0.9)	Low (1.0-10)	Medium (11-100)	High (100+)	Mean	Range	
Chlordane										
AG-1	1975-77	115	114	0	1	0	0	<0.4	ND-4	-
AG-2	"	63	62	0	1	0	0	<0.4	ND-4	-
AG-3	"	113	111	0	1	1	0	<0.4	ND-11	-
AG-4	"	77	76	0	1	0	0	<0.4	ND-4	-
AG-5	"	111	107	0	3	1	0	<0.4	ND-47	9.0
AG-6	"	99	98	0	1	0	0	<0.4	ND-4	-
AG-7	"	47	47	0	0	0	0	ND	ND	-
AG-10	"	61	60	0	1	0	0	<0.4	ND-4	-
AG-11	"	23	23	0	0	0	0	ND	ND	-
AG-13	"	149	146	0	3	0	0	<0.4	ND-10	-
AG-14	"	91	90	0	1	0	0	<0.4	ND-4	-
TOTAL	1975-77	949	934	0	13	2	0	<0.4	ND-47	-
Heptachlor Epoxide										
AG-1	1975-77	115	108	3	4	0	0	<0.4	ND-2	-
AG-2	"	63	59	2	1	1	0	<0.4	ND-23	-
AG-3	"	113	111	2	0	0	0	<0.4	ND-0.7	-
AG-4	“	77	77	0	0	0	0	ND	ND	-
AG-5	"	111	107	0	3	1	0	<0.4	ND-15	-
AG-6	"	99	99	0	0	0	0	ND	ND	-
AG-7	"	47	47	0	0	0	0	ND	ND	-
AG-10	"	61	59	1	1	0	0	<0.4	ND-2	-
AG-11	"	23	22	0	1	0	0	<0.4	ND-1	-
AG-13	1975-76	62	55	0	3	3	1	7.6	ND-370	94
	1976-77	87	57	1	20	9	0	2.9	ND-25	12
AG-14	1975-77	91	91	0	0	0	0	ND	ND	-
TOTAL	1975-77	949	892	9	33	14	1	0.8	ND-370	24

TABLE 3-9 Unit area loadings of chlordane plus heptachlor epoxide and total endosulfan in 11 agricultural watersheds from May 1975 to April 1977

	Chlordane & Heptachlor Epoxide (mg/ha)				Σ-Endosulfan (mg/ha)			
Watershed	May-Aug	Sep-Dec	Jan-Apr	Total	May Aug	Sep-Dec	Jan-Apr	Total
<u>1975-76 (May-April)</u>								
AG-1	0.0	0.0	0.0	0.0	0.1	2.7	6.0	8.8
AG-2	0.0	0.0	1.0	1.0	1.1	4.0	10.0	15.1
AG-3	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.4
AG-4	0.0	0.0	0.0	0.0	0.0	0.0	3.1	3.1
AG-5	0.0	0.0	2.3	2.3	0.0	0.0	4.6	4.6
AG-6	0.0	0.0	0.0	0.0	3.4	1.4	9.4	14.2
AG-7	0.0	0.0	0.0	0.0	0.0	4.2	0.0	4.2
AG-10	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.7
AG-il	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.8
AG-13	4.0	0.5	0.0	4.5	37.9	15.1	36.9	89.9
AG-14	0.0	0.0	0.0	0.0	0.0	0.0	5.2	5.2
MEAN	0.4	0.0	0.3	0.7	3.9	2.6	6.9	13.4
<u>1976-77 (May to April)</u>								
AG-1	0.0	0.0	3.5	3.5	0.3	0.0	0.6	0.9
AG-2	0.4	3.4	0.0	3.8	2.0	0.0	0.5	2.5
AG-3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AG-4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AG-5	0.3	0.0	0.0	0.3	0.0	0.0	0.4	0.4
AG-6	0.7	0.0	0.0	0.7	0.0	0.1	0.0	0.1
AG-7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AG-10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AG-11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AG-13	1.5	0.0	3.0	4.5	8.8	0.8	18.1	27.7
AG-14	0.9	0.0	0.0	0.9	0.0	0.0	0.0	0.0
MEAN	0.3	0.3	0.6	1.2	1.0	0.1	1.8	2.9

Water Quality

A water quality objective of 60 ng/L and 1 ng/L for chlordane and heptachlor epoxide, respectively, has been adopted by the I.J.C. (1977). During the two-year sampling period from May 1975 to April 1977, no samples of water contained chlordane above the adopted standard but 4.8% of samples contained HE which exceeded the adopted standard. Use of chlordane on corn was deleted as of January 1, 1978 (Agriculture Canada, 1977).

3.3.3 Total Endosulfan

Presence in Water

Endosulfan as formulated is a mixture of cis and trans isomers in an approximate ratio of 7:3. The insecticide is applied for the control of foliar insects on tobacco, fruits and vegetables. It oxidizes rapidly to the sulfate metabolite on plant tissues and in water it is converted into either the diol or sulfate, depending upon the pH (NRCC, 1975). The frequency of endosulfan found in the water samples from the 11 agricultural watersheds was:

α - endosulfan - 9.5%
β- endosulfan - 17.8%
endosulfan sulfate - 17.7%
total endosulfan - 19.2%

Endosulfan diol was not detectable by the screening procedure used in the analysis. The mean annual residues of endosulfan in water for all 11 watersheds was 3.7 and 2.9 ng/L for 1975-76 and 1976-77, respectively (Table 3-10, Appendix XVII); all watersheds exhibited lower residues in 1976-77 than in 1975-76 although the decline in water from AG-13 was only slight. Annual mean residues in water ranged from <0.4 ng/L in AG-3,4,10 and 11 to 16 ng/L in AG-13 in 1975-76 and from non-detectable in AG-7 and 11 to 15 ng/L in AG-13 in 1976-77. AG-13 consistently exhibited the highest residues in water reflecting the use of endosulfan in the production of tobacco, fruits and vegetables (Frank and Ripley, 1977).

Annual losses of total endosulfan ranged from 1.8 g in AG-11 to 178.9 g in AG-13 during 1975-76 and from 0 in AG-4,7,11 and 14 to 55.2 g in AG-13 during 1976-77 (Appendix XVIII). This represented unit area loadings that ranged from 0.4 mg/ha/yr in AG-3 to 89.9 mg/ha/yr in AG-13 in 1975-76. These losses declined in 1976-77 with a range from 0 mg/ha/yr in AG-3,4,7, 10,11 and 14 to 27.7 mg/ha/yr in AG-13 (Table 3-9).

Sources of Endosulfan and Entry into Stream Water

The highest endosulfan losses occurred in AG-2 and AG-13 watersheds in which the insecticide is used to control foliar insects on tobacco and vegetables. The incidence of endosulfan in the remaining watersheds cannot be completely explained since there is little or no documented use of the compound in these areas (Frank and Ripley, 1977); it may be explained in part as originating from small uses around residential homes and gardens (properties of less than 4.5 ha were not included in the use survey); endosulfan residues in water from AG-3 and AG-6 appeared mainly during the appropriate spray season. Most other losses, however, occurred at times of the year when there would be no active use. To elucidate the possible sources, the sampling period was divided into sub-periods of May-August, September-December, and January April and then further divided into periods associated with storm runoff events, spills and/or spray drifts. The remaining losses were considered to originate mainly from the drainage in base flow (Table 3-11). In 1975-76 the major losses (83.4%) were associated with erosion and surface runoff of water. Only 1.8% entered the streams via tile drainage and the remaining 14.8% was presumably lost as the result of spills, spray drift and carelessness around water (Table 3-11, Appendix XIX). In 1976-77 losses associated with runoff and erosion amounted to 54.6 g total endosulfan or 66.8% of the total loss; spills and spray drift accounted for 21.2% of the losses, while the drainage losses were 12.0%. These losses were measured throughout the whole year and were not confined to the spray period.

Endosulfan losses consisted of 5-18% of the α isomer, 25-28% of the β isomer, and 54-70% as endosulfan sulfate (Table 3-11, Appendix XIX). Endosulfan residues have been identified as persisting from one season to the next in soils used for the production of fruit, vegetables and tobacco in Ontario (Frank et al, 1976, 1977 and Harris et al, 1977).

Endosulfan in stream bed sediment was detected in only one watershed (AG-1) and amounted to 16.1 ng/g (Table 3-4); since 80% of this residue consisted of the cis isomer, a recent endosulfan spill at the test site was indicated. Endosulfan was not detected in stream sediments of the remaining 10 watersheds although Miles and Harris (1971, 1973) have reported its presence in several stream sediments in the vicinity of known use areas. Endosulfan could not be detected in any rainwater samples collected in 1975 (Table 3-5).

Endosulfan appeared in the waters of AG-13 on two occasions in February and March 1977, when high flow events were being sampled (Table 3-6 and Appendix XII). Concentrations in water fluctuated considerably over the period of the two events as did the amounts carried in the stream. In only one event did the peak load coincide with the peak flow volume. In both cases, however, the amount carried declined as the flow volume declined towards base line flow.

Water Quality

Endosulfan is acutely toxic to fish as a direct toxicant (NRCC 1975). *As* a result, the I.J.C. water quality objective (1977) for endosulfan is set low at 3 ng/L. Over the two year study period 14.1% of the water samples exceeded the objective; these higher readings were confined mainly to AG-1, 5 and 13. The use of endosulfan on tobacco is likely to decline since it was dropped

TABLE 3-10 Frequency and concentrations of total endosulfan in water collected from 11 agricultural watersheds between May 1975 and April 1977

Watershed	Period (May-Apr)	Analysis (#)	Frequency of ∑Endosulfan in water (ng/L)					Mean	Range	SD
			Not Det. (<0.4)	Trace (0.4- 0.9)	Low (1.0- 10.0)	Medium (11-100)	High (101+)			
AG-1	1975-76	61	42	0	17	2	0	2.7	ND-41	12.3
	1976-77	54	45	2	7	0	0	0.5	ND-9	2.5
AG-2	1975-76	29	21	0	5	3	0	2.2	ND-17	9.6
	1976-77	34	30	0	3	1	0	1.0	ND-17	6.5
AG-3	1975-76	52	46	2	4	0	0	<0.4	ND-6	1.7
	1976-77	61	60	0	1	0	0	<0.4	ND-8	2.0
AG-4	1975-76	34	33	0	1	0	0	<0.4	ND-6	2.0
	1976-77	43	41	1	1	0	0	<0.4	ND-4	0.4
AG-5	1975-76	55	50	0	5	0	0	0.5	ND-6	2.6
	1976-77	56	54	1	1	0	0	<0.4	ND-6	1.6
AG-6	1975-76	58	51	0	5	0	2	5.5	ND-173	52.
	1976-77	41	39	1	1	0	0	<0.4	ND-2	0.6
AG-7	1975-76	28	27	0	0	0	1	4.8	ND-128	49.
	1976-77	19	19	0	0	0	0	ND	ND	-
AG-10	1975-76	24	22	0	2	0	0	<0.4	ND-4	1.6
	1976-77	37	35	0	2	0	0	<0.4	ND-3	1.1
AG-11	1975-76	18	17	0	1	0	0	<0.4	ND-4	2.1
	1976-77	5	5	0	0	0	0	ND	ND	-
AG-13	1975-76	62	22	1	9	30	0	16.	ND-100	38.
	1976-77	87	22	3	18	44	0	15.	ND-52	29.
AG-14	1975-76	48	44	1	2	1	0	0.5	ND-11	3.9
	1976-77	43	41	2	0	0	0	<0.4	ND-0.7	0.3
TOTAL	1975-76	469	375	4	51	36	3	3.7	ND-173	28.
	1976-77	480	391	10	34	45	0	2.9	ND-52	17.
GRAND TOTAL	1975-77	949	766	14	85	81	3	3.3	ND-173	23.

TABLE 3-11 Losses to water of Σ-endosulfan and its components from 11 agricultural watersheds (47072 ha) from May 1975 to April 1977

Item	Losses of Σ Endosulfan & Components (g)				
	May-Aug	Sep-Dec	Jan-Apr	Total	º%
1975-76 Σ endosulfan					
Storm runoff	84.8	47.7	279.2	411.7	83.3
Base flow	0.0	7.5	1.2	8.7	1.8
Spill and Drift	19.8	53.7	0.0	73.5	14.9
Total	104.6	108.9	280.4	493.9	
1976-77 Σ endosulfan					
Storm runoff	10.8	2.4	41.4	54.6	66.8
Base flow	6.7	0.3	2.8	9.8	12.0
Spill and Drift	17.3	0.0	0.0	17.3	21.2
Total	34.8	2.7	44.2	81.7	
1975-76 Components					
α endosulfan	5.2	12.1	72.8	90.1	18.2
β endosulfan	17.8	23.3	97.5	138.6	28.1
endosulfan sulfate	81.6	73.5	110.1	265.2	53.7
Σ endosulfan	104.6	108.9	280.4	493.9	
1976-77 Components					
α endosulfan	4.1	0.0	0.0	4.1	5.0
β endosulfan	8.4	1.2	10.5	20.1	24.6
endosulfan sulfate	22.4	1.5	33.7	57.6	70.4
Σ endosulfan	34.9	2.7	44.2	81.8	

from the recommended list in 1975 for hornworm control because of unacceptably high residue levels in cured tobacco leaf (O.M.A.F. 1975-76).

3.3.4 Other Cyclodienes

Throughout the course of the two-year study, no residue of endrin could be identified in stream water, stream sediments or rainwater (detection limit of 1 ng/L in water, 1 ng/g in sediment). Endrin is not recorded as having been applied in any of the 11 watersheds in 1975 to 1977 (Frank and Ripley, 1977).

3.4 Organochlorine Herbicides - Chlorophenoxy and Benzoic Acids

Ten herbicides belonging to this group were in use in the 11 agricultural watersheds (Appendix II) of which seven were included in the analytical screening methodology (Table 2-1), i.e. three compounds in use were not detectable by the screening method employed. Four herbicides belonging to this group were identified in water samples.

3.4.1 2,4-D

Uses of 2,4-D and Presence in Stream Water

2,4-D is used for the control of weeds in corn and cereal crops and along public rights-of-way. Of the 949 water samples collected from the 11 watersheds over the two-year study period, 66 or 7.0% were found to contain 2,4-D (Table 3-12). Only two samples contained residues above 10 µg/L; the highest residue found was 320 µg/L in a sample collected in July, 1975 from AG-13 at a time when the ditch bank, located upstream from the sampling station, was being sprayed with 2,4-D; the second highest level was found in June 1975 in water from AG-1. This water sample contained 15.9 µg/L which was also derived from a stream bank spraying (Appendix XX).

Over the two-year study period, only AG-1 and AG-13 were found to contain mean residue levels of 0.1 µg/L or higher; no 2,4-D residues were found in AG-11 and the remaining watersheds contained mean levels between ND and 0.1 µg/L; the higher mean levels in AG-1 and AG-13 were the result of the two high readings mentioned above. The mean annual concentrations for the two-year period for all 11 watersheds was 0.4 µg/L.

Annual losses of 2,4-D from the combined 11 agricultural watersheds amounted to 4.54 kg in 1975-76 and 2.22 kg in 1976-77 (Table 3-13, Appendix XXI); this loss represented 0.15% and 0.07%,respectively, of the total volume of 2,4-D used in the watersheds. The major losses in 1975-76 occurred as the result of ditch bank spraying and from spraying rights-of-way; only minor losses are associated with agricultural uses. In 1976-77 the losses from agricultural and non-agricultural uses were about equal (Table 3-13). Unit area loadings for 2,4-D ranged from 0 to 553 mg/ha/yr in 1975-76 and from 0 to 134 mg/ha/yr in 1976-77 (Table 3-14); the highest unit area losses again were in AG-1 and AG-13, primarily as the result of ditch bank spraying

TABLE 3-12 Frequency and concentration of chlorophenoxy and chlorobenzoic acid herbicides in water collected from 11 agricultural watersheds between May 1975 and April 1977

Watershed	Period (May-Apr)	Analysis (#)	Frequency and content in water (µg/L)					Range	SD
			Not Det.	Low (0.1- 1.0)	Medium (1.1- 10.0)	High (10.1+)	Mean		
2,4-D									
AG-1	1975-76	61	52	6	2	1	0.3	ND-15.9	4.1
	1976-77	54	45	8	1	0	0.1	ND-3.9	1.1
AG-2	1975-76	29	28	1	0	0	<0.1	ND-0.3	-
	1976-77	34	30	3	1	0	<0.1	ND-1.1	-
AG-3	1975-76	52	46	6	0	0	<0.1	ND-0.7	-
	1976-77	61	60	1	0	0	<0.1	ND-0.3	-
AG-4	1975-76	34	31	3	0	0	<0.1	ND-0.8	-
	1976-77	43	41	2	0	0	<0.1	ND-0.8	-
AG-5	1975-76	55	50	5	0	0	<0.1	ND-0.3	-
	1976-77	56	54	2	0	0	<0.1	ND-0.3	-
AG-6	1975-76	58	54	4	0	0	<0.1	ND--0.8	-
	1976-77	41	39	0	2	0	<0.1	ND-2.1	-
AG-7	1975-76	28	26	2	0	0	<0.1	ND-0.3	-
	1976-77	19	17	2	0	0	<0.1	ND-0.4	-
AG-10	1975-76	24	23	1	0	0	<0.1	ND-0.3	-
	1976-77	37	37	0	0	0	ND	ND	-
AG-11	1975-77	23	23	0	0	0	ND	ND	-
AG-13	1975-76	62	55	6	0	1	5.2	ND-320.	81.
	1976-77	87	83	4	0	0	<0.1	ND-0.6	-
AG-14	1975-76	48	48	0	0	0	ND	ND	-
	1976-77	43	41	2	0	0	<0.1	ND-0.8	-
TOTAL	1975-76	469	431	34	2	2	0.7	ND-320.	29.
	1976-77	480	452	24	4	0	<0.1	ND-3.9	0.5
GRAND TOTAL	1975-77	949	883	58	6	2	0.4	ND-320.	20.

Continued ....

TABLE 3-12 Continued

Watershed	Period (May-Apr)	Analysis (#)	Frequency and content in water (µg/L)					Range	SD
			Not Det.	Low (0.1- 1.0)	Medium (1.1- 10.0)	High (10.1+)	Mean		
2,4,5-T									
AG-1	1975-76	61	55	5	1	0	< 0.1	ND-l.1	-
	1976-77	54	50	4	0	0	< 0.1	ND-0.8	-
AG-3	1975-77	113	111	2	0	0	<0.1	ND-0.3	-
AG-4	1975-77	77	76	1	0	0	<0.1	ND-0.8	-
AG-7	1975-77	47	46	1	0	0	<0.1	ND-0.3	-
AG-10	1975-77	61	60	1	0	0	<0.1	ND-0.3	-
AG-13	1975-77	149	143	6	0	0	<0.1	ND-0.3	-
AG-2, 5, 6, 11, 14		387	387	0	0	0	ND	ND	-
TOTAL	1975-77	949	928	20	1	0	<0.1	ND-1.1	-
MCPA									
AG-4	1975-77	77	75	2	0	0	<0.1	ND-0.3	-
AG-6	1975-77	99	98	1	0	0	< 0.1	ND-0.3	-
AG-13	1975-77	149	148	1	0	0	<0.1	ND-0.3	-
AG-14	1975-77	91	89	2	0	0	<0.1	ND-0.3	-
AG-1, 2, 3, 5, 7, 10, 11		533	533	0	0	0	ND	ND	-
TOTAL	1975-77	949	943	6	0	0	<0.1	ND-0.3	-
dicamba									
AG-13	1975-77	149	148	1	0	0	<0.1	ND-0.7	-
AG-1, 2, 3, 4, 5, 6, 7, 10, 11, 14		800	800	0	0	0	ND	ND	-
TOTAL	1975-77	949	948	1	0	0	<.0.1	ND-0.7	-

AG-13: One sample contained 320 µg/L and was associated with the spraying of the stream bank.

TABLE 3-13 Uses and losses of 2,4-D, 2,4,5-T, MCPA and dicamba in 11 agricultural watersheds between May 1975 and April 1977

Uses & Losses		Ditchbanks & rights-of-way		Farm Crops		Total	
		(kg)	(%)	(kg)	(%)	(kg)	(%)
2,4-D							
Amount applied (1975)		791	25.5	2307	74.5	3098	100
Amount lost	May-Aug	3.732	82.2	0.342	7.5	4.074	89.7
(1975-76)	Sep-Dec	0.200	4.4	0.265	5.9	0.465	10.3
	Total	3.932	86.6	0.607	13.4	4.539	
	lost/used (%)	0.50		0.03		0.15	
Amount lost	May-Aug	1.181	53.2	0.766	34.5	1.947	87.7
(1976-77)	Sep-Dec	0.016	0.7	0.257	11.6	0.273	12.3
	Total	1.197	53.9	1.023	46.1	2.220	
	lost/used (%)	0.15		0.04		0.07	
2,4,5-T							
Amount applied	(1975)	277	99.3	2	0.7	279	100
Amount lost	May-Aug	1.36	100	0	0	1.36	100
(1975-76)	lost/used (%)	0.49		0.00		0.49	
(1976-77)	May-Aug	0.321	100	0	0	0.321	100
	lost/used (%)	0.12		0.00		0.12	
MCPA							
Amount applied	(1975)	0	0	697	100	697	100
Amount lost	May-Aug	0	0	0.268	84.3	0.268	84.3
(1975-76)	Sep-Dec	0	0	0.050	15.7	0.050	15.7
	Total	0	0	0.318	100	0.318	100
	lost/used (%)			0.05		0.05	
Amount Lost	1976-77	0	0	0	0	0	0
Dicamba	(1975)						
Amount applied		?		58	100	58	100
Amount lost	1975	0.025	100	0	0	0.025	100

as previously mentioned. In 1976-77 the highest unit areas losses were in AG-4 and AG-6; losses from AG-4 resulted mainly from runoff events from treated fields while losses from AG-6 resulted from rights-of-way application.

Sources of 2,4-D

The presence of 2,4-D in stream water appeared to be closely correlated to the spray activities in the watershed. The herbicide is used for weed control on corn in only two watersheds, namely, AG-1 and AG-3, where 33% and 15%, respectively, of the corn hectarage was sprayed (Frank and Ripley, 1977). Between 1.9% and 85.5% (mean 40.9%) of the total cereal hectarage in all watersheds except AG-13 was treated with 2,4-D at a rate of 0.5 kg/ha. Roadside rights-of-way in 10 of 11 watersheds were treated; 24-D was used alone in one watershed and in combination with 2,4,5-T in the other nine watersheds (Appendix II); many roadsides followed ditches and streams with the result that watercourses were subjected to 2,4-D and/or 2,4,5-T by over-spray or drift. In AG-3 and AG-6 parts of the roadside received 2,4-D application at 2.5 kg/ha and other roadsides received a combination 2,4-D/2,4,5-T treatment at 0.9 to 1.7 kg/ha. Of the total nonagricultural land, 15.4% (490.3 ha) was sprayed with 2,4-D or 2,4-D/2,4,5-T combination (Frank and Ripley, 1977).

Entry into Water

In 1975 86.6% of the 2,4-D residue in water originated from non agricultural use while in 1976 the figure was 53.9% (Table 3-13). Entry into water appeared to be the result of the following practices and runoff events:

A) Non-Agricultural Uses
- spraying of dried-up ditch followed by heavy rain, e.g. AG-1
- spraying of ditch bank with overspray into stream water e.g. AG-13
- spraying of ditch bank followed by heavy rains and runoffs, e.g. AG-1 and AG-3
- spraying of ditch bank and roadside with drift into stream water, e.g. AG-7 and AG-10
- spill of 2,4-D on stream banks or into stream water e.g. AG-1

B) Agricultural Uses
- spray drift from cereal crop treatment, e.g. AG-4 and AG-5
- runoff water carrying 2,4-D from fields, e.g. AG-2
- spills of 2,4-D on stream banks and water, e.g. AG-1

No losses of 2,4-D were observed in the January to April period; major losses occurred from May to August, i.e. 89.7% in 1975 and 87.7% in 1976 during the period when the major part of crop and rights-of-way treatments occur; minor losses, 10.3% in 1975 and 12.3% in

TABLE 3-14 Unit area loadings of 2,4-D, 2,4,5-T, MCPA and dicamba in 11 agricultural watersheds between May 1975 and April 1977

Watershed	2,4-D (mg/ha)			2,4,5-T (mg/ha)	MCPA (mg/ha)			DICAMBA (mg/ha)
	May-Aug	Sep-Dec	Total	Total May-Aug	May-Aug	Sep-Dec	Total	May-Aug
1975-76 (May-April)								
AG-1	553	0	553	240	0	0	0	0
AG-2	32	0	32	0	0	0	0	0
AG-3	38	0	38	0	0	0	0	0
AG-4	1	28	29	0	1	27	28	0
AG-5	20	0	20	0	0	0	0	0
AG-6	56	39	95	0	42	0	42	0
AG-7	16	0	16	15	0	0	0	0
AG-10	18	0	18	18	0	0	0	0
AG-11	0	0	0	0	0	0	0	0
AG-13	219	12	231	0	18	0	18	13
AG-14	0	0	0	0	1	0	1	0
MEAN	87	7	94	25	6	2	8	1
1976-77 (May-April)								
AG-1	54	0	54	3	0	0	0	0
AG-2	68	10	78	0	0	0	0	0
AG-3	51	0	51	49	0	0	0	0
AG-4	134	0	134	0	0	0	0	0
AG-5	8	1	9	0	0	0	0	0
AG-6	114	0	114	0	0	0	0	0
AG-7	25	25	50	0	0	0	0	0
AG-10	0	0	0	0	0	0	0	0
AG-11	0	0	0	0	0	0	0	0
AG-13	1	8	9	0	0	0	0	0
AG-14	0	6	6	0	0	0	0	0
MEAN	41	5	46	5	0	0	0	0

1976, occurred in the September to December period and coincided with the fall spraying of winter wheat and additional spraying on rights-of-way (Table 3-13). There are no indications that 2,4-D residues persist from one season to the next in Ontario soils; hence 2,4-D incidence in water was associated directly with the same years' spraying events.

In a rainfall event on 24 June 1975 in AG-1, where 2,4-D had previously been applied to a dried stream bed, the flow volume rose from 0.09 to 16.75 m^3/sec over a six hour period. During this period, the 2,4-D discharge in the water rose from 0.16 mg/hr to 253 mg/hr, an eight-fold increase over the flow volume (Table 3-6, Appendix XII).

Residues of 2,4-D were detected in stream bed sediments at 2 to 6 µg/g in 5 of 11 watersheds (Table 3-4); in all cases these residues were accompanied by residues of 2,4,5-T at levels ranging from 3 to 14 µg/g, indicating that the residues resulted from non-agricultural uses. 2,4-D was not detected in rain water collected in 1975 from six of the watersheds (Table 3-5).

Water Quality

The I.J.C. (1977) has adopted a water quality objective for 2,4-D of either 100 µg/L or 5% of the median lethal dose over a 96 hour period to the most sensitive fish species; the most sensitive local species was bluegill with a TLM (48 hr) of 8 mg/L (Agriculture Canada, 1974-76) which gives a calculated objective of 400 µg/L; hence the 100 µg/L concentration was adopted as the 2,4-D standard. Over the two years of the study, only one water sample (0.1% of total samples) contained a level of 2,4-D which exceeded the proposed objective.

3.4.2 2,4,5-T

Use of 2,4,5-T and Presence in Stream Water

With the exception of 2 kg of 2,4,5-T applied to 2 ha of fence rows in AG-1 and AG-3, 2,4,5-T was used exclusively on non-agricultural land. The incidence of 2,4,5-T in stream water was 2.2% of the total collected from the 11 agricultural watersheds (Table 3-12). The mean annual concentration in water for all watersheds and for both years of the study was below the detection level of 0.1 µg/L. Of the 21 water samples which were found to contain measurable levels of 2,4,5-T, eleven also contained 2,4-D (Table 3-12, Appendix XX). Twenty of these samples had concentrations of 2,4,5-T between 0.1 and 1.0 µg/L and one sample contained 1.1 µg/L 2,4,5-T plus 1.3 µg/L 2,4-D; this sample was collected from AG-1 where a dried up ditch had been sprayed and was followed by heavy rain.

Annual losses of 2,4,5-T were 1.36 kg in 1975 and 0.32 kg in 1976; all losses occurred in the May-August period and the losses represented 0.49% and 0.12% of the total annual applications; these losses are associated with non-agricultural practices as discussed in the previous section for 2,4-D (Table 3-13, Appendix XVI). Unit area loadings of 2,4,5-T ranged from 0 to 240 mg/ha/yr in 1975 and from 0 to 49 mg/ha/yr in 1976 (Table 3-14). The largest losses occurred in AG-1 for reasons discussed previously.

Entry into Water

In a rainfall event on June 24, 1975 in AG-1 where 2,4,5-T had previously been applied to a dried stream bed, the flow volume rose from 0.09 to 16.75 m^3/sec over a six hour period. During this period the 2,4,5-T discharge in the water rose from 0.1 mg/hr to 42 mg/hr (Table 3-6, Appendix XII).

There is no evidence that 2,4,5-T persists from one season to another in Ontario soils and hence its presence in water can be associated with recent applications within the watersheds. 2,4,5-T was used at a rate of 0.6 kg/ha on 458.5 ha of rights-of-way in 9 of the 11 watersheds (Frank and Ripley, 1977); in all cases, 2,4,5-T was used in mixture with 2,4-D. 2,4,5-T was detected in three watersheds in 1975 and in two watersheds in 1976. It was also detected in stream bed sediments of five watersheds at levels ranging from 3 to 14 µg/g and was accompanied by 2,4-D in all cases (Table 3-4). 2,4,5-T was not detected in rainwater collected from five watersheds in 1975 (Table 3-5).

Water Quality

The water quality objective for 2,4,5-T adopted by the I.J.C. (1977) is either 100 µg/L or 5% of the median lethal dose for the most sensitive local fish species over a 96 hour period (McKee and Wolf, 1971). On this basis, a TLM of 55 mg/L for perch produces a calculated criterion of 2.7 mg/L. No water samples in the two year survey were found to exceed the standard of 100 µg / L 2,4,5-T.

3.4.3 MCPA

MCPA was used to control weeds in cereal crops in all 11 watersheds; 11% of total cereal hectarage was sprayed at a mean rate of 0.67 kg/ha (Frank and Ripley, 1977). MCPA was found in only six water samples (0.6%) and in all cases the level approximated 0.3 µg/L or close to the detection limit (Table 3-12, Appendix XX). Five of these samples were collected in June and one in November, corresponding with the spraying of spring and winter grains. The six samples with positive MCPA presence were located in AG-4,6,13 and 14. Losses of MCPA amounted to 318 g in 1975; no losses were recorded in 1976 (Table 3-13, Appendix XXI). Losses are attributed to the result of spills (229 g) and from spray drift (89 g). Unit area loadings ranged from 0 to 42 mg/ha/yr in 1975 (Table 3-14) and zero in 1976.

MCPA is not known to persist in soil and was not found in stream bed sediments or in rainwater (Table 3-4, 3-5) and hence its presence in water is correlated directly with cereal crop applications.

The I.J.C. objective for MCPA was calculated at 250 µg/L based on the most sensitive species, rainbow trout and bluegill, that had a 24 hr LC_{50} of 5 mg/L (Agriculture Canada 1974-76). No water sample exceeded this objective or the proposed 100 µg/L objective (I.J.C. 1977) that was applied since the former calculation exceeded the latter.

3.4.4 Dicamba

Dicamba was used for weed control in 0.6 and 0.9% of cereals in only AG-1 and AG-3 respectively (Frank and Ripley, 1977). One water sample (0.1%) of those collected over two years was found to contain dicamba at a level of 1.0 µg/L (Table 3-12); this sample came from AG-13 where no dicamba was recorded as being used for cereal production. Dicamba is used for nonagricultural purposes and it is concluded that the calculated loss of 25 g into the water resulted from the treatment of non-agricultural land (Table 3-13, Appendix XX); this event occurred in May 1976 (Appendix XX) and gave a calculated unit area loading of 13 mg/ha/yr (Table 3-14). Few, if any, farmers in AG-13 would risk the use of dicamba because of injurious properties to the many susceptible crops grown there. Dicamba is not known to persist in soil and was not found in either stream bed sediments or in rainwater (Table 3-4, 3-5).

The I.J.C. objective (1977) for dicamba was calculated to be 23 mg/L based on the most sensitive local species, carp, that exhibited a TLM of 465 mg/L over 48 hrs (WSSA 1974). No water sample exceeded this objective or the proposed 100 µg/L objective.

3.4.5 Other Chlorophenoxy and Benzoic Acids

No 2,4-DB, chloramben, dichlorprop, MCPB, mecoprop or silvex were identified in stream water samples, stream sediment samples or rainwater samples in the 11 watersheds over the survey period. Frank and Ripley (1977) have reported that chloramben was used to the extent of 2000 kg/year in AG-1 and AG-13; 2,4-DB and mecoprop had only limited use (Appendix II).

3.5 Other Organochlorine Insecticides and Fungicides

Neither lindane nor dichloran were identified in stream water samples over the two year study. According to Frank and Ripley (1977) no lindane was in use in the 11 agricultural watersheds (Appendix I). Dichloran was used only in AG-13 but only in small amounts (Appendix III).

3.6 Industrial Organochlorines

3.6.1 Polychlorinated Biphenyls (PCB)

PCB are used as industrial chemicals and have no known or identified use in agricultural production. The main source of PCB in the watershed is thought to be from electrical transformers; no electrical power lines, (except AG-5) cross the other 10 watersheds, although each watershed does have transformers at each farm operation for step-down conversion of electrical energy (the exact number is not known but can be estimated by the number of farms in each watershed) .

Presence in Water

PCB were identified in stream water from all 11 agricultural watersheds (Table 3-15). In only 5.6% of samples analyzed were PCB levels below the limit of detection of 2 ng/L. The mean residue in water ranged from 20 to 46 ng/L while individual samples ranged from a low of non-detectable to a high of 200 ng/L in the two years of the study (Table 3-15, Appendix XXII). The mean concentrations in water were 38 ng/L in 1975-76 and 25 ng/L in 1976-77. The majority of samples contained residues between 11 and 100 ng/L.

PCB are known to persist for long periods of time. Soils could act as a reservoir and as a source of water contamination. Analysis of agricultural soils has failed to identify PCB at levels which could account for the magnitude of residue found in water (Frank et al, 1977).

PCB were identified in stream bed sediments of all 11 watersheds at levels ranging from below the detection limit of 2 ng/g to a high of 8 ng/g and with an overall mean of 5 ng/g (Table 3-4). PCB were also present in rainwater from all six agricultural watersheds that were sampled; the concentrations ranged from non-detectable (<2 ng/L) to 100 ng/L in individual samples. The mean PCB residue in rainwater for all watersheds sampled ranged from 40 to 60 ng/L, i.e. the mean residues in rainwater appeared to be higher than in stream water samples (Table 3-5). Annual PCB losses in 1975-76 ranged from 278 g in AG-4 to 2132 g in AG-2; the mean annual loss in 1975-76 from the 11 watersheds was 913 g/year. In 1976-77 the annual losses ranged from 68 g in AG-11 to 937 g in AG-2 with a mean annual loss for 11 watersheds of 337 g/year (Appendix XXIII). Unit area loadings ranged from 128 mg/ha/yr in AG-10 to 269 mg/ha/yr in AG-2 in 1975-76 and from 28 mg/ha/yr in AG-11 to 119 mg/ha/yr in AG-2 during 1976-77 (Table 3-16).

Entry into Water

Removal of PCB in stream waters could be correlated with all six rainfall events (Table 3-6, Appendix XII). Following a rainfall in AG-1, the stream flow rate rose from 0.09 to 16.75 m^3/sec over a six hour period; measurements of PCB in the water showed that removal rates rose from 16 to 6030 µg/hr over the same six hour period; i.e. a slightly higher build-up than the increase in flow volume. In AG-3 where a moderately high flow event was subsiding, PCB losses in µg/hr showed little or no decline over a 4 hour period and was actually followed by an increase in PCB discharge as the flow volume declined. In AG-4 where base flows were being measured, losses of PCB varied from 0 to 47 µg/hr.

TABLE 3-15 Frequency and concentration of PCB in stream water collected from 11 agricultural watersheds between May 1975 and April 1977

Watershed	Period May-Apr.	Analysis (#)	Frequency and content in water (ng/L) Not Det. (<2)	Low (2- 10)	Medium (11- 100)	High (100+)	Mean	Range	SD
AG-1	1975-76	61	2	5	53	1	40	10-110	43
	1976-77	54	0	19	35	0	24	ND-60	31
AG-2	1975-76	29	0	2	27	0	46	4-100	53
	1976-77	34	2	6	25	1	30	ND-200	68
AG-3	1975-76	52	1	3	48	0	39	10-100	37
	1976-77	61	3	11	46	1	28	ND-200	57
AG-4	1975-76	34	2	6	26	0	36	ND-90	50
	1976-77	43	6	11	26	0	20	ND-50	32
AG-5	1975-76	55	1	6	48	0	40	ND-80	41
	1976-77	56	8	9	39	0	24	ND-100	41
AG-6	1975-76	58	3	8	47	0	35	ND-80	43
	1976-77	41	2	9	30	0	25	ND-60	31
AG-7	1975-76	28	0	1	27	0	41	10-100	45
	1976-77	19	1	3	15	0	22	ND-60	24
AG-10	1975-76	24	2	3	18	1	35	ND-110	23
	1976-77	37	5	7	25	0	23	ND-60	38
AG-11	1975-76	18	2	1	15	0	36	ND-100	50
	1976-77	5	0	1	4	0	24	10-40	62
AG-13	1975-76	62	2	6	54	0	39	10-100	38
	1976-77	87	5	20	61	1	24	ND-120	35
AG-14	1975-76	48	4	8	36	0	36	ND-100	49
	1976-77	43	2	9	32	0	23	ND-60	31
Total	1975-76	469	19	49	399	2	38	ND-110	43
	1976-77	480	34	105	338	3	25	ND-200	41
Grand Total:	1975-77	949	53	154	737	5	31	ND-200	42

TABLE 3-16 Unit area loadings of PCB and organophosphorus insecticides in 11 agricultural watersheds between May 1975 and April 1977

Watershed	PCB Losses (mg/ha)				Losses mg ha/yr			
					Chlorpyriphos	Diazinon	Ethion	Malathion
	May-Aug	Sep-Dec	Jan-Apr	Total	Total	Total	Total	Total
1975-76 (May-April)								
AG-1	44	30	74	148	0	0	0	0
AG-2	45	62	162	269	4	174 [1/]	0	0
AG-3	18	28	146	192	0	0	1	0
AG-4	16	41	93	150	0	0	0	0
AG-5	22	19	176	217	0	0	0	0
AG-6	76	68	74	218	0	0	0	0
AG-7	54	81	127	262	0	0	0	0
AG-10	19	30	79	128	0	0	0	0
AG-11			(82)		0		0	0
AG-13	31	35	126	192	0	9875 [1/]	0	0
AG-14	7	29	117	153	0	0	0	0
Mean	33	42	117	192	0	914 [1/]	0	0
1976-77 (May-April)								
AG-1	6	0	61	67	0	0	0	0
AG-2	21	33	65	119	0	0	0	0
AG-3	29	11	42	82	0	0	0	0
AG-4	2	8	43	53	0	0	0	0
AG-5	23	14	76	113	5	0	0	0
AG-6	21	20	35	76	0	0	0	0
AG-7	30	16	29	75	0	0	0	0
AG-10	16	2	26	44	0	0	0	0
AG-11	2	0	26	28	0	0	0	0
AG-13	7	2	54	63	1	1210 [1/]	0	36 [1/]
AG-14	4	21	48	73	0	0	0	
Mean	15	12	46	73	1	110 [1/]	0	3 [1/]

[1/] Indoor use

In three rainfall events in 1977 peak removal of PCB appeared to coincide with peak flow volume of water (Table 3-6) at the same time concentrations of PCB in the water also peaked (Appendix XII). At the height of runoff in AG-13, almost 4 mg/hr were being carried out of the watershed; this declined to only 0.07 mg/hr as the flow dropped towards the base flow.

Water Quality

No I.J.C. (1977) water quality objective for PCB in water has, as yet, been officially adopted but levels of 2 ng/L and 10 ng/L have been suggested, being based upon the bioaccumulation in fish so as not to exceed 0.1 µg/g in tissue. The 2 ng/L is a practical limit of detection by current methods of analysis. Over the two year survey period, 94.4 of water samples contained PCB residue at or above the 2 ng/L concentration while 78.2% contained residues above 10 ng/L.

3.6.2 Other Industrial Organochlorines

Mirex (dechlorane), used primarily as a fire retardant in the Ontario Great Lakes basin, was not detected in any of the 949 water samples from the 11 agricultural watersheds (minimum detectable amount of 1 ng/L).

3.7 Organophosphorus Insecticides

According to Frank and Ripley (1977) fifteen organophosphorus (OP) insecticides were used in the 11 agricultural watersheds (Appendix I). Thirteen of these were identifiable by the analytical screening procedure followed in this project (Table 2-1, Appendix I). The screening procedure included 21 OP, i.e. 8 additional OP which were not used in the watersheds according to the farm-to-farm survey. Of the 21 OP insecticides, four were identified in stream water and one was identified in rainwater.

3.7.1 Chlorpyrifos

This OP insecticide was used in watersheds AG-2, AG-7 and AG-13 for the control of cutworms in tobacco and vegetable production (Frank and Ripley, 1977). Chlorpyrifos was detected on single occasions in three watersheds, once in 1975 on July 10 in AG-2, twice in 1976 on May 21 in AG-5, and on June 28 in AG-13 (Table 3-17, Appendix XXIV). The concentrations in water during the three events were (1) 0.15 µg/L in AG-2 which resulted in a calculated loss of 35 g chlorpyrifos to water, (2) 1.6 µg/L in AG-5 with a loss of 15 g, and (3) 0.25 µg/L in AG-13 with a loss of 1 g (Table 3-17, Appendix XXV). The loss of chlorpyrifos on July 10, 1975 in AG-2 occurred as a runoff event from a treated tobacco field. The losses of chlorpyrifos in the other two watersheds (AG-5 and AG-13) were associated with the spraying of vegetables and appeared to be the result of either spillage, spray drift or carelessness around the stream.

Unit area loadings were between 0 and 4 mg/ha/yr in 1975-76 and 0 to 5 mg/ha/yr in 1976-77 (Table 3-16). Chlorpyrifos does not appear to persist in soil from one year to the next

TABLE 3-17 Frequency and concentrations of organophosphorus insecticides in water collected from 11 agricultural watersheds between May 1975 and April 1977

Watershed	Period May-Apr.	Analysis (#)	Frequency and content in water(µg/L)					Mean	Range	SD
			Not Det. (<0.01)	Low (0.01-0.10)	Medium (0.11-1.0)	High (1.1-10.0)	Very High (10+)			
Chlorpyrifos.										
AG-2	1975-77	63	62	0	1	0	0	<0.01	ND-0.15	-
AG-5	1975-77	111	110	0	0	1	0	0.01	ND-1.60	0.29
AG-13	1975-77	149	148	0	1	0	0	<0.01	ND-0.25	-
AG-1,3,4,6,7,10,11,14		626	626	0	0	0	0	ND	ND	-
Total	1975-77	949	946	0	2	1	0	<0.01	ND-1.60	-
Diazinon										
AG-2	1975-77	63	62	0	0	0	1	0.42	ND-25.	6.4
AG-3	1975-77	113	112	1	0	0	0	<0.01	ND-0.03	-
AG-13	1975-76	62	41	1	11	5	4	5.75	ND-140.	45.
	1976-77	87	23	14	32	17	1	1.02	ND-26.	5.8
AG-1,4,5,6,7,10,11,14		624	624	0	0	0	0	ND	ND	-
Total	1975-77	949	862	16	43	22	6	0.49	ND-140.	12.
Ethion										
AG-3	1975-77	113	112	1	0	0	0	<0.01	ND-0.04	-
AG-5	1975-77	111	110	1	0	0	0	<0.01	ND-0.02	-
AG-1,2,4,6,7,10,11, 13,14		725	725	0	0	0	0	ND	ND	-
Total	1975-77	949	947	2	0	0	0	<0.01	ND-0.04	-
Malathion										
AG-13	1975-77	149	145	0	3	1	0	0.02	ND-1.80	0.32
AG-1,2,3,4,5,6,7,10, 11,14		800	800	0	0	0	0	ND	ND	-
Total	1975-77	949	945	0	3	1	0	<0.01	ND-1.80	-

(Harris and Turnbull, 1977) but it has been detected in soil during the year of use (Frank et al, 1977). Chlorpyrifos was not detected in stream bed sediments norrainwater (Tables 3-4, 3-5); hence losses to water are associated with the use of chlorpyrifos within the spray season.

The I.J.C. (1977) has proposed a water quality objective for chlorpyrifos based on 5% of the median lethal dose to the most sensitive local species (bluegill) over a 96 hour period. The LC_{50} for bluegill is recorded as 2.6 µg/L for a 96 hour period (McKee and Wolf, 1971) which by calculation gives a water quality objective of 130 ng/L. Over the two year sampling period, no water was found to contain chlorpyriphos which exceeded this proposed level.

3.7.2 Diazinon

This OP insecticide is used for the control of foliar insects in vegetables and according to Frank and Ripley (1977), it was used only in AG-5 and AG-13 at rates of 0.7 kg/ha on a total area of 11 ha.

Diazinon was detected in water from three watersheds, namely, AG-2, AG-3 and AG-13. An unexplained water contamination occurred in October 1975 in AG-2 (Table 3-17, Appendix XXIV and XXV) which amounted to a loss of 1376 g; this could not be associated with outdoor use because the loss occurred in the non-growing part of the season, therefore, it could be attributed to indoor use or spillage. Diazinon was detected in a water sample in AG-3 at a level of 30 ng/L on June 18, 1975 resulting in a loss of 2 g; since diazinon was not used on any farm in AG-3 larger than 4.5 ha, the source was probably a small property which was not surveyed in Project 5 (Frank and Ripley, 1977).

Diazinon was repeatedly detected in the water of Hillman Creek, AG-13. During 1975-76, 34% of water samples were found to contain diazinon and 74% contained diazinon in 1976-77 (Table 3-17, Appendix XXIV). The actual losses over the two years are estimated at 19.65 kg and 2.41 kg for 1975-76 and 1976-77, respectively (Appendix XXV). The source of diazinon was traced to an indoor use in which it was used for fly control in a series of mushroom houses that were linked directly to the stream by a pump and drainage tile. Subsequent sampling above and below the outlet confirmed the origin of these diazinon losses (Table 3-18). In 1975-76 the mean residue in the AG-13 stream water was 5.75 µg/L and for 1976-77 it was 1.02 µg/L (Table 3-17); the highest individual levels for the two year period were 140 µg/L and 26 µg/L, respectively. The peak concentration occurred in August 1975, which was preceded by a lower peak in June, 1975 and followed by a second peak in October, 1976 (Appendix XXIV).

The total losses of diazinon from outdoor use over the two year period were calculated at 2 g while losses from indoor use and out-of-season use are estimated at 21 kg. Unit area loadings had little meaning since 99% of the losses originated from point sources (Table 3-16).

TABLE 3-18 Concentrations of diazinon up and down stream of a mushroom house, a point source in AG-13

	Dates of sampling, diazinon in water (µg/L)				
Location	8 Oct.	15 Oct.	22 Oct.	20 Jan.	20 May
Upstream	ND[1]	31[2]	ND[1]	ND	<0.05
Downstream	2.0-15.6	49-93	14-29	150	0.04-0.43

[1] Good flow of water in stream
[2] Low flow with some back flow in stream

Diazinon was not detected in stream bed sediments or in rainwater (Table 3-4 and 3-5). Diazinon appeared in two runoff events that were sampled in AG-13 during February-March 1977 (Table 3-5 and Appendix XII). Concentrations remained constant or increased with flow and the amount lost increased to a peak that coincided with the peak flow volumes in the stream. This was not in keeping with a point source loss and could not be explained.

A water quality objective of 80 ng/L has been adopted by the I.J.C. (1977). The point source losses accounted for 77 individual samples (8.1%) from the 11 watersheds over the two year study period which exceeded this objective. All except one were in the Hillman Creek (AG-13).

3.7.3 Ethion

Ethion is used for the control of soil insects in vegetables, with heaviest use in onions. In the farm survey, Frank and Ripley (1977) did not record the use of ethion in any of the 11 agricultural watersheds. The survey, however, did not include residential properties or small farms of less than 4.5 ha where the landlord was absent.

Ethion was detected on single occasions in AG-3 and AG-5 in 1975 only (Table 3-17, Appendix XXIV). Both events were recorded in June, 1975 at concentrations of 0.04 and 0.02 µg/L respectively, in water samples from AG-3 and AG-5 resulting in respective total losses of 4 g and 1 g (Appendix XXV). Both could have resulted from spray drift or carelessness near streams while spraying. Ethion has been reported as persisting in muck soils from one year to the next (Miles et al, 1978) but in this study the losses appeared to be from current use. No ethion was found in either stream bed sediments or in rainwater (Tables 3-4 and 3-5) .

Under the I.J.C. water quality objective the most sensitive species of fish is harlequin (Parmentel 1971), a tropical species, with an LC50 of 700 ng/L resulting in a calculated criterion of 35 ng/L. The most sensitive local species of fish, however, is the bluegill with a TLm (48 hr) of 230 µg/L, which gives a proposed level of 11.5 µg/L. If the lower objective is used (35 ng/L), one water sample was found which exceeded this proposed concentration.

3.7.4 Leptophos

This OP insecticide, like chlorpyriphos, was used for the control of cutworms in tobacco and vegetables and is normally applied prior to planting of the crop. According to the farm survey by Frank and Ripley (1977), leptophos was used in AG-2, AG-7 and AG-13 primarily in connection with tobacco production.

Leptophos was not identified in stream water or stream bed sediments but was identified in one rainwater sample collected from AG-1 during May-June, 1975 (Table 3-5) at a level of 1.1 µg/L. Its presence in rainwater is difficult to explain since there was only one hectare of tobacco planted in AG-l; possibly the leptophos originated from spray drift from areas adjacent to this watershed which practice tobacco production.

Leptophos has recently been removed from registered use because of its delayed mammalian neural toxicity.

3.7.5 Malathion

Malathion is used for the control of foliar insects in fruits and vegetables; it is used both commercially and domestically. According to the farm survey (Frank and Ripley, 1977), malathion was used commercially in AG-1, AG-2 and AG-13 at a rate of 0.6 kg/ha on 32 ha of fruits and vegetables (Appendix I).

Malathion was detected in stream water only in AG-13 and on five occasions. The concentrations were 0.25 µg/L on July 8, 1976, 0.38, 0.32 and 1.80 µg/L on December 6, 16 and 17, 1976, respectively, and 1.70 µg/L on April 20, 1977 (Table 3-17, Appendix XXIV). Losses amounted to 1 g (July 1976), 53 g (December 1976) and 18 g (April 1977) (Appendix XXV). Unit area loadings for AG-13 in 1976-77 were calculated as 36 mg/ha/yr (Table 3-16). These losses occurred during periods of the year when field uses of malathion would not have occurred and the source was traced to the same mushroom grower previously discussed with respect to the diazinon contamination. Losses of malathion, therefore, were also due to point sources and not as a diffuse source as the result of field use.

Malathion was not detected in either stream bed sediments or in rainwater (Table 3-4, 3-5). The calculated I.J.C. (1977) water quality objective for malathion was 5.1 µg/L based on 5% of the 96 hr TL_{50} for the most sensitive fish species (cohoe salmon and bluegill) being 101 mg/L (Macek and McAllister, 1970). No water samples exceeded this objective.

3.7.6 Other Organophosphorus Insecticides

The following OP insecticides were also in use in the various watersheds: azinphosmethyl, chlorfenvinphos, demeton, dimethoate, fensulfothion, mevinphos, parathion, phorate, phosalone and phosmet. None of these insecticides were detected in stream water, stream bed sediment or rainwater.

3.8 Organonitrogen Compounds (s-Triazines)

Five triazine herbicides are used in the 11 agricultural watersheds including atrazine, simazine, cyprazine, metribuzin and cyanazine (Table 3-1, Appendix XX); of this group, cyanazine was the only triazine which was not included in the analytical screening procedure. In addition to the above, prometone was identified in some samples but did not appear to be used in agriculture.

3.8.1 Atrazine and Desethylatrazine

Atrazine is currently the most widely applied herbicide in Ontario being used mainly for the control of weeds in corn. Between 9.5 to 31.3% (mean 17.6%) of each of the eleven watersheds was devoted to corn production of which 53.3 to 93.6% (mean 73.1%) received atrazine treatments at rates ranging from 1.1 to 2.6 kg/ha (Frank and Ripley, 1977). Total corn hectarage amounted to 6153 ha which received 10,570 kg of atrazine (Appendix XXVI).

Presence in Water

Atrazine and/or desethylatrazine (the de-ethylated degradation product of atrazine) were found to be present in 80.2% of water samples from the eleven watersheds over the two year sampling period at an overall mean concentration of 1.4 µg/L (Table 3-19). Mean residues in water during 1975-76 varied from 0.10 µg/L in *AG-7* to 3.2 µg/L in AG-3 with individual samples containing residues as high as 31.7 µg/L; in the 1976-77 period the mean residues by watershed ranged from <0.02 µg/L in *AG-7* to 5.5 µg/L in AG-10 with the highest individual sample reading of 32.8 µg/L. The mean concentrations for all watersheds were 1.1 µg/L in 1975-76 and 1.6 µg/L in 1976-77. There appeared to be little variation in atrazine levels from year to year for most watersheds, with the notable exception of AG-10 where a marked increase was observed in the second year. Of the 949 water samples analyzed over the two year period, 78% contained measurable amounts of atrazine and 59% contained measurable amounts of desethylatrazine; only 2% contained desethylatrazine alone while 21% contained only atrazine.

The levels of atrazine and its metabolite in stream water showed definite seasonal variations. From a level of around 1 µg/L during the winter months, atrazine levels started to increase in May and peaked sharply in June in watersheds AG-1, 5, 10 and 13 during 1975 and AG-4 in 1976; peak periods occurred in July 1975 for watersheds AG-2 and 14 and in July 1976 for watersheds AG-1,3,5 and 14. A broad 2-month peak period for AG-3 and AG-4 was observed in 1975 while in 1976 peak periods for AG-10 and AG-13 were noted in August and October, respectively (Figure 2-4, Appendix XXVII). Levels generally declined rapidly after the peak period to less then 1 µg/L over a one to two month period; occasionally the decline in concentration was followed by a second and smaller peak, e.g. AG-3 in September 1976, AG-10 in October 1975 and AG-10 in November, 1976.

The proportion of atrazine and desethylatrazine appeared to be associated with the time of year at which samples were taken. During the spray period, residue of the parent atrazine predominated and desethylatrazine was absent in a number of samples. A high ratio of atrazine to its metabolite, or the absence of desethylatrazine, was interpreted as an indication of a spill, drift, or direct loss into water either immediately after use or shortly thereafter. Conversely, a low atrazine/desethylatrazine ratio was interpreted as a loss of herbicide from soil sometime after application, either as a runoff event or via tile drainage.

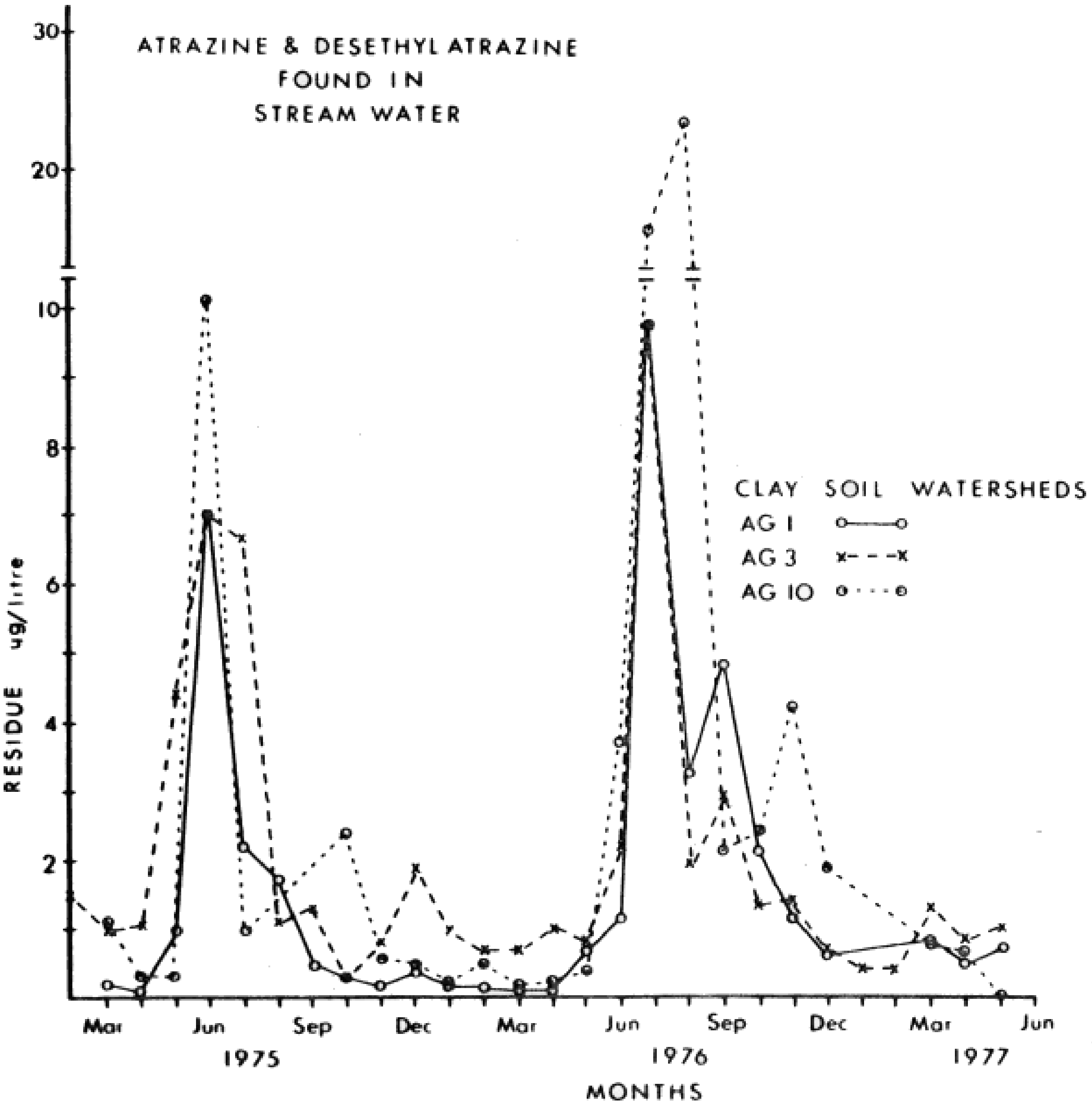
ATRAZINE & DESETHYL ATRAZINE
FOUND IN
STREAM WATER
RESIDUE ug/litre
30
20
10
8
6
4
2
CLAY SOIL WATERSHEDS
AG 1
AG 3
AG 10
Mar
Jun
Sep
Dec
Mar
Jun
Sep
Dec
Mar
Jun
1975
1976
1977
MONTHS

Fig. 2

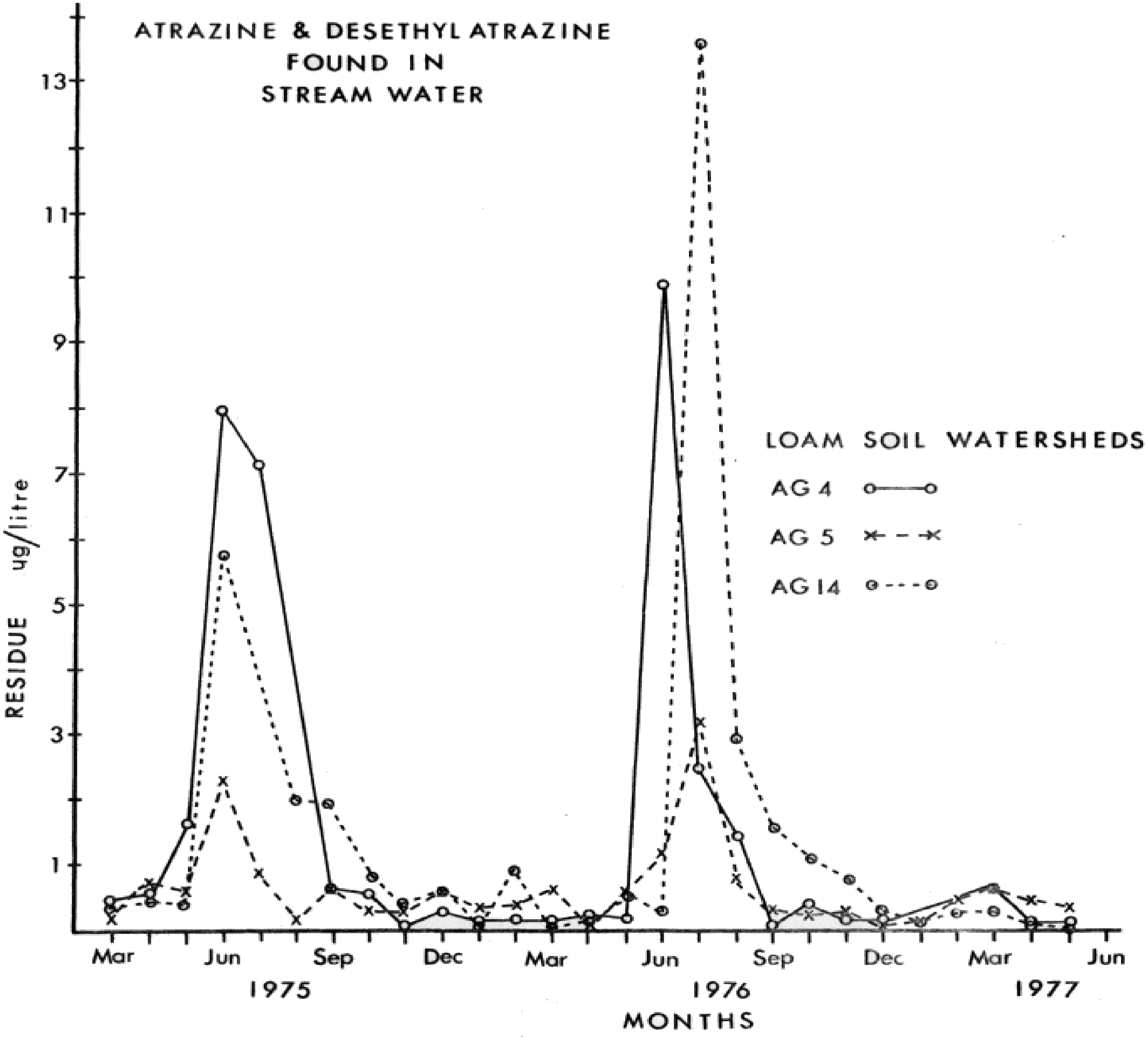
ATRAZINE & DESETHYL ATRAZINE
FOUND IN
STREAM WATER
RESIDUE ug/litre
13
11
9
7
5
3
1
LOAM SOIL WATERSHEDS
AG 4
AG 5
AG 14
Mar
Jun
Sep
Dec
Mar
Jun
Sep
Dec
Mar
Jun
1975
1976
1977
MONTHS

Fig. 3

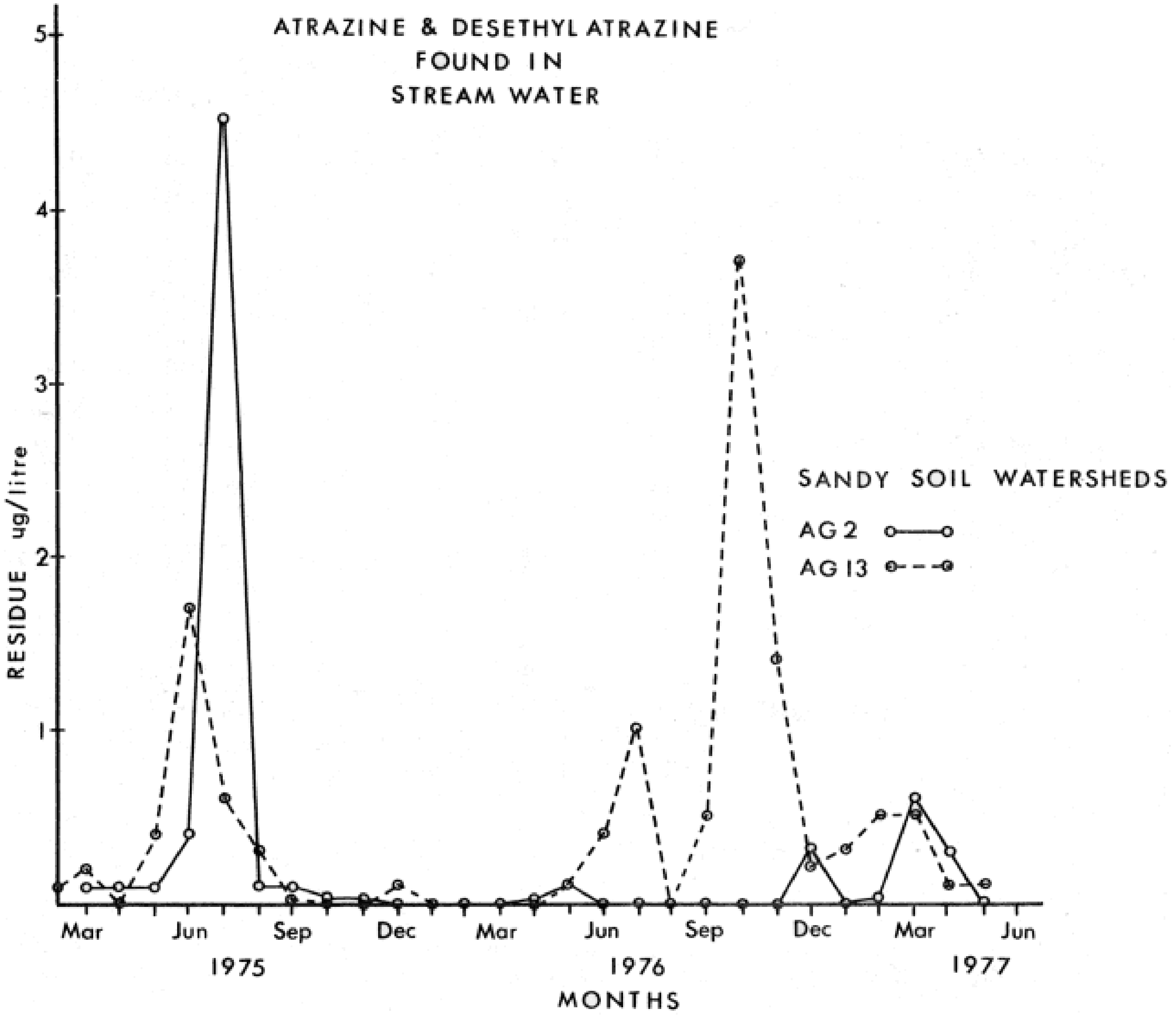
ATRAZINE & DESETHYL ATRAZINE
FOUND IN
STREAM WATER
RESIDUE ug/litre
5
4
3
2
1
SANDY SOIL WATERSHEDS
AG 2
AG 13
Mar
Jun
Sep
Dec
Mar
Jun
Sep
Dec
Mar
Jun
1975
1976
1977
MONTHS

Fig. 4

TABLE 3-19 Frequency and concentrations of atrazine and desethylatrazine in water collected from 11 agricultural watersheds between May 1975 and April 1977

		Atrazine and its metabolite - Frequency and content in water (µg/L)								
Watershed	Period May-Apr.	Analysis (#)	Not Det. (<0.04)	Trace (0.04- 0.09)	Low (0.1- 1.0)	Medium (1.1- 10.0)	High (10.1 +)	Mean	Range	SD
AG-1	1975-76	61	5	10	30	14	2	2.2	<0.04-18.2	5.7
	1976-77	54	1	1	27	20	5	3.2	<0.04- 22.6	9.9
AG-2	1975-76	29	13	8	7	0	1	0.57	<0.04-13.1	4.9
	1976-77	34	22	3	8	1	0	0.17	<0.04-1.8	0.73
AG-3	1975-76	52	0	0	22	24	6	3.2	<0.4 -31.7	10.8
	1976-77	61	1	0	33	25	2	2.0	<0.04-24.7	7.0
AG-4	1975-76	34	2	3	25	3	1	1.2	0.07-14.7	5.9
	1976-77	43	2	4	27	9	1	1.5	<0.04-27.1	8.5
AG-5	1975-76	55	4	2	37	12	0	1.0	<0.04 -6.6	3.1
	1976-77	56	3	2	38	13	0	0.89	<0.04- 7.7	2.1
AG-6	1975-76	58	23	11	23	1	0	0.13	<0.04- 1.2	0.44
	1976-77	41	26	3	12	0	0	0.07	<0.04-0.52	0.18
AG-7	1975-76	28	11	9	8	0	0	0.10	<0.04- 0.6	0.35
	1976-77	19	19	0	0	0	0	<0.04	<0.04	-
AG-10	1975-76	24	0	0	20	3	1	1.4	0.07-10.3	5.6
	1976-77	37	1	2	18	8	8	5.5	<0.04-32.8	18.2
AG-11	1975-76	18	0	0	16	2	0	0.49	0.1 - 1.2	0.61
	1976-77	5	1	2	2	0	0	0.09	<0.04- 0.3	0.28
AG-13	1975-76	62	32	7	15	8	0	0.39	<0.04- 4.4	1.6
	1976-77	87	20	11	46	9	1	0.66	<0.04-10.8	2.9
AG-14	1975-76	48	2	6	32	7	1	1.0	<0.04-13.3	13.5
	1976-77	43	0	1	33	7	2	1.6	<0.04-18.0	21.
Total	1975-76	469	92	56	235	74	12	1.1	<0.04-31.7	6.6
	1976-77	480	96	29	244	92	19	1.6	<0.04-32.8	9.8
Grand Total:	1975-77	949	188	85	479	166	31	1.4	<0.04-32.8	8.4

Flow Volume and Atrazine Loss

The effect of changing stream flow volumes as the result of rainfall events was clearly reflected in the atrazine:desethylatrazine ratios (Table 3-6, Appendix XII). Under base flow conditions in AG-4 on September 11-12, 1975, the atrazine:desethylatrazine ratio ranged from 1:2 to 2:1 while actual losses varied from 25-1170 µg/hr atrazine and 29-583 µg/hr desethylatrazine. Under constant medium flow conditions in AG-6 on March 21, 1977, atrazine and desethylatrazine again approximated a 1:1 ratio with losses of about 290 µg/hr for both compounds. On June 24, 1975 following a field application of atrazine a rainstorm resulted in a sharp stream flow increase from 0.09 to 16.75 m^3/sec over a short period of time; during the same time losses of atrazine rose from 0.9 to 561 mg/hr while losses of desethylatrazine rose from 0.02 to 103 mg/hr, i.e. during the peak period of runoff and flow volume the atrazine:desethylatraine ratio approximated 5:1. In a decreasing flow rate situation in AG-3 on December 15-16, 1975, several months after the use of atrazine on the land, atrazine and desethylatrazine declined from 29 to 10 mg/hr and from 26 to 10 mg/hr, respectively, with an accompanying flow volume decline from 4.61 to 3.23 m^3/sec. With rising flow rates in AG-13 on February 24-25, 1977 and on March 4-5, 1977, atrazine again predominated over the desethylated metabolite by a factor of over five times. The major losses of atrazine and desethylatrazine were accounted for by high flow rates which, in turn, were associated with high runoff events.

Annual Losses to Water

Total annual losses of atrazine plus its metabolite from the watersheds were 101 kg in 1975-76 (10 watersheds) and 89 kg in 1976-77 (11 watersheds) Appendix XXVIII); these amounts represented losses of 0.95% and 0.84% of the annual 10,570 kg of atrazine applied on the watersheds. Percentage losses of the amounts applied per watershed ranged from 0.2% from AG-7 in 1975-76 to 3.1% from AG-1 in 1975-76. Losses per treated hectare of corn ranged from 0.0 to 34.0 g/ha/yr (mean 16.4) in 197 5-7 6 and 0.0 to 29.0 g/ha/yr (mean 12.8) in 1976-77 (Table 3-20). On a watershed basis, unit area loadings of atrazine ranged from 129 to 5431 mg/ha/yr in 1975-76 and from 0 to 5969 mg/ha/yr in 1976-77 (Table 3-21).

The factors which influence the degree and nature of atrazine losses from the land into stream waters are summarized as follows (Appendix XXIX and XXX).

Period:	May-Aug:	period of application, canopy development following spraying, medium to low stream flows.
	Sep-Dec:	harvest and post-harvest period, ground protected with fall plowing, medium to low stream flows.
	Jan-Apr:	spring thaw and runoff, no ground cover, high stream flows.

Cause:	Storm Runoff:	High stream flows (flows in excess of 1200 to 1400 L/sec) indicated runoff events.
	Spills:	Carelessness around streams, appearance of high concentrations in absence of runoff events, high atrazine:desethylatrazine ratio (above 3:1).
	Base Flow:	Absence of runoff event or spill, base flow conditions (below 1200 to 1400 L/sec) indicated mainly internal soil drainage.

Spills included losses of the pesticide to the water as the result of back-siphoning of spray equipment during filling operations, empty containers left in or near streams, washing spray equipment, overfilling, loss of chemical foam while filling, spray drift and direct over-spray of streams.

Actual losses of atrazine by watershed are tabulated in Appendix XXIX and XXX; unit area losses in milligrams per hectare per year for both atrazine and desethylatrazine are calculated for the 1975-76 period (Table 3-22) and for the 1976-77 period (Table 3-23). In the two years of the study, runoff from all soils accounted for 62.1 and 56.8% of the total losses representing a unit area loss of 1362 and 1056 mg/ha/yr respectively. Tile drainage accounted for 20.3 and 20.8% of the losses or an input of 446 and 386 mg/ha/yr for the two years. Spills were calculated as representing 17.6 and 22.4% of the total loss or 385 and 419 mg/ha/yr (Table 3-22, 3-23). In the May-Aµgust period, losses due to storm runoff and spills were of the same magnitude in both years while in the January-April period most of the losses resulted from storm runoff and no spills were recorded. One-third to two-fifths of the total atrazine loss in both years occurred during storm runoff conditions in the January-April period.

Atrazine losses from clay and clay-loam soils, as compared to sandy and sandy - loam soils, were almost 10 times higher in 1975-76 and 6.5 times higher in 1976-77; losses from loam and silt-loam soils were intermediate between these two extremes. In clay soils, storm runoff accounted for 66.5 and 54.5% of the annual loss respectively for the two years and was equally divided between the May-August and January-April periods for 1975-76 while in 1976-77 the largest loss occurred in the January-April period. On loams and silt loams the losses were primarily from storm runoff events in the January-April period, and accounted for 42.1 and 46.5% of the total annual loss. The largest losses from sandy and sandy loam soils were by means of base flow (tile drainage) (38.2%) and spills (32.4%) in 1975-76 and these occurred mainly in the May-August period. However, in the 1976-77 period losses from sandy soils were mainly as runoff events (49.1%) and especially in the May-August period (46.2%).

Seasonal Differences

Examining atrazine losses on a seasonal basis, the May to August period was characterized by medium to low flow conditions (6.0 to 31.3% of the total annual flow) but with a number of runoff events that carried freshly-sprayed atrazine into stream water. Together with several incidents of spills, concentrations of atrazine in water rose sharply from 1 to between 7 and 28 µg/L, coinciding with the main spray season (Tables 3-22, 3-23 and Fig. 2-4).

TABLE 3-20 Rates of application and losses of atrazine and its metabolite from treated corn and the whole watershed 1975-77

Watershed	Watershed			Treatedcornarea		
	Atrazine Application 1975 kg/ha/yr	Losses[1] 1975-76 g/ha/yr	Losses[1] 1976-77 g/ha/yr	Atrazine Application 1975 kg/ha/yr	Losses[1] 1975-76 g/ha/yr	Losses[1] 1976-77 g/ha/yr
AG-1	0.14	4.45	2.31	1.11	34.0	17.7
AG-2	0.17	0.75	0.61	1.94	8.6	6.9
AG-3	0.34	5.43	5.97	1.59	25.1	27.5
AG-4	0.38	1.62	2.57	2.64	11.4	18.0
AG-5	0.66	2.27	3.10	2.01	7.0	9.5
AG-6	0.19	0.96	0.67	1.84	9.2	6.4
AG-7	0.08	0.13	0.00	1.28	2.2	0.0
AG-10	0.17	2.87	2.52	1.93	33.2	29.0
AG-11	0.13	-	0.20	1.43	-	2.3
AG-13	0.29	0.57	0.66	1.36	2.7	3.1
AG-14	0.18	2.84	1.80	2.04	31.8	20.1
MEAN	0.25	2.19	1.85	1.74	16.5	12.8

[1] Atrazine plus desethylatrazine

TABLE 3-21 Unit area loadings of atrazine plus desethyl atrazine and simazine in 11 agrucultural watersheds between May 1975 and April 1977.

Watershed	Total Atrazine (mg/ha)				Simazine (mg/ha)			
	May-Aug	Sep-Dec	Jan-Apr	Total	May-Aug	Sep-Dec	Jan-Apr	Total
1975-76 (May-April)								
AG-1	3896	401	150	4447	56	19	0	75
AG-2	674	33	48	755	0	0	0	0
AG-3	1300	771	3360	5431	0	0	0	0
AG-4	704	124	790	1618	0	0	0	0
AG-5	440	277	1557	2274	0	0	168	168
AG-6	495	183	280	958	9	0	0	9
AG-7	111	18	0	129	0	0	0	0
AG-10	949	707	1216	2872	1	0	0	1
AG-11			(974)					
AG-13	387	70	111	568	6	0	0	6
AG-14	320	1170	1354	2844	1	3	0	4
Mean	928	375	887	2190	7	2	17	26
1976-77 (May-April)								
AG-1	1523	16	774	2313	245	1	1	247
AG-2	48	21	538	607	0	0	0	0
AG-3	2216	848	2905	5969	66	0	0	66
AG-4	1285	91	1183	2559	32	0	0	32
AG-5	1183	153	1760	3096	32	3	80	115
AG-6	38	9	621	668	0	0	0	0
AG-7	0	0	0	0	0	0	0	0
AG-10	1223	274	1018	2515	6	0	150	156
AG-11	55	0	146	201	0	0	0	0
AG-13	126	211	322	659	2	0	23	25
AG-14	155	690	957	1802	0	0	0	0
Mean	714	210	929	1853	35	0	23	58

TABLE 3-22 Losses of atrazine and desethylatrazine from different soil types between May 1975 and April 1976

Soil Type (watersheds)	Reason	Mean Losses[1] (mg/ha) and (%)							
		May-Aug		Sep-Dec		Jan Apr		Total	
		(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)
Clay & clay loam	Storm runoff	1216	(27.2)	408	(9:1)	1349	(30.2)	2973	(66.5)
(AG-1,3,10)	Base flow	179	(4.0)	218	(4.9)	225	(5.0)	622	(13.9)
	Spills	727	(16.3)	148	(3.3)	0	(0.0)	875	(19.6)
	TOTAL	2122	(47.5)	774	(17.3)	1574	(35.2)	4470	
Loam & silt loam	Storm runoff	92	(4.8)	172	(8.9)	809	(42.1)	1073	(55.8)
(AG-4,5,6,14)	Base flow	175	(9.1)	155	(8.1)	185	(9.6)	515	(26.8)
	Spills	223	(11.6)	111	(5.8)	0	(0.0)	334	(17.4)
	TOTAL	490	(25.5)	438	(22.8)	994	(51.7)	1922	
Sands & sandy	Storm runoff	96	(20.6)	0	(0.0)	41	(8.8)	137	(29.4)
loams (AG-2,7,13)	Base flow	142	(30.5)	24	(5.1)	12	(2.6)	178	(38.2)
	Spills	151	(32.4)	0	(0.0)	0	(0.0)	151	(32.4)
	TOTAL	389	(83.5)	24	(5.1)	53	(11.4)	466	
All soils (AG-1,2,	Storm runoff	430	(19.6)	191	(8.7)	741	(33.8)	1362	(62.1)
3,4,5,6,7,10,13,14)	Base flow	166	(7.6)	135	(6.1)	145	(6.6)	446	(20.3)
	Spills	341	(15.5)	44	(2.0)	0	(0.0)	385	(17.5)
	TOTAL	937	(42.7)	370	(16.9)	886	(40.4)	2193	
		Mean Flow Volumes $m^3 \times 10^3$/yr (%)							
Flow volumes	Clays	1130	(6.0)	2532	(13.5)	1,5046	(80.5)	18,708	
	Loams	2447	(13.1)	4267	(22.8)	11,980	(64.1)	18,694	
	Sands	5197	(19.7)	6259	(23.7)	14,949	(56.6)	26,405	
	MEAN	2877	(13.7)	4344	(20.7)	13,791	(65.6)	21,012	

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[1] Mean losses weighted to size watershed and not arithmetical means of Tables 3-20 and 3-22.

TABLE 3-23 Losses of atrazine and desethylatrazine from different soil types between May 1976 and April 1977

Soil Type (watersheds)	Reason	Mean Losses[1] (mg/ha) and (%)							
		May-Aug		Sep-Dec		Jan-Apr		Total	
		(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)
Clay & clay loam (AG-1,3,10,11)	Storm runoff	425	(15.5)	109	(4.0)	961	(35.0)	1495	(54.5)
	Base flow	199	(7.2)	108	(3.9)	250	(9.1)	557	(20.2)
	Spills	630	(22.9)	67	(2.4)	0	(0.0)	697	(25.3)
	TOTAL	1254	(45.6)	284	(10.3)	1211	(44.1)	2749	
Loam & silt loam (AG-4,5,6,14)	Storm runoff	164	(8.1)	146	(7.2)	946	(46.5)	1256	(61.8)
	Base flow	100	(4.9)	90	(4.4)	187	(9.2)	377	(18.5)
	Spills	401	(19.7)	0	(0.0)	0	(0.0)	401	(19.7)
	TOTAL	665	(32.7)	236	(11.6)	1133	(55.7)	2034	
Sands & sandy looms (AG-2,7,13)	Storm runoff	12	(2.9)	0	(0.0)	194	(46.2)	206	(49.1)
	Base flow	35	(8.3)	14	(3.3)	92	(21.9)	141	(33.5)
	Spills	10	(2.4)	63	(15.0)	0	(0.0)	73	(17.4)
	TOTAL	57	(13.6)	77	(18.3)	286	(68.1)	420	
All soils (AG-1,2,3, 4,5,6,7,10,11,13,14)	Storm runoff	217	(11.6)	93	(5.0)	746	(40.1)	1056	(56.7)
	Base flow	118	(6.3)	85	(4.6)	184	(9.9)	387	(20.8)
	Spills	377	(20.2)	42	(2.2)	0	(0.0)	419	(22.4)
	TOTAL	712	(38.2)	220	(11.8)	930	(50.0)	1862	
		Mean Flow Volumes $m^3 \times 10^3$/yr (%)							
Flow volumes	Clay	2465	(23.9)	985	(9.5)	6868	(66.6)	10,318	
	Loams	2984	(20.0)	2710	(18.1)	9244	(61.9)	14,938	
	Sands	5769	(31.3)	4059	(22.1)	8577	(46.6)	18,405	
	MEAN	3739	(25.7)	2585	(17.8)	8230	(56.5)	14,554	

[1] See note on Table 3-22

The September-December period was also characterized by medium to low flow conditions (9.5 to 23.7% of total annual flow) but there were fewer runoff events and spills and generally atrazine concentrations were low <1 µg/L, with a few minor peaks occurring in this period with levels up to 3 to 4 µg/L (Table 3-22, 3-23 and Fig. 2-4). These peaks appeared to coincide with a minor spray period for perennial weeds in the fall.

The January to April period represents the highest flow volume period at 46.6 to 80.5% of the annual total; concentrations of atrazine in stream water during this period were generally low but because of the flow factor, losses of atrazine during this period were comparable to losses during the spray season (Tables 3-22, 3-23 and Fig.2-4).

Storm runoff losses of atrazine from individual watersheds were much lower than would be expected on the basis of the report by Smith et al (1974) who measured losses from treated fields; the discrepancy may be due to relative sizes of land areas investigated i.e. by studying only an area adjacent to the stream as compared to the total watershed under investigation in this survey.

Movement in and from Soils

Kojlowski and Kurtz (1963), Rodger (1966) and Montgomery and Freed (1959) have reported on atrazine movement into the soil profile and in some cases penetration to a depth of 90 cm was observed. Von Stryk (1977) reported atrazine losses of between 0.75 to 14.1 g/ha into stream water; these values are considerably higher than the 0.13 to 0.86 g/ha reported here (Table 2-33, 3-23). Sheets (1970) reported that the degradation of atrazine in subsoil was much slower than at the surface; the presence of atrazine in tile drainage waters may be interpreted, therefore, as being the result of applications from the previous season.

Twelve groundwater samples were collected from the sandy soils in AG-13 in piezometers at 3.4 and 7.0 m during the May-June period of 1975. No triazine herbicides were found in these samples to a detection limit of 4.0.04 µg/L.

Atrazine can and frequently does persist in soils in Ontario from one season to the next and may cause injury to susceptible crops such as sugar beets as reported by Frank (1966). In a review on the persistence of striazines, Sheets (1970) points out that persistence is dependent on a number of factors that include soil pH, moisture, temperature and microbiological activity. Soils in Ontario vary from slightly acid to slightly alkaline and hence do not promote the rapid breakdown of atrazine. Decomposition by hydrolysis proceeds more rapidly in acid soils than in neutral or alkaline soils. Cool and dry weather lengthens the persistence while warm and moist conditions promote degradation. Under the conditions found in Ontario, atrazine would remain un-ionized (Boitron *et al* 1973, Weber 1970); adsorption to colloidal particles would be weak and reversible, being held by hydrogen bonding and van der Waal's forces (Frissel, 1961); under runoff conditions, atrazine can be readily removed from soil particles (Smith *et al,* 1974) by being hydrogen-bonded to moving water molecules (Ward and Weber, 1968).

Weber (1970) reported that biological or non-biological hydrolysis of atrazine in calcareous or neutral soils is not an active process of degradation; in such soils, degradation of the chloro-s-triazines appears to be by microbial dealkylation (Kaufman and Kearney, 1970). Sirons et al (1975) have reported that desethylatrazine appears to be the major metabolite under Ontario conditions and that this metabolite is phytotoxic at a level of 1 µg/g soil. The atrazine:desethylatrazine ratio throµghout this study varied from 8:1 to 1:1 when both were present. On some occasions, either one or the other was absent from stream water.

Presence in Sediments

Atrazine was detected in watercourse bottom sediments in four watersheds; levels of 7 µg/g were found in AG-6 and AG-14 and 20 µg/g in AG-4; desethylatrazine was not identified in these sediments which were collected during the spray season or shortly thereafter. In the fourth watershed (AG-11) both atrazine and desethylatrazine were detected at levels of 7.6 and 8.2 µg/g, respectively; this sample was collected just prior to the commencement of the spray season. Waldron and Bailey (1964) studied atrazine movement in five watersheds in the Lake Erie basin and reported 11 of 156 bottom sediments (7%) contained atrazine at levels ranging from 4.5 to 95 ng/g.

Neither atrazine nor desethylatrazine was detected in rainwater samples (Table 3-5).

Water Quality

The water quality objective for atrazine and desethylatrazine were calculated on the basis of the I.J.C. proposals (1977). The most sensitive fish species was the harlequin fish, a tropical species with a 48 hr LC_{50} of 0.55 mg/L (Pimentel 1971); data on the local species, rainbow trout, was a 48 hr LC_{50} of 12.5 mg/l. By applying a 5% tolerance to the toxicity to harlequin fish, a level of 28 µg/L was calculated as the I.J.C. objective. If this objective is placed on the 949 water samples analyzed for atrazine and desethylatrazine over the two year study period, only three samples (0.3%) exceeded the calculated level. With the local species a level of tolerance of 625 µg/L was calculated and no water sample exceeded this concentration or the 100 µg/L maximum also proposed by I.J.C.

3.8.2 Cyprazine

Cyprazine is an s-triazine herbicide which has been used for weed control in corn but because of poor sales, supplies were discontinued in 1976-77. According to the survey by Frank and Ripley (1977) cyprazine was used in only one watershed (AG-4) with a total amount of only 18 kg being applied. However, because of the similarity between cyprazine and cyanazine, some confusion of identification may have occurred in the survey and more cyprazine may have actually been used than was recorded.

Presence in Stream Water

Cyprazine was identified in 14 water samples from 7 of the 11 watersheds (Table 3-24, Appendix XXXI). With the exception of one sample, all residues were below 1 µg/L; the exception (from AG-3) had a level of 18 µg/L. The presence of cyprazine appeared to result from runoff in 10 of the samples and from spills in the remaining four samples (Table 3-25). Total losses in 1975-76 were 130 g from runoff and 541 g from spills (total 671 g) and in 1976-77 losses amounted to 540 g from runoff and 5 g from spills. Unit area loadings ranged from 0 to 80 mg/ha/yr in 1975-76 and from 0 to 42 mg/ha/yr in 1976-77 (Table 3-26).

Sources of Loss

Cyprazine was not detected in stream sediments or in rainwater (Tables 3-4, 3-5) and was also not detected in groundwater samples analyzed from AG-13. Losses of cyprazine would appear to originate from current rather than past uses; hence the recorded losses from spills and runoff would indicate a more extensive use of this herbicide than was determined by the farm-to-farm survey. The persistence of cyprazine in Ontario soils is not documented.

Water Quality

The I.J.C. (1977) water quality objective for cyprazine is calculated at 310 µg/L using rainbow trout as the most sensitive species with a LC50 of 6.2 ± 1.75 mg/L (WSSA, 1974). Since the calculated objective exceeds the maximum proposed level of 100 µg/L, the laLLer is used as the criterion. All samples with positive cyprazine readings were well below this objective.

3.8.3 Metribuzin

Metribuzin is a triazine herbicide used for the control of weeds in potatoes, tomatoes and soybeans. Reported uses of metribuzin (Frank and Ripley, 1977) occurred only in AG-1, AG-5 and AG-13 at a rate of 0.79 kg/ha on 303 ha of land.

Presence in Water

Metribuzin was detected in 14 water samples (1.5%) over the two year period (Table 3-24); it was detected inthree watersheds in 1975-76 but only in two watersheds in 1976-77. All losses occurred in the May-August period with maximum levels of 1.4 µg/L. Total losses amounted to 127g in 1975-76 and 274 g in 1976-77 (Table 3-27). These losses were attributed to 41 g in

TABLE 3-24 Frequency and concentration of several organonitrogen herbicides in water collected from 11 agricultural watersheds between May 1975 and April 1977

Watershed	Period May - Apr.	Analysis (#)	Frequency and content in water (µg/L)					Mean	Range	SD
			Not Det. (<0.04)	Trace (0.04- 0.09)	Low (0.10- 1.0)	Medium (1.1- 10.)	High (10.1+)			
Alachlor										
AG-3	1975-77	113	111	1	0	1	0	0.08	ND-9.0	1.70
AG-11	1975-77	23	22	1	0	0	0	<0.04	ND-0.07	-
AG-1,2,4,5,6,7,10, 13,14		813	813	0	0	0	0	ND	ND	-
Total	1975-77	949	946	2	0	1	0	<0.04	ND-9.0	-
Cyprazine										
AG-1	1975-77	115	113	2	0	0	0	<0.04	ND-0.07	-
AG-2	1975-77	63	60	3	0	0	0	<0.04	ND-0.07	-
AG-3	1975-77	113	111	1	0	0	1	0.16	ND-18.0	-
AG-4	1975-77	77	76	0	1	0	0	<0.04	ND-0.3	-
AG-5	1975-77	111	109	0	2	0	0	<0.04	ND-0.3	-
AG-10	1975-77	61	59	1	1	0	0	<0.04	ND-0.3	-
AG-14	1975-77	91	89	0	2	0	0	<0.04	ND-0.3	-
AG-6,7,11,13	1975-77	318	318	0	0	0	0	ND	ND	-
Total	1975-77	949	935	7	6	0	1	<0.04	ND-18.0	-
Metribuzin										
AG-1	1975-77	115	110	0	4	1	0	<0.04	ND-1.2	0.18
AG-5	1975-77	111	110	0	0	1	0	<0.04	ND-1.4	-
AG-6	1975-77	99	98	1	0	0	0	<0.04	ND-0.07	-
AG-13	1975-77	149	142	2	5	0	0	<0.04	ND-1.0	-
AG-2,3,4,7,10,11,14	1975-77	475	475	0	0	0	0	ND	ND	-
Total	1975-77	949	935	3	9	2	0	<0.04	ND-1.4	-

Continued .....

TABLE 3-24 Continued

Watershed	Period May-Apr	Analysis (#)	Frequency and content in water(µg/L) Not Det. (<0.04)	Trace (0.04 - 0.09)	Low (0.10-1.0)	Medium (1.1-10.)	High (10.1+)	Mean	Range	SD
Prometone										
AG-5	1975-77	111	110	1	0	0	0	<0.04	ND-0.07	-
AG-6	1975-77	99	97	2	0	0	0	<0.04	ND-0.07	-
AG-10	1975-77	61	57	4	0	0	0	<0.04	ND-0.07	-
AG-13	1975-77	149	148	1	0	0	0	<0.04	ND-0.07	-
AG-1,2,3,4,7,11,14		529	529	0	0	0	0	ND	ND	-
Total	1975-77	949	941	8	0	0	0	0.04	ND-0.07	-
Simazine										
AG-1	1975-76	61	45	12	4	0	0	0.04	ND-0.20	0.08
	1976-77	54	29	5	17	3	0	0.37	ND-3.40	1.30
AG-3	1975-76	52	50	2	0	0	0	<0.04	ND-0.07	-
	1976-77	61	55	3	3	0	0	<0.04	ND-0.50	0.14
AG-4	1975-76	34	34	0	0	0	0	ND	ND	-
	1976-77	43	39	2	2	0	0	<0.04	ND-0.20	-
AG-5	1975-77	111	103	8	0	0	0	<0.04	ND-0.07	-
AG-6	1975-77	99	98	0	1	0	0	<0.04	ND-0.10	-
AG-10	1975-76	24	23	1	0	0	0	<0.04	ND-0.07	-
	1976-77	37	26	6	5	0	0	0.04	ND-0.30	0.13
AG-13	1975-76	62	57	5	0	0	0	<0.04	ND-0.07	-
	1976-77	87	83	4	0	0	0	<0.04	ND-0.07	-
AG-14	1975-77	91	88	3	0	0	0	<0.04	ND-0.07	-
AG-2,7,11	1975-77	133	133	0	0	0	0	ND	ND	-
Totals	1975-76	469	442	22	5	0	0	<0.04	ND-0.20	0.04
	1976-77	480	421	29	27	3	0	0.06	ND-3.40	0.48
Grand Total:	1975-77	949	863	51	32	3	0	0.04	ND-3.40	0.35

TABLE 3-25 Uses of three organonitrogen herbicides and losses to stream water in 11 agricultural watersheds between May 1975 and April 1977.

Watershed	Treated Area		Amount Used 1975 (kg)	Losses			Remarks
	Corn (ha)	Soybean (ha)		Date	Concentration (µg/L)	Amount (g)	
Alachlor							
AG-1	54	7	90				
AG-2	138	20	297				
AG-3	392	0	740	May 31 & June 5/75	9.0 & <0.1	249 + 15	Two spills
AG-4	10	0	25				
AG-5	544	0	1090				
AG-6	10	0	12				
AG-7	131	0	148				
AG-10	0	0	0				
AG-11	0	61	225	June 5/75	< 0.1	0	No flow
AG-13	17	0	36				
AG-14	67	0	92				
Total	1363	88	2755			264	
Cyprazine							
AG-1	0	0	0	May 18/76, Mar.18/77	< 0.1	5+30	Spill & Runoff
AG-2	0	0	0	Mar.11/76, Mar.11 & Apr.15/77	<0.1	100+46+48	Runoff
AG-3	0	0	0	May.31/75, Mar.13/77	18, <0.1	498+205	Spill & runoff
AG-4	16	0	14	Mar. 10/75	< 0.1	2	Spill
AG-5	0	0	0	Jul.31/75, Mar.28/77	0.2, 0.3	41+125	Spill & Runoff
AG-10	0	0	0	Oct.6/75, Mar.11/77	0.3, <0.1	40+34	Runoff
AG-14	0	0	0	Oct.3/75, Nov.29/76	0.3, 0.2	0+52	Runoff
Total	16	0	14			1226	
Prometone - No known uses							
AG-5				Apr. 5/77	< 0.1	19	Runoff
AG-6				Nov.12/75, Mar.7/77	< 0.1	44+21	Runoff
AG-10				10 &11 Mar./76 10811 Mar./77	< 0.1	1+54	Spill & Runoff
AG-13				Aug.26/76	< 0.1	<1	Spill
Total						140	

TABLE 3-26 Unit area loading of 4 organonitrogen herbicides in 11 watersheds between May 1975 and April 1977

Watershed	Unit area loadings (mg/ha/yr) Alachlor Total (May-Aug)	Cyprazine Total	Metribuzin Total (May-Aug)	Prometone Total
1975-76 (May-April)				
AG-1	0	0	8	0
AG-3	0	13	0	0
AG-3	43	80	0	0
AG-4	0	1	0	0
AG-5	0	14	21	0
AG-6	0	0	0	8
AG-7	0	0	0	0
AG-10	0	10	0	0
AG-11	0	0	0	0
AG-13	0	0	11	0
AG-14	0	0	0	0
Mean	4	11	4	1
1976-77 (May-April)				
AG-1	0	7	27	0
AG-2	0	12	0	0
AG-3	0	33	0	0
AG-4	0	0	0	0
AG-5	0	42	0	6
AG-6	0	0	0	4
AG-7	0	0	0	0
AG-10	0	11	0	18
AG-11	0	0	0	0
AG-13	0	0	70	1
AG-14	0	11	0	0
Mean	0	10	9	3

runoff water and 86g in spills during the 1975-76 period and 135g in runoff waters plus 139g in spills in 1976-77. Runoff losses originated from soybean field in AG-1 (Table 3-27 and Appendix XXXII). Losses from AG-5 and AG-13 were judged to arise from carelessness around streams or from spray drift. Unit area loadings ranged from 0 to 21 mg/ha/yr in 1975-76 and from 0 to 70 mg/ha/yr in 1976-77 (Table 3-26).

Sharom and Stephenson (1976) have reported that metribuzin may persist from one season to the next in Ontario soils. However, since the incidence of positive metribuzin in water occurred in the spray season, it was concluded that it resulted from current uses. Metribuzin was not detected in sediments or rainwater (Tables 3-4, 3-5) nor was it detected in groundwaters of AG-13 sampled at 3.4 to 7.0 m below the surface.

Water Quality

The I.J.C objective for metribuzin in water was calculated at 5 mg/L as based on rainbow trout and bluegill, the most sensitive species, with an LC$_{50}$ value of >100 mg/L over 96 hours (WSSA, 1974). No water samples were found which exceeded the proposed objective of 100 µg/L.

3.8.4 Prometone

Prometone is used for total vegetation control on industrial sites, rights-of-way, driveways and fence rows; it was not used for agricultural purposes in the 11 watersheds (Frank and Ripley, 1977) although it could have had use on non-cropped areas or on non-agricultural areas which were not covered in the use-survey.

Entry and Presence in Stream Water

Prometone was present in 0.8% of water samples at a mean residue of less than the detection limit of 0.04 µg/L (Table 3-24, Appendix XXXI). In 1975-76, prometone was detected in only one sample (AG-6) with a calculated loss of 44 g (Table 3-25); this loss was associated with a runoff event in November (Appendix XXXII). In 1976-77 losses were observed from AG-5,6,10 and 13 with a combined total loss of 96g. Losses in August (AG-13) and November (AG-10) appeared to be from spray drift (2 g) since concentrations were at trace levels and were not associated with a rainfall event; the remaining loss (94g) appeared to be caused by runoff events in AG-5,6 and 10. Unit area loadings ranged from 0 to 8 mg/ha/yr in 1975-76 and 0-18 mg/ha/yr in 1976-77 (Table 3-26).

Prometone was not identified in stream sediments and rainwater or in groundwaters of AG-13 (Tables 3-4, 3-5). Prometone has been shown to persist for several years in soil when used for total vegetation control.

Water Quality

No toxicity data to local species of fish is available (WSSA, 1974); using 100 µg/L as an

TABLE 3-27 Uses of metribuzin and simazine with losses to stream water in 11 agricultural watersheds between May 1975 and April 1977

Watershed	1975 Crops Treated		Losses in stream water(g)					
			1975 - 76			1976 - 77		
	(ha)	(kg)	May-Aug	Sep-Dec	Jan-Apr	May-Aug	Sep-Dec	Jan-Apr
Metribuzin:	Potato (P) Soybean (S) Tomato (T)							
AG-1	201(S)	131	41(R)	0	0	135(R)	0	0
AG-5	30(P)	30	64(S)	0	0	0	0	0
AG-13	72(P,S,T)	78	22(S)	0	0	139(S)	0	0
Total	303	239	127	0	0	274	0	0
Simazine:	Asparagus (A) Corn (C)							
AG-1	31(C)	23	286(S)	94(R)	0	1245(S)	6(R)	7(R)
AG-2	0	0	0	0	0	0	0	0
AG-3	220(C)	335	12(D)	0	0	411(S)	2(D)	0
AG-4	0	0	0	0	0	29(R) 30(S)	0	0
AG-5	16	18	10(D)	0	505(R)	95(R)	10(D)	241(R)
AG-6	0	0	52(R)	0	0	0	0	0
AG-7	0	0	0	0	0	0	0	0
AG-10	0	0	0	0	0	19(S)	0	453(R)
AG-11	0	0	0	0	0	0	0	0
AG-13	6 (A)	13	11(S)	0	0	3(D)	0	45(R)
AG-14	0	0	3(D)	0	0	0	0	0
Total	273	389	374	94	505	1832	18	746

Simazine:		1975-76	1976-77
Storm Runoff	(R)	651 (66.9%)	876(33.7%)
Base Flow	(D)	25 (2.6%)	15(0.6%)
Spill	(S)	297(30.5%)	1705(65.7%)
	Total	973	2596

objective, no water samples were found which exceeded or even approached this level of prometone concentration.

3.8.5 Simazine

Simazine is used as a pre-emergence herbicide for weed control in several areas of crop production. In corn production it may be used alone or in combination with atrazine; it is used alone in asparagus and in ornamental and tree nurseries; lesser uses are for vegetation control on rights-of-way, driveways, fence rows and industrial sites and is also used for aquatic weed control in streams, lakes and ponds. The use survey (Frank and Ripley, 1977) tabulated only the use of simazine on corn; many farmers did not recognize the combination of atrazine and simazine in formulations e.g. Echo with the result that the survey does not represent a full inventory of simazine use on corn.

Presence in Stream Water and Mode of Entry

Simazine was identified in 9.5% of the water samples analyzed over the two year period (Table 3-24); it was present in water from four watersheds for which simazine was not recorded for use in crop production (Appendix II and XXXI). In those watersheds where its use was identified, a total of 389 kg was applied resulting in a calculated loss of 973 g in the water during 1975-76 i.e. a loss of 0.25% (Table 3-27, Appendix XXXII); this percentage loss is inaccurate and erroneously high because of the incompleteness of the use survey. Losses of simazine in 1975-76 were categorized as 66.9% in storm runoff waters, 30.5% due to spills and 2.6% from base flow (mainly tile drainage) (Table 3-27). In 1976-77 losses amounted to 2596g of which 1245g or 47.9% originated from a single spill along with atrazine in AG-1; total spills represented 65.7% of the annual loss in 1976-77. Losses due to runoff events were 876 g or slightly higher than in the previous year, but, because of the single spill incident, this represented less than half the total loss from AG-1. Losses through tile drainage were very low at 25g and 15g in the two respective years.

Spills of simazine in AG-1, 3, 4 & 10 occurred in conjunction with atrazine spills, again revealing that simazine was not recognized as a component of the herbicide formulation for the purpose of the use survey (Frank and Ripley, 1977). The highest spill in AG-1 resulted in atrazine: simazine concentration ratios that ranged from 4:1 to 6:1 in water. Spills appeared to be a significant pathway for emergence into water. Unit area loadings in 1975-76 varied from 0 to 168 mg/ha/yr and in 1976-77 from 0 to 247 mg/ha/yr (Table 3-21).

In general, the behaviour of simazine in soil is similar to that of atrazine; it is more strongly adsorbed to organic matter and colloidal particles and is less soluble and less readily leached from soils (Bailey et al, 1968, Harris and Warner 1964, and Nearpass 1965). Under neutral or slightly alkaline soil conditions, simazine appears to be stable and it tends to persist longer in soils than does atrazine (Sheets, 1970).

Simazine was detected in stream sediment samples only in AG-11 at a level less than 1 µg/g; it was not detected in rainwater from six watersheds collected in 1975 (Table 3-5) or in groundwater collected to depths of 3.4 to 7.0 m in AG-13.

Water Quality

Based on chinook salmon as the most sensitive local fish species with a TL_m value of 6.6 mg/L over 48 hr, an I.J.C. water quality objective of 300 µg/L is calculated; since this value is higher than the proposed maximum of 100 µg/L the latter was accepted as the objective. All water samples in which simazine was identified contained levels well below this 100 µg/L objective.

3.8.6 Other Triazines

No prometryne was detected in stream water, stream sediments, rainwater or groundwater during the study. The survey of Frank and Ripley (1977) showed no use of prometryne in the 11 agricultural watersheds.

3.9 Organonitrogen insecticides - Methyl Carbamates

The analytical screening procedure covered the detection of four methyl carbamate insecticides, three of which were used in the 11 watersheds for commercial agricultural purposes. The screening of methyl carbamate insecticides was confined to only three watersheds (AG-3,6 and 13) and only for a limited sampling period between June and August, 1976.

3.9.1 Carbofuran

Carbofuran is used for the control of insects in corn, potatoes, rutabagas and vegetables (Frank and Ripley, 1977). It was identified in 10 of 43 samples (23%) at levels up to 1.0 µg/L (Table 3-28, Appendix XXXIII). In the period from June to August, 1976, a total loss of only 21 g of carbofuran by means of the stream water was observed in the three watersheds (AG-3,6,13) under investigation. This represented a unit area loading of 1.5 mg/ha/yr.

The I.J.C. objective for carbofuran in water was calculated at 6.0 µg/L based on bluegill as the most sensitive species with a 96 hr TL_m value of 120 µg/L (Hughes, 1969). No residue in water even approached the objective.

3.9.2 Other Methyl Carbamates

Of the remaining methyl carbamates in use in AG-3, AG-6 and AG-13, neither carbaryl nor metalkamate were detected in stream water in the June-August 1976 period; carbaryl and metalkamate were used agriculturally in AG-2 and AG-4 (Appendix I). The screening procedure also included methiocarb which was not used in any of the watersheds; none was detected.

TABLE 3-28 Frequency and concentration of carbamates in water collected from 5 agricultural watersheds between June-August 1976

Watershed	Period	Analysis	Frequency and contents in water (µg/L)					Amount
			Not det. (absent)	Trace (<0.5)	Low (0.5-1.0)	Mean	Range	(g)
Carbofuran								
AG-3	June-Aµg. 1976	13	8	1	4	<0.5	ND-1.0	20.7
AG-6	July-Aug. 1976	5	5	0	0	ND	ND	0.0
AG-13	June-Aug. 1976	25	20	1	4	.0.5	ND-1.0	0.3
	TOTAL	43	33	2	8	<0.5	ND-1.0	21.0
EPTC			(absent)	(0.1-0.5)				
AG-2	June-Aug. 1976	5	5	0	0	ND	ND	0.0
AG-3	June-Aug. 1976	13	13	0	0	ND	ND	0.0
AG-6	June-Aug. 1976	8	8	0	0	ND	ND	0.0
AG-7	Aug. 1976	2	2	0	0	ND	ND	0.0
AG-13	June Aug. 1976	25	22	3	0	<0.1	ND-0.2	0.1
	TOTAL	53	50	3	0	<0.1		0.1

ND - not detected

3.10 Organonitrogen Herbicides - Thiocarbamates

The screening procedure included the detection of seven thiocarbamate herbicides of which four were in use in the 11 agricultural watersheds (Frank and Ripley, 1977). Water samples were analyzed from five watersheds (AG-2,3,6,7 and 13) for the brief period of June to August, 1976.

3.10.1 EPTC

EPTC is used for weed control in white beans and potatoes in AG-2, 3,5 and 13 (Appendix II). EPTC was identified in three of 53 water samples (Table 3-28, Appendix XXXIII); all three samples came from AG-13. Residues of EPTC in water ranged from non-detectable to 0.2 µg/L and amounted to a total calculated loss of only 0.1 g over the three-month sampling period in 1976.

The I.J.C. objective for EPTC in water is calculated at 950 µg/L based on rainbow trout as the most sensitive species with a 96 hr LC_{50} value of 19 mg/L (WSSA 1974). If the proposed 100 µg/L is used as the maximum permissible concentration, EPTC levels in water are well below proposed objective.

3.10.2 Other Thiocarbamates

No butylate, cycloate, diallate, molinate, pebulate or vernolate was detected in the stream water of the five agricultural watersheds (AG-2,3,6, 7 and 13) which were sampled between June and August, 1976 (Table 3-28). Butylate was used in six watersheds while diallate and pebulate were used in one watershed (Appendix II).

3.11 Other Organonitrogen Pesticides

Alachlor, a herbicide, was the only other organonitrogen pesticide which was included in the analytical screening procedure.

3.11.1 Alachlor

Alachlor is used for pre-emergence weed control in corn and soybean. Its use included about 4.4% of the total hectarage of soybeans grown in three watersheds and an average of 16.2% of the corn hectarage in the 11 watersheds. Application rates were 1.9 kg/ha on 1451 ha (Frank and Ripley, 1977 and Appendix II).

Presence in Stream Water

Alachlor was identified in only three of the 949 water samples analyzed from the 11 watersheds over the two-year study (Table 3-24); on two of the occasions (AG-3 and AG-11) trace levels of alachlor were found (< 0.1 µg/L); the third sample from AG-3 contained alachlor at a level of 9.0 µg/L (Appendix XXXI). These incidences appeared to be the result of spills in which a total of 264 g was lost to the stream water, representing about 0.001% of the total applied to the land (Table 3-25). Unit area loadings were 0 to 43 mg/ha/hr in 1975-76 with no observed loss in 1976-77 (Table 3-26).

Alachlor was not identified in stream sediments (Table 3-4), in rainwater (Table 3-5), or in groundwater from AG-13 collected at depths of 3.4 to 7.0 m.

Water Quality

The most sensitive fish species to alachlor is rainbow trout which have exhibited a 96 hr TL_m of 2.3 mg/L (WSSA, 1974). Based on a 5% safety objective, a level of 115 µg/L is calculated and the proposed level of 100 µg/L is applied. Alachlor incidence and quantities in stream water were well below this objective.

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APPENDIX I Insecticide Use[a] in the Agricultural Watersheds 1975

	USE OF INSECTICIDES (kg a.i.)							
Common Name	AG-1	AG-2	AG-3	AG-4	AG-5	AG-7	AG-13	TOTAL
azinphos-methyl	4						2,326	2330
B.thuringiensis		114			9		24	147
carbaryl	6	96		1			615	718
carbofuran			619		119		354	1092
chinomethionate	0.4							0.4
chlordane			383					383
chlordimeform							43	43
chlorfenvinphos			79					79
chlorpyrifos		958				38	7	1003
cyhexatin							13	13
demeton					6			8
diazinon							2[b]	
dicofol							36	36
dimethoate							2	2
endosulfan	11	545			33	26	67	682
fensulfothion			94					94
leptophos		596				22	33	651
malathion	1	7					11	19
metalkamate			11		7			18
methomyl							24	24
methoxychlor	1						11	12
mevinphos							0.8	0.8
parathion			57					57
phorate					107			107
phosalone				0.4			205	205.4
phosmet							638	638
trichlorfon		392						392
Total	23.4	2708	1243	1.4	281	86	4414.8	8757.6

[a] No insecticides were used in AG-6, 10, 11 or 14

[b] One mushroom farm used diazinon but rate is not known

APPENDIX II Herbicides Used in the Agricultural Watersheds (including road allowance) 1975

	USE OF HERBICIDES (kg a.i.)											
Common Name	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
alachlor	90	297	740	25	1090	12	148		225	36	92	2755
amitrole	4	53			1							58
atrazine	737	1353	2132	700	1972	1047	430	504	303	572	820	10570
bentazon	48		47							14		109
bromacil			0.5									0.5
butylate		270				256	554	152	167	309		1708
chloramben	1806									173		1979
chlorthal										32		32
cyanazine	14	315	1138	14	388	6	555				38	2468
cyprazine				14								14
2,4-D	449	653	592	131	197	318	268	83	198	51	158	3098
2,4-DB			34		3	94		33	19		16	199
diallate						39						39
dicamba	12		46									58
dinitramine					16							16
dinoseb	12									0.3		12.3
diphenamid		276								139		415
EPTC		46	408		72					14		540
linuron	42	87			7				4	163		303
MCPA	8		297	151	16	169	56					697
mecoprop	7		31									38
metobromuron		9	656		72					275		1012
metribuzin	131				30					78		239
monolinuron										39		39
monuron										5		5
naptalam	24									0.7		24.7
niclofen										3		3
paraquat	7	1				8			26	140		182

Continued .....

APPENDIX II Continued

USE OF HERBICIDES (kg a.i.)

Common Name	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
pebulate										97		97
picloram							2					2
simazine	23		335		18					13		389
2,4,5-T	15		32	13	51	23	25	25	41		54	279
terbacil										13		13
trifluralin	118		188		24					367		697
Total:	3547	3360	6676.5	1048	3957	1972	2063	797	958	2534	1178	28090.5
Herbicidal [a/] Oil (liters)	350	1380	1138		2212						1043	6123

[a/] Oil used to apply atrazine to corn

APPENDIX III Fungicide and Pesticidal Oils Use [a] in the Agricultural Watersheds

	1975			
	USE OF FUNGICIDES (kg a.i.)			
Common Name	AG-1	AG-4	AG-13	TOTAL
benomyl			107	107
captan		2	1354	1356
captafol	231		745	976
chlorothalonil			5	5
copper (fixed)	308		1174	1482
dichloran			11	11
dodine		0.3		0.3
EBDC	357		1563	1920
folpet			3	3
sulphur			1369	1369
Total:	896	2.3	6331	7229.3
Pesticidal Oil [b]			7780 L	

[a] No fungicides were used in AG-2, 3, 5, 7, 10,11 or 14

[b] Liters of dormant or superior oil (Fruit Production Recommendations, 1976, Publication 360, O.M.A.F.)

APPENDIX IV Nematocides and Growth Regulators Use in the Agricultural Watersheds

1975

Common Name	USE OF PESTICIDE (kg a.i.)				
	AG-1	AG-2	AG-7	AG-13	TOTAL
<u>Nematocides</u>					
1,2-dichloropropane + 1,3-dichloropropene		87,101	7,159	4,121	98,381
methyl isothiocyanate		7,800	384	1,002	9,186
Total:	0	94,901	7,543	5,123	107,567
<u>Growth Regulators</u>					
fatty alcohols		27,690	679		28,369
ethephon	5				5
Total:	5	27,690	679	0	28,374

APPENDIX V Sample Frequency that Water Samples Were Collected for Pesticide Analysis 1974-77

Number of Sampling Dates, Samples and Analyses

DATE		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
<u>Waters - Sampling Dates</u>													
1974	Apr.	3	5	2	2	1	1	2	2	1	3	2	24
	May	6	6	2	2	2	3	2	2	3	6	2	36
	June	3	4	3	2	2	2	3	3	2	3	2	29
	July	4	5	3	1	2	3	2	1	2	3	3	29
	Aug.		4	2		2	2	2	2	2		2	18
	Sept.		3	2		3		2	1	2	1	1	15
	Oct.		1			2		1		1	3		8
	Nov.	1	1	1	1						4		8
	Dec.										3		3
1974	-TOTALS:												
	Samples	17	29	15	8	14	11	14	11	13	26	12	170
	Analysis	17	29	15	8	14	11	14	11	13	26	12	170
1975	Jan.		1	1[d]									2
	Feb.		1[d]	1			1				1		4
	Mar.	3	1[d]	1[d]	2	1	2		1	1	4	1	17
	Apr.	6	3	6[d]	3	7	4[d]	4	2	5	7	4	51
	May	6[d]	6	9	5	10[d]	6	6	3	4	6[d]	6[d]	67
	June	11[e]	4	8	2	10	4	8	2	6	11[d]	4	70
	July	2	3	6	1	10	5	3	1		11		42
	Aug.	1	2	1		1	6	4			3		18
	Sept.	6	3	4	3[d,e]	3	4	4			6	4	37
	Oct.	5	3	3	1	4	5		2		14	5	32
	Nov.	6	2	5	1[d]	5	6		1		6	5	37
	Dec.	4	1	4[e]	4	3	5		2		4	4	31

Continued ...

APPENDIX V Continued

DATE	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
Days	50	30	49	22	54	48	29	14	16	63	33	408
Duplicates	1	2	3	2	1	1	0	0	0	2	1	13
Rain Ev.	1(3)[n]	0	1(4)[n]	1(11)[n]	0	0	0	0	0	0	0	3(18)[n]
1975- TOTALS:												
Samples	54	32	56	35	55	49	29	14	16	65	34	439
Analysis	324	187	334	210	330	294	174	84	96	384	204	2621
1976 Jan.	3		1	2	2	2		1		3	2	16
Feb.	4	2	4	1	4	1		5		4	1	26
Mar.	5	1	4	8	3	8	2	3[d]	7	5	10	56
Apr.	8[d]	1	3	6	4	6	1	2	1	8	6	46
May	11[d]	2	4	7	5	5	2[d]	5		10[d]	5	56
June	11	4	6	4	5	3		5		10[d]	3	51
July	12	2	5	3	5	3	1	4		13[d]	3	51
Aug.	3	2	5	3	5	4	3	4	1	10[d]	3	43
Sept.		2	5	3	5	3		3		8[d]	2	31
Oct.	3	4	6	1	6	3	4	4	2	5[d]	3	41
Nov.	1	3	4	5	4[d]	3	4	1		8[d]	3	36
Dec.	1	1	3	3	3	2	2	1		2[d]	2	20
Days	62	24	50	46	51	43	19	38	11	86	43	473
Duplicates	2	0	0	0	1	0	1	1	0	10	0	15
Rain Ev.	0	0	0	0	0	0	0	0	0	0	0	0
1976-TOTALS:												
Samples	64	24	50	46	52	43	20	39	11	96	43	488
Analysis	384	149	326	276	312	271	122	234	66	626	256	3022

Continued ...

APPENDIX V Continued

DATE		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
1977	Jan.		2	4		3	3	1			5	3	21
	Feb.		3	2		3	3				7[e]	3	21
	Mar.	8	5	9	9	8	9[d,e]	1	8	1	7[e]	11[d]	76
	Apr.	4	5	4	3	4	2	1	3		3	2	31
	May	2	2	6	2	5	3	2		1	2	3	28
	DAYS	14	17	25	14	23	20	5	11	2	24	22	177
Duplicates		0	0	0	0	0	1	0	0	0	0	2	3
	Rain Ev.	0	0	0	0	0	1(3)[n]	0	0	0	2(7)[n]	0	3(10)[n]
1977	Totals:												
	Samples	14	17	25	14	23	24	5	11	2	31	24	190
	Analysis	84	102	150	84	138	144	30	66	12	185	144	1139
SPECIAL SAMPLES:													
(1)	Groundwater												
	Samples										12		12
	Analysis										12		12
(2)	Contaminations												
	Samples										16		16
	Analysis										16		16
(3)	Rainfall												
	Samples	4		4	4	3			4		4		23
	Analysis	16		16	16	12			16		16		92
1974-1977													
	Samples	153	102	150	107	147	127	68	79	42	250	113	1338
	Analysis	825	467	841	594	806	720	340	411	187	1267	616	7074
SEDIMENT													
1976-1977													
	Samples	1	1	1	1	1	1	1	1	1	1	1	11
	Analysis	6	6	6	6	6	6	6	6	6	6	6	66

d = Duplicate e = Rainfall event n = Number of samples per rainfall event

APPENDIX VI Results of Duplicate Samples Collected between 1975-77 from 10 of the 11 Watersheds

Watershed and Date	Content in Duplicate Water Samples (µg/L)													
	DDE	TDE	DDT	HE	DLD	END	DIA	MAL	PCB	24-D MCPA	ATR	deAT	SIM	MET
AG-1														
May 28/75	.008	-	-	-	<0.001	-	-	-	.060	-	2.2	0.3	<0.1	-
	.008	.006	.002	-	-	-	-	-	.030	-	2.2	<0.1	<0.1	-
Apr.27/76	.006	.002	.004	-	-	-	-	-	ND	-	0.3	-	-	-
	-	-	-	-	-	.008	-	-	.020	-	0.2	-	-	-
May 18/76	.011	.004	-	-	-	-	-	-	.03	-	1.4	0.2	-	-
	.008	.003	-	-	.002	-	-	-	.03	-	1.3	0.2	<0.1	-
AG-2														
Feb.25/75	.035	.003	.057	-	.014	.013	-	-	.140	-	0.3	0.5	-	-
	.037	.003	.056	-	.013	.014	-	-	.160	-	0.3	0.9	-	-
Mar.19/75	.004	.003	.001	-	-	-	-	-	.032	-	<0.1	-	-	-
	.006	-	.010	-	-	-	-	-	.080	-	<0.1	-	-	-
AG-3														
Feb.24/75	.003	.003	<0.001	-	.002	-	-	-	.040	-	0.7	0.2	-	-
	.007	.007	.002	-	<0.001	.022	-	-	.050	-	1.5	0.6	-	-
Apr.21/75	.005	-	-	-	-	.002	-	-	.050	-	1.7	0.4	<0.1	-
	. 004	-	-	-	-	-	-	-	.100	-	1.6	<0.1	<0.1	-
May 30/75	.004	-	-	-	-	-	-	-	.050	-	1.1	0.5	-	-
	.004	-	-	-	-	-	-	-	.060	-	1.1	0.5	-	-
AG-4														
Sep.12/75	.008	.004	.004	-	-	.004	-	-	.040	-	0.5	0.6	-	-
	.009	.003	-	-	.002	-	-	-	.040	-	0.5	0.4	-	-
Nov.27/75	.010	.003	-	-	-	-	-	-	.060	<0.5	<0.1	-	-	-
	.007	-	-	-	-	-	-	-	.020	<0.5 (d,m)	<0.1	<0.1	-	-

Continued ....

APPENDIX VI Continued

Watershed and Date	Content in Duplicate Water Samples (µg/L)													
	DDE	TDE	DDT	HE	DLD	END	DIA	MAL	PCB	24-D MCPA	ATR	deAT	SIM	MET
AG-5														
May 21/75	-	-	-	-	-	-	-	-	.05	-	0.2	0.2	-	-
	-	-	-	-	-	-	-	-	.08	-	0.2	0.5	-	-
Nov.9/76	.001	-	-	-	-	-	-	-	.04	-	0.1	0.3	<0.1	-
	.001	-	-	-	-	-	-	-	.04	-	0.1	0.2	<0.1	-
AG-6														
Apr.17/75	.006	-	-	-	-	-	-	-	.08	-	0.1	<0.1	-	-
	.007	-	-	-		-	-	-	.02	-	0.1	-	< 0.1	-
Mar.13/77	-	-	-		-	-	-	-	.010	-	0.3	0.2	-	--
	.002	-	-	-	-	-	-	-	.006	-	0.3	0.2	-	-
AG-7														
May 11/76	.006	.003	.004	-	-	-	-	-	.03	-	-	-	-	-
	.008	.003	.001	-	-	-	-	-	.04	-	-	-	-	-
AG-10														
Mar.24/76	.005	.003	-	-	-	-	-	-	.01	-	0.3	-	-	-
	.002	.001	.001	-	-	-	-	-	.06	-	0.3	-	-	-
AG-13														
May 28/75	.002	.001	.002	-	.017	.050	.35	-	.06	-	0.4	-	-	1.0
	.002	.001	.003	-	.019	.052	.58	-	.06	--	0.4	0.3	<0.1	0.9
June 24/75	.005	.003	.005	-	-	-	-	-	.07	-	0.9	<0.1	-	-
	.022	.075	.045	-	-	-	-	-	.05	-	3.6	0.6	-	-
Apr.27/76	.004	.001	.002	-	.002	.006	.054	-	.02	-	-	-	-	-
	-	-	-	-	.003	.008	-	-	-	-	-	-	-	-
May 18/76	.004	.002	-		<0.001	<0.001	-	-	.03	-	<0.1	-	-	-
	.008	.004	.001	-	.009	.032	.066	-	.03	-	0.2	<0.1	-	-

Continued ....

APPENDIX VI Continued

	Content in Duplicate Water Samples (µg/L)													
Watershed and Date	DDE	TDE	DDT	HE	DLD	END	DIA	MAL	PCB	24-D MCPA	ATR	deAT	SIM	MET
AG-13 (continued...)														
Aug.16/76	.002	-	-	.004	.017	.031	.23	-	.004	-	-	-	-	-
	.002	-	-	.001	.006	.008	.17	-	-	-	-	-	-	-
Sep.27/76	.001	-	-	-	-	-	-	-	.01	-	3.6	1.2	<0.1	-
	.002	-	-	-	.003	.019	6.0	-	.03	-	<0.1	-	-	-
Oct.7/76	.001	-	-	-	.002	.02.6	3.5	-	.03	-	<0.1	-	-	-
	.002	-	-	-	<0.001	.009	3.0	-	.04	-	-	-	-	-
Oct.25/76	.002	-	-	-	-	.002	2.1	-	.01	0.3	10.8	-	-	-
	.002	-	-	-	-	<0.001	2.5	-	.04	0.3	10.8	-	-	-
Nov.4/76	.001	-	-	.002	-	.003	.50	-	.05	-	3.1	-	-	-
	.001	-	-	.002	-	.003	.26	-	.04	-	2.1	-	-	-
Nov.18/76	.002	-	-	-	.001	.001	.50	-	.03	-	0.8	-	-	-
	.002	-	-	--	.002	.001	.26	-	.04	-	0.7	-	-	-
Nov.26/76	.002	-	-	-	.002	.006	l.3	-	.03	-	0.6	-	-	-
	.002	-	-	-	<0.001	.005	l.8	-	.02	-	0.6	-	-	-
Dec.6/76	.022	-	-	-	.003	.005	2.6	1.9	.034	-	0.2	-	-	-
	.018	-	-	-	.004	.007	2.0	l.7	.032	-	0.3	-	-	-
AG-14														
May 14/75	.004	-	-	-	-	-	-	-	.06	-	0.3	< 0.1	-	-
	.002	-	-	-	-	-	-	-	.05	-	0.3	<0.1	-	-
Mar.16/77	.001	-	-	-	-	-	-	-	.008	-	0.2	0.1	-	-
	.001	-	-	-	-	-	-	-	.007	-	0.2	<0.1	-	-
Mar.17/77	.001	.001	-	-	-	-	-	-	-	-	0.2	0.1	-	-
	.001	.001	-	-	-	-	-	-	.008	-	0.2	0.1	-	-

HE= heptachlor epoxide
END = endosulfan
DIA = diazinon
MAL = malathion

ATR= atrazine
de-AT= desethylated atrazine
SIM= simazine
MET= metribuzin
DLD= dieldrin

APPENDIX VII Interpretation of Trace and Not Detected Levels of Pesticides for Concentrations in Water and for Loading Purposes

Pesticide	Trace (ng/L)		Not Detected (ng/L)	
	Conc. in Water	For Loading	Conc. in Water	For Loading
p,p'-DDE	0.4 - 0.9	0.7	<0.4	0.2
p,p'-TDE	0.4 - 0.9	0.7	<0.4	0.1
o,p' & p,p'-DDT	0.4 - 0.9	0.7	<0.4	0.1
dieldrin	0.4 - 0.9	0.7	<0.4	0.2
chlordane	0.4 - 0.9	0.7	<0.4	0.0
endosulfan	0.4 - 0.9	0.7	<0.4	0.0
heptachlor epoxide	0.4 -0.9	0.7	<0.4	0.0
PCB	2.0 -6.0	4.0	<2.0	1.0

Pesticide	Trace (µg/L)		Not Detected (µg/L)	
	Conc. in Water	For Loading	Conc. in Water	For Loading
atrazine	0.04 - 0.09	0.07	<0.04	0.02
desethylated atrazine	0.04 - 0.09	0.07	<0.04	0.02
simazine	0.04 - 0.09	0.07	<0.04	0.02
cyprazine	0.04 - 0.09	0.07	<0.04	0.00
prometone	0.04 - 0.09	0.07	<0.04	0.00
metribuzin	0.04 - 0.09	0.07	<0.04	0.00
2,4-D	0.1- 0.4	0.3	<0.1	0.0
a,4,5-T	0.1- 0.4	0.3	<0.1	0.0
MCPA	0.1- 0.4	0.3	<0.1	0.0
dicamba	0.1- 0.4	0.3	< 0.1	0.0
alachlor	0.04 - 0.09	0.07	<0.04	0.00

APPENDIX VIII(a) Total monthly flow volumes for 11 agricultural watersheds between May 1975 and April 1977

	Flow Volume (m^3 x 10^3)											
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
1975-76												
May	6	2319	993	92	429	(2979)[1/]	1998	173		160	(357)	9,506
June	43	2430	640	257	475	(1472)	1665	338		245	(7)	7,572
July	2	1702	169	1	76	(1018)	1205	0		85	(0)	4,258
August	29	1788	386	170	211	1924	1058	612		935	319	7,432
Sept.	42	2812	532	343	226	1718	1394	532		19	699	8,317
Oct.	3	2344	103	139	129	1716	1381	454		6	268	6,543
Nov.	3	2751	865	311	338	1554	1542	464		197	1381	9,406
Dec.	59	3811	2985	1003	963	2985	1739	1554		781	3293	19,173
Jan.	102	3343	1924	200	1517	2072	1153	1052	[43][2/]	697	1108	13,168
Feb.	6883	7327	9411	1135	3281	4021	3466	4983	[3306]	2849	3145	46,501
March	2627	8388	9251	3787	4009	1026	7549	3429	[2640]	1677	16,035	57,778
April	630	4737	3182	1050	1068	4169	3158	1665	[523]	504	298	20,461
TOTAL	10,429	43,752	30,441	8,488	12,722	26,654	27,308	15,256	[6,512]	8,155	26,910	210,115
1976-77												
May	501	4305	1788	535	1020	2997	2479	1061	408	352	310	15,756
June	269	2319	292	144	92	1142	1603	60	24	154	355	6,454
July	762	2085	2985	197	845	1517	1591	126	6	173	804	11,091
August	0	2011	1517	4	1163	810	1215	40	19	20	0	6,799
Sept.	5	1690	222	33	208	988	1270	39	0	30	7	4,492
Oct.	17	1838	287	169	461	1153	1456	74	38	74	121	5,688
Nov.	1	1813	2529	259	820	1105	1196	41	11	67	3071	10,913
Dec.	9	1764	592	141	606	1058	907	69	6	71	640	5,863
Jan.	0	1645	311	45	385	1051	629	2	0	20	220	4,308
Feb.	0	1698	246	33	499	864	916	120	124	602	88	5,190
March	4520	6140	11,023	3834	5515	3515	4641	2706	1645	1122	8878	58,539
April	3445	4926	2091	516	1484	3297	2356	879	360	1037	1750	22,141
TOTAL	9,529	32,234	23,883	5,910	13,098	24,497	20,259	5,217	2,641	3,722	16,244	157,234

[1/] In brackets - rough estimate of flow volume

[2/] AG-11 not included in 1975-76 totals

APPENDIX VIII(b) Monthly losses of suspended solids leaving 11 agricultural watersheds between May 1975 and April 1977

	Suspended solids lost (kg x 10^3)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
<u>1975-76</u>												
May	2	70	17		6	16	26	11		2	3	153
June	1749	29	23		10	9	38	28		19	0	I,905
July	3	255	2		1	5	5	0		0	0	271
August	1507	42	10		3	4	6	1		39	3	1,615
Sept.	72	62	8		3	4	7	1		14	7	178
Oct.	1	27	1		1	5	3	89		1	2	130
Nov.	1	38	14		5	2	3	34		1	15	113
Dec.	76	60	4		26	33	33	120		22	22	396
Jan.	20	75	26	(1)	18	9	10	19		25	14	216
Feb.	4241	239	255	(27)	130	18	18	166		246	33	5,346
March	529	409	369	(681)	114	158	58	264		207	494	2,602
Apri1	22	127	478	(24)	12	93	25	336		114	2	1,209
TOTAL	8223	1433	1207		329	356	232	1069		690	595	14,134
<u>1976-77</u>												
May	42	96	30	25	36	19	6	328	1	22	4	609
June	26	42	3	5	1	5	9	2	0	14	14	121
July	140	27	335	4	327	13	12	11	0	1	8	878
August	0	34	31	0	404	7	5	1	0	1	0	483
Sept.	0	15	2	2	1	6	4	1	0	2	0	33
Oct.	1	9	3	5	3	5	3	2	0	2	1	R4
Nov.	0	11	54	16	21	4	8	1	0	1	39	155
Dec.	0	17	5	1	2	5	4	4	0	2	3	43
Jan.	0	7	3	0	1	5	2	0	0	1	1	20
Feb.	0	49	3	0	5	8	8	15	2	28	0	118
March	723	417	857	799	529	149	70	235	31	203	443	4,456
April	945	172	64	40	14	16	50	50	26	219	17	1,613
TOTAL	1877	896	1390	897	1344	242	181	650	60	496	530	8,563

Ref. R. Coote (1978)

APPENDIX IX Monthly concentration means of DDT, TDE and DDE in stream waters collected between February 1975 and May 1977 with mean and range for ∑DDT

Date	Com-ponent	Content in water (ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
<u>1975</u>												
Feb.	DDE		36	5			4					
	TDE		3	3			4					
	DDT		57	1			1					
	∑ DDT		96	8			9					
Mar.	DDE	3	5	NT)	7	ND	2		4	ND	10	ND
	TDE	ND	2	ND	ND	ND	ND		ND	ND	2	ND
	DDT	ND	6	ND	ND	ND	ND		ND	ND	15	ND
	∑ DDT	3	13	ND	7	ND	2		4	ND	27	ND
		ND-7	-	-	ND-7		T-3				6-66	
Apr.	DDE	7	7	35	8	104	9	8	12	7	93	8
	TDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	∑ DDT	7	7	35	8	104	9	8	12	7	93	8
		1-13	1-11	4-71	6-11	1-470	5-13	5-10	7-16	3-12	3-520	5-14
May	DDE	1	2	1	1	2	1	4	1	3	2	1
	TDE	ND	ND	ND	ND	ND	ND	2	ND	ND	ND	ND
	DDT	ND	ND	ND	ND	ND	ND	17	ND	ND	ND	ND
	∑ DDT	1	2	1	1	2	1	23	1	3	2	1
		ND-5	ND-4	ND-4	ND-5	ND-3	ND-2	ND-120	ND-2	1-5	ND-4	ND-3
June	DDE	2	4	2	2	2	2	3	2	3	5	2
	TDE	ND	2	ND	ND	ND	ND	1	ND	ND	3	ND
	DDT	ND	33	ND	ND	ND	ND	ND	ND	ND	4	ND
	∑ DDT	2	39	2	2	2	2	4	2	3	12	2
		1-7	1-142	1-2		1-5	1-3	2-12		3-4	2-59	

Continued ......

APPENDIX IX Continued . . . .

Date	Com - ponent	Content in water (ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975 (cont'd.)												
July	DDE	3	24	2	2	3	2	3	4		4	
	TDE	T	8	ND	ND	ND	T	ND	ND		ND	
	DDT	2	86	ND	ND	ND	1	1	ND		ND	
	Σ DDT	6	118	2	2	3	4	4	4		4	
		3-7	3-347	1-4		1-4	1-13	2-7			3-4	
Aug.	DDE	19	2	1		2	4	4			3	
	TDE	2	ND	ND		ND	T	ND			ND	
	DDT	1	ND	ND		ND	2	1			ND	
	Σ DDT	22	2	1		2	7	5			3	
							1-27	2-9			3-4	
Sept.	DDE	15	8	10	6	7	16	14			12	14
	TDE	2	3	3	1	3	2	4			3	5
	DDT	T	1	ND	ND	ND	ND	ND			2	ND
	Σ DDT	18	12	13	7	10	18	18			17	19
		8-39	8-18	9-15	5-9	2-15	2-55	12-28			6-25	12-27
Oct.	DDE	3	3	2	7	3	5		4		5	4
	TDE	T	T	ND	NI)	T	ND		ND		1	ND
	DDT	ND	ND	ND	ND	ND	ND		ND		ND	ND
	Σ DDT	4	4	2	7	4	5		4		6	4
			2-7	2-3		1-7	2-7		2-5		4-8	2-6
Nov.	DDE	10	9	9	9	8	6		10		8	6
	TDE	ND	3	1	2	T	ND		3		1	1
	DDT	ND	ND	ND	ND	ND	ND		ND		ND	ND
	Σ DDT	10	12	10	11	9	6		13		9	7
		2-18	10-14	8-13		3-15	3-15				5-17	5-12

Continued .....

APPENDIX IX Continued

Date	Com - ponent	Content in water (ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
<u>1975 (cont'd.)</u>												
Dec.	DDE	2	1	13	3	3	2		T		3	2
	TDE	ND	ND	2	ND	ND	ND		ND		ND	ND
	DDT	ND	ND	ND	ND	ND	ND		ND		ND	ND
	∑DDT	2	1	15	3	3	2		T		3	2
		ND-6		T-46	1-6	2-14	1-5		ND-1		1-6	1-3
<u>1976</u>												
Jan.	DDE	6		17	7	11	7		4		7	5
	TDE	ND		ND	ND	ND	ND		ND		ND	ND
	DDT	ND		ND	ND	ND	ND		ND		ND	ND
	∑DDT	6		17	7	11	7		4		7	5
		ND-13			ND-13	5-17	T-13		ND-7		2-12	3-6
Feb.	DDE	8	5	10	4	6	1		4		7	ND
	TDE	ND	ND	ND	ND	ND	ND		ND		ND	ND
	DDT	ND	ND	ND	ND	ND	ND		ND		ND	ND
	∑DDT	8	5	10	4	6	1		4		7	ND
		5-12	3-7	7-11		2-12			ND--7		2-12	
March	DDE	8	4	5	4	6	7	2	6	7	8	7
	TDE	3	3	ND	ND	ND	ND	2	T	2	T	T
	DDT	ND	ND	ND	ND	ND	ND	ND	ND	T	ND	ND
	∑DDT	11	7	5	4	6	7	4	7	10	9	8
		3-22		3-7	ND-7		1-16	3-4	6-7	ND-17	2-20	1-17
April	DDE	2	10	1	2	T	2		1	1	2	1
	TDE	T	ND	T	ND	ND	ND		ND	ND	T	ND
	DDT	T	ND	T	1	ND	ND		ND	ND	T	ND
	∑DDT	3	10	2	3	T	2		1	1	3	1
		1-6		ND-4	1-14		ND-4		ND-2		ND-6	ND-3

Continued ....

APPENDIX IX **Continued**

Date	Com - ponent	Content in water (ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976 (con'd.)												
May	DDE	4	5	3	4	5	5	8	5		3	5
	TDE	1	3	T	1	1	2	2	2		1	1
	DDT	ND	T	T	2	T	1	2	2		T	T
	∑DDT	5	9	4	7	7	8	12	9		5	7
		ND-14	5-12	ND-8	ND-14	1-15	T-14	11-13	2-13		ND-15	1-17
June	DDE	2	6	10	5	52	5		3		3	6
	TDE	ND	ND	1	ND	3	ND		ND		T	ND
	DDT	ND	ND	ND	ND	2	ND		ND		ND	ND
	∑DDT	2	6	11	5	57	5		3		4	6
		ND-7	T-13	ND-29	T-10	ND-253	1-10		ND-10		ND-17	ND-13
July	DDE	2	1	2	2	1	1	1	1		1	2
	TDE	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
	DDT	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
	∑DDT	2	1	2	2	1	1	1	1		1	2
		1-3		1-4		T-1	1-2				T-3	1-2
Aug.	DDE	1	1	1	1	1	1	1	1	1	2	2
	TDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	∑DDT	1	1	1	1	1	1	1	1	1	2	2
		1-2		T-1	1-2	1-2			1-2		T-3	1-4
Sept.	DDE		2	1	1	3	2		1		2	1
	TDE		ND	ND	ND	ND	ND		ND		T	ND
	DDT		ND	ND	ND	ND	ND		ND		T	ND
	∑DDT		2	1	1	3	2		1		3	1
			1-2	T-2		1-10	T-3		ND-3		T-8	

Continued ...

APPENDIX IX **Continued**

Date	Com - ponent	Content in water (ng/L)										
		AD-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976 (cont'd.)												
Oct.	DDE	1	1	1	1	1	1	1	2	1	1	1
	TDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	∑DDT	1	1	1	1	1	1	1	2	1	1	1
		T-2	T-2	T-1	T-1	T-1	T-1	T-1	1-2	T-1	T-2	T-1
Nov.	DDE	1	1	1	1	1	2	1	1		3	2
	TDE	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
	DDT	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
	∑DDT	1	1	1	1	1	2	1	1		3	2
				T-1	T-2	T-1	1-2	1-2			1-10	1-3
Dec.	DDE	4	6	5	4	4	2	6	6		8	11
	TDE	1	1	2	T	1	T	1	2		T	6
	DDT	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
	∑DDT	5	7	7	5	5	3	7	8		9	17
				5-7	3-7	4-8	1-4	6-8			ND-20	7-24
1977												
Jan.	DDE		5	2		4	4	2			2	2
	TDE		ND	ND		ND	ND	ND			ND	ND
	DDT		ND	ND		ND	ND	ND			ND	ND
	∑DDT		5	2		4	4	2			2	2
			2-7	ND-6		ND-10	2-8				T-4	
Feb.	DDE		6	2		T	T				5	T
	TDE		2	ND		ND	ND				2	ND
	DDT		45	ND		ND	ND				12	ND
	∑DDT		53	2		T	T				19	T
			ND-158	1-2		ND-1	ND-1				ND-69	ND-1

Continued ....

APPENDIX IX Continued

Date	Com - ponent	Content in water (ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
<u>1977 (cont'd.)</u>												
March	DDE	4	11	5	5	8	8	5	9	5	22	5
	TDE	4	4	T	2	2	1	6	2	7	11	2
	DDT	T	13	1	ND	1	1	ND	2	ND	35	ND
	∑DDT	9	28	7	7	11	10	11	13	12	68	7
		4-13	4-44	2-16	3-16	4-22	2-23		6-29		11-211	1-15
April	DDE	2	5	5	2	4	T	ND	5		2	1
	TDE	2	4	6	6	3	ND	ND	5		2	2
	DDT	ND	48	41	27	26	ND	ND	35		ND	ND
	∑DDT	4	57	52	35	33	T	ND	45		4	3
		1-7	7-113	6-114	ND-97	6-64	ND-1		2-126		1-6	ND-6
May	DDE	8	2	1	6	2	T	5		5	4	1
	TDE	6	4	3	2	1	2	4		4	9	T
	DDT	44	ND	1	30	ND	ND	31		64	48	ND
	∑DDT	58	6	5	38	3	3	40		73	61	2
		12-112	1-11	ND-7	3-72	ND-12	ND-7	1-77			26-95	1-2
<u>Feb.1975-May 1977</u>												
Mean	DDE	4	5	5	4	11	4	4	4	5	8	4
	TDE	1	2	T	T	T	T	1	T	T	1	T
	DDT	1	12	1	2	1	T	3	2	2	3	ND
	∑DDT	6	20	7	7	13	5	8	7	8	12	5
Total	Samples	126	70	123	83	128	110	52	62	29	170	94

ND - not detected <0.4 ng/L
T - trace 0.4 - 0.9 ng/L

APPENDIX X Amount of ∑DDT leaving 11 agricultural watersheds between May 1975 and April 1977

	Amount leaving watersheds (g)											
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
<u>1975-76</u>												
May	0	2	5	0	0	6	28	1		3	0	45
June	28	10	2	0	0	3	7	0		0	0	50
July	0	175	0	0	0	5	3	0		0	0	183
Aug.	9	4	1	0	0	12	5	3		4	1	39
Sept.	32	38	5	2	1	29	19	1		5	9	141
Oct.	0	15	0	0	0	6	15	1		0	0	37
Nov.	0	20	10	2	1	9	17	6		1	12	78
Dec.	10	29	45	3	4	12	20	7		2	5	137
Jan.	8	11	14	1	7	20	12	2	(0)	5	5	85
Feb.	56	59	112	11	14	42	41	18	(9)	23	13	389
Mar.	42	50	89	13	16	89	43	18	(35)	18	10	388
April	2	54	14	1	1	7	6	2	(1)	0	0	87
TOTAL	187	467	297	33	44	240	216	59		61	55	1659
<u>1976-77</u>												
May	2	42	11	1	4	14	24	7	0	0	0	105
June	1	13	2	0	1	5	18	0	0	0	6	46
July	2	1	14	0	0	5	11	0	0	0	7	40
Aug.	0	1	5	0	2	0	0	0	0	0	0	8
Sept.	0	2	0	0	0	1	0	0	0	0	0	3
Oct.	0	2	0	0	0	0	0	0	0	0	0	2
Nov.	0	1	9	0	0	0	1	0	0	0	3	14
Dec.	0	5	3	0	1	1	3	0	0	0	8	21
Jan.	0	10	0	0	1	3	0	0	0	0	0	14
Feb.	0	47	0	0	0	2	1	0	0	14	44	108
Mar.	44	360	156	23	40	40	19	33	4	50	15	784
April	28	214	13	1	8	24	22	5	3	10	8	336
TOTAL	77	698	213	25	57	95	99	45	7	74	91	1481

APPENDIX XI Amount of DDE, TDE, DDT and ∑DDT leaving 11 agricultural watersheds between May 1975 and April 1977

Watersheds	Amount leaving watersheds (g)							
	1975-76 (May-April)				1976-77 (May-April)			
	DDE	TDE	DDT	∑DDT	DDE	TDE	DDT	∑DDT
AG-1	110	64	13	187	27	49	1	77
AG-2	219	113	135	467	217	99	382	698
AG-3	196	98	3	297	118	79	16	213
AG-4	33	0	0	33	19	6	0	25
AG-5	44	0	0	44	43	7	7	57
AG-6	227	12	1	240	62	29	4	95
AG-7	140	56	20	216	60	31	8	99
AG-10	57	2	0	59	34	10	1	45
AG-11					4	3	0	7
AG-13	60	0	1	61	28	13	33	74
AG-14	51	4	0	55	70	21	0	91
TOTAL	1137	349	173	1659	682	347	452	1481
	68.5%	21.1%	10.4%		46.1%	23.4%	30.5%	

APPENDIX XII Residues of pesticides in six series of waters taken during six flow events between June 1975 and March 1977

WATER-SHED			Mean Content in water (µg/L)												
	DATE	TIME	DDE	TDE	DDT	HE	DLD	ENDO	DIA	PCB	2,4-D	2,4,5-T	ATR	deATR	SIM
AG-1	June 24/75	1130	.003	ND	ND	ND	ND	ND	ND	.05	0.5	<0.5	2.8	<0.1	<0.1
		1600	.003	.001	.002	ND	ND	ND	ND	.10	0.7	<0.5	41.1	<0.1	ND
		1725	.008	.003	.005	ND	ND	ND	ND	.10	4.2	0.7	9.3	1.7	ND
AG-3	Dec.15/75	2330	.040	.006	ND	ND	ND	ND	ND	.030	ND	ND	1.8	1.6	ND
	Dec.16/75	0030	.003	ND	ND	ND	ND	ND	ND	.010	ND	ND	1.5	1.4	ND
		0130	.004	ND	ND	ND	ND	ND	ND	.030	ND	ND	1.3	1.2	ND
		0330	.007	ND	ND	ND	ND	ND	ND	.030	ND	ND	1.3	1.1	ND
AG-4	Sep.11/75	0930	.024	.001	ND	ND	ND	ND	ND	.090	ND	ND	0.9	0.9	ND
		1020	.008	ND	ND	ND	ND	ND	ND	.07	1.6	1.5	0.3	0.3	ND
		2330	.008	ND	ND	ND	ND	ND	ND	.03	ND	ND	0.1	0.2	ND
	Sep.12/75	0020	.005	.003	ND	ND	ND	ND	ND	.040	ND	ND	0.2	0.1	ND
		0120	.005	ND	ND	ND	ND	ND	ND	.050	ND	ND	0.1	0.1	ND
		0150	.004	.003	ND	ND	ND	ND	ND	.050	ND	ND	0.2	0.l	ND
		0250	.008	.004	.004	ND	ND	ND	ND	.040	ND	ND	0.5	0.3	ND
		0400	.004	.003	ND	ND	ND	ND	ND	.040	ND	ND	0.7	0.4	ND
		0530	.008	.004	.004	ND	ND	ND	ND	.050	ND	ND	1.2	0.6	ND
		0700	.008	.003	ND	ND	ND	ND	ND	.040	ND	ND	1.3	0.6	ND
		0830	.008	.004	.004	ND	ND	ND	ND	.070	ND	ND	0.7	0.6	ND
		1050	.004	.003	ND	ND	ND	ND	ND	.040	ND	ND	0.7	0.6	ND
		1300	.008	.004	.004	ND	ND	.004	ND	.040	ND	ND	0.5	0.6	ND
		1410	.009	.003	ND	ND	.002	ND	ND	.040	ND	ND	0.5	0.4	ND
AG-6	Mar.21/77	1200	.003	.004	ND	ND	ND	ND	ND	.020	ND	ND	<0.1	<0.1	ND
		1430	.006	.005	ND	ND	ND	ND	ND	.033	ND	ND	<0.1	<0.1	ND
		1630	.009	.006	ND	ND	ND	ND	ND	.016	ND	ND	<0.1	<0.1	ND
AG-13	Feb.24/77	0930	.015	.012	.065	ND	.007	.002	.092	.045	ND	ND	0.5	<0.1	ND
		1340	.012	.006	.036	ND	.025	.040	.79	.10	ND	ND	0.5	<0.1	ND
		1600	.012	.006	.032	ND	.020	.018	.62	.10	ND	ND	0.4	<0.1	ND
		1900	.016	.005	.060	ND	.019	.028	.75	.09	ND	ND	0.4	<0.1	ND

Continued ...

APPENDIX XII Continued

WATER- SHED	DATE	TIME	Mean Content in water (µg/L)												
			DDE	TDE	DDT	HE	DLD	ENDO	DIA	PCB	2,4-D	2,4,5-T	ATR	deATR	SIM
AG-13	Feb.25/77	1010	.010	.002	.015	ND	.014	.022	.65	.02	ND	ND	0.4	<0.1	ND
	Mar.4/77	1440	.038	.010	.168	ND	.038	.050	.37	.07	ND	ND		Lost	
		1800	.042	.020	.154	.002	.031	.040	.33	.14	ND	ND	0.5	0.1	ND
		2100	.044	.018	.166	.004	.031	.046	.44	.15	ND	ND	0.5	0.l	ND
	Mar.5/77	1405	.024	.010	.024	.002	.015	.019	.15	.03			0.5	<0.1	ND

HE	heptachlor epoxide	DIA	diazinon
DLD	dieldrin	ATR	atrazine
ENDO	endosulfan	deATR	desethylated atrazine
SIM	simazine		

APPENDIX XIII Monthly concentration of dieldrin in water collected in 11 agricultural watersheds between February 1975 and May 1977 (mean and range)

		Content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975	Feb.		14	1			ND					
	Mar.	ND	ND	ND	ND	ND	ND		ND	ND	6	ND
											ND-16	
	April	1	T	ND	ND	ND	1	ND	ND	ND	2	ND
		ND-5					ND-4				ND-8	
	May	ND	ND	ND	ND	ND	ND	ND	ND	ND	6	ND
		ND-1	ND-1			ND-1	ND-1				ND-18	ND-1
	June	3	ND	ND	ND	T	ND	ND	ND	ND	20	ND
		ND-32	ND-1			ND-1		ND-T			ND-120	
	July	ND	21	ND	ND	ND	ND	T	ND		T	
			ND-63				ND-T	ND-3			ND-T	
	Aug.	ND	ND	ND		ND	ND	T			12	
								ND-2			11-15	
	Sep.	T	2	ND	ND	ND	1	2			8	ND
		ND-3	ND-4			ND-T	ND-4	ND-9			ND-16	ND-T
	Oct.	T	T	ND	ND	ND	ND		T		2	ND
		ND-1	ND-T						ND-T		ND-12	
	Nov.	ND	ND	ND	ND	ND	ND		ND		3	ND
		ND-T					ND-T				ND-10	
	Dec.	T	ND	ND	ND	ND	ND		T		6	ND
		ND-2							ND-T		ND-10	ND-T

Continued ....

APPENDIX XIII Continued

		Content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976	Jan.	10		4	ND	ND	ND		ND		3	ND
		ND-29									ND-6	
	Feb.	1	T	ND	ND	ND	ND		ND		5	ND
		T-2	ND-1			ND-1					ND-8	
	Mar.	T	ND	ND	ND	ND	ND	ND	ND	ND	8	ND
		ND-2									2-15	
	April	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	ND
		ND-T		ND-T							ND-12	
	May	ND	ND	ND	ND	ND	ND	ND	ND		5	ND
		ND-1			ND-T						ND-15	ND-T
	June	T	ND	ND	ND	1	ND		3		6	ND
		ND-3				ND-5			ND-12		ND-14	
	July	T	ND	ND	ND	ND	ND	ND	ND		9	ND
		ND-4									ND-31	
	Aug.	ND	ND	ND	ND	ND	ND	ND	ND	ND	13	ND
											ND-18	
	Sep.		ND	ND	ND	ND	1	ND	ND		6	ND
							ND-4				ND-16	
	Oct.	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	ND
		ND-T									ND-3	

Continued ...

APPENDIX XIII Continued

		Content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976	Nov.	T	ND	ND	ND	ND	ND	ND	ND		2	ND
											ND-4	
	Dec.	T	ND	ND	ND	ND	ND	ND	ND		2	ND
											ND-4	
1977	Jan.		ND	ND		ND	ND	ND			4	ND
											ND-6	
	Feb.		3	ND		ND	ND				5	T
			ND-5								ND-18	ND-1
	Mar.	ND	T	ND	ND	T	T	ND	ND	ND	15	ND
			ND-3	ND-T		ND-2	ND-1				5-33	
	April	T	T	ND	ND	ND	ND	1	ND		6	ND
		ND-1	ND-l								1-9	
	May	ND	ND	ND	ND	ND	ND	ND		ND	4	ND
											3-5	

ND - not detected, <0.4 ng/L
T - trace 0.4-0.9 ng/L

APPENDIX XIV Amount of dieldrin leaving 11 agricultural watersheds between May 1975 and April 1977

	Losses of dieldrin per month (g)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
1975-76												
May	0	0	0	0	0	0.5	0	0	0	0.5	0	1.0
June	3.6	0.5	0	0	0	0	0	0	0	3.2	0	7.3
July	0	34.0	0	0	0	0	0	0	0	0	0	34.0
Aug.	0	3.2	0	0	0	0	0	0	0	13.6	0	16.8
Sept.	0.9	5.0	0	0	0	2.7	4.1	0	0	5.0	0	17.7
Oct.	0	0	0	0	0	0	0	0	0	0.5	0	0.5
Nov.	0	I.4	0	0	0	0	0	0	0	0.4	0	1.8
Dec.	1.8	0	0	0	0	0	0	0	0	3.2	1.4	6.4
Jan.	10.4	0	1.4	0	0	0	0	0	0	1.8	0	13.6
Feb.	6.4	1.8	0.9	0	0	0	0	0	0	11.8	0	20.9
Mar.	6.8	6.8	0	0	0	0	0	0	0	14.5	0	28.1
April	0.5	0	1.4	0	0	0	0	0	0		0	3.3
TOTAL	30.4	52.7	3.7	0	0	3.2	4.1	0	0	55.9	1.4	151.4
1976-77												
May	0	0	0	0	0	0	0	0	0	1.4	0	1.4
June	0.5	0	0	0	0	0	0	0	0	1.4	0	1.9
July	0.5	0	0	0	0	0	0	0	0	1.4	0	1.9
Aug.	0	0	0	0	0	0	0	0	0	0	0	0.0
Sept.	0	0	0	0	0	0.5	0	0	0	0	0	0.5
Oct.	0	0	0	0	0	0.4	0	1.8	0	0	0	2.2
Nov.	0	0	0	0	0	0	0	0	0	0	0	0.0
Dec.	0	0	0	0	0	0	0	0	0	0	0	0.0
Jan.	0	0	0	0	0	0	0	0	0	0	0	0.0
Feb.	0	0.9	0	0	0	0	0	0	0	5.9	0	6.8
Mar.	4.0	18.1	6.4	0	0.5	1.8	0	0	0	16.3	0	47.1
Apr.	6.4	14.1	1.4	0	0	2.3	0	0	0	16.3	0	40.5
TOTAL	11.4	33.1	7.8	0	0.5	5.0	0	1.8	0	42.7	0	102.3

APPENDIX XV Monthly concentrations of cis- and trans-chlordane & heptachlor epoxide in water collected from 11 agricultural watersheds between February 1975 and May 1977 (mean and range)

YEAR	MONTH	Content in water(ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975	Feb.		ND	ND			ND					
	Mar.	ND	ND	ND	ND	ND	ND		ND	ND	1(H)	ND
											ND-3	
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	May	ND	ND(H)	ND	ND	ND	ND	ND	ND	ND(H)	ND	ND
			ND-T							ND-1		
	June	ND	ND	ND	ND	ND	ND	ND	ND	ND	40(H)	ND
											N	
	July	ND	ND	ND	ND	T(H)	ND	ND	ND		14(H)	
						ND-2					ND-28	
	Aug.	ND	ND	ND		ND	ND	ND			ND	
	Sept.	ND	ND	ND	ND	ND	ND	ND			1(H)	ND
											ND-5	
	Oct.	ND	ND	ND	ND	ND	ND		T(H)		ND(H)	ND
									ND-T		ND-T	
	Nov.	ND	ND	ND	ND	ND	ND		ND		ND(H)	ND
											ND-1	
	Dec.	ND	ND	ND	ND	ND	ND		ND		ND	ND

Continued ...

APPENDIX XV **Continued**

YEAR	MONTH	Content in water (ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976	Jan.	ND		ND	ND	3(H)	ND		ND		ND	ND
						2-4						
	Feb.	ND	T(H)	ND(H)	ND	4(H)	ND		T(H)		6(H)	ND
			ND-T	ND-T		ND-15			ND-2		ND-22	
	Mar.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		ND-T(H)										
	May	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
	June	T(C)	1(C)	3(C)	1(C)	5(C)	1(C)		1(C)		7(H)2(C)	1(C)
		ND-4	ND-4	ND-11	ND--4	ND-10	ND-4		ND-4		ND-24,ND-10	ND-4
	July	ND(H)	ND	ND	ND	ND	ND	ND	ND		11(H)	ND
		ND-2									ND-25	
	Aug.	ND	ND	ND	ND	9(C)	ND	ND	ND	ND	3(H)	ND
						ND-47					ND-8	
	Sept.		8(H)	ND	ND	ND	ND		ND		T(H)	ND
			ND-23								ND-3	
	Oct.	ND	ND	ND	ND	ND	ND	ND	ND	ND	T(H)	ND
											ND-2	
	Nov.	ND	ND	ND	ND	ND	ND	ND	ND		T(H)	ND
											ND-2	

Continued

APPENDIX XV Continued

YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
		Content in water (ng/L)										
1976 (continued....)												
	Dec.	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
1977	Jan.		ND	ND		ND	ND	ND			1 ND-3	ND
	Feb.		ND	ND		ND	ND				ND(H) ND-1	ND
	Mar.	T(H) ND-2	ND	ND	ND	ND	ND	ND	ND	ND	T(H) ND-2	ND
	Apr.	T ND-2	T ND-2	ND ND-T(H)	ND	ND	ND	ND	ND		3(H) ND-6	ND
	May	ND	ND	ND ND-T(H)	ND	ND	ND	ND		ND	2(H) 1-3	ND

C -	chlordane	ND -	not detected <0.4 ng/L
H -	heptachlor epoxide	T -	trace 0.4-0.9 ng/L

APPENDIX XVI Amount of chlordane and heptachlor epoxide leaving 11 agricultural watersheds between May 1975 and April 1977

	Amount leaving watersheds (g)											
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
Chlordane												
1976-77 (May-April)												
June	0	3	0	0	0	2	0	0	0	0	1	6
July	0	0	0	0	0	2	0	0	0	0	3	5
Aug.	0	0	0	0	1	0	0	0	0	0	0	1
TOTAL	0	3	0	0	1	4	0	0	0	0	4	12
Heptachlor epoxide												
1975-76 (May--April)												
July	0	0	0	0	0	0	0	0	0	8	0	8
Oct.	0	0	0	0	0	0	0	0	0	1	0	1
Jan.	0	0	0	0	2	0	0	0	0	0	0	2
Feb.	0	1	0	0	5	0	0	0	0	0	0	6
Mar.	0	7	0	0	0	0	0	0	0	0	0	7
TOTAL	0	8	0	0	7	0	0	0	0	9	0	24
1976-77 (May-April)												
June	0	0	0	0	0	0	0	0	0	1	0	1
July	0	0	0	0	0	0	0	0	0	2	0	2
Sept.	0	22	0	0	0	0	0	0	0	0	0	22
Oct.	0	5	0	0	0	0	0	0	0	0	0	5
Mar.	5	0	0	0	0	0	0	0	0	2	0	7
April	13	0	0	0	0	0	0	0	0	4	0	17
TOTAL	18	27	0	0	0	0	0	0	0	9	0	54

APPENDIX XVII Monthly concentrations of Σ endosulfan in water collected from 11 agricultural watersheds between February 1975 and May 1977 (mean and range)

		Content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975	Feb.		14				ND					
	Mar.	T	ND	1	ND	3	ND		ND	ND	17	ND
		ND-1									ND-41	
	Apr.	T	2	ND	1	1	1	ND	ND	ND	2	T
		ND-3	ND-5		ND-3	ND-10	ND-3				ND-6	ND-2
	May	1	ND	ND	ND	ND	ND	ND	ND	ND	10	2
		ND-7									ND-51	ND-6
	June	ND	ND	ND	ND	ND	ND	ND	ND	ND	15	ND
											ND-45	
	July	ND	7	1	ND	1	2	ND	ND		ND	
			ND-16	ND-6		ND-6	ND-6					
	Aug.	9	ND	ND		ND	20	ND			41	
							ND-107				10-75	
	Sept.	5	10	ND	ND	ND	2	33			15	ND
		ND-18	ND-17				ND-9	ND-128			ND-50	
	Oct.	3	1	ND	ND	ND	ND		2		11	ND
		ND-7	ND-2						ND-3		ND-27	
	Nov.	3	ND	ND	ND	ND	1		ND		8	ND
		ND-8					ND-8				ND-22	
	Dec.	3	ND	ND	ND	ND	ND		2		16	ND
		ND-10							ND-3		ND-24	ND-T

Continued ...

APPENDIX XVII Continued

		Content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976	Jan.	14		ND	ND	2	ND		ND		7	ND
		ND-41				ND-4					ND-22	
	Feb.	2	4	T	ND	3	ND		ND		11	ND
		ND-8	ND-8	ND-2		ND-6					ND-22	
	Mar.	1	ND	ND	1	ND	21	ND	ND	T	19	1
		ND-5			ND-6		ND-173			ND-4	ND-34	ND-11
	Apr.	3	1	ND	ND	ND	ND	ND	ND	ND	19	ND
		ND-9				ND-1					7-32	
	May	ND	ND	ND	ND	ND	ND	ND	ND		13	ND
				ND-T							ND-38	ND-T
	June	2	5	ND	1	ND	ND		ND		26	ND
		ND-5	ND-17		ND-4						ND-43	
	July	ND	ND	ND	ND	ND	ND	ND	T		18	ND
									ND-2		ND-51	
	Aug.	ND	ND	ND	ND	ND	ND	ND	ND	ND	23	ND
											ND-36	
	Sept.		ND	ND	ND	ND	T		1		24	ND
							ND-2		ND-3		ND-51	
	Oct.	1	ND	ND	ND	ND	ND	ND	ND	ND	12	ND
		ND-3				ND-T	ND-T				ND-31	
	Nov.	ND	ND	ND	ND	ND	ND	ND	ND		3	ND
											ND-9	

Continued ...

APPENDIX XVII Continued

YEAR	MONTH	Content in water (ng/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976 (continued....)												
	Dec.	ND	ND	ND	ND	ND	ND	ND	ND		4	ND
											ND-7	
1977	Jan.		ND	ND		ND	ND	ND			2	ND
				ND-8							ND-8	
	Feb.		ND	ND		ND	ND				8	ND
											ND-22	
	Mar.	ND	1	ND	ND	T	ND	ND	ND	ND	16	ND
			ND-5			ND-6					T-45	ND-T
	Apr.	T	T	ND	ND	ND	ND	ND	ND		9	ND
		ND-2	ND-2								ND-18	
	May	ND	ND	ND	ND	ND	ND	ND		ND	5	ND
											2-8	

ND -	not detected	0.4 ng/L
T -	Trace	0.4 - 0.9 ng/L

APPENDIX XVIII Amount of ∑endosulfan leaving 11 agricultural watersheds between May 1975 and April 1977

	Amount leaving watersheds (g)											
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
1975-76												
May	0.4	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	2.5
June	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.2	0.0	5.2
July	0.0	9.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	10.0
Aug.	0.0	0.0	0.0	0.0	0.0	17.8	0.0	0.0	0.0	69.1	0.0	86.9
Sept.	2.7	30.3	0.0	0.0	0.0	7.5	23.6	0.0	0.0	17.4	0.0	81.5
Oct.	0.0	0.2	0.0	0.0	0.0	0.0	0.0	2.0	0.0	1.9	0.0	4.1
Nov.	0.2	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	4.2
Dec.	10.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.3	0.0	19.1
Jan.	13.6	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	11.7	0.0	2.6.2
Feb.	1.9	16.5	1.2	0.0	7.3	0.0	0.0	0.0	0.0	26.8	0.0	53.7
Mar.	11.8	57.4	0.0	5.7	5.5	51.7	0.0	0.0	0.5	25.9	23.4	181.9
April	3.2	4.9	0.0	0.0	0.2	0.0	0.0	0.0	1.3	9.0	0.0	18.6
TOTAL	44.6	119.8	2.2	5.7	13.9	78.0	23.6	2.0	1.8	178.9	23.4	493.9
1976-77												
May	0.0	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.3	0.0	11.0
June	1.2	13.2	0.0	0.0	0.0	0.0	0.0	0.1	0.0	2.1	0.0	16.6
July	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.6	0.0	6.8
Aug.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.5
Sept.	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.1	0.0	0.7	0.0	1.1
Oct.	0.0	0.0	0.0	0.0	0.2	0.3	0.0	0.0	0.0	0.4	0.0	0.9
Nov.	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.1	0.0	0.3
Dec.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.4
Jan.	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Feb.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.9	0.0	6.9
Mar.	0.0	3.0	0.0	0.0	l.3	0.0	0.0	0.0	0.0	14.2	0.0	18.5
April	2.8	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.0	0.0	18.5
TOTAL	4.2	19.6	0.3	0.0	1.5	0.8	0.0	0.2	0.0	55.2	0.0	81.8

APPENDIX XIX Amounts of endosulfan components leaving 11 agricultural watersheds between May 1975 and April 1977

	Amount leaving watershed (g)											
Period	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	Total
1975 (May-Aug)												
cis-endosulfan	0.0	1.7	0.1	0.0	0.0	0.7	0.0	0.0	0.0	2.7	0.0	5.2
trans-endosulfan	0.1	1.7	0.5	0.0	0.0	3.7	0.0	0.0	0.0	11.8	0.0	17.8
endosulfan sulfate	0.3	5.6	0.4	0.0	0.0	14.4	0.0	0.0	0.0	60.9	0.0	81.6
Total	0.4	9.0	1.0	0.0	0.0	18.8	0.0	0.0	0.0	75.4	0.0	104.6
(Sep -Dec)												
cis-endosulfan	5.6	0.0	0.0	0.0	0.0	0.0	1.8	0.0	0.0	4.7	0.0	12.1
trans-endosulfan	2.8	7.0	0.0	0.0	0.0	1.9	5.6	0.4	0.0	5.6	0.0	23.3
endosulfan sulfate	5.3	25.0	0.0	0.0	0.0	5.6	16.2	1.6	0.0	19.8	0.0	73.5
Total	13.7	32.0	0.0	0.0	0.0	7.5	23.6	2.0	0.0	30.1	0.0	108.9
1976 (Jan-Apr)												
cis-endosulfan	9.3	27.7	0.0	4.4	0.0	5.4	0.0	0.0	0.9	14.5	10.6	72.8
trans-endosulfan	4.5	20.1	0.6	0.9	6.1	38.8	0.0	0.0	0.9	17.1	8.5	97.5
endosulfan sulfate	16.7	31.0	0.6	0.4	7.8	7.5	0.0	0.0	0.0	41.8	4.3	110.1
Total	30.5	78.8	1.2	5.7	13.9	51.7	0.0	0.0	1.8	73.4	23.4	280.4
Grand Total	44.6	119.8	2.2	5.7	13.9	78.0	23.6	2.0	1.8	178.9	23.4	493.9
(May - Aug.)												
cis-endosulfan	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.3	0.0	4.1
trans-endosulfan	0.6	4.3	0.0	0.0	0.0	0.0	0.0	0.1	0.0	3.4	0.0	8.4
endosulfan sulfate	0.0	11.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.8	0.0	22.4
Total	1.4	15.9	0.0	0.0	0.0	0.0	0.0	0.1	0.0	17.5	0.0	34.9
(Sep-Dec)												
cis-endosulfan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
trans-endosulfan	0.0	0.0	0.0	0.0	0.1	0.6	0.0	0.0	0.0	0.5	0.0	1.2
endosulfan sulfate	0.0	0.0	0.0	0.0	0.1	0.2	0.0	0.1	0.0	1.1	0.0	1.5
Total	0.0	0.0	0.0	0.0	0.2	0.8	0.0	0.1	0.0	1.6	0.0	2.7
1977 (Jan-Apr)												
cis-endosulfan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
trans-endosulfan	0.0	0.5	0.2	0.0	0.7	0.0	0.0	0.0	0.0	9.1	0.0	10.5
endosulfan sulfate	2.8	3.2	0.1	0.0	0.6	0.0	0.0	0.0	0.0	27.0	0.0	33.7
Total	2.8	3.7	0.3	0.0	1.3	0.0	0.0	0.0	0.0	36.1	0.0	44.2
Grand Total	4.2	19.6	0.3	0.0	1.5	0.8	0.0	0.2	0.0	55.2	0.0	81.8

APPENDIX XX Monthly concentrations of chlorophenoxy and chlorobenzoic acid herbicides in water collected from 11 agricultural watersheds between April 1974 and May 1977

(mean and range)

		Content in water (µg/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7$^{1/}$	AG-10	AG-11	AG-13	AG-14
1974	Apr.				T(D)		ND	ND		ND		ND
					ND-T							
	May				ND		ND(D)	ND		ND		ND
							ND-T					
	June				ND		ND	0.4(D)ND(BM)T(P)		ND		ND
								T-0.6,ND-T,ND-0.5				
	July				1.6(D)1.2(T)		ND(D)	ND		ND(D)0.7(T)		ND(D)
							ND-T			ND-T,T-1.0		ND-T
	Aug.						T(D)	ND		0.6(D)ND(T)		T(D)
							T			ND-1.1,ND-T		
	Sept.							ND(T)		T(T)		T(D)
								ND-T		T		ND-T
	Oct.									ND		
1975	Feb.		ND	ND			ND				ND	
	Mar.	ND	ND	ND	ND	ND	T(B)		ND	ND	ND	ND
							ND-1.0					
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	May	ND	ND	ND(D)	ND	ND	ND	ND	ND	ND	ND	ND
		ND-T(D,T)		ND-T								

Continued ....

APPENDIX XX Continued

		Content in water (µg/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975 (continued...)												
	June	1.8(D) T(T) ND-15.9 ND-1.1	ND	T(D) ND-T	T(D,M) ND-T	ND(D) ND-T	T(M) ND-T	ND	T(D,T) ND-T	ND	T(D,M) ND-0.8	T(M) ND-T
	July	T(D) ND-T	T(D) ND-T	T(D) ND-T	T(D)	T(D) ND-T	T(D) ND-0.8	T(D,T) ND-T	ND		160(D) T-320	
	Aug.	ND	ND	ND		ND	ND	ND			ND	
	Sept.	T(D) ND-T	ND	ND	T(D,T) ND-0.8 (D,T)	ND	ND	ND			ND	ND
	Oct.	ND	ND	ND	ND	ND	T(D) ND-T		ND		ND	ND
	Nov.	ND	ND	ND	T(D,M)	ND	ND		ND		T(D) ND-T	ND
	Dec.	ND	ND	ND	ND	ND	ND		ND		ND	ND
1976	Jan.	ND		ND	ND	ND	ND		ND		ND	ND
	Feb.	ND	ND	ND	ND	ND	ND		ND		ND	ND
	Mar.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Continued ....

APPENDIX XX **Continued**

YEAR	MONTH	Content in water (µg/L)										
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976 (continued....)												
	May	ND	ND	T(T) ND-T	T(D) ND-T	ND	ND	ND	ND		ND(B,D) ND-T	T(D) ND-0.8
	June	0.5(D) T(T) ND-3.9 ND-0.8	ND(D) ND-T	ND(T) ND-T	ND	ND(D) ND-T	0.5(D) ND-1.4		ND		ND	T(M) ND-T
	July	T(D) ND-T	ND	ND (D) ND-T	T(D) ND-T	T(D) ND-T	ND	ND	ND		ND	ND
	Aug.	T(D) ND-T	0.6(D) ND-1.1	ND	ND		0.7(D) ND-2.1	T(D) ND-T	ND	ND	ND	ND
	Sept.		ND	ND	ND	ND	ND		ND	ND	ND	ND
	Oct.	ND	T(D) ND-T	ND	ND	ND	ND	T(D) ND-T	ND		T(D) ND-0.6	T(D) ND-T
	Nov.	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
	Dec.	T(D) T	ND	ND	ND	ND	ND	ND	ND		ND	ND
1977	Jan.		ND	ND		ND	ND	ND			T(T) ND--T	ND
	Feb.		ND	ND		ND	ND				T(T) ND-T	ND

Continued ....

APPENDIX XX Continued

YEAR MONTH	Content in water (µg/L)										
	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1977(continued...)											
Mar.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Apr.	ND	ND	ND	ND	ND	ND	ND	ND		ND	ND
May	ND	ND	ND	ND(D)	ND	ND	ND		ND	ND	T(D)
			ND-T(D)	ND-T							ND-T

[1/] AG-7 in 1974 was Ganaraska River
AG-7 in 1975-77 was Shelter Valley Creek

D = 2,4-D B = dicamba M = MCPA T = 2,4,5-T

ND = not detected <0.1 µg/L
T = trace 0.4 - 0.1 µg/L

APPENDIX XXI Amount of chlorophenoxy and chlorobenzoic acid herbicides leaving 11 agricultural watersheds between May 1975 and April 1977

Herbicides	Amount leaving watersheds (g)											
(Month)	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
2,4-D												
1975-76 (May-April)												
May	28	0	27	0	0	0	0	0	0	0	0	55
June	2305	0	144	1	35	0	0	55	0	18	0	2.558
July	300	255	64	0	25	309	91	0	0	407	0	1451
Aug.	0	0	0	0	0	0	0	0	0	11	0	11
Sept.	176	0	0	1	0	0	0	0	0	0	0	177
Oct.	0	0	0	0	0	212	0	0	0	0	0	212
Nov.	0	0	0	23	0	0	0	0	0	24	0	47
Dec.	0	0	0	28	0	0	0	0	0	0	0	28
TOTAL	2809	255	235	53	60	521	91	55	0	460	0	4539
2,4-D												
1976-77 (May-April)												
May	0	0	0	230	0	0	0	0	0	0	0	230
June	14	103	0	0	0	420	0	0	0	0	0	537
July	60	0	315	0	13	0	0	0	0	0	0	388
Aug.	0	433	0	0	11	205	143	0	0	2	0	794
Sept.	0	0	0	0	6	0	0	0	0	0	0	6
Oct.	0	70	0	0	0	0	141	0	0	16	27	254
Nov.	0	13	0	0	0	0	0	0	0	0	0	13
TOTAL	74	619	315	230	30	625	284	0	0	18	27	2222
2,4,5-T												
1975-76 (May-April)												
May	24	0	0	0	0	0	0	0	0	0	0	24
June	1195	0	0	0	0	0	86	55	0	0	0	1336
TOTAL	1219	0	0	0	0	0	86	55	0	0	0	1360

Continued....

APPENDIX XXI Continued

Herbicides	Amount leaving watersheds (g)											
(Month)	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
2,4,5-T												
1976-77 (May-April)												
May	0	0	32	0	0	0	0	0	0	0	0	32
June	15	0	88	0	0	0	0	0	0	0	0	103
July	0	0	186	0	0	0	0	0	0	0	0	186
TOTAL	15	0	306	0	0	0	0	0	0	0	0	321
MCPA												
1975-76 (May-April)												
May	0	0	0	0	0	0	0	0	0	25	0	25
June	0	0	0	1	0	228	0	0	0	10	4	243
Nov.	0	0	0	22	0	0	0	0	0	0	0	22
Dec.	0	0	0	28	0	0	0	0	0	0	0	28
TOTAL	0	0	0	51	0	228	0	0	0	35	4	318
dicamba												
1975-76 (May-April)												
May	0	0	0	0	0	0	0	0	0	25	0	25

APPENDIX XXII Monthly concentration of PCB in water collected from 11 agricultural watersheds between February 1975 and May 1977 (mean and range)

		PCB Content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975	Feb.		150	50			5					
	Mar.	20	60	40	60	50	15		50	30	17	10
		10-40			30-90		10-20				10-20	
	Apr.	80	143	137	120	217	68	100	60	100	137	83
		10-120	90-180	40-320	80-140	50-800	30-130	50-180	20-180	30-200	10-600	50-110
	May	63	70	51	62	57	52	53	73	38	58	53
		30-110	40-90	40-70	30-80	40-70	40-60	20-90	50-110	20-60	40-80	50-60
	June	46	38	48	50	45	50	34	35	40	45	50
		30-80	30-50	30-80	20-80	20-80	30-70	20-60	30-40	20-60	20-90	20-100
	July	30	20	25	20	23	26	47	40		25	
				20-40		10-30	20-30	10-100			10-40	
	Aug.	50	60	70		40	52	43			37	
			50-70				30-90	30-60			30-40	
	Sept.	47	50	58	50	53	43	48			40	43
		30-70	40-60	30-70	30-70	40-70	10-80	20-70			30-50	30-50
	Oct.	28	27	37	30	35	32		25		40	46
		10-50	10-50	20-50		20-50	20-40		10-40		30-50	20-60
	Nov.	35	25	20	40	10	28		40		32	26
		20-70	20-30	10-30		1-20	10-60				20-40	10-50
	Dec.	30	10	28	50	30	42		25		33	23
		10-50		20-40	10-90	10-60	10-90		20-30		10-60	10-40

Continued ....

APPENDIX XXII Continued

		PCB content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976	Jan.	43	65	30	16	30	10		20		43	25
		20-70	40-90		1-30		1-20				10-90	10-40
	Feb.	50		52	40	55	1		32		45	
		30-70		40-60		20-80			1-70		30-60	
	Mar.	42	5	33	24	50	33	25	30	36	46	44
		20-60		10-50	1-50	30-70	10-80	20-30	20-40	1-100	10-60	10-100
	Apr.	15	20	14	18	28	17	20	5	10	15	4
		1-50		1-20	5-30	1-60	1-40		1-10		1-30	1-10
	May	32	20	20	12	24	30	30	28		23	38
		10-50	10-30	1-50	1-30	1-40	1-50		1-60		1-40	1-60
	June	26	18	47	23	138	23		20		26	30
		10-60	10-40	20-100	1-40	1-600	10-40		1-50		10-50	10-50
	July	12	8	20	8	12	8	5	14		11	13
		5-30	5-10	5-40	5-10	5-30	5-10		5-20		5-20	10-20
	Aug.	10	15	19	13	20	15	13	17	15	20	21
		5-15	10-20	5-35	10-20	10-40	8-20	10-16	10-21		2-34	1-38
	Sept.		14	14	12	29	17		12		14	113
			8-20	5-32	8-16	1-100	10-30		1-32		4-20	16-210
	Oct.	33	30	28	33	28	35	30	37	35	32	23
		30-40	20-40	10-40	20-40	10-60	30-40	20-40	10-60	30-40	20-40	10-40
	Nov.	30	30	35	34	22	25	28	40		29	25
			20-40	20-40	20-50	10-40	20-30	10-40			10-50	20-30

Continued .....

APPENDIX XXII Continued

		PCB Content in water (ng/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976 (continued...)												
	Dec.	22	20	14	20	10	18	13	1		14	14
				1-28	1-30	1-28	16-20	1-26			1-33	12-16
1977	Jan.		39	82		25	35	22			43	38
			38-40	32-200		10-40	22-46				36-52	30-48
	Feb.		38	27		16	17				54	27
			16-74	24-30		1-30	1-40				10-190	24-32
	Mar.	29	19	29	20	29	20	17	25	27	38	18
		5-53	ND-32	10-90	ND-42	13-90	6-44		14-60		12-120	4-40
	Apr.	27	31	28	22	30	44	26	36		19	10
		16-40	20-53	ND-80	7-46	13-53	40-47		16-73		16-20	7-12
	May	30	4	11	27	9	6	10		20	4	5
		13-46	ND-7	ND-33	26-27	ND-30	ND-7	ND-20			ND-7	ND-7

APPENDIX XXIII Amount of PCB leaving 11 agricultural watersheds between May 1975 and April 1977

	Amount of PCB leaving watersheds (g)											
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
<u>1975-76</u>												
May	12	151	52	6	32	171	118	18		12	17	589
June	157	89	31	20	25	71	58	12		10	0	473
July	1	48	3	0	1	25	86	0		2	0	166
Aug.	51	72	27	3	8	149	42	26		38	14	430
Sept.	66	142	37	12	11	69	134	18		19	28	536
Oct.	2	89	4	3	4	68	96	10		8	12	296
Nov.	5	60	29	10	8	45	108	16		6	44	331
Dec.	80	199	101	51	35	188	120	46		36	47	903
Jan.	34	329	42	2	66	25	79	23	(1)	13	19	632
Feb.	228	574	454	10	192	10	249	94	(98)	160	34	2005
Mar.	112	300	381	143	233	290	325	99	(92)	71	474	2428
April	2	79	29	18	38	78	66	23	(5)	6	1	340
TOTAL	750	2132	1190	278	653	1189	1481	385		381	690	9129
<u>1976-77</u>												
May	16	80	35	1	24	50	71	48	4	9	1	339
June	7	59	11	2	4	26	49	0	0	3	10	171
July	7	6	89	0	8	29	32	0	0	1	5	177
Aug.	0	18	42	0	34	10	15	0	0	0	0	119
Sept.	0	21	2	0	5	22	15	0	0	0	0	65
Oct.	0	52	7	5	14	35	40	2	1	1	2	159
Nov.	0	54	52	8	16	35	29	1	0	1	84	280
Dec.	0	135	6	2	7	18	9	2	0	1	9	189
Jan.	0	213	21	0	10	21	12	0	0	0	6	283
Feb.	0	57	7	0	9	10	20	0	4	37	2	146
Mar.	130	159	175	64	191	105	96	63	50	42	159	1234
April	182	83	56	16	18	54	35	17	9	29	51	550
TOTAL	342	937	503	98	340	415	423	133	68	124	329	3712

APPENDIX XXIV Monthly concentrations of organophosphorus insecticides in water collected from 11 agricultural watersheds between February 1975 and May 1977

(mean and range)

		Content in water (µg/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975	Feb.		ND	ND			ND					
	Mar.	ND	ND	ND	ND	ND	ND		ND	ND	0.39(D)	ND
											ND-1.16	
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01(D)	ND
											ND-0.08	
	May	ND	ND	ND	NI)	ND	ND	ND	ND	ND	0.08(D)	ND
											ND-0.47	
				0.004(D)								
	June	ND	ND	0.005(E)	ND	0.002(E)	ND	ND	ND	ND	5.15(D)	ND
				ND-0.030		ND-0.018					ND-48.0	
				ND-0.042								
	July	ND	0.05(C)	ND	ND	ND	ND	ND	ND		0.38(D)	
			ND-0.15								ND-0.73	
	Aug.	ND	ND	ND		ND	ND	ND			95(D)	
											60-140	
	Sept.	ND	ND	ND	ND	ND	ND	ND			0.03(D)	ND
											ND-0.24	
	Oct.	ND	ND	ND	ND	ND	ND		ND		ND	ND
	Nov.	ND	ND	ND	ND	ND	ND		ND		0.33(D)	ND
											ND-1.00	

Continued ....

APPENDIX XXIV Continued

		Content in water (µg/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975 (continued)												
	Dec.	ND	ND	ND	ND	ND	ND		ND		0.23(D)	ND
											ND-0.91	
1976	Jan.	ND		ND	ND	ND	ND		ND		ND	ND
	Feb.	ND		ND	ND	ND	ND		ND		ND	ND
	Mar.	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.40(D)	ND
											ND-6.00	
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.42(D)	ND
											ND-2.40	
	May	ND	ND	ND	ND	0.32(C)	ND	ND	ND		0.15(D)	ND
						ND-1.60					ND-1.10	
	June	ND	ND	ND	ND	ND	ND		ND		0.13(D)	ND
											0.03(C)	
											ND-0.60	
											ND-0.27	
	July	ND	ND	ND	ND	ND	ND	ND	ND		0.82(D)	ND
											0.02(H)	
											ND-7.00	
											ND-0.25	
	Aug.	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.26(D)	ND
											ND-0.86	

Continued

APPENDIX XXIV Continued

		Content in water (µg/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
<u>1976</u> (continued...)												
	Sept.		ND	ND	ND	ND	ND		ND		0.75(D)	ND
											ND-6.00	
	Oct.	ND	6.3(D)	ND	ND	ND	ND	ND	ND	ND	7.63(D)	ND
			ND-25.0								2.10-26.0	
	Nov.	ND	ND	ND	ND	ND	ND	ND	ND		0.74(D)	ND
											0.21-2.00	
	Dec.	ND	ND	ND	ND	ND	ND	ND	ND		2.52(D)	ND
											0.75(M)	
											0.88-5.80	
											0.38-1.80	
1977	Jan.		ND	ND		ND	ND	ND			1.09(D)	ND
											0.15-2.40	
	Feb.		ND	ND		ND	ND				0.71(D)	ND
											ND-2.80	
	Mar.	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.18(D)	ND
											0.04-0.48	
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND		0.60(D)	ND
											0.57(M)	
											0.19-1.40	
											ND-1.70	
	May	ND	ND	ND	ND	ND	ND	ND		ND	ND	ND

C = chlorpyrifos D = diazinon E = ethion M = malathion

APPENDIX XXV Amount of organophosphorus insecticides leaving 11 agricultural watersheds between May 1975 and April 1977

	Amount leaving watersheds (g)											
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
<u>Chlorpyrifos</u>												
1975-76 (May-April)												
July	0	35	0	0	0	0	0	0	0	0	0	35
1976-77 (May-April)												
May	0	0	0	0	15	0	0	0	0	0	0	15
June	0	0	0	0	0	0	0	0	0	1	0	1
TOTAL	0	0	0	0	15	0	0	0	0	1	0	16
<u>Diazinon</u>												
1975-76 (May-April)										see		
June	0	0	2	0	0	0	0	0	0	below	0	2
Oct.	0	1376	0	0	0	0	0	0	0		0	1376
TOTAL	0	1376	2	0	0	0	0	0	0		0	1378
<u>Ethion</u>												
1975-76 (May-April)												
June	0	0	4	0	1	0	0	0	0	0	0	5
<u>Malathion</u>												
1976-77 (May-April)												
July	0	0	0	0	0	0	0	0	0	1	0	1
Dec.	0	0	0	0	0	0	0	0	0	53	0	53
April	0	0	0	0	0	0	0	0	0	18	0	18
TOTAL	0	0	0	0	0	0	0	0	0	72	0	72

<u>Diazinon: AG-13 (1975-76)</u>

May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	TOTAL
10	4050	11	7190	7778	0	113	112	137	0	194	55	19,650
<u>Diazinon: AG-13 (1976-77)</u>												
185	3	597	7	73	494	56	315	93	260	179	146	2,408

APPENDIX XXVI Atrazine use on corn in 11 watersheds 1975

Watershed		Corn Area		Corn Treated		atrazine
(#)	(ha)	(ha)	(%)[1]	(ha)	(%)[1]	(kg)
AG-1	5080	1168	23.0	665	13.1	736
AG-2	7913	797	10.1	698	8.8	1353
AG-3	6200	1941	31.3	1343	21.7	2132
AG-4	1860	347	18.7	265	14.2	700
AG-5	3000	1270	42.3	980	32.7	1972
AG-6	5472	670	12.3	568	10.4	1047
AG-7	5645	589	10.4	336	6.0	431
AG-10	3025	491	16.2	262	8.7	504
AG-11	2383	269	11.3	212	8.9	303
AG-13	1990	454	22.8	421	21.2	572
AG-14	4504	430	9.5	403	8.9	820
TOTAL	47072	8426		6153		10570
MEAN	4279	766	17.9	559	13.1	961

1/ Percent area of watershed

APPENDIX XXVII Monthly concentrations of atrazine and desethylatrazine in water collected from 11 agricultural watersheds between April 1974 and May 1977

	Content in water (µg/L)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
(1974)											
Apr.											
ATR	T	0.2	0.3		0.2			0.1		0.1	
De-A	ND	ND	ND		ND			ND		ND	
Total	T	0.2	0.3		0.2			0.1		0.1	
Range	ND-0.1	ND-0.6	0.2-0.4					ND-0.2		T-0.1	
May											
ATR	2.8	0.1	0.5		0.2			0.5		1.5	
De-A	0.1	T	0.3		0.1			T		0.1	
Total	2.9	0.2	0.8		0.3			0.6		1.6	
Range	T-10.7	T-0.3	0.2-1.4		0.1-0.6			0.4-0.7		0.5-3.6	
June											
ATR	2.8	0.3	35.9		5.8			0.5		1.2	
De-A	0.3	T	1.0		0.4			T		0.2	
Total	3.1	0.4	36.9		6.2			0.6		1.4	
Range	2.4-3.9	ND-0.8	0.6-108.		0.4-12.			0.1-1.2		0.3-2.9	
July											
ATR	4.3	0.6	0.7		2.9			1.7		6.5	
De-A	0.6	0.1	0.3		0.3			0.1		0.5	
Total	4.9	0.7	1.0		3.2			1.8		7.0	
Range	4.0-6.4	0.1-2.8	0.2-1.7		2.0-4.4					4.1-11.8	
Aug.											
ATR		T	0.3		0.8			0.4			
De-A		ND	T		T			ND			
Total		T	0.4		0.9			0.4			
Range		ND-0.1	T-0.7		0.4-1.3			ND-0.8			

Continued ....

APPENDIX XXVII Continued

	Content in water(µg/L)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AC-10	AG-11	AG-13	AG-14
(1974-continued...)											
Sept.											
ATR		ND	ND		0.8			1.3		0.3	
De-A		ND	ND		ND			ND		ND	
Total		ND	ND		0.8			1.3		0.3	
Range					0.6-1.1						
Oct.											
ATR		ND								ND	
De-A		ND								ND	
Total		ND								ND	
Range											
Nov.											
ATR	0.8	ND	ND							0.2	
De-A	ND	ND	ND							ND	
Total	0.8	ND	ND							0.2	
Range										T-0.3	
Dec.											
ATR					2.3					T	
De-A					ND					ND	
Total					2.3					T	
Range					0.2-4.3					ND-0.1	
(1975)											
Jan.											
ATR		0.2									
De-A		ND									
Total		0.2									
Range											

Continued ....

APPENDIX XXVII Continued

	Content in water (µg/L)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
(1975-continued...)											
Feb.											
ATR		0.3	1.1			0.1				0.1	
De-A		0.7	0.4			0.1				ND	
Total		1.0	1.5			0.2				0.1	
Range											
Mar.											
ATR	0.1	T	0.4	0.3	0.1	ND		0.7	1.1	0.1	0.3
De-A	T	ND	0.6	0.1	T	ND		0.5	ND	0.1	ND
Total	0.2	T	1.0	0.4	0.2	ND		1.2	1.1	0.2	0.3
Range	0.1-0.3			0.3-0.5						ND-0.4	
Apr.											
ATR	0.1	T	0.8	0.4	0.3	0.1	T	0.3	0.7	ND	0.3
De-A	ND	T	0.3	0.2	0.3	0.1	0.1	ND	0.2	ND	0.1
Total	0.1	0.1	1.1	0.6	0.6	0.2	0.2	0.3	0.9	ND	0.4
Range	T-0.1	ND-0.2	0.6-2.1	0.3-0.9	0.4-0.9	T-0.4	ND-0.6	0.2-0.3	0.6-2.6	ND-T	0.3-0.8
May											
ATR	0.9	0.9	4.1	1.4	0.4	T	ND	0.2	0.4	0.3	0.3
De-A	0.1	0.1	0.4	0.3	0.2	T	ND	T	0.3	0.1	0.1
Total	1.0	1.0	4.5	1.7	0.6	0.1	ND	0.3	0.7	0.4	0.4
Range	0.2-2.4	0.2-2.4	0.6-31.7	0.2-7.3	0.4-1.3	0.1-0.2		0.2-0.4	0.3-1.2	T-0.7	0.3-0.7
June											
ATR	5.8	0.3	5.6	6.5	1.7	0.3	T	9.3	0.2	1.4	3.9
De-A	1.2	T	1.3	1.5	0.6	T	T	0.9	0.1	0.3	1.9
Total	7.0	0.4	6.9	8.0	2.3	0.4	0.1	10.2	0.3	1.7	5.8
Range	1.-18.2	ND-1.0	2.0-14.1	1.3-14.7	0.3-6.6	0.1-1.2	ND-0.3	10.-10.3	0.2-0.4	0.7.4.4	0.2-13.3

Continued ....

APPENDIX XXVII Continued

	Content in water (µg/L)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
(1975-continued...)											
July											
ATR	2.0	2.8	5.4	5.7	0.7	0.1	ND	0.8		0.4	
De-A	0.2	1.7	1.3	1.5	0.2	0.1	0.1	0.2		0.2	
Total	2.2	4.5	6.7	7.2	0.9	0.2	0.1	1.0		0.6	
Range	1.6-2.8	T-13.1	1.7-14.3		0.3-2.6	ND-0.5	T-0.2				
Aug.											
ATR	1.4	ND	0.7		0.1	0.2	ND			0.1	
De-A	0.3	ND	0.4		0.1	0.2	0.2			0.2	
Total	1.7	ND	1.1		0.2	0.4	0.2			0.3	
Range		ND-T				ND-0.9	T-0.4			T-0.7	
Sept.											
ATR	0.5	0.1	0.6	0.4	0.2	ND	0.1			T	1.2
De-A	ND	ND	0.7	0.3	0.4	0.1	ND			ND	0.7
Total	0.5	0.1	1.3	0.7	0.6	0.1	0.1			T	1.9
Range	0.2-0.9	ND-0.3	0.8-1.8	0.4-1.0	0.5-0.8	ND-0.4	ND--0.4			ND-0.2	0.8-2.6
Oct.											
ATR	0.2	ND	0.2	0.3	0.1	ND		2.1		ND	0.7
De-A	0.1	ND	0.1	0.3	0.2	ND		0.3		ND	0.2
Total	0.3	ND	0.3	0.6	0.3	ND		2.4		ND	0.9
Range	T-0.5	ND-T	0.3-0.4		T-0.4	ND-T		1.8-2.9			0.6-1.1
Nov.											
ATR	0.2	ND	0.3	T	T	ND		0.6		ND	0.3
De-A	ND	ND	0.5	ND	0.2	ND		ND		ND	0.1
Total	0.2	ND	0.8	T	0.3	ND		0.6		ND	0.4
Range	T-0.3	ND-T	0.5-1.3		0.1-0.5	ND-T					0.1-0.8

Continued ....

APPENDIX XXVII Continued

PERIOD	Content in water (µg/L)										
	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
(1975-continued...)											
Dec.											
ATR	0.4	ND	1.0	0.1	0.4	ND		0.5		0.1	0.5
De-A	T	ND	0.9	0.1	0.3	0.1		ND		ND	0.2
Total	0.5	ND	1.9	0.2	0.7	0.1		0.5		0.1	0.7
Range	0.2-0.8		1.1-3.4	0.1-0.6	ND-1.4	ND-0.2		0.4-0.6		ND-0.2	ND-1.1
(1976)											
Jan.											
ATR	0.2		0.5	0.1	0.2	ND		0.2		ND	T
De-A	ND		0.5	T	0.2	ND		ND		ND	ND
Total	0.2		1.0	0.2	0.4	ND		0.2		ND	T
Range	ND-0.2			0.1-0.2	0.3-0.5						
Feb.											
ATR	0.1	ND	0.4	0.2	0.2	ND		0.5		ND	0.9
De-A	ND	ND	0.3	ND	0.2	ND		ND		ND	ND
Total	0.1	ND	0.7	0.2	0.4	ND		0.5		ND	0.9
Range	ND-0.2		0.2-1.7		0.3-0.5			0.3-0.9		ND-T	
Mar.											
ATR	0.1	ND	0.3	0.1	0.3	T	ND	0.2	0.4	ND	0.1
De-A	ND	ND	0.3	T	0.4	ND	ND	ND	0.2	ND	T
Total	0.1	ND	0.6	0.2	0.7	T	ND	0.2	0.6	ND	0.2
Range	ND-0.2		0.2-1.1	T-0.4	0.6-0.8	ND-0.1		0.2-0.3	0.1-1.1	ND-T	ND-0.4
Apr.											
ATR	0.1	T	0.7	0.1	T	ND	ND	0.2	0.3	ND	0.2
De-A	ND	ND	0.3	0.1	T	ND	ND	ND	ND	ND	ND
Total	0.1	T	1.0	0.2	T	ND	ND	0.2	0.3	ND	0.2
Range	ND-0.3		0.1-2-2	ND-0.6	ND-0.3	ND-0.2		0.1-0.2			ND-0.4

Continued ....

APPENDIX XXVII Continued

	Content in water (µg/L)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
(1976-continued...)											
May											
ATR	0.5	0.1	0.4	0.1	0.3	T	ND	0.4		0.1	0.4
De-A	T	ND	0.4	0.1	0.3	ND	ND	ND		ND	0.1
Total	0.6	0.1	0.8	0.2	0.6	T	ND	0.4		0.1	0.5
Range	0.3-2.4	ND-0.2	0.1-2.2	ND-0.3	0.4-1.0	ND-0.1		0.2-0.6		ND-0.3	0.1-0.9
June											
ATR	1.0	ND	1.7	8.9	1.0	ND		3.7		0.4	0.2
De-A	0.1	ND	0.5	1.0	0.2	ND		ND		ND	T
Total	1.1	ND	2.2	9.9	1.2	ND		3.7		0.4	0.3
Range	T-4.2		0.7-3.6	0.4-27.1	0.4-2.7			ND-17.9		ND-0.7	0.2-0.5
July											
ATR	9.4	ND	7.4	1.8	2.4	ND	ND	13.2		0.9	11.9
De-A	1.3	ND	2.3	0.7	0.8	ND	ND	2.4		0.1	1.8
Total	10.7	ND	9.7	2.5	3.2	ND	ND	15.6		1.0	13.7
Range	4.0-22.6		5.2-24.7	1.9-3.0	1.8-7.7			0.1-32.8		0.2-0.6	7.1-18.
Aug.											
ATR	2.6	ND	1.2	1.1	0.5	ND	ND	21.4	T	ND	2.3
De-A	0.6	ND	0.7	0.4	0.3	ND	ND	2.0	ND	ND	0.7
Total	3.2	ND	1.9	1.5	0.8	ND	ND	23.4	T	ND	3.0
Range	2.7-3.6		0.9-2.5	1.2-2.0	0.2-1.4			16.9-31.5		ND-T	2.5-3.9
Sept.											
ATR		ND	2.5	0.1	0.3	ND		1.9		0.4	1.3
De-A		ND	0.4	ND	ND	ND		0.2		0.1	0.3
Total		ND	2.9	0.1	0.3	ND		2.1		0.5	1.6
Range			0.1-12.2	T-0.1	ND-1.1			0.5-3.6		ND-2.5	1.0-2.2

Continued .....

APPENDIX XXVII Continued

	Content in water (µg/L)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
(1976-continued)											
Oct.											
ATR	1.9	ND	0.7	0.3	0.1	ND	ND	2.1	ND	3.7	0.8
De-A	0.2	ND	0.6	0.1	0.2	ND	ND	0.3	ND	ND	0.4
Total	2.1	ND	1.3	0.4	0.3	ND	ND	2.4	ND	3.7	1.2
Range	1.6-2.8		0.3-3.3	T-1.2	ND-0.8	ND-T		1.2-3.6	ND-T	ND-10.8	0.4-1.7
Nov.											
ATR	0.9	ND	0.7	0.1	0.1	ND	ND	3.8		1.4	0.6
De-A	0.2	ND	0.7	0.1	0.2	ND	ND	0.4		ND	0.2
Total	1.1	ND	1.4	0.2	0.3	ND	ND	4.2		1.4	0.8
Range			0.9-1.6	T-0.4	0.1-0.4					0.4-3.7	0.6-0.9
Dec.											
ATR	0.5	T	0.4	T	T	ND	ND	1.6		0.2	0.1
De-A	T	0.2	0.3	T	0.1	ND	ND	0.2		ND	0.1
Total	0.6	0.3	0.7	0.1	0.2	ND	ND	1.8		0.2	0.2
Range			0.3-0.8	ND-0.1	0.1-0.3					T-0.3	0.1-0.3
(1977)											
Jan.											
ATR		ND	0.2		T	ND	ND			ND	0.1
De-A		ND	0.3		T	ND	ND			0.3	T
Total		ND	0.5		0.1	ND	ND			0.3	0.2
Range			0.4-0.5		ND-0.1					ND-0.6	T-0.3
Feb.											
ATR		ND	0.2		0.2	ND				ND	T
De-A		ND	0.2		0.3	ND				0.4	0.2
Total		ND	0.4		0.5	ND				0.4	0.3
Range		ND-T	ND-0.8		0.1-0.7	ND-0.1				T-0.7	0.1-0.3

Continued ....

APPENDIX XXVII Continued

	Content in water (µg/L)										
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
(1977-continued...)											
Mar.											
ATR	0.7	0.4	0.7	0.4	0.4	0.1	ND	0.7	0.2	0.2	0.2
De-A	0.2	0.3	0.6	0.3	0.3	0.1	ND	0.1	0.1	T	0.1
Total	0.9	0.7	1.3	0.7	0.7	0.2	ND	0.8	0.3	0.3	0.3
Range	0.5-1.3	0.1-1.8	0.4-1.8	0.2-1.0	0.3-1.4	T-0.5		0.6-1.0		T-0.6	0.2-0.5
Apr.											
ATR	0.4	0.1	0.3	0.1	0.2	ND	ND	0.6		0.1	0.1
De-A	T	0.2	0.5	0.1	0.3	ND	ND	0.1		ND	0.1
Total	0.5	0.3	0.8	0.2	0.5	ND	ND	0.7		0.1	0.2
Range	0.2-0.7	ND-0.9	0.6-1.1	0.1-0.2	0.3-0.6			0.6-0.9		0.1-0.2	
May											
ATR	0.5	ND	0.5		0.2	ND	ND		0.1	T	0.1
De-A	0.2	ND	0.5		0.2	ND	ND		T	T	ND
Total	0.7	ND	1.0		0.4	ND	ND		0.2	0.1	0.1
Range	0.2-1.2		T-2.2		0.1-0.7					T-0.2	T-0.1
RATIO:	ATR/De-A										
1974-1977	7.1	1.9	4.3	3.9	3.1	1.4	0.7	8.9	3.4	9.0	3.6

ATR = atrazine
De-A = desethylated atrazine

ND = not detected <0.04 ng/L
T = trace 0.04-0.09 ng/L

APPENDIX XXVIII Amount of atrazine plus desethylatrazine leaving monthly from 11 agricultural watersheds between May 1975 and April 1977

	Amount of atrazine and its metabolite leaving watersheds (kg)											
PERIOD	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	TOTAL
1975-76												
May	0.12	0.27	0.79	0.01	0.25	0.59	0.04	0.06		0.05	0.14	2.32
June	17.61	0.82	5.40	0.28	0.87	0.54	0.17	2.14		0.38	0.03	28.24
July	0.20	4.01	1.41	0.01	0.11	0.31	0.19	0.00		0.05	0.03	6.32
Aug.	1.86	0.23	0.46	1.01	0.09	1.27	0.23	0.67		0.29	1.24	7.35
Sept.	1.33	0.19	0.59	0.07	0.12	0.50	0.10	0.47		0.07	2.19	5.63
Oct.	0.03	0.02	0.07	0.03	0.05	0.05	0.00	1.28		0.00	0.26	1.79
NOV .	0.03	0.05	0.69	0.06	0.07	0.06	0.00	0.03		0.00	0.44	1.43
Dec.	0.65	0.00	3.43	0.07	0.59	0.39	0.00	0.36		0.07	2.38	7.94
Jan.	0.24	0.00	1.05	0.04	0.39	0.07	0.00	0.29	0.01	0.01	0.16	2.26
Feb.	0.14	0.00	10.23	0.23	1.87	0.01	0.00	2.34	0.67	0.14	1.32	16.95
Mar.	0.31	0.00	7.29	1.05	2.20	1.23	0.00	0.79	1.53	0.07	4.57	19.04
April	0.07	0.38	2.26	0.15	0.21	0.22	0.00	0.26	0.11	0.00	0.05	3.71
TOTAL	22.59	5.97	33.67	3.01	6.82	5.24	0.73	8.69	2.32	1.13	12.81	102.98
1976-77												
May	0.83	0.38	1.57	0.11	0.54	0.19	0.00	0.39	0.12	0.04	0.05	4.22
June	0.32	0.00	1.11	1.46	0.10	0.02	0.00	0.65	0.01	0.07	0.26	4.00
July	6.60	0.00	8.15	0.82	2.19	0.00	0.00	1.97	0.00	0.14	0.39	20.26
Aug.	0.00	0.00	2.91	0.00	0.72	0.00	0.00	0.69	0.00	0.00	0.00	4.32
Sept.	0.03	0.00	0.62	0.01	0.03	0.00	0.00	0.16	0.00	0.00	0.01	0.86
Oct.	0.05	0.00	0.32	0.10	0.16	0.03	0.00	0.22	0.00	0.31	0.17	1.36
Nov.	0.00	0.00	3.71	0.04	0.20	0.02	0.00	0.16	0.00	0.10	2.74	6.97
Dec.	0.00	0.17	0.61	0.02	0.07	0.00	0.00	0.29	0.00	0.01	0.19	1.36
Jan.	0.00	0.35	0.15	0.01	0.04	0.00	0.00	0.00	0.00	0.02	0.04	0.61
Feb.	0.00	0.01	0.13	0.01	0.27	0.03	0.00	0.22	0.01	0.14	0.02	0.84
Mar.	2.97	2.08	16.22	2.10	4.42	3.06	0.00	1.90	0.23	0.33	3.61	36.92
April	0.96	1.82	1.51	0.10	0.55	0.31	0.00	0.96	0.11	0.15	0.64	7.11
TOTAL	11.76	4.81	37.01	4.78	9.29	3.66	0.00	7.61	0.48	1.31	8.12	88.83

APPENDIX XXIX Losses of atrazine and desethylatrazine from 10 agricultural watersheds between May 1975 and April 1976

Watershed		Amount in stream water (kg)			
		May-Aug	Sep-Dec	Jan-Apr	Total
AG-1	Storm runoff	16.79	1.42	0.35	18.56
	Base flow	0.86	0.62	0.41	1.89
	Spill	2.14	0.00	0.00	2.14
	TOTAL	19.79	2.04	0.76	22.59
AG-2	Storm runoff	1.27	0.00	0.30	1.57
	Base flow	1.38	0.26	0.38	2.02
	Spill	2.68	0.00	0.00	2.68
	TOTAL	5.33	0.26	0.68	6.27
AG-3	Storm runoff	0.17	3.01	18.66	21.84
	Base flow	1.09	1.77	2.17	5.03
	Spill	6.80	0.00	0.00	6.80
	TOTAL	8.06	4.78	20.83	33.67
AG-4	Storm runoff	0.00	0.00	0.91	0.91
	Base flow	0.22	0.23	0.56	1.01
	Spill	1.09	0.00	0.00	1.09
	TOTAL	1.31	0.23	1.47	3.01
AG-5	Storm runoff	0.00	0.37	3.62	3.99
	Base flow	1.07	0.46	1.05	2.58
	Spill	0.25	0.00	0.00	0.25
	TOTAL	1.32	0.83	4.67	6.82
AG-6	Storm runoff	2.01	0.34	1.41	3.76
	Base flow	0.70	0.66	0.12	1.48
	Spill	0.00	0.00	0.00	0.00
	TOTAL	2.71	1.00	1.53	5.24
AG-7	Storm runoff	0.00	0.00	0.00	0.00
	Base flow	0.63	0.10	0.00	0.73
	Spill	0.00	0.00	0.00	0.00
	TOTAL	0.63	0.10	0.00	0.73
AG-10	Storm runoff	0.42	1.39	2.94	4.75
	Base flow	0.44	0.75	0.74	1.93
	Spill	2.01	0.00	0.00	2.01
	TOTAL	2.87	2.14	3.68	8.69
AG-13	Storm runoff	0.26	0.00	0.17	0.43
	Base flow	0.28	0.14	0.05	0.47
	Spill	0.23	0.00	0.00	0.23
	TOTAL	0.77	0.14	0.22	1.13

Continued ....

APPENDIX XXIX Continued

Watershed		Amount in stream water (kg)			
		May-Aug	Sep-Dec	Jan-Apr	Total
AG-14	Storm runoff	0.00	2.27	5.79	8.06
	Base flow	0.44	1.00	0.31	I.75
	Spill	1.00	2.00	0.00	3.00
	TOTAL	1.44	5.27	6.10	12.81
TOTAL	Storm runoff	20.92	8.80	34.15	63.87
	Base flow	7.11	5.99	5.79	18.89
	Spill	16.20	2.00	0.00	18.20
	TOTAL	44.23	16.79	39.94	100.96

APPENDIX XXX Losses of atrazine and desethylatrazine from 11 agricultural watersheds between May 1976 and April 1977

Watershed		Amount in stream water (kg)			
		May-Aug	Sep-Dec	Jan-Apr	Total
AG-1	Storm runoff	4.45	0.00	3.08	7.53
	Base flow	0.54	0.08	0.85	1.47
	Spill	2.76	0.00	0.00	2.76
	TOTAL	7.75	0.08	3.93	11.76
AG-2	Storm runoff	0.30	0.00	3.62	3.92
	Base flow	0.08	0.17	0.64	0.89
	Spill	0.00	0.00	0.00	0.00
	TOTAL	0.38	0.17	4.26	4.81
AG-3	Storm runoff	4.93	2.71	16.22	23.86
	Base flow	2.97	2.55	1.79	7.31
	Spill	5.84	0.00	0.00	5.84
	TOTAL	13.74	5.26	18.01	37.01
AG-4	Storm runoff	0.06	0.00	1.89	1.95
	Base flow	0.16	0.17	0.33	0.66
	Spill	2.17	0.00	0.00	2.17
	TOTAL	2.39	0.17	2.22	4.78
AG-5	Storm runoff	1.39	0.08	3.99	5.76
	Base flow	0.30	0.38	1.29	2.47
	Spill	1.06	0.00	0.00	1.06
	TOTAL	3.55	0.46	5.28	9.29
AG-6	Storm runoff	0.09	0.00	3.29	3.38
	Base flow	0.12	0.05	0.11	0.28
	Spill	0.00	0.00	0.00	0.00
	TOTAL	0.21	0.05	3.40	3.66
AG-7	Storm runoff	0.00	0.00	0.00	0.00
	Base flow	0.00	0.00	0.00	0.00
	Spill	0.00	0.00	0.00	0.00
	TOTAL	0.00	0.00	0.00	0.00
AG-10	Storm runoff	0.03	0.00	1.74	1.77
	Base flow	0.54	0.02	1.34	1.90
	Spill	3.13	0.81	0.00	3.94
	TOTAL	3.70	0.83	3.08	7.61

APPENDIX XXX Continued

Watershed		Amount in stream water (kg) May-Aug	Sep-Dec	Jan-Apr	Total
AG-11	Storm runoff	0.05	0.00	0.11	0.16
	Base flow	0.08	0.00	0.24	0.32
	Spill	0.00	0.00	0.00	0.00
	TOTAL	0.13	0.00	0.35	0.48
AG-13	Storm runoff	0.00	0.00	0.25	0.25
	Base flow	0.19	0.04	0.39	0.62
	Spill	0.06	0.38	0.00	0.44
	TOTAL	0.25	0.42	0.64	1.31
AG-14	Storm runoff	0.20	2.50	3.77	6.47
	Base flow	0.11	0.61	0.54	1.26
	Spill	0.39	0.00	0.00	0.39
	TOTAL	0.70	3.11	4.31	8.12
TOTAL	Storm runoff	11.80	5.29	37.96	55.05
	Base flow	5.59	4.07	7.52	17.18
	Spill	15.41	1.19	0.00	16.60
	TOTAL	32.80	10.55	45.48	88.83

APPENDIX XXXI Monthly concentrations of organonitrogen herbicides in water collected from 11 agricultural watersheds between April 1974 and May 1977 (mean and range)

		Content in water (µg/L)				
YEAR	MONTH	AG-1	AG-2	AG-3	AG-10	AG-13
1974	April	0.2(S)	ND	ND	ND	ND
		ND-0.5				
	May	0.2(S)	ND	ND	T(S)	T(S) 0.3(C) 0.8(M)
		ND-0.3			ND-T	ND-T ND-1.5 ND-4.2
	June	0.4(S)	ND	3.1(S) 0.3(M)	ND	T(S)
		0.2-0.8		ND-9.1 ND-0.9		ND-0.2
	July	0.8(S)	ND	ND	ND	ND(S)
		0.6-0.9				ND-T
	Aug.		ND	ND	ND	
	Sept.		ND	ND	ND	0.3(S)
	Oct.		ND			T(S)
						ND-T
	Nov.	ND	ND	ND		T(S)
						ND-0.2
						ND

Continued ....

APPENDIX XXXI Continued

		Content in water (µg/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1975	Feb.	ND	ND	ND			ND				ND	
	Mar.	ND	ND	ND	ND	ND	ND		ND	ND	ND	ND
	Apr.	T(S)	ND	ND(S)	ND	ND(S)	ND	ND	ND	ND	ND	ND
		ND-T		ND-T		ND-T						
	May	T(S)	ND	1.0(A)	ND	ND	ND(S)	ND	ND(S)	ND	0.2(M)	ND
		ND-0.1		ND-9.0			ND-0.1		ND-T		ND-1.0	
	June	T(M,S)	ND	ND(A,S)	ND	ND	ND	ND	ND	ND(A)	T(M,S)	ND
		ND-0.3		ND-T						ND-T	ND-T	
	July	T(S)	ND	ND	ND	0.2(M)	ND(M)	ND	ND		ND	
		ND-T				ND-1.4	ND-T					
	Aug.	0.2(S)	ND	ND		ND	ND	ND			ND(M)	
											ND-T	
	Sept.	ND(S)	ND	ND	ND	ND	ND	ND			ND	ND
		ND-T										
	Oct.	ND	ND	ND	ND	ND	ND		0.2(C)		ND	T(C)
									ND-0.3			ND-0.3
	Nov.	ND(S)	ND	ND	ND	ND	ND(P)		ND		ND	ND(S)
		ND-T					ND-T					ND-T
	Dec.	ND	ND	ND	ND	ND	ND		ND		ND	ND

APPENDIX XXXI Continued

YEAR	MONTH	Content in water (µg/ L) AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1976	Jan.	ND		ND	ND	ND	ND		ND		ND	ND
	Feb.	ND	ND	ND	ND	ND	ND		ND		ND	ND
	Mar.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Apr.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	May	ND(S) ND-T	ND	ND	T(C,S) ND-0.3(C)T(S)	ND ND-T	ND	ND	ND(S) ND-T		T(M)ND(S) ND-0.8(M) T(S)	ND(S)
	June	T(M,S) ND-0.7(M)T(S)	ND	ND	T(S) ND-0.2	ND	ND		ND		ND	ND
	July	0.2(M)1.3(S) ND-1.2,0.5-3.4	ND	0.2(S) ND-0.5	ND(S) ND-T	T(S) ND-T	ND	ND	ND(S) ND-T	ND-0.4	T(M)ND(S) (M)0.2(S)	ND
	Aug.	0.7(S) 0.5-0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND(P) ND-T	ND
	Sept.		ND	ND	ND	ND	ND		ND		ND(S) ND-T	ND
	Oct.	0.6(S) 0.5-0.6	ND	ND(S) ND-T	ND	ND	ND	ND	ND	ND	ND	ND
	Nov.	0.3(S)	ND	ND	ND	ND(S) ND-T	ND	ND	ND		ND	T(C) ND-0.2
	Dec.	ND	ND	ND	ND	ND	ND	ND	ND		ND(M) ND-T	ND

APPENDIX XXXI Continued

		Content in water (µg/L)										
YEAR	MONTH	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14
1977	Jan.		ND	ND		ND	ND	ND			ND	ND
	Feb.		ND	ND		ND	ND				ND	ND
									ND(P,C)			
	Mar.	ND(C,S)	ND(C)	ND(C)	ND	T(C)ND(S)	ND(P)	ND	0.1(S)	ND	ND(S)	ND
						ND-0.2(C)			ND-T			
		ND--T	ND-T	ND-T		T(S)	ND-T		T-0.3		ND-T	
	Apr.	ND	ND(C)	ND	ND	ND(P)	ND	ND	T(S)		ND	ND
		ND-T				ND-T			ND-0.1			
	May	ND	ND	ND(S)	ND	ND	ND	ND		ND	ND	ND
				ND-T								

A - alachlor
C - cyprazine
M - metribuzin
P - prometone

ND - not detected <0.04 µg/L
T- trace 0.04-0.09 µg/L

APPENDIX XXXII Amount of organonitrogen herbicides leaving 11 agricultural watersheds between May 1975 and April 1977.

Herbicide (period)	Amount leaving watershed (g)											
	AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	Total
<u>alachlor</u>												
1975-76 (May-April.)												
May	0	0	249	0	0	0	0	0	0	0	0	249
June	0	0	15	0	0	0	0	0	0	0	0	15
TOTAL	0	0	264	0	0	0	0	0	0	0	0	264
<u>cyprazine</u>												
1975-76 May-April)												
May	0	0	498	2	0	0	0	0	0	0	0	500
July	0	0	0	0	41	0	0	0	0	0	0	41
Oct.	0	0	0	0	0	0	0	30	0	0	0	30
Mar.	0	100	0	0	0	0	0	0	0	0	0	100
TOTAL	0	100	498	2	41	0	0	30	0	0	0	671
1976-77 (May- April)												
May	5	0	0	0	0	0	0	0	0	0	0	5
Nov.	0	0	0	0	0	0	0	0	0	0	52	52
Mar.	0	46	205	0	85	0	0	34	0	0	0	370
Apr.	30	48	0	0	40	0	0	0	0	0	0	118
TOTAL	35	94	205	0	125	0	0	34	0	0	52	545
<u>metribuzin</u>												
1975-76 (May-April)												
May	0	0	0	0	0	0	0	0	0	15	0	15
June	0	0	0	0	0	0	0	0	0	5	0	5
July	39	0	0	0	1	0	0	0	0	0	0	40
Aug.	2	0	0	0	63	0	0	0	0	2	0	67
TOTAL	41	0	0	0	64	0	0	0	0	22	0	127
1976-77 (May-April)												
May	0	0	0	0	0	0	0	0	0	106	0	106
July	135	0	0	0	0	0	0	0	0	33	0	168
TOTAL	135	0	0	0	0	0	0	0	0	139	0	274

Continued ....

APPENDIX XXXII Continued

Herbicide (period)		Amount leaving watershed (g)											
		AG-1	AG-2	AG-3	AG-4	AG-5	AG-6	AG-7	AG-10	AG-11	AG-13	AG-14	Total
<u>prometone</u>													
1975-76 (May-April)													
	Nov.	0	0	0	0	0	44	0	0	0	0	0	44
1976-77	(May-April)												
	Aug.	0	0	0	0	0	0	0	0	0	1	0	1
	Nov.	0	0	0	0	0	0	0	1	0	0	0	1
	Mar.	0	0	0	0	0	21	0	54	0	0	0	75
	April	0	0	0	0	19	0	0	0	0	0	0	19
	TOTAL	0	0	0	0	19	21	0	55	0	1	0	96
<u>simazine</u>													
1975-76	(May-April)												
	May	10	0	12	0	10	52	0	0		5	3	92
	June	70	0	0	0	0	0	0	0		6	0	76
	July	1	0	0	0	0	0	0	0		0	0	1
	Aug.	205	0	0	0	0	0	0	0		0	0	205
	Sept.	94	0	0	0	0	0	0	0		0	0	94
	Nov.	0	0	0	0	0	0	0	0		0	0	0
	Feb.	0	0	0	0	505	0	0	0		0	0	505
	TOTAL	380	0	12	0	515	52	0	0		11	3	973
1976-77	(May-April)												
	May	6	0	0	29	14	0	0	19	0	2	0	70
	June	0	0	0	16	0	0	0	0	0	0	0	16
	July	1239	0	405	14	79	0	0	0	0	1	0	1738
	Aug.	0	0	6	0	2	0	0	0	0	0	0	8
	Oct.	6	0	2	0	0	0	0	0	0	0	0	8
	Nov.	0	0	0	0	10	0	0	0	0	0	0	10
	Mar.	0	0	0	0	221	0	0	387	0	31	0	639
	April	7	0	0	0	20	0	0	66	0	14	0	107
	TOTAL	1258	0	413	59	346	0	0	472	0	48	0	2596

APPENDIX XXXIII Monthly concentration of methyl (carbofuran) and thio carbamates (EPTC) in water collected from 5 agricultural watersheds between June and August 1976 (µg/L)

Year	Month	AG-2		AG-3			AG-6			AG-7		AG-13		
		Thio	(#)	Thio	Meth	(#)	Thio	Meth	(#)	Thio	(#)	Thio	Meth	(#)
1976	June	ND	1	ND	T(C)	3	ND		2			0.1(E)	<0.5(C)	4
					ND-0.5							ND-0.2	ND-1.0	
	July	ND	2	ND	0.5(C)	5	ND	ND	3			ND	ND(C)	12
					ND-1.0								ND-1.0	
	August	NT)	2	ND	ND	5	ND	ND	3	ND	2	ND	ND (C)	9
													ND- <0.5	

C - carbofuran ND - not detected
E - EPTC