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Contamination of Rural Ponds with Pesticide, 1971-85, Ontario, Canada

R. Frank, H. E. Braun, B. D. Ripley, and B. S. Clegg

Agriculture Laboratory Services, Ontario Ministry of Agriculture and Food, Guelph, Ontario, Canada N1H 2W1

When applying pesticides to their crops Ontario farmers use water as the major diluent and carrier. This water is drawn from farm wells, farm ponds, ditches, streams, or rivers. Over the past 15 years, analyses have been performed on farm water supplies to determine the degree of contamination by pesticides. Many have been found to be contaminated and the main sources have been a) surface water runoff from treated fields during storm events, (b) deposits from spray drift and (c) accidental pesticide spills leaching into ground water to contaminate well waters. These findings have been published by Frank et al (1987a, 1987b) on both randomly surveyed wells and wells suspected of contamination and by Braun and Frank (1980), Frank (1981) and Frank et al (1980, 1981, 1982) on pesticide concentrations in surface water and loadings to major rivers in Ontario. In this paper the pesticides most frequently found as contaminants of farm ponds are examined.

METHODS AND MATERIALS

Owners of rural ponds contacted the Ministries of Agriculture and Food or Environment when water supplies were suspected of being contaminated and requested pesticide analyses. Local officials investigated the complaints and recorded the location of the pond with respect to adjacent fields and sprayed crops, the pesticides used, the soil type, the slope of the land and any protection of the pond. Information was obtained on recent rainfalls and a reason found for suspecting contamination. Sufficient water was collected for conducting analyses for all pesticides involved. One-litre glass or polyethylene bottles were used, one for each chemical group involved. Samples were obtained by dipping into the pond as far away from the edge as possible. Occasionally sediments or soils (0.5 kg) were taken from around the edge of the pond. In some instances, plant damage was the first sign of a problem and this was especially severe among greenhouse crops. In other cases, fish being raised in the ponds were found dying or dead. Samples were transported to the laboratory and analysed within two days.

Send reprint requests to Dr. R. Frank, Ag. Lab Services Branch, OMAF, c/o University of Guelph, Guelph, Ontario N1G 2W1

Unfiltered water samples were analyzed for suspected pesticides in each of the chemical groups listed below. Before water samples were extracted, sediments were resuspended. Soils and bottom sediments were drained of water before being extracted.

For bipyridylium herbicides, sodium borohydride (50 mg) was added to 100 ml of water in a beaker and the contents were stirred for 30 min. The procedure followed was described by King (1978). Determination was made by packed column GLC with a nitrogen-phosphorus detector. Recoveries from water were 70±5%. For chlorophenoxy and chlorobenzoic acid and chlorthal-methyl herbicides, one liter of water or 25 g of soil or sediment was extracted and esterified according to a procedure described by Yip (1971). Gas-liquid chromatography (GLC) determinations were made using the electrolytic conductivity detection system (halogen mode) with a column packing of 5% Dexil on Varaport 30 (Frank and Sirons 1982). Recoveries from spiked water samples were 83±2%.

For chloroacetamide, triazine and uracil herbicides, one liter of water of 25g of soil or sediment were extracted with trichloromethane. The three herbicide groups were measured using a GLC with electrolytic conductivity detector (N-mode) according to the procedure described by Ramsteiner et al. (1974) and Sirons et al. (1973). Recoveries from fortified samples were 85±5% for residue concentrations close to the detection limit and 93±2% for higher concentrations.

For glyphosate, one liter of water was extracted and derivatized before determination by GLC following a procedure described in the Pesticide Analytical Manual (1986). Recovery was 25%.

For phenylurea herbicides, water samples (1.5 L) were adjusted to pH 9-10 with 10% NaOH and extracted twice with 50 ml dichloromethane. The extract was filtered through pre-washed cotton, evaporated just to dryness and redissolved in 5 ml hexane. Residues were determined by high pressure liquid chromatography (HPLC) on a silica column (0.25 x 25 cm) with UV detection (Lawrence 1976).

For picloram, one liter samples of water were extracted with diethyl ether followed by methylation and quantification by GLC-electron capture detection using the procedure of Sirons et al. (1977).

For thiocarbamate herbicides, one liter samples were extracted twice with isooctane. Residues were determined by GLC using a flame photometric detector (S mode) as described by Frank et al. (1978) or capillary gas chromatography with nitrogen-phosphorus detector (NPD) (Ripley and Braun, 1983). Mean recovery was 95±5%.

For trifluralin, water samples (1.5 L) were made up to 5% NaCl, thoroughly shaken and extracted three times with 50 ml

dichloromethane and filtered through sodium sulfate. Hexane (20 ml) and isooctane (2 ml) were added and evaporated almost to dryness. Residues were dissolved in 5 ml isooctane prior to analysis by capillary GC with a nitrogen-phosphorus detector.

For chlorophenols, chlorinated phenolics, one liter water samples were extracted into benzene, methylated, and cleaned up on a Florisil column. Quantification was by GLC - electron capture detection and electrolytic conductivity detector. The procedure was described by Frank et al. (1983).

Captan and dichloran were determined after cleanup and fractionation of the organochlorine insecticide extract as described below. Metalaxyl, chlorothalonil and anilazine were determined in the carbamate procedure described below.
For organochlorine and organophosphorus insecticides, water samples (1.5 L) were extracted twice with 50 ml dichloromethane after the addition of 50 ml saturated aqueous NaCl solution by shaking vigorously for 60 sec. The extracts were dried through anhydrous Na_2SO_4, evaporated just to dryness, and redissolved in hexane to give a 500-fold concentration factor. An aliquot (0.5 ml) was removed for analysis of organophosphorus insecticides. The remainder was cleaned up for determination of organochlorine insecticides (Mills et al. 1972). The parameters used for GLC determinations are described by Frank et al. (1978, 1982) and Braun and Frank (1980).

For N-methylcarbamate insecticides, one liter samples of water were extracted, hydrolyzed, derivatized, and fractionated for GLC determination by electron capture detection according to the procedure described by Coburn et al. (1976). In later years, one-liter samples were acidified, extracted with 2 x 50 ml dichloromethane, evaporated, redissolved in methanol and examined by capillary column-nitrogen-phosphorus detection (Ripley and Braun 1983). Recoveries from spiked water were $90\pm5\%$.

Duplicate field samples and internal laboratory check samples were analyzed at random as an ongoing 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 Cl- and N-specific modes and flame photometric detection in the P- and S-specific 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 (iii) using GC-MS. The data are presented uncorrected for recoveries.

RESULTS AND DISCUSSION

Between 1971 and 1985, water samples from 211 rural ponds were analyzed for pesticides. Contamination was found in 132 or 63% of the ponds (Table 1). These ponds were located in all six

Table 1. Pond data (1971 to 1985)

Mode of Contamination	Contributing Cause	Number of Ponds Examined	Number of Ponds Contaminated
Surface Runoff or/and Spray Drift	Mainly cornfields	59	45
	Mainly cereal fields	30	11
	Rotational crops including corn	51	31
	Fruit, vegetables, cash crops excluding corn	24	11
	Nurseries	4	4
	Rights-of-ways	26	14
Accidental Spills	Backsiphoning and/or overfilling	11	11
	Dumping and buried containers	6	5
All Causes	Total	211[1]	132

[1] 211 ponds analyzed, 63 in 1971-75, 53 in 1976-1980 and 95 in 1981-85. Ponds were located in southwestern (61), southeastern (60), eastern (14), western (48), central (24) and northern (4) regions of Ontario.

Table 2. Pesticide numbers detected in the 132 contaminated ponds.

Pesticides Detected	Number of Ponds	Runoff/Spill (number)	Pestcidies H/F/I[1]
None	79	-	
One	92	84/9	H-(84), F-(1), I-(8)
Two	37	31/5	2H-(30), H+F-(3), 2I-(1), H+I-(2)
Three	1	0/1	3H-(1)
Four	1	1/0	3H+F-(1)
Five	1	0/1	3H+2I(1)
Total	211	116/16	H-(122), F-(5), I-(12)

[1] H/F/I - Herbicides/Fungicides/Insecticides

agricultural regions of the province. There were 168 ponds adjacent to sprayed crops and upon analysis 102 or 60% of ponds were contaminated. The offending pesticides were either carried into the ponds along with surface runoff water following storm events or deposited into the pond water from airborne spray drift. The greatest number of contaminations were associated with treated corn fields or rotational crops which included corn (Table 1). Spraying of rights-of-way resulted in 14 of 26 ponds (54%) becoming contaminated primarily from spray drift. Of the remaining 17 ponds, 16 were contaminated by accidental spillage from spray equipment or failure to dispose of empty pesticide containers left adjacent to ponds.

Ninety-three or 70% of the 132 contaminated ponds contained a single pesticide and in 84 ponds, herbicides were found, in 8 ponds insecticides were present and in one pond a fungicide was involved (Table 2). Thirty-six or 27% of the pond waters contained two pesticides. Thirty ponds had two herbicides, 5 had one herbicide and either a fungicide or an insecticide, and a single pond had two insecticides. Individual ponds had three, four, or five pesticides. In total, 122 ponds were contaminated with herbicides, 5 with fungicides and 12 with insecticides. The distributions of the residue concentrations for herbicides, fungicides, and insecticides appear in Table 3. The highest residues were associated with spills and failure to remove empty containers that subsequently lost their contents.

Pond water was analyzed for pesticides by chemical group and the results are presented in Table 3. Triazine herbicides were suspected in 124 ponds and identified in 82 (66%). The residues of all pesticides found in each pond were combined to give a single concentration. These were grouped by magnitude of the combined concentrations, <0.2, 0.2 - 2, 2- 20, 20- 200 and 200+ ug/L (Table 3). It is worth noting that the highest concentrations were the results of accidental spills. Seven ponds had combined residues of herbicides over 200 ug/L, six of these were due to triazines. Thirteen ponds had combined residues of 20 - 200 ug/L and seven involved triazines.

Twenty-two different herbicides, one fungicide and six different insecticides were identified in pond water (Table 4). The causes of the contamination were determined during the investigations and these were found to result from (a) accidental loss of chemical adjacent to and into the pond or (b) movement of airborne spray and/or movement of runoff waters carrying pesticides into the pond. The largest number of contaminations involved atrazine, which was detected in 73 ponds. Sixty five contaminations were caused by spray drift and water runoff events combined and eight resulted from spills. The higher residue concentrations of atrazine were caused by spills. The second most frequently found pesticide was 2,4-D, identified in 29 ponds, 27 caused by spray drift and water runoff and two due to spills.

Table 3. Pesticide groups identified in the 132 contaminated ponds with the frequency and levels of the contaminations.

Pesticidal Group	Number Ponds Analyzed	Number Ponds Contaminated	No. of wells contaminated by Total residue concentration (ug/L) <0.2	0.2-2	2-20	20-200	200+	Spills
1. Herbicides (Total)	197	122	12	55[3]	35[3]	13[2]	7[1]	12
triazines	124	82	5	40[2]	24[2]	7[3]	6[1]	10
chloroacetamides	124	8	0	4	2	1[1]	1[1]	2
chlorophenoxy acids	88	30	6	14	8[2]	2	0	1
chlorobenzoic acids	88	3	1	1	1	0	0	0
chloropicolinic acids	12	2	0	2	0	0	0	0
bipyridilium	10	3	2	0	0	1	0	0
phenylureas	11	3	0	0	1	2[2]	0	1
thiocarbamates	4	1	0	0	1[1]	0	0	1
miscellaneous	14	5	0	1	1[1]	3[3]	0	3
2. Fungicides (Total)	11	5	3	2	0	0	0	0
3. Insecticides (Total)	30	12	6[2]	4[2]	2[1]	0	0	4
organochlorine	16	9	6	3	0	0	0	0
organophosphorous	19	3	0	1[1]	2[1]	0	0	3
methylcarbamate	11	1	1[1]	0	0	0	0	1

[1] All Spills; [2] One Spill Included; [3] Two Spills Included

Table 4. Identity of the pesticides found in ponds, their frequency and range of concentrations in water.

Pesticide Identified	Major Cause[1]	Number of Ponds[2]	Residue in Pond Water (ug/L) Mean + SD	Range
Herbicides:				
alachlor	R/D	3	2.6 ± 2.3	0.6-15
	Spill	1	960	960
atrazine	R/D	65	5.7 ± 11.3	0.1-57
	Spill	8	201 ± 246	1.1-681
butylate	Spill	1	15	15
chlorthal-methyl	Spill	1	11	11
cyanazine	R/D	2	0.6 ± 0.6	0.2,1.0
	Spill	2	485 ± 629	40,930
2,4-D	R/D	27	2.5 ± 4.8	0.1-22
	Spill	2	2.3 ± 2.5	0.5-4.0
dicamba	R/D	3	1.6 ± 1.8	0.1-3.6
dichlorprop	R/D	5	6.5 ± 9.5	0.1-23
	Spill	1	0.3	0.3
diquat	R/D	2	0.01	0.01
diuron	R/D	2[3]	15 ± 15	4,25
glyphosate	R/D	1	42	42
	Spill	1	112	112
linuron	Runoff	1	12	12
MCPA	Runoff	2	0.3 ± 0.2	0.1,0.5
mecoprop	Runoff	2	1.1 ± 0.1	1.0,1.1
metobromuron	Runoff	1	76	76
metolachlor	Runoff	3	5.7 ± 8.1	0.6-15
	Spill	1	190	190
paraquat	Spill	1	70	70
picloram	Runoff	2	0.7 ± 0.5	0.3,1.0
prometryn	Runoff	1	3.0	3.0
simazine	Runoff	8	1.0 ± 1.0	0.1-3.0
	Spill	2	1470 ± 1731	246-2694
2,4,5-T	Runoff	4	7.4 ± 5.5	0.7-14
	Spill	1	0.1	0.1
terbacil	Runoff	1	0.2	0.2
	Spill	1	4.5	4.5
Fungicide:				
PCP	Runoff	5	0.40 ± 0.50	0.01-0.95
Insecticide:				
carbofuran	Spill	1	0.01	0.01
chlorpyrifos	Spill	1[4]	4.4	4.4
diazinon	Spill	2	1.2 ± 0.8	0.6,1.7
DDT	Runoff	5	0.010 ± 0.009	0.002-0.024
endosulfan	Runoff	4[5]	1.1 ± 0.9	0.11-2.0
parathion	Spill	1	1.0	1.0

[1] R/D. = runoff/drift. [2] Six ponds tested, for PCB, two contaminated 0.08, 0.12 ug/L diuron. [3] Sediment, 30 and 280 ug/L diuron. [4] Resulted in fish kills [5] Residue of endosulfan in three of four ponds resulted in fish kills.

Endosulfan was measured in the water of four ponds at a mean residue to 1.1 ± 0.9 ug/L. In three of these four ponds, a fish kill occurred. In one of the ponds with an endosulfan residue of 0.56 ug/L, large goldfish were found dying at the time of sampling. In a second pond, where fish had already died and the water residue was 2.0 ug/L, poisoning of a dog also occurred. In all three ponds where fish died, spraying had occurred up to the edge of the pond. A fish kill also occurred in a pond where chlorpyrifos was spilled.

In several of the ponds, the sediment was analyzed and found to contain residues many times higher in concentration than the water. Three ponds with atrazine residues of between 0.7 and 8.9 ug/L in the water had sediment levels of 28 to 50 ug/kg. All three were contaminated as a result of surface water runoff from an adjacent corn field. Another pond, where a spill had occurred, the atrazine residue in the water was 17 ug/L while in sediment the level was 6430 ug/kg. In three ponds, where 2,4-D had entered the water, residue concentrations of 1.8 to 3.0 ug/L were observed and the sediment levels were between 10 and 20 ug/kg.

Residues of chlorophenoxy, chlorobenzoic and chloropicolinic acid herbicides injuriously affected seedling crop plants raised in greenhouses when water was used from these contaminated ponds. In one case, 2,4-D at 0.6 ug/L plus mecoprop at 1.0 ug/L severely affected tomato plants approaching the fruiting stage.

Agricultural chemicals can be deposited or carried into farm ponds through accidental spills or in surface runoff waters following storm events. Herbicides were the most widely used group of pesticides appearing in pond waters. Ponds should therefore be protected with berms. Many ponds were stocked with fish, however, only insecticides caused their demise; this was particularly evident with endosulfan and chlorpyrifos. On the other hand, plants watered from contaminated ponds were most often injured by herbicides having hormonal growth properties similar to 2,4-D.

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