

Survey of Farm Wells for Pesticides, Ontario, Canada, 1986 and 1987

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In 1983, 8,720 metric tonnes of pesticides were applied to 2.14 million hectares of agricultural land in Ontario, Canada (Magee 1984). Most of the pesticides, 7,200 metric tonnes (82%), were applied to crops or soils with water as a diluent and carrier. It was estimated that 400 million L of water were used to apply these chemicals to soils and crops. The three main sources of water were farm wells, farm ponds, and surface waters (ditches and streams). The residues of pesticides found in surface water of eleven agricultural watersheds were studied between 1975-77 (Braun and Frank 1980, Frank 1981, Frank et al. 1978, 1982 and Frank and Sirons 1979) and the results indicated that spills contributed significantly to contamination.

A study was conducted in 1984 on wells of cash-crop farms located on mineral soils across Southern Ontario (Frank et al. 1987). Water samples were collected from 91 wells during 1984 and analyzed for pesticide residues. Many of the 11 wells contaminated were the result of spills that were extremely difficult to clean-up.

The present study of 179 wells is an extension of the 1981-84 study (Frank et al. 1987). The aim of the present surveys was to determine 1) if normal field use of pesticides contaminated well waters, 2) if careless handling of pesticides was the main source of contamination, and 3) if provincial educational programs were reducing the incidence of pesticide contamination of well water.

METHODS AND MATERIALS

In 1986 and 1987, 103 and 76 wells, respectively, were sampled by cooperators across Ontario. Each cooperator completed a questionnaire on the type of well on his home farm and listed the pesticides used on the farm. Representative samples of water from each well identified in the survey were collected into 4.5-L glass bottles. Water was run for a short period to empty the metal pipes before samples were collected over a 5 to 10 min period. Samples were collected over two weekends, one in late November and the second in mid December, in both 1986 and 1987. After collection, water samples were refrigerated until delivery to the laboratory within two days. Multi-residue and compound specific analyses were performed on the water within a few days of receipt. Samples were held at 4°C while in storage awaiting analysis.

Organochlorine (OCl) and organophosphorus insecticides (OPI): Water samples (1.5 L) were extracted twice with 50 mL of dichloromethane by shaking vigorously for 60 sec after the addition of 50 mL of saturated aqueous NaCl solution. The extracts were dried with anhydrous Na_2SO_4 and evaporated just to dryness. The residual material was dissolved in hexane to give a 500-fold concentration factor. An aliquot of 0.5 mL was removed for determination of organophosphorus insecticides. The remainder was cleaned up for determination of organochlorine insecticides (Mills et al. 1972). The parameters used for gas liquid chromatography (GLC) determinations are described by Frank et al. (1978, 1981) and Braun and Frank (1980).

N-Methylcarbamate insecticides and thiocarbamate herbicides: Samples were acidified prior to extraction as described above for OCl and OPI. Compounds were determined by capillary column GC with nitrogen-phosphorus detection (Ripley and Braun 1983).

Fungicides: Captan and dichloran were determined after cleanup and fractionation of the OCl extract described above. Metalaxyl, chlorothalonil and anilazine were determined in the carbamate procedure described above. Ethylenebisdithiocarbamate compounds were determined, using the CS_2 evolution technique (Keppel 1969, Ripley 1979).

Acetanilide and triazine herbicides: Water samples (1.0 L) were adjusted to pH 9.5 with $\text{NH}_4\text{OH}:\text{H}_2\text{O}$ (1:2) and extracted twice with 50 mL of chloroform. The extracts were dried with anhydrous Na_2SO_4 and evaporated just to dryness. The residual material was dissolved in 5.0 mL of methanol. Residues were determined by packed column GLC with an electrolytic conductivity detector in the nitrogen mode (Ramsteiner et al. 1974) or by capillary column GC with a nitrogen-phosphorus detector.

Chlorophenoxy alkanoic and chlorobenzoic acid herbicides: Samples of water (1.5 L) were extracted and esterified according to the procedure of Yip (1971). GLC determinations were made with an electrolytic conductivity detector in the halogen mode or with an electron-capture detector (Frank and Siron 1980; Frank et al. 1978).

Bipyridium herbicides: Sodium borohydride (50 mg) was added to 100 mL of water in a beaker and the contents were stirred for 30 min, and thereafter the procedure followed that described by King (1978). Determination was made by packed column GLC with a nitrogen-phosphorus detector.

Trifluralin: Water samples (1.0 L) were adjusted to contain 5% NaCl, shaken well, and extracted three times with 50 mL of dichloromethane; the extracts were filtered through sodium sulfate. Hexane (20 mL) and isoctane (2 mL) were added to the sample extract and evaporated almost to dryness. Residues were dissolved in 5 mL of isoctane prior to analysis by capillary GC with a nitrogen-phosphorus detector.

Phenylurea herbicides: Water samples (1.0 L) were adjusted to pH 9-10 with 10% NaOH and extracted two times with 50 mL of dichloromethane. Each extract was filtered through pre-washed cotton and evaporated just to dryness. The residual material was dissolved in 5 mL of hexane. Residues were determined by high pressure liquid chromatography (HPLC) on a silica column (0.26 x 25 cm) with UV detection at 254 nm (Lawrence 1976).

Duplicate field samples and internal laboratory check samples were analysed at random as part of an on-going quality assurance program. Confirmation techniques were applied when residues were high enough to allow alternative procedures to be used. These included (i) the use of element-specific GLC detectors, e.g. conductivity detection in the halogen and N-selective modes and flame photometric detection in the P- and S-selective modes; (ii) the use of alternate-column GLC, i.e. using column packings of different polarity so that characteristic retention times were significantly changed, or by capillary column GC; and (iii) low resolution mass spectroscopy where necessary.

Recoveries of the different chemical groups ranged from 70 to 95% for thio- and N-methylcarbamates, phenylureas and triazines and 70 to 96% for organochlorine and organophosphorus insecticides. Data are presented uncorrected for recoveries. Detection limits for the pesticides tested appear in Table 1.

RESULTS AND DISCUSSION

The 179 wells surveyed by questionnaire in 1986 and 1987 were located in 20 counties and 66 townships across Southern Ontario, an area which represents the main agricultural region of the province. Almost half the wells were located on clay type soils, 30% on sandy or gravelly loams and the remainder on silt loams (Table 2). Most wells (91%) were protected by cement or steel caps. Fourteen percent of the wells were located in or on the edge of treated fields, the remainder were located near the house or near the barn. Of the 41 wells used to draw water to spray pesticides in 1986, all except two were also used as a source of drinking water. In 1986 and 1987, 42 (40%) and 24 (32%) of wells respectively were used for spraying pesticides and as domestic drinking water (Table 2).

Forty nine (27%) wells were either sand points or dug and the remainder were drilled. Two wells were dug and subsequently drilled (Table 2).

The use of pesticides on the 179 farms is recorded in Table 1; 23 farms used no pesticides, 155 used herbicides, 78 used insecticides, 39 used fungicides and 5 used nematocides. These pesticide uses involved 30 different herbicides, 28 different insecticides, 15 different fungicides and 2 nematocides. The

Table 1. Frequency of use of 30 herbicides, 28 insecticides, 15 fungicides and 2 nematicides on crops produced on 103 farms surveyed in 1986 and 76 farms in 1987, pesticides analysed and their detection limits.

Generic Name	Farms	Detection	Common Name	Farms	Detection	Common Name	Farms	Detection	Common Name	Farms	Detection	Common Name
	1986/87	Limit		1986/87	Limit		1986/87	Limit		1986/87	Limit	
	(ug/L)			(ug/L)			(ug/L)			(ug/L)		
Herbicides												
alachlor	2/5	0.1	sethoxydim	7/4		parathion	1/0	0.05				
allidochlor	1/0	0.1	simazine	4/4	0.1	permethrin	2/5					
amitrole	0/1	0.1	terbacil	3/10	0.1	phorate	1/2	0.1				
atrazine	59/44	0.1	triaallate	1/0		phosalone	2/0	0.5				
bentazon	16/14		trifluralin	15/16	0.05	phosmet	0/2	0.5				
bromoxynil	15/6	0.1				terbufos	0/2	0.1				
butylate	2/3											
chloramben	6/1	0.1	acephate	1/2								
cyanazine	15/6	0.1	azinphosmethyl	4/0	5.0							
2,4-D	32/32	0.1	carbaryl	10/10	1.0	benomyl ¹	3/3					
2,4-DB	5/5	0.1	carbofuran	4/2	1.0	captan	9/8	0.5				
dicamba	13/19	0.1	chlorpyrifos	3/2	0.1	captafol	4/0	0.5				
dichlorprop	2/0	0.1	cyhexatin	1/0		carbathin	0/2					
EPTC	2/3		deltamethrin	1/0		chlorothalonil	7/1					
glyphosate	28/28		demeton	1/0	0.1	ferbam	0/2					
linuron	17/11	0.1	diazinon	15/13	0.05	fixed copper	1/1					
MCPA	15/7	0.1	dimethoate	1/1	0.25	iprodione	2/2					
MCPB	2/1	0.1	dinocap	1/1	0.01	mancozeb	7/1					
mecoprop	4/6	0.1	endosulfan	4/3	0.01	maneb	3/2					
metobromuron	4/11	0.1	fensulfothion	1/0	0.5	metalaxy1	1/1					
metolachlor	18/34	0.1	fonofos	0/5	0.1	metiram	3/1					
metribuzin	27/15	0.1	lindane	14/13	0.01	sulfur	0/1					
monolinuron	1/1	0.1	malathion	0/4	0.1	thiram	2/2					
oxyfluorfen	1/0		methidathion	1/0	0.5	zineb	1/0					
paraquat	6/1		methomyl ¹	1/0		Nematicides¹						
			oxydemeton-methyl ¹	0/1	0.5	1,3-DCP	3/3					
						IMTC	1/2					

¹IMTC - isomethyl thiocyanate, 1,3-DCP 1-3 dichloropropenes

Table 2. Information on 179 Wells Surveyed 1986-87.

1. Soil Surface		2. Well Use ¹	
Clay soils	87	Pesticide spraying	66
Loam soils	38	Human drinking water	144
Sandy soils	54	Livestock drinking	101

¹39 wells used for drinking and spraying.

3. Well Description		4. Pesticide use	
Sand point	1.5-7.5 m deep (6)	No pesticides	23 farms
Dug	2.4-15 m deep (43)	Herbicides	155 farms
Drilled	8.4-30 m deep (71)	Insecticides	78 farms
	31-60 m deep (47)	Fungicides	39 farms
	61-100 m deep (12)	Nematocides	5 farms

number of farms using herbicides was much greater than for other pesticides hence four of the most widely used pesticides were herbicides. There were 103 farms using atrazine, 64 using 2,4-D, 56 using glyphosate and 52 using metribuzin. The insecticides with the widest use were diazinon on 28 farms, lindane on 27 farms and carbaryl on 20 farms. The fungicides with the widest use were captan on 17 farms (mainly as a seed treatment), chlorothalonil and mancozeb each on 8 farms.

Water Quality - Pesticides. Well waters were analysed for 25 of the 30 herbicides listed in Table 1, 20 of the 28 insecticides and 2 of the 15 fungicides. The limits of detection appear in Table 1 for the 47 pesticides checked in the waters of the farms where they were used. Triazines and acetanilides were analysed in all waters and in 1986 all waters were analysed for organophosphorus and organochlorine insecticides.

The results of the analyses of well waters for pesticides revealed that in 1986 10 wells contained residues of pesticides and in 1987 the number was four. These findings appear in Tables 3 and 4. Atrazine and its metabolite desethyl atrazine appeared in nine of the 10 wells in 1986. Residues ranged from 0.2 to 34 ug/L. In four cases the owner had used well water to mix and load atrazine and spray field corn, in one of these cases it was used in 1985 but not 1986. In these four cases the water could have become contaminated as a result of carelessness around the well. In one of these wells, a 72 m drilled well, a spill must have occurred to result in the high concentration of 34 ug/L. In four cases the owner sprayed his corn with atrazine but did not use the well sampled for spray water yet the well was contaminated. This may have resulted from runoff water or leaching entering the well since all wells were on the edge of fields and residues ranged from 0.2 to 2.9 ug/L. One well was

Table 3. Characteristics of ten wells in which pesticides residues were detected in 1986 (Interim Maximum Acceptable Concentration for atrazine and its metabolite is 60 ug/L).

Type of Well	Well depth (m)	Distance of well from sprayed fields (m)	Well Used for spraying	Atrazine used in 1986	Atrazine ¹ (parent & metabolite) (ug/L)	Location and soil type
Dug	2.4	50	Yes	Yes	1.3 (0.7+0.6)	SW ⁴ - silt loam
Dug	4.5	1	No	No	3.3 (1.1+1.2)	SW - sand
Dug	5.4	45	Yes	No ²	34 (17+17)	SW - sandy loam
Dug	6.0	240	No	Yes	0.5	W - clay
Dug	6.0	6	No	Yes	2.9 (0.7+2.20)	W - loam
Dug	9.0	30	Yes	Yes	0.4	SW - sandy loam
Dug	15	15	No	Yes	0.4	SW - clay
Drilled	25	30	No	Yes	0.2	SW - sandy loam
Drilled	72	6	Yes	Yes	1.8 (0.8+1.0) 0.003 lindane ³	SW - loam clay
Drilled	31	1	Yes	Yes	0.1 diazinon ³	SW - sand

¹Metabolite - desethyl atrazine. ²Applied 1985. ³Lindane and diazinon were used as seed treatments on the two farms. ⁴SW - Southwest, W - West regions

contaminated and the owner had not sprayed his corn or used the well in 1987 but had in 1986. In this case the well was close to a neighbours field. The presence of lindane at very low levels and diazinon at 0.1 ug/L could only be traced to the use of seed treatments on the two farms; careless handling or washing equipment probably accounted for this contamination.

In 1987 four wells were identified with herbicide residues. All four contained atrazine and three also contained metolachlor (Table 4). Three of the four owners used their well water to spray atrazine and metolachlor and contamination could have occurred as a result of activities around the well, the fourth who did not use atrazine in 1987 must have contaminated the well from a spill the year before.

Table 4. Residues in waters of 4 wells collected and analyzed December 1987 in survey of 76 wells (Interim Maximum Acceptable Concentration for atrazine 60 ug/L, metolachlor 50 ug/L).

Type	Well depth (m)	Well to field	Water for spray	Atrazine ¹ 1985-86	Residues (ug/L) metolachlor	Location
				1985	atrazine ¹	Soil type
Dug	36	Edge	Yes	1985-86	43	52 ² SW-sandy loam
Dug	10	Edge	No	1985-86	0.9	1.4 ³ SW-sandy
Dug	10	Lawn	Yes	1985	0.8	W-gravel/clay
Drilled	35	In field	Yes	1986	ND	W-clay loam

¹The four growers used atrazine in 1986 and/or 1985, all residues were present as the parent herbicide, no desethyl atrazine was detected in the initial samples.

²Follow up 24 March 88, 55 ug/L metolachlor, 54 ug/L atrazine (6.5% desethylatrazine)

³Follow up 24 March 88, 3.3 ug/L metolachlor, 1.2 ug/L atrazine (38% desethylatrazine)

In addressing the three objectives of the study it was necessary to include findings from the 1984 survey (Frank et al. 1987). Over the three surveys 270 wells were analysed and 26 were found to be contaminated with pesticides. The questions were:

1. Do pesticides enter well waters from normal use?
2. Do pesticides enter well water during loading and mixing operations?
3. Have educational programs reduced the incidences of contamination?

The summary of three years' data, 1984, 1986 and 1987 appears in Table 5 along with those pesticides found in wells and the

number of farms using the particular compounds. Of 10 wells found to contain atrazine and one well with metolachlor, the only known means of entry was through leaching down the profile or from surface runoff water entering directly into the well.

Table 5. Summary of pesticides found in wells in surveys conducted in 1984 (Frank et al. 1987), 1986 and 1987.

Pesticide	Number of Farms	Number of wells contaminated	<u>Cause of contamination</u>	
			leaching/runoff	spill-mixing/loading
alachlor	45	1	0	1
atrazine	172	24	10	14
diazinon	44	1	0	1
dimethoate	3	1	0	1
lindane	39	1	0	1
metolachlor	77	3	1	2
metribuzin	58	1	0	1
trifluralin	45	1	0	1
Total	271	26	10	16

Year	Number	Contamination (all pesticides) ug/L				Total
		<1.0	1.1-10	11-100	101+	
1984	91	6	2	3	1	12(13%)
1986	103	5	4	1	0	10(9.7%)
1987	76	1	2	0	1	4(5.3%)
Total	271	12	8	4	2	

Eight pesticides were found in the wells where the water was used for spraying and they could have therefore entered as a result of mixing and loading. Since many of the wells were drilled and were as deep as 72 m this source is the most likely cause of contamination. The most probable leading causes were due to either back-siphoning, overfilling the spray tank, spilling of concentrate, or washing equipment too close to the well. The depth of the well and the concentration in the water virtually ruled out leaching.

During the last three to four years Ontario Ministry of Agriculture and Food extension programs have stressed protection of farm water supplies and grant monies have been made available to assist in this protection. In 1984, 12 of 91 wells (13%) were contaminated whereas in 1986 and 1987 10 wells (9.7%) and four wells (5.3%) respectively were found to contain pesticide

residues. The totals of all pesticide residues per well appears in Table 9 and the incidences of contamination appear to have declined but the levels of contamination do not appear to have changed.

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