Occurrence and fate of selected agricultural pesticides in water and sediments of Lake Erie coastal marshes

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1. Rationale and objectives

With continued application of pesticides in the Great Lakes basin, nonpoint source pollution of nearshore wetlands is becoming a major concern. Unlike point sources of contamination such as at the outlet of an effluent pipe, nonpoint sources are more difficult to define. An estimated 21 million kg of pesticides are used annually on agricultural crops in the Canadian and American Great Lakes Watershed (GAO 1993). Herbicides account for about 75% of this. These pesticides are frequently transported via sediment, ground or surface water flow from agricultural land into the aquatic ecosystem. With mounting concerns and evidence of the effects of certain pesticides on wildlife and human health (Colborn et al. 1993), it is crucial that we determine the occurence and fate of agricultural pesticides in sediments found in marshes draining into the Great Lakes.

Limited information exists on contamination of sediments by contemporary agricultural pesticides. Transport of pesticides adsorbed to particulate material may be an important mechanism in pesticide movement from agricultural land to fresh water systems. The deposition of pesticide-carrying particulates could potentially contaminate sediments. The extent of sediment contamination caused by pesticides and the fate of pesticides in sediments in near-shore marshes is unclear. Furthermore, there have been very few studies in agricultural watersheds which address the question of bioavailability and, thus, toxicity of pesticides to organisms which live in or near sediments.

A multidisciplinary study was initiated to assess nonpoint source contaminant transport from agricultural land into near-shore zones and wetlands of the Great Lakes Basin. A region located in Essex County of southwestern Ontario was selected due to its extensive agricultural land use, encompassing more than 2200 farms (OMAF 1993), and due to the presence of environmentally sensitive marshes adjacent to Lake Erie.

The objectives of the study were 1) to examine selected near-shore and wetland locations in the Canadian Great Lakes Basin, and agricultural sources of sediments contaminated by toxic agricultural chemicals (esp. pesticides); 2) estimate the quantity of chemicals present; 3) evaluate their bioavailability and impact on wetland ecology; and 4) identify the options for remedial action.

This report summarizes some of the data collected during the life of the study. Unfortunately, it is not possible to include all of the detailed data on sediment quality until the authors have had some time to interpret the results. A separate report is being prepared on sediments that were sampled from the areas studied. Additional scientific papers and presentations will be prepared by the authors to communicate the results of our study.

2. Methods

2.1 Background

Initial investigations began in 1990 and continued in 1991 to identify near-shore areas where sediments may contain measurable levels of pesticides. A total of 15 sampling sites bordering Lake Erie and Lake Ontario were selected for sediment analysis for various pesticides. From the preliminary results of this survey, it became clear that many basic processes remained to be studied before an extensive survey should be undertaken. A number of questions needed to be answered, such as: What are the existing levels of pesticides in water and sediments? What is the mobility of these compounds from agricultural fields to the marsh sediments? Is particulate material the main medium for moving contaminants from the field to the marsh? If so, to what degree do these compounds partition themselves between the water column and the marsh sediment? These questions could be best answered by focusing the study on a particular marsh system. As a result, Malden and Hillman Creek Watersheds in Essex county were selected for conducting a more detailed study in 1992. Later that year, it was determined that Hillman Creek Watershed was too big and complex to analyze in such a short period of time (2 years). Instead Muddy Creek Watershed, which drains into Wheatley Harbour, was deemed more suitable because of its size and well defined shape.

2.2 Description of watersheds

The two watersheds studied in greatest detail were Malden Watershed (MAL) and Muddy Creek Watershed (MUD) (Fig.1). MAL is located 25 km south of Windsor, Ontario, and MUD drains into Wheatley Harbour 12 km west of Leamington, Ontario. The areas of the watersheds are about 415 and 784 ha for MAL and MUD, respectively. The land use in both watersheds as determined by this study is mainly agriculture with soybean, corn, wheat and tomato as major crops (Table 1). Agricultural statistics for Essex County reported in OMAF (1993) indicate similar land use.

The topography of both watersheds is characteristic of all of Essex County--almost level to undulating (Fig. 2 topo map plus agnps cells). The average slopes are 0.2 and 0.24% for MUD and MAL, respectively. Near the creeks or major drains the slope can exceed 3%. The drop in elevation ranged from 12 to 14 m from the top to the bottom of the watersheds. The soil texture in MAL is mostly clay to clay loam (Perth and Brookston Series, (Richards et al. 1989)). The soil texture in MUD is more variable. The southern section is composed of Brookston Clay (Richards et al. 1989). The remainder is a mixture of mostly Brookston Clay Sand and Berrien Sandy Loam.

Drainage in both watersheds varies from poor to imperfect depending on soil texture and therefore subsurface drainage is prevalent. The natural drainage is supplemented with municipal drains, open ditches, and dredge cuts to serve as outlets for subsurface drains. Muddy Creek collects surface and drainage water from all MUD and drains into Wheatley Harbour. Two municipal drains serve MAL--Ong and McGee Drain. During high intensity rainfall events, surface runoff occurs on the clay soils and in between row crops such as corn and tomatoes.

The climate in Essex county is classified as humid continental, with hot summers and humid winters. The mean annual precipitation is about 792 mm (need Harrow Research Station values).

Table 1. Land use in the Malden and Muddy Creek Watersheds.

Crops	Land Area (ha)		
	Malden Watershed		Muddy Creek Watershed
	1992	1993	1993
Apples	0	0	8.1
Corn	80.7	76.7	228.2
Cucumber	0.5	0	0
Hay	0	0	4.2
Peas	12.3	0	0
Soybean	184.8	211.1	175.2
Tomato	42.6	36.7	4.1
Wheat	92.5	88.8	3.8
Not planted	0	0	8
Total crop area	413.4	413.3	431.6
Forest	0	0	36.8
Marshland	2	2	27.8
Water	0	0	16.1
No information	0	0	271.2
Total land area	415.4	415.3	783.5

2.3 Data collection:

2.3.1 Determination of Farm Practices and watershed topography

All farmers in MAL were contacted individually and voluntariliy provided information on their agricultural practices[1]. Not all farmers in MUD responded and therefore the information is incomplete. Information collected from the farmers included identification of exact field locations, cropping practices, and the quantities and dates of application of nutrients and pesticides. The pesticide and crop data were tabulated and used to calculate values in Tables 1 and 2. The pesticide application rate that the farmer provided during the interview corresponded in most cases to the recommended rate. Therefore, the herbicide usage calculation shown in Table 2 for each watershed was based on the lowest recommended rate found in the *Guide to Weed Control* (OMAF 1994). For calculation of insecticide and fungicide usage, application rates were obtained from the suppliers and farmers. Tables 3A and 3B summarize some of the properties of the pesticides used and of other pesticides that were detected in the watershed.

Air photos and hard copies of topographical maps at a scale of 1:10000 were obtained. The two watersheds were divided into cells (polygons) using the AGNPS model approach and numbering scheme (Young et al. 1989). The watershed cells and contour lines were digitized with a Geographic Information System (GIS) called ILWIS (Integrated Land and Water Information System; Valenzuela 1988). The land management (eg. crops, fertilizers, tillage), pesticide and topographic (land slope, slope direction and length) data were related to each cell in the watersheds.

2.3.2 Creek Sampling

Water and sediment samples in MUD and MAL were collected throughout the year at 5 and 2 locations, respectively (Fig. 1). Sampling was most intensive (bi-weekly) during the growing season. Surficial sediments were collected with a mini-Ponar grab sampler. Sediment cores were obtained with a modified hand-operated Kajak-Brinkhurst corer. Sixty liters of water were centrifuged using a Westfahlia continuous flow centrifuge at a rate of 2 L/min. Outflowing water from the centrifuge was collected into precleaned pressurizable stainless steel cans. About 20 to 60 g (wet weight) of suspended particulate matter was obtained.

All collected material was either frozen or kept at 0E C until analyzed. Water, surficial sediment and suspended particulate matter were analyzed for pesticides (extraction/GC-MS). Dissolved and particulate phosphorous were also measured along with a variety of relevant water quality parameters including dissolved organic carbon, alkalinity, turbidity, hardness, pH, calcium, magnesium and dissolved oxygen. Some sediment samples were analyzed for Al, Ca, Mg, K, Na, P, Ti, Fe, Mn,

[1] In order to maintain farmer confidentiality, the pesticide data presented in this report is pooled and not presented on an area basis.

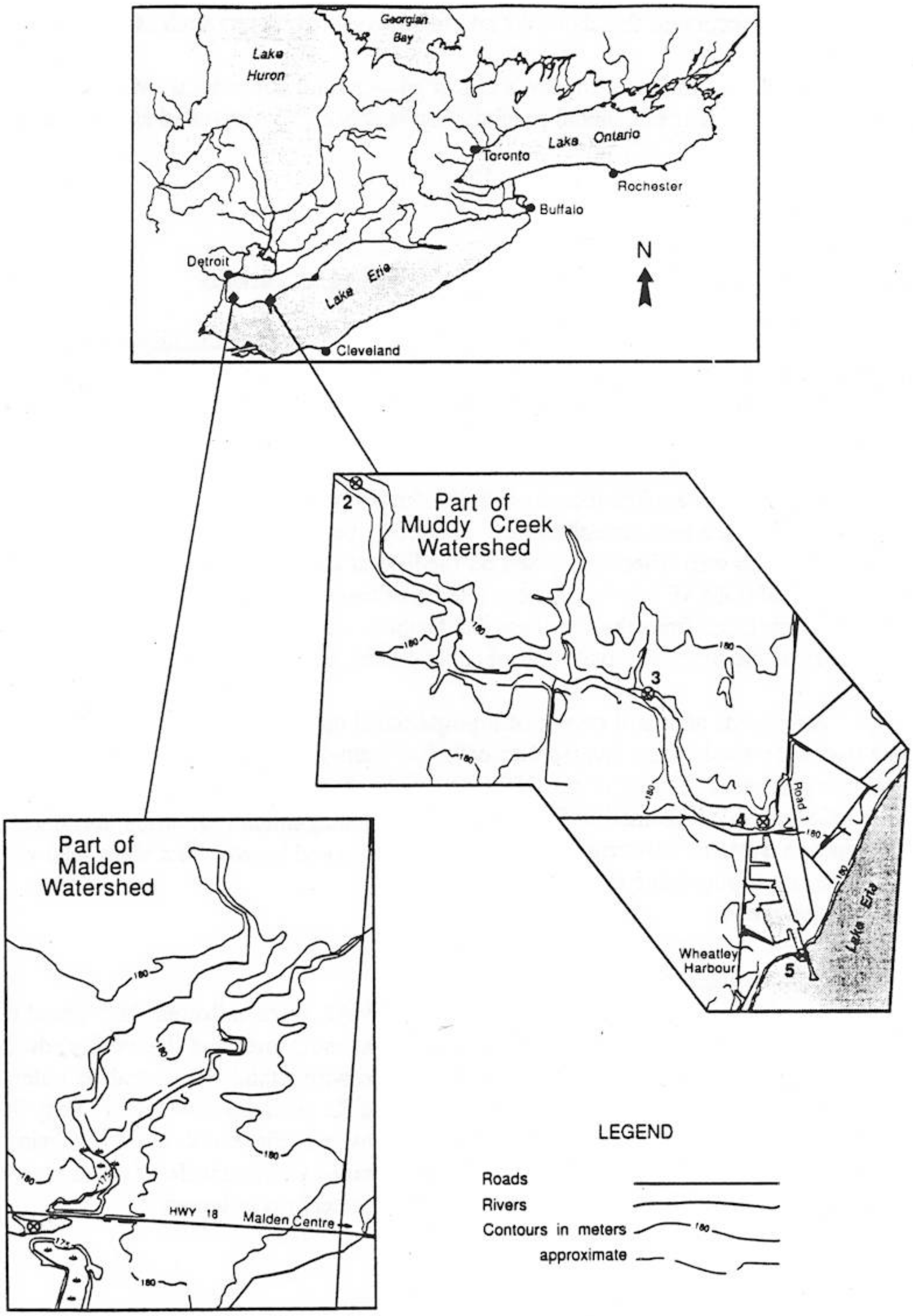

Figure 1. Location of sampling sites and watersheds in the Great Lakes Basin. Site MUD1 is located 1.5 km further upstream.

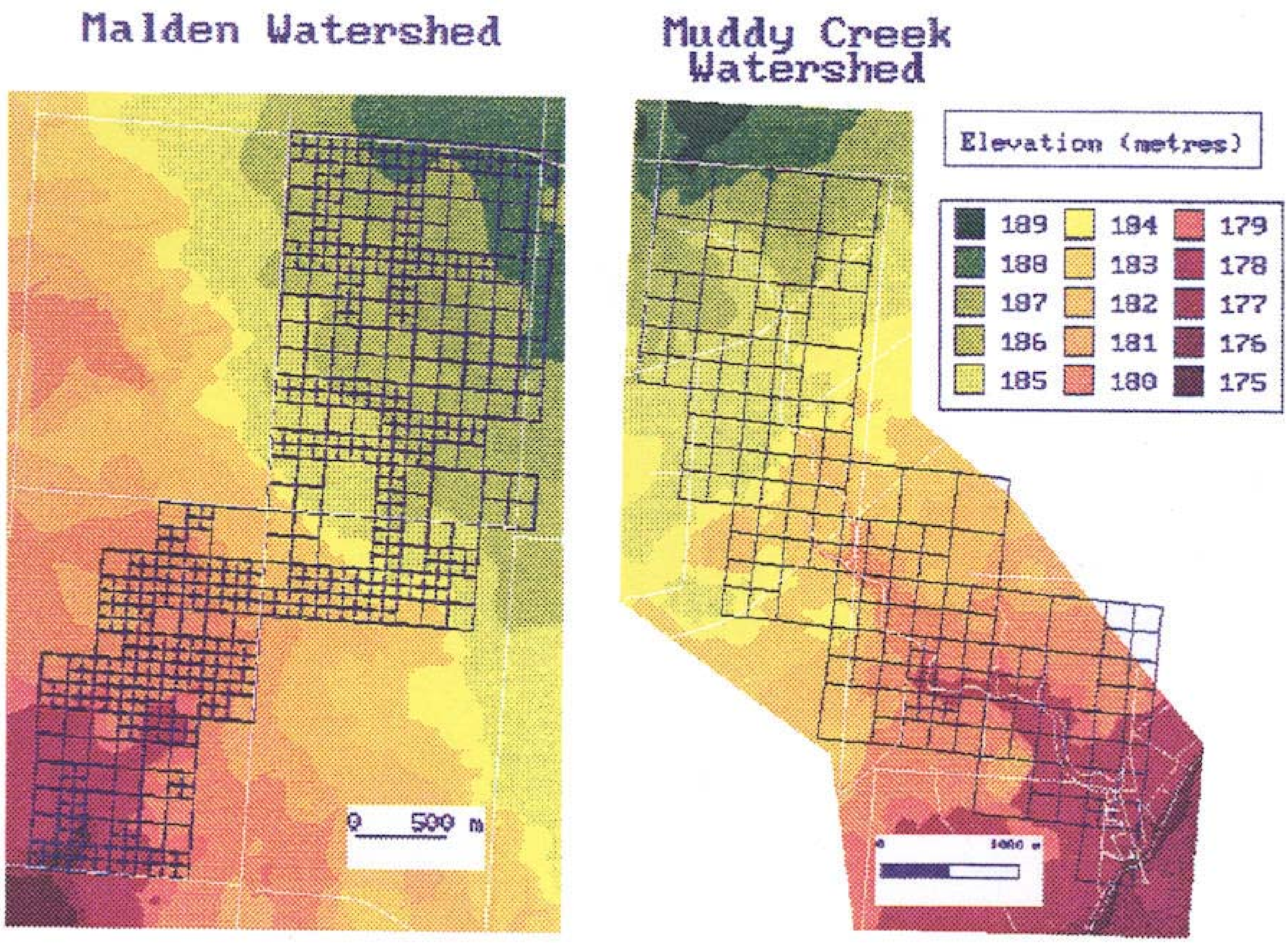

Figure 2. Topographic maps of the watersheds overlayed by AGNPS cells (Young *et al*, 1989) which depict the shape and size of each watershed.

organic C, particle size distribution, major oxides and trace elements. Chronological age of two sediment cores was evaluated using the 210Pb method (Turner 1994).

2.3.3 Pesticide "speciation"

A novel method combining high pressure liquid chromatography (HPLC) with in-line microfiltration allowed experimental differentiation of pesticide "species" such as that dissolved in water, bound to the surface of sediment particles or diffused to the particle interior. Details of the experimental method appear in the literature (Gamble 1990). Results obtained in this manner allow greater understanding of the rates and extents of pesticide binding to sediment particles. The nature of the information is also indicative of bioavailability of pesticides to living organisms.

Table 2. Pesticide application in Malden and Muddy Creek Watersheds.

Common Name[1] of pesticide	Trade Name[2]	Crops	Recommended[3] Rate (l/ha)	Active[4] Component (g/l)	Usage in Watershed[5]					
					Malden				Muddy Creek	
					1992		1993		1993	
					ha	kg	ha	kg	ha	kg
Atrazine (H)	Atrazine Primextra Marksman	corn	2 - 3 6.5 - 8.5 3.70 - 4.50	500 200 260	55.5	61.1	44.5	44.2	100.8	100.8
Bentazon (H)	Basagran+	soybean	1.75 - 2.25	480	99.7	83.7	62.2	52.2	69.0	58.0
Bromoxynil (H)	Pardner Buctril	corn	1.0 - 1.2 1.00	280 280	23.7	6.6	37.9	10.6	20.1	5.6
Butylate (H)	Sutan+	corn	4.25 - 8.50	800	0	0	21.6	73.4	0	0
Chlorothalonil (F)	Bravo	cucumber tomato	(2.5 kg/ha)	NA	42.7	NA	0	0	0	0
Clomazone (H)	Merit	soybean	1.40 - 1.80	480	0	0	0	0	20.2	13.6
Copper sulfate (A,F)	Kocide 101	tomato	(2.5 kg/ha)	NA	42.3	NA	23.6	NA	0	0
Cyanazine (H)	Bladex	corn	3.75 - 7.00	480	21.7	39.1	50.9	91.6	16.0	28.8
Cypermethrin (I)	Cymbush	tomato	0.14 - 0.28	250	32.3	1.1	23.6	0.8	0	0
2,4-D (H)	Kilmore 2,4-D	wheat	0.85 - 1.75 0.35 - 1.10	295 500	23.3	5.8	38.0	7.4	0	0
Dicamba (H)	Banvel Kilmore Marksman	wheat corn	0.23 - 0.29 0.85 - 1.10 3.70 - 4.50	480 110 130	39.1	3.9	25.4	8.3	0	0
Dyfonate (I)	Fonofos	corn	5.65 kg/ha	20 %	34.9	39.4	0	0	0	0
Ethalfluralin (H)	Edge	soybean	1.4 - 2.2 kg/ha	50 %	17.2	12.0	5.9	4.1	0	0
Glyphosate (H)	Roundup	soybean	2.35 - 7.00	356	0	0	0	0	25.5	21.3
Imazethapyr (H)	Pursuit	soybean	0.42	240	30.3	3.0	71.0	7.2	0	0
Linuron (H)	Lorox	corn	0.76 - 2.2 kg/ha	50 %	0	0	0	0	24.1	9.2
Maneb (F)	Manzate	tomato	(2.5 kg/ha)	200	32.3	16.2	0	0	0	0
MCPA (H)	MCPA Amine Tropotox Plus Buctril	wheat	0.7 - 1.7 2.75 - 4.25 1.00	500 25 280	8.8	2.9	8.2	2.9	3.8	1.1
MCPB (H)	Tropotox Plus	wheat	2.75 - 4.25	375	0.9	0.9	0	0	0	0
Mecoprop (H)	Kilmore	wheat	0.85 - 1.1	80	23.3	1.6	10.1	0.7	0	0
Metolachlor (H)	Primextra Dual	corn soybean tomato	6.5 - 8.5 2.0 - 2.75	300 960	167.3	319.8	162.7	312.4	192.7	370.0
Metribuzin (H)	Lexone Sencor	soybean tomato peas	0.70 - 1.13 0.85 - 2.25	480 500	177.0	67.2	139.4	52.9	28.2	10.7
Naptalam (H)	Alanap	cucumber	9.5 - 30	240	0.5	1.1	0	0	0	0
Pendimethalin (H)	Prowl	corn	3.50	480	0	0	0	0	16.0	26.9
Permethrin (I)	Ambush	corn	0.200 - 0.275	500	0	0	21.6	2.2	0	0
Sethoxydim (H)	Poast	soybean	0.81 - 2.72	184	0	0	0	0	25.5	3.8
Tefluthrin (I)	Force	corn	NA	NA	0	0	2.0	NA	0	0
Thifensulfuron-methyl (H)	Pinnacle	soybean	0.0053 - 0.0080	75 %	99.7	0.4	62.2	0.2	0	0
Trifluralin (H)	Treflan	soybean	1.10 - 2.00	545	57.8	34.6	5.9	3.5	0	0
No pesticide applied on cropland					73.7		95.5		57.2	
Pesticide application unknown					0		0		379.2	

NA - Not Available

[1] A-algicide; F-fungicide; H-herbicide; I-insecticide

[2] Trade names are listed in association with EACH active ingredient ("common name of pesticide") which they contain.
[3] Recommended rates taken from "Guide to Weed Control", Ontario Ministry of Agriculture and Food, Publication no. 75, 1992 or 1994, or by communication with the supplier (cypermethrin, dyfonate, permethrin). Where recommended rates could not be obtained, the applied rate as estimated by the farmers is given in brackets.
[4] Active components of the specific pesticide ("Common Name") contained in the "Trade Name" product.
[5] Calculations based on the lowest recommended rates.

Table 3A. Properties of pesticides applied in Malden and/or Muddy Creek watersheds.

Common Name[1] of Pesticide	Solubility[2] in water (µg/ml)	Soil K_{OC}[2] (ml/g)	Half-life[2] (days)	Toxicity[2]	
				LD_{50} oral, rat (mg/kg)	LC_{50} fish (mg/l)
Atrazine (H)	33	100	60	1780	4.5
Bentazon (H)	2300000	34	20	2063	>100
Bromoxynil (H)	0.08	10000	7	260	0.05
Butylate (H)	46	400	13	3500	5.2
Chlorothalonil (F)	0.6	1380	30	>10000	0.049
Clomazone (H)	1100	NA	NA	1369	NA
Copper sulphate (A,F)	316000	NA	NA	472	$1
Cyanazine (H)	170	190	14	288	9.0
Cypermethrin (I)	0.004	100000 e	30 e	250	0.002
2,4-D (H)	890	20	10	699	1.1
Dicamba (H)	400000	2	14	1707	35
Dyfonate (I)	16.9	870	40	8	0.05
Ethalfluralin (H)	0.3	4000	60	>10000	NA
Glyphosate (H)	900000 e	24000 e	47	5000	86
Imazethapyr (H)	miscible	NA	NA	>5000	NA
Linuron (H)	81	400	60	4000	16
Maneb (F)	6 e	2000 e	70	7990	2.2
MCPA (H)	825	20 e	25	1160	117
MCPB (H)	44	20 e	14	680	75
Mecoprop (H)	660000	20 e	21	1166	nontoxic
Metolachlor (H)	530	200	90	2780	3.9
Metribuzin (H)	1200	60 e	40	1100	64
Naptalam (H)	231000	20 e	14	1770	76
Pendimethalin (H)	0.275	15000	NA	2679	0.138
Permethrin (I)	0.006	100000	30	430	0.005
Sethoxydim (H)	4700	100 e	5	3200	moderately toxic
Tefluthrin (I)	very low	NA	NA	1531	highly toxic
Thifensulfuron-methyl (H)	2400	NA	NA	>5000	NA
Trifluralin (H)	0.3	8000	60	>10000	0.011

Table 3B. Properties of other relevant pesticides.

Common Name[1] of pesticide	Solubility[2] in water (µg/ml)	Soil K_{OC}[2] (ml/g)	Half-life[2] (days)	Toxicity[2]	
				LD_{50} oral, rat (mg/kg)	LC_{50} fish (mg/l)
Alachlor (H)	242	170	15	1800	1.8
	Removed from market 1988				
Carbofuran (I,N,M)	351	22	50	11	0.28
á-Endosulfan (I) â-Endosulfan (I)	0.32	12400	50	23	0.0003
Fensulfothion (I,N)	1600	78	NA	2.2	8.8
	Discontinued in 1990				
Pebulate (H)	100	430	14	921	7.4
Simazine (A,H)	3.5	130	60	>5000	56
Terbufos (I,N)	15	500	5	4.5	10

[1] A-algicide; H-herbicide; I-insecticide; M-miticide; N-nematicide

[2] Solubility and toxicity data taken, where available, from "Farm Chemicals Handbook '92", Meister Publishing, Willoughby, OH, USA, 1992. LD_{50} median lethal dose resulting in a 50% kill, LC_{50} median lethal concentration. Soil K_{oc}, pesticide half-life and solubility (where necessary) taken from J. Stover and A.S. Hamill, "Pesticide Contamination of Surface Waters Draining Agricultural Fields: Pesticide Contamination Classification and Abatement Measures", Agriculture Canada, Harrow Research Station. LC_{50} values for atrazine, metolachlor and cyanazine from "Canadian Water Quality Guidelines", Task Force on Water Quality Guidelines, Canadian Council of Resource and Environment Ministers, 1987 and updates. Data for fensulfothion taken from "Guide to the Chemicals Used in Crop Protection", Agriculture Canada, Research Branch, Pub. No. 1093, 6th ed., 1973. Some fish LC_{50} and soil K_{oc} data from J.H. Montgomery, "Agrochemicals desk reference: Environmental data", Lewis publishing, Chelsea, MI, USA, 1993.

e estimated value

2.3.4 Ecotoxicological tests

A battery of bioassay tests were carried out using aquatic plants and invertebrates. Four species of benthic invertebrates (an amphipod *Hyalella azteca*; midge *Chironomus riparius*; mayfly *Hexagenia spp.* and oligochaete worm *Tubifex tubifex*) were placed in vessels containing creek sediment and overlying water. Test durations ranged from 10 to 28 days indicating effects of chronic exposure on either reproduction (*T. tubifex*) or survival and growth (others). Endpoint parameters were compared to a reference sediment taken from a nearby wildlife sanctuary.

Phytochemical toxicity of compounds in creek water was determined using filter sterilized water diluted from 0 to 100%. Growth of the green algae *Selenastrum capricornutum* was measured after 72 hours following the method of Environment Canada, 1992. A standard procedure (ASTM, 1993) was also used to measure change in biomass over 7 days of the vascular plants duckweed (*Lemna gibba*) and a rooted macrophyte (*Myriophyllum sibriricum*).

3. Findings

3.1 Watershed characteristics and land management practices

The direction of overland flow of water as estimated by AGNPS Model for both watersheds is shown in Fig. 3. The overland flow in MAL travels up to 1.5 km in a southwesterly direction in the northern part of the watershed before reaching a municipal drain (Ong Drain). The potential for soil/sediment transport is however low because the slope in the area is 0.1 to 0.15%. Areas along the two drains in the southern half of the watershed where land slope exceeds 3% could contribute to sediment loading at the outlet. The change in land use from year to year as shown in Fig. 4 could account for some of the changes in pesticide levels found in the water and sediment. The data obtained from MUD was similar.

Dates, quantities and types of pesticides and fertilizers applied to each field in the watersheds and for each year represents a considerable volume of data. This is particularly so when trying to quantify relationships between parameters. To facilitate this task, data of this type has been handled, represented and analyzed using the relational database of ILWIS (Valenzuela 1988). Detailed discussion of these relationships is beyond the scope of this report.

Several general observations can be made. Approximately 30 different herbicides were applied in 1992 and 1993 (Table 2). Some farmers reported applying up to six pesticides on certain crops. Metolachlor, bentazon, metribuzin, atrazine, cyanazine and trifluralin were amongst the most widely applied pesticides. Crops in the two watersheds include (in decreasing order of crop area) soybean, corn, wheat, tomato, peas, apples, hay and cucumber.

3.2 Creek samples

The following pesticides were routinely monitored in creek water and sediment samples: alachlor, atrazine, cyanazine, cypermethrin, dyfonate, fensulfothion, metolachlor, metribuzin, simazine, terbufos and trifluralin. Several others were monitored on different occasions during the evolution of the research. Table 4 shows a sample of the results for the Malden watershed in 1992.

Atrazine and metolachlor were consistently detected in water in both watersheds with mean concentrations as high as 2.6 and 4.8 µg/L (parts per billion), respectively. Cyanazine, metribuzin and trifluralin were detected in greater than 50% of the samples. Metolachlor and trifluralin (and metribuzin in one core sample) were also found in particulate matter.

Table 4. Detection of pesticides in the Malden Watershed.

Pesticide	Drinking Water Quality (ng/l)	Fresh Water Quality (ng/l)	Malden Watershed 1992					
			Water			Particulate		
			Fraction	Average (ng/l)	Maximum (ng/l)	Fraction	Average (ng/kg)	Maximum (ng/kg)
Alachlor (H)	NA	NA	2 / 7	1.7	6	0 / 6	---	---
Atrazine (H)	60000	2000	7 / 7	448	1230	0 / 6	---	---
Carbofuran (I,N,M)	90000	1750	1 / 5	172	862	0 / 6	---	---
"-Endosulfan (I)	NA	NA	0 / 5	---	---	0 / 6	---	---
$-Endosulfan (I)	NA	NA	0 / 5	---	---	0 / 6	---	---
Fensulfothion	NA	NA	---	---	---	0 / 6	---	---
Linuron (H)	NA	NA	0 / 5	---	---	0 / 6	---	---
Metolachlor (H)	50000	8000	7 / 7	405	668	6 / 6	14000	23000
Metribuzin (H)	80000	1000	5 / 7	43	114	0 / 6	---	---
Pebulate (H)	NA	NA	0 / 6	---	---	0 / 6	---	---
Simazine (A,H)	10000	10000	4 / 7	6.3	14	0 / 6	---	---
Trifluralin (H)	45000	100	4 / 7	1.3	4	5 / 6	620	1000

NA - Data not available

"Drinking water quality" and "Fresh water quality" (for aquatic life) guidelines obtained from "Canadian Water Quality Guidelines", Task Force on Water Quality Guidelines, Canadian Council of Resource and Environment Ministers, 1987 and updates.

"Fraction" indicates the frequency of detection of the pesticide.

"Particulate" concentrations refer to suspended particulate matter (SPM), surficial sediment (S^2) and cores of #6 cm depth.

The following were also monitored in 1991 and early 1992, but were not detected in any cases: captan, chlorpyrifos (Dursban), diphenamid, diuron, guthion, methidathion and phosmet.

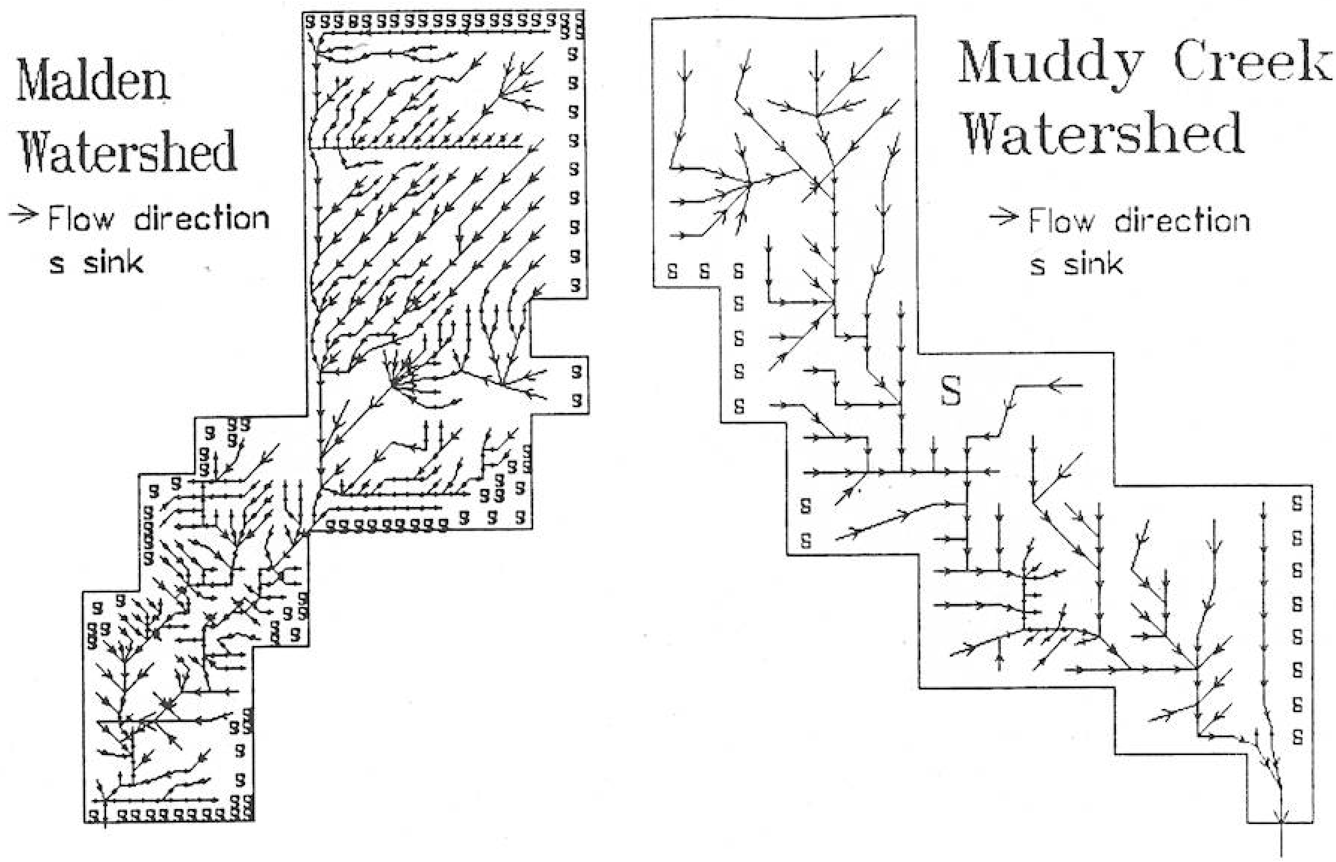

Figure 3. Estimated flow direction from each cell of Muddy Creek and Malden Watersheds. Computer output from AGNPS model.

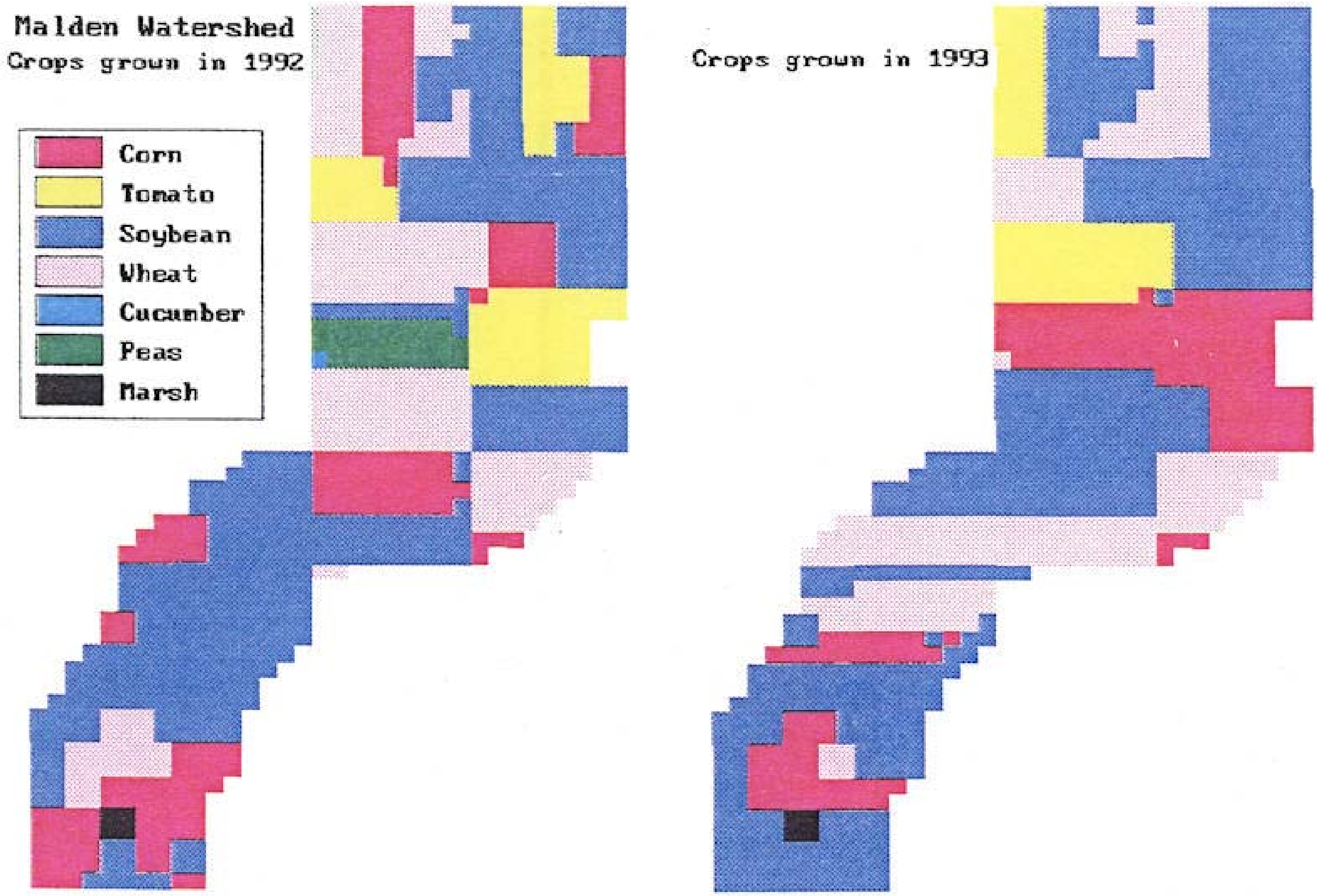

Figure 4. Changes in land use in Malden Watershed during the study period.

Of importance are profiles of pesticide distribution over time and down the creek such as those shown in Fig 5. Relating such data with locations and dates of pesticide application helps in the elucidation of transport and fate processes.

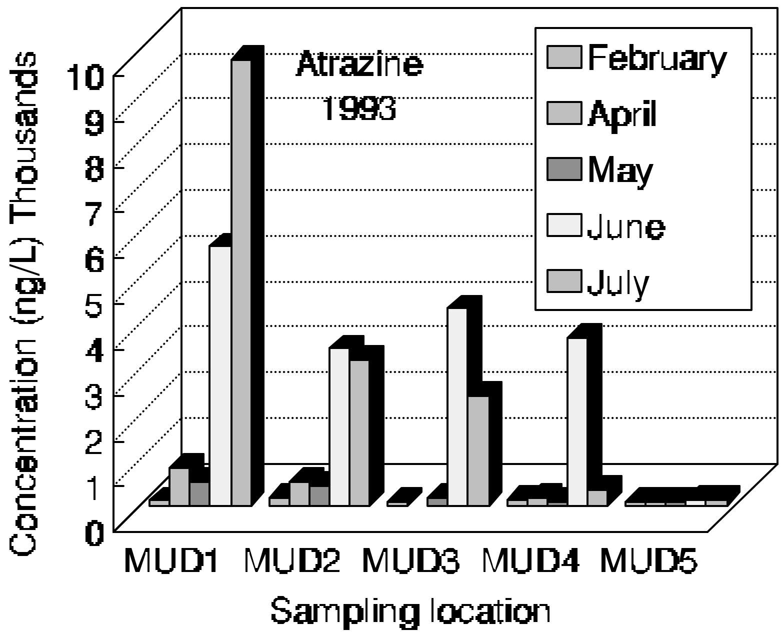

Figure 5A. Profile of atrazine dispersion over time as measured down Muddy Creek. (see Fig. 1 for sampling location)

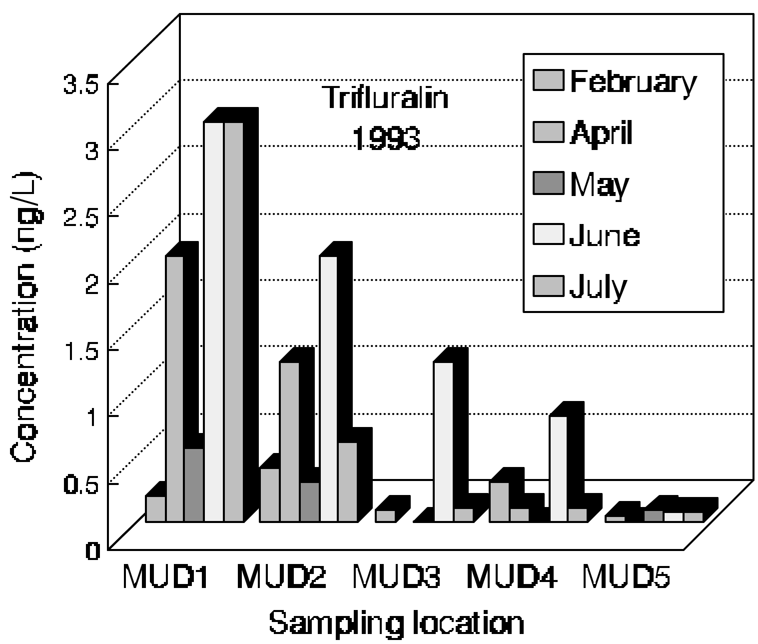

Figure 5B. Profile of trifluralin dispersion over time as measured down Muddy Creek. (see Fig. 1 for sampling location)

3.3 Microbiological degradation

During the early stages of measuring atrazine binding to creek sediment from Malden watershed, it was serendipitously found that rapid microbiological degradation of the pesticide was occurring. As seen in Fig. 6, an initial lag of about 15 days was followed by a decrease in atrazine concentration. Upon readdition of atrazine at 27 days, degradation occurred at a high rate and with no lag. This behaviour is consistent with microbiological degradation. Sediment which was sterilized by gamma-irradiation (indicated by triangles in Fig. 6) showed no sign of this degradation. Sterilized sediment was therefore used for studies of chemical interaction of pesticides with the sediments.

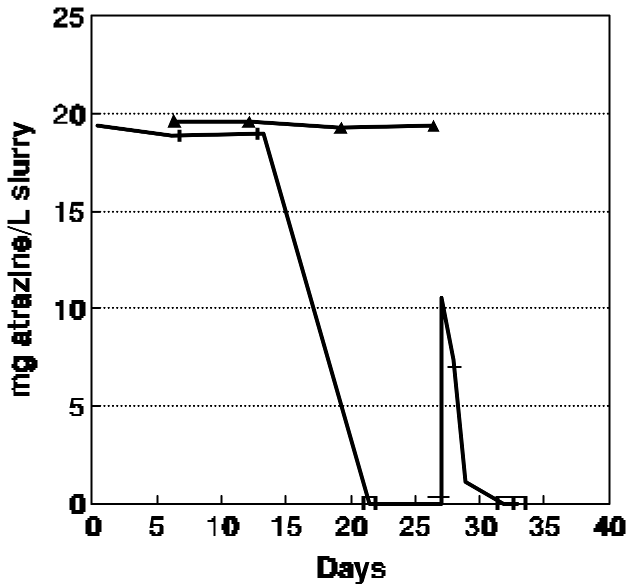

Figure 6. Degradation of atrazine by micro-organisms present in creek sediments is seen at about 15 and 27 days (squares). Gamma-irradiated sediments lack this acitivity (triangles).

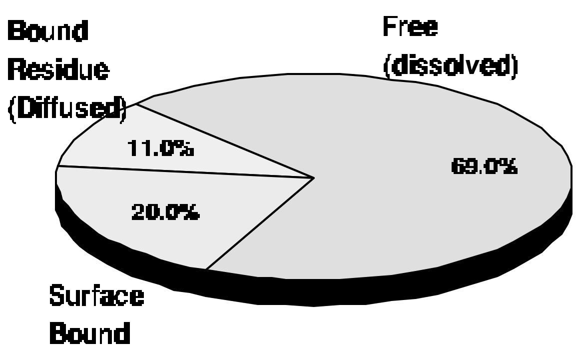

Figure 7. Species distribution ("speciation") of metolachlor after 14 days in the presence of Muddy Creek sediment .

It is interesting to note that all samples of surficial sediment tested from this region were found to degrade atrazine. This spans a range of about 60 km. Further, degradation was very rapid and resulted in complete mineralization of the triazine ring to CO_2. Investigation of this finding is the subject of a separate publication (Topp, 1994). Its potential importance to agricultural practices is clear.

3.4 Pesticide-sediment interaction

In evaluating transport of contaminants (such as pesticides) it is necessary to consider how the contaminant interacts with soils present. Knowledge of soil/sediment transport is also needed. Current models of transport generally assume that the soil particles are an infinite sink, and treat the interaction as a simple partitioning. This ignores the true chemical nature of the binding process. Models using equilibrium constants accept that binding requires a free site to which the pesticide can attach, and include a measure of the concentration of sites available. Further, binding of pesticide to sediment particles is not an instaneous process. Indeed, it may be quite slow. As such, any meaningful calculation of bound pesticide must take residence time into account.

Mechanistic studies of pesticide binding to soils (Gamble, 1990; Gamble, 1992) and clay minerals (Gilchrist, 1993) have revealed a two-stage process. Dissolved pesticides first bind to sites on the surface of the soil particles. From there they slowly diffuse to the particle interior through small cracks or pores. Once diffused into the particle, the pesticides are less available to organisms. However, diffusion back out of the particles may occur for a long period of time. For example, in Malden watershed in 1992 alachlor, carbofuran and simazine were detected (Table 4) although none were applied that year (Table 2).

For the first time, this method has been applied to quantify binding by creek sediments. The findings, using both atrazine and metolachlor, are consistent with the mechanism observed for interaction with soils. An example of the species distribution after 14 days found for metolachlor binding to Muddy creek sediment (experimental conditions of 25°C; 20 g/L suspended solids; 293 ppb metolachlor) appears in Fig. 7. Even at the high suspended solids concentration used experimentally, the majority of metolachlor remained as the free species. Atrazine was found to have an even lower tendency to bind. The kinetic (rate) and thermodynamic (equilibrium) parameters determined allow improved predictive capabilities for pesticide transport and fate.

Sediment cores from both MAL and MUD were found to have insufficient ranges of activity to allow dating by the ^{210}Pb method. Therfore, it was concluded that either the sampling locations were non-depositional environments (no sediment accumulation over the last 150 years) or sediment deposition and removal was cyclic (Turner 1994). In either case, elevated levels of sediment transport to Lake Erie are indicated.

3.5 Bioassays

In general, survival of the 4 species of invertebrates was little affected by the exposure to creek sediments from agricultural watersheds. One exception was a reduction in survival of 20-40% of the midge in one sediment collected September 1993. In contrast, slight enhancement in growth of the midge and mayfly in creek *vs*. reference sediment were frequently observed.

Benthic invertebrates (eg. tubifex, mayfly) are considered the best indicators of sediment contaminaiton since they have direct contact with both sediment solids and interstitial waters. The lack of an observable response by them is not unexpected. Only two pesticides (metolachlor and trifluralin) were detected in the particulate samples collected in 1992 (Results for 1993 not available at the time of this report). The highest detected concentrations of 35 ng/g metolachlor and 2 ng/g trifluralin are well below those expected to have a toxic effect on invertebrates.

Plant toxicity tests revealed a somewhat greater sensitivity. Although the vascular plant *M. sibiricum* was only slightly affected, duckweed and particularly the green algae routinely demonstrated reduced growth in sample *vs*. control water. In the worst case, a 50% reduction in algal growth was observed in sample water which had been diluted to 22% with control water. Several pesticides (particularly triazines) have routinely been measured during the growing season at concentrations equal to or exceeding those which have been shown in laboratory and some field studies to have a toxic effect on algae.

4. Study conclusion

Field results indicate that some pesticides appear to be released from soil or sediment particles over a time scale of years. Pesticides applied in this watershed appear to have long-term and cumulative effects within the boundaries of the watershed. This is consistent with chemical binding studies which indicate slow diffusion of pesticides into and out of soil/sediment particles. Of those monitored, trifluralin and metolachlor were the only pesticides detected in sediments. The reasons for this are not yet clear. Ecotoxicological studies showed contaminant levels in sediment samples to be below those necessary to have a significant effect on benthic invertebrates. Some toxic effect on plants, especially algae was noted, however. Although the relation was not conclusively demonstrated, some pesticides (particularly triazines) were measured in water samples at concentrations known to cause a detrimental effect. The low strength of binding to sediments observed for some pesticides implies that they remain largely in the more bioavailable "free" form. This limits accumulation in sediments, but may enhance transport into the Great Lakes. The presence of atrazine-degrading microorganisms in sediments may reduce the amount of this herbicide transported.

5. New technologies and benefits

Several bioassays which have not been previously used to determine the toxicity of sediment samples from agricultural watersheds were developed and used in this study. The toxicity test with invertebrates measures reproductive effort and therefore is very useful in the determination of chronic toxicity. The rooted macrophyte bioassay is an innovative technique under development at the University of Guelph and was used for the first time in the field scenario.

New methods of extracting pesticides from water samples were tested. The technique using solid phase extraction discs was shown to effectively recover pesticides from water without the need for the large volumes of high purity solvents required by traditional methods (Triska et al.1994).

The HPLC micro-filtration method to versatile and was applied to sediments for the first time. It was observed that similar binding mechansims apply to soils and sediments.

Microorganisms capable of mineralizing atrazine completely were discovered in Essex County sediments (Topp et al 1994). This clearly offers potential benefits for farmers and environmentalists. To take maximum advantage of this, we must find ways of increasing the residence time of pesticides in wetland sediments.

6. Implications for Great Lakes ecosystem

Most of the research was conducted on two watersheds. However, the uniform conditions existing in Essex County likely allow extrapolation to other watersheds and marsh areas along Lake Erie and Lake St. Clair. Chemical speciation studies were conducted on two widely applied herbicides: atrazine and metolachlor.

The lack of contamination of sediments with pesticides in agricultural watersheds is encouraging with regards to the minimal toxic effect on benthic invertebrates. However, this does not preclude contamination of marshland water. The growth of two species of plants was inhibited when placed in water samples collected following rainfall events. Although this water was found to contain herbicides (atrazine, simazine, metribuzin) which are known to inhibit photosynthesis (Day 1993), this relationship has yet to be confirmed.

Microorganisms in sediments having the ability to rapidly degrade atrazine may reduce environmental contamination with this herbicide. This potential could be exploited in managed drainage systems for ensuring that atrazine loss from agricultural areas does not enter the Great Lakes system.

Greater farmer participation in the process is encouraged so that they can understand why the research is done. Some farmers that were interviewed were skeptical and refused to answer questions pertaining to their agricultural practices.

7. Technology transfer potential

- Atrazine mineralizing microorganisms for bioremediation
- HPLC micro-filtration technique for chemical speciation
- The "battery of bioassay tests" approach to ecotoxicological evaluation of water and sediments

8. Gaps/needs for future research

- More bioassays with additional species of aquatic plants especially rooted macrophytes
- Field assessment of the impact of herbicides on aquatic plant species in wetlands
- Information on the impact of pesticides on amphibians and reptiles
- Quantification of the transport of pesticides in water and sediments moving down a watershed and application of watershed models (ILWIS, AGNPS)
- Evaluation of groundwater quality and movement in watersheds
- Extention of chemical speciation to other pesticides such as trifluralin and metribuzin
- Examination of the degradation of other herbicides in sediments
- Assessment of the biodegradation of pesticides under field conditions in natural and constructed drainage systems designed to reduce off farm movement of agrochemicals.

9. Selected References

ASTM (American Society for Testing & Materials) 1993. *Standard guide for conducting static toxicity tests with Lemna gibba G3*. ASTM 1993 Annual Book of Standards, Vol. 11.04, E1315-91, Philadelphia, PA.

Colborn, T., vom Saal, F.S. and Soto, A.M. 1993. *Development effects of endocrine-disrupting chemicals in wildlife and humans*. Environmental Health Perspectives 101(5):378-384.

Day, K.E. 1993. Short-term effects of herbicides on primary productivity of periphyton in lotic environments. Ecotoxicology 2:123-138.

Environment Canada. 1992. *Biological tests methods: growth inhibition test using the freshwater algae, Selenastrum capricornutum.* EPS 1/RM/25 Ottawa, Ontario, Canada.

Gamble, D.S.; Khan, S.U. 1990. *Atrazine in organic soil: Chemical speciation during heterogeneous catalysis*. Journal of Agricultural and Food Chemistry, 38:297-308.

Gamble, D.S.; Ismaily, L.A. 1992. *Atrazine in mineral soil: The analytical chemistry of speciation*. Canadian Journal of Chemistry, 70:1590-1596.

GAO (U.S. General Accounting Office). 1993. *Pesticides: Issues concerning pesticides used in the Great Lakes watershed*. Pub. No. GAO/RCED-93-128, GAO, Washington, D.C. 20548.

Gilchrist, G.F.R.; Gamble, D.S.; Kodama, H.; Khan, S.U. 1993. *Atrazine interactions with clay minerals: Kinetics and equilibrium of sorption*. Journal of Agricultural and Food Chemistry, 41:1748-1755.

Ontario Ministry of Agriculture and Food (OMAF). 1994. *Guide to weed control.* Publicaiton 75, Queen's Printer for Ontario, Toronto, Ontario.

Ontario Ministry of Agriculture and Food (OMAF). 1993. *Agricultural Statistics for Ontario.* Publication 20, Queen's Printer, Toronto, Ontario.

Richards, N.R., A.G. Caldwell and F.F.Morwick. Reprinted March 1989. *Soil survey of Essex County. Report No. 11 of the Ontario Soil Survey.* OMAF, Guelph, Ontario.

Turner, L.J. 1994. *^{210}Pb dating of sediments from Malden Creek (core 053) and Muddy Creek (Core 054), Ontario.* Technical note RAB-TN-93-43, 16p. National Water Research Institute, Burlington, Ontario.

Valenzuela, C.R. 1988. *ILWIS overview.* International Institute for Aerospace Survey and Earth Sciences (ITC),Enschede, Netherlands, ITC Journal (Special ILWIS issue) 1:4-14.

Young, R.A., C.A. Onstad, D.D. Bosch and W.P. Anderson. 1989. *AGNPS: A nonpoint-source pollution model for evaluating agricultural watersheds.* J. Soil and Water Conservation 44(2):168-173.

10. Publications

10.1 Scientific

Topp, E, D.W. Gutzman, B.P. Bourgoin *(in memoriam),* J.A. Millette and D.S. Gamble. 1994. *Rapid mineralization of the herbicide atrazine in alluvial sediments and enrichment cultures.* Paper in preparation.

10.2 Miscellaneous

Bourgoin, B.P., A. Mudroch, K. Day, J.A. Millette, D.S. Gamble, D.W. Gutzman, R. Roshon, E. Topp. 1993. *The impact of agricultural activities on Lake Erie coastal marshes.* Poster at the 1st Annual Environment and Health Symposium, June 23, 1993, University of Toronto, Ontario.

Gutzman, D.W., D.S. Gamble, E. Topp. 1993. *Chemical speciation of atrazine in a biologically active creek sediment.* Oral presentation at the 76th Canadian Society for Chemistry Conference, Sherbrooke, Quebec.

Millette, J.A., E. Topp, D.W. Gutzman, D.S. Gamble, B.P. Bourgoin, A. Mudroch, K.Day and R. Roshon. 1994. *Effects of agricultural non-point source contaminants on Canadian Great Lakes coastal marshes.* Proceedings of the XII CIGR World Congress and AgEng'94 Conference on Agricultural Engineering, Aug.29-Sept.1, 1994, Milan, Italy.

Millette, J.A., D.W. Gutzman, E.Topp, D.Gamble, A. Mudroch, B. Bourgoin and L. Emili. 1994. *Watershed analysis to assess sediment and contamination transport.* Oral paper 94-292, abstract published in the proceedings of the Fifth Annual Northeast Agricultural/Biological Engineering Conference, July 24-27, 1994, ASAE, University of Guelph, Guelph, Ont.

Millette, J.A., D.W. Gutzman, E. Topp, D.S. Gamble, L. Emili, B.P. Bourgoin (in memoriam), A. Mudroch. 1994. *Role of sediments in the transport of nonpoint source contaminants in the Canadian Great Lakes coastal region.* Oral presentation at the 37th Annual Conference on Great Lakes Research, June 5-9, 1994, Windsor, Ontario.

Triska, J., G. Garbai, B. Bourgoin and A. Mudroch. 1994. *New solid phase extraction materials in studies of contamination of water by pesticides.* Paper presented at the 29th Central Canadian Symposium on Water Pollution Research, February 1994, Burlington, Ontario.

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