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Propachlor and *N*-Isopropylaniline Residues in Onions (*Allium cepa*) and Muck Soils

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Onion (*Allium cepa* L.) is a major crop grown on organic soils in Ontario and Quebec. The Ontario crop covered 2534 ha in 1985, and had an estimated value of 14 million dollars. The Quebec crop covered 600 ha, and had an estimated value of 3.3 million dollars (OMAF 1985, Statistics Canada 1985). According to Tolman et al. (1986), onions fail to produce unless weeds are controlled, and this cannot be done economically without herbicide use. Presently only a few chemicals are registered for control of broadleaf and grass weeds on this crop (MAPAQ 1985, OMAF 1989). Chlorpropham and dacthal are recommended as preemergence or directed postemergence applications for the control of some germinating annuals and seedling grasses but cannot be used on bunching onions and are often rendered ineffective during the high summer temperatures.

In recent years several herbicides have been lost from the market, namely, nitrofen and allidochlor because of toxicological problems. Allidochlor the herbicide most extensively used in a pre- or post-emergence treatment for control of both broadleaf weeds and grasses has been discontinued. Others such as ioxynil and aziprotryn have been removed due to lack of control on seedling annual grasses and have not been used extensively due to phytotoxicity to onions under hot conditions. Annual grasses are controlled by postemergence treatments of either diclofop-methyl or sethoxydim while broadleaf weeds may be controlled by fenoxaprop-ethyl and oxyfluorfen. Propachlor has been a very effective preemergence, broadleaf-weed killer and has been used for weed control in many onion producing countries in Europe and the United Kingdom and in Holland. In the USA, onion growers in many states have applied propachlor to their crops under Sections 18 Insecticide and 24 of FIFRA (Federal Insecticide, Fungicide and Rodenticide Act). A new toxicological package on long-term health-effects of propachlor is expected in the near future. To gain Canadian registration additional residue data are required on the persistence and degradation of propachlor and its metabolites in muck soils. The studies reported in this paper are intended to supplement and extend the above knowledge on this promising herbicide for onion growers.

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MATERIALS AND METHODS

Four field trials and one monitoring trial were conducted during 1984-1985. Onions treated with propachlor under research permits were examined to determine terminal residues.

Experiment 1 was conducted at the Muck Research Station operated by the Ontario Ministry of Agriculture and Food located on the Holland Marsh at Kettleby, Ontario. The marsh soil is approximately 80% organic matter. Four replications with 3.4 by 15 m plots in a randomized block were seeded on May 9, 1984 with 'Rocket' onions using a Stan Hay precision planter in a bed of four double rows. Propachlor at 6.7 kg ha^{-1} (50% WP) was applied with a tractor-mounted sprayer delivering 550 L water ha^{-1} as either preemergence (May 14), early postemergence (June 20) or late postemergence (July 16) treatments. Onion plants were sampled on July 16 and August 15 and the dried harvest onions from windrows were sampled on September 14.

Experiment 2 was conducted at the same location as Experiment 1. A randomized block design was employed with four replications and 1.8 by 5 m plots. 'Rockets' onions were seeded into plots on May 4 with a precision planter. Propachlor (50% WP) at 6.7 kg ai ha^{-1} was applied using a manually-operated, two-nozzle sprayer powered by compressed carbon dioxide at 210 kPa. Propachlor was applied on May 17 as a preemergence treatment and on June 6 as an early postemergence treatment. These applications were followed by treatments of pendimethalin and/or chlorpropham.

Soil core samples were collected by compositing multiple areas (five) from each of the replicated plots to a depth of 15 cm. Onions were sampled during the harvesting of the windrow-dried crop on September 27.

Experiment 3 was conducted on an organic soil located in Quebec at the Ste-Clotilde Experimental Farm operated by Agriculture Canada. Four replications of 1.8 by 5 m plots in a randomized block were seeded May 1, 1984 with 'Canada Maple' onions at a rate of 50 seeds/m using a precision planter.

Propachlor (50% WP) was applied preemergence to onions on May 7 at 6.7 kg ai ha^{-1} using a tractor-mounted sprayer delivering 300 L water ha^{-1}. A postemergence treatment was applied manually by distributing granular (20%") propachlor at 6.7 kg ai ha^{-1} incorporated in sand on June 21. Onions were pulled August 30 and allowed to dry in windrows until harvest on September 13, 1984. The first soil samples were collected on July 8 and on September 10, 1984. Soil samples were cored (five cores per sample) to depths of 0 to 7 cm and 7 to 15 cm on plots of each replicate.

Experiment 4 was conducted at the same location as experiments 1 and 2. 'Autumn Keeper' onions were seeded April 26, 1985 into four replicate 3.4 by 15 m plots in a randomized block design. On July 12, 1985, when the onions were in true 2-leaf stage, propachlor (50% WP) at 3.2 kg ai ha^{-1} was applied postemergence with a tractor-mounted sprayer delivering 550 L water ha^{-1}.

Samples of onions and soil were collected prior to pretreatment on July 10, 1985, and after herbicide application on days 0, 10 and 40 while onions were growing in the field and on day 70 when onions were being pulled. Onions were collected from storage (dry barn) on days 130 and 143 after propachlor application.

Onions from 12 growers with Research Permits to use propachlor were monitored for residues at the time of crop harvest. The permits allowed growers to use on or both of the following treatments: a) preemergence application of propachlor at kg ai ha^{-1} and/or b) an early postemergence application of propachlor at 4.1 kg ai ha^{-1}. The growers' farms were located on organic soils on three marshes in central Ontario. Green onion samples were obtained from the growers on July 10, 1985. Dry onions and soils were received from the field or storage between September 1985 and January 1986.

Onion and soil samples were analyzed for propachlor and for both the free and bound N-isopropylaniline using a modified procedure described by Frank et al. (1977).

A Perkin-Elmer Model 8320B capillary gas-chromatograph, equipped with a nitrogen-phosphorus detector, and a Perkin-Elmer GP 100 plotting integrator were used. The column used was a J & W fused-silica capillary-column, 30 m x 0.25 mm, with a 0.25 um coating of SE-54. Chromatographic conditions were as follows. Temperatures: inlet, 225°C; detector 300°C; column oven, initial temperature of 90°C programmed at 20°C min^{-1} to 150°C and then 10°C min^{-1} to 250°C with a hold time of 7 min to allow elution of late compounds. Cas flows: helium carrier pressure of 70 kPa, 2 mL min^{-1}, air 20 mL min^{-1}, hydrogen, 8 mL min^{-1}. Injections were 2 µL with capillary inlet system configured in splitless mode with vent valve open for 30 sec. Under the described conditions, the retention times of N-isopropylaniline and propachlor were 4.5 and 8.6 min, respectively.

Confirmation of propachlor and N-isopropylaniline were made using a Tracor model 550 gas chromatograph equipped with a Hall, electrolytic conductivity detector operated in the halogen and/or nitrogen mode. Operating conditions were: inlet, 230°C; transfer line, 250°C; pyrolyzer, 910°C; helium carrier, 50 ml min^{-1}; hydrogen reaction gas, 50 mL min^{-1}. Data generated were recorded and processed using a Shimadzu C-R3A Chromatopac data processor. Recoveries of propachlor and N-isopropylaniline from soil and onions fortified prior to extraction ranged from 88 top 96%, and 85 to 95% respectively. The detection limit for each compound was 0.01 mg kg^{-1}.

RESULTS AND DISCUSSION

No propachlor or free N-isopropylaniline was detected in onion or soil samples in the three experiments (1, 2 and 3) conducted in 1984. Residues of bound N-isopropylaniline were released by a hydrolysis procedure, and residues ranged from not detected (<0.01) to 0.03 mg kg^{-1} in harvest onions (Table 1-3). The highest levels of bound N-isopropylaniline (1.2 and 0.66 mg kg^{-1}) were observed in bunching green onion samples within 10 days of the two late postemergence treatments with propachlor (Table 1). The residue levels also declined significantly by Day 40 (0.11 and 0.14 mg kg^{-1}) and by Day 70 levels were 0.04 and 0.05 mg kg^{-1}. Regression analysis of the residue data (Table 1) indicated that an equation: log (residue concentration = 1.4 - 1.5 log (time days) produced the best fit ($R^2 = 0.94$).

Table 1. Residues (mg kg^{-1}) of N-isopropylaniline (bound metabolite) in onions following application of propachlor at 6.7 kg ha^{-1}, Muck research Station, Kettleby, 1984 (Experiment #1).

Application Date (stage)	Sampling Date	Growth Stage	Post Application (days)	Onions[1] Bound Metabolite[2] (mg kg^{-1})
14 May	16 July	immature	63	0.07 + 0.01
(Pre-em)	16 Aug.	immature	93	<0.01
	15 Sept.	dried	123	0.03 + 0.01
20 June	16 July	immature	26	0.15 + 0.06
(Early post)	15 Aug.	immature	56	<0.01
	14 Sept.	dried	86	0.02 + 0.01
6 July	16 July	immature	10	1.2 + 0.10
	15 Aug.	immature	40	0.14 + 0.03
	14 Sept.	dried	70	0.04 + 0.02
14 May/6 July	16 July	immature	10	0.66 + 0.25
(Pre and	15 Aug.	immature	40	0.11 + 0.03
late post)	14 Sept.	dried	70	0.05 + 0.01

[1]Seeded 4 May, 1984 with Autumn Rocket; [2]No propachlor or free N-isopropylaniline detected (<0.01 mg kg^{-1})

A similar equation was proposed by Stamper et al. (1979) for the dissipation of organophosphorus insecticides based on the diffusion of the chemical from leaf surfaces. With propachlor on onions, the early rapid decline of residue (Table 1) probably resulted from the rapid early growth of the seedling causing a dilution effect. First-order kinetics produced a regression correlation coefficient of 0.79 and suggested a half-residue persistence of about 21 days.

A preemergence application of propachlor produced "negligible" residue (<0.1 mg kg^{-1}) at harvest and levels were 0.07 mg ka^{-1} at Day 63, the approximate date of harvesting pickling onion grades (Table 1). Propachlor applied as a late postemergence application left a negligible residue by Day 70, i.e., 0.04 and 0.05 mg kg^{-1} with levels only marginally higher at Day 40, i.e, 0.14 and 0.11 mg kg^{-1}.

No propachlor or free N-isopropylaniline was detected in onions or soil samples for Experiments 2 and 3 (Table 2 and 3). Total residues, including bound

N-isopropylaniline, are reported for harvest onions only. Levels were 0.01 mg kg^{-1} following a preemergence treatment of propachlor while levels increased only slightly to 0.03 mg kg^{-1} following an early postemergence application (Table 2). In both cases, levels were below the negligible residue tolerance of 0.1 mg kg^{-1} normally allowed under the Canadian Food and Drug Act (Health and Welfare Canada, 1986) where no maximum residue limit is granted. As with onions, hydrolysis of soil samples liberated the bound N-isopropylaniline and levels ranged from 0.38 to 2.2 mg kg^{-1}. Higher levels were observed when propachlor was applied preemergence and early postemergence (Table 3). The bound aniline was also stratified in the soil and was found to decrease in concentration with increasing depth. levels of 2.2 mg kg^{-1} were observed at 0 to 7 cm while levels of 1.2 mg kg^{-1} were observed at the 7 to 15 cm depth. Residues of the total soil depth of 0 to 15 cm were 0.51 and 1.2 mg kg^{-1} at Day 16 and 81, respectively.

Table 2. Residues (mg kg^{-1}) of N-isopropylaniline (bound metabolite) in onions and soils following use of propachlor at 6.7 kg ai ha^{-1}, Muck Research Station, Kettleby, 1984. (Experiment #2).

Propachlor	Pendimethalin (P) Chlorpropham (C)	Sampling Date (days)	Pre & Post Application	Bound Metabolite[2]	
				onions[1]	soil
Pre treatment		16 May	-1	NA[4]	0.34+0.32
17 May[3]	24 May (P)	27 Sept.	133	0.01+0.01	0.38+0.34
17 May	6 June (P)	27 Sept.	133	0.01+0.01	0.52+0.39
17 May	24 May (P) 6 June (C)	27 Sept.	133	0.02+0.02	0.98+0.39
17 May 6 June[5]	17 May (C) 6 June (C)	27 Sept.	113	0.03+0.01	2.20+0.84

[1]Seeded 4 May, 1984 with Autumn Rocket; [2]No propachlor or free N-isopropylaniline detected (<0.01 mg kg^{-1}); [3]May application Pre emergence, June application early post emergence; [4]NA: not analyzed; [5]Two applications of 6.7 kg ha^{-1}.

In Experiment 2, background levels in soil of N-isopropylaniline were found to be 0.34 mg kg^{-1} and did not increase significantly following preemergence treatment of propachlor, ie. 0.38 mg kg^{-1} (Table 2). The background levels of Experiment 2 were likely the result of previous experiments with propachlor on these plots. The data presented in Table 2 also suggest that the residue levels may persist longer or even increase as other herbicides are applied in addition to propachlor. For example, the level of bound N-isopropylaniline increased from 0.38 to 0.98 mg kg^{-1} when pendimethalin and chlorpropham (postemergence) were applied after the propachlor preemergence treatment. These results indicate that soil retention or microbial breakdown of propachlor may be dependent upon the presence of other herbicides.

Table 3. Residues (mg kg^{-1}) of N-isopropylaniline (bound metabolite) in onions and soils following the use of propachlor at 6.7 kg ai ha^{-1}. Agriculture Canada Ste-Clotilde Farm, Quebec, 1984. (Experiment #3).

Sample	Application date	Onion stage[1]	Sampling date	Post Application (days)	Onions (Bound Metabolite[2])
Onions	7 May	Pre-em	13 Aug.	53	<0.01
	21 June	early post	13 Sept.	84	<0.01
Soil	7 May	Pre-em	8 July	16	0.75+0.88
(0-7 cm)	21 June	early post	10 Sept.	81	2.2 +1.8
Soil	7 May	Pre-em	8 July	16	0.26+0.22
(7-15 cm)	21 June	early post	10 Sept.	81	0.23+0.30
Soil - mean				16	0.51
(0-15 cm)				81	1.2

[1]Seeded 1 May, 1984 with Canada Maple; [2]No propachlor or free N-isopropylaniline was detected (<0.01 mg kg^{-1}).

Table 4. Residues (mg kg^{-1}) of propachlor and N-isopropylaniline (bound metabolite) in onions and organic soil following the use of propachlor at 3.4 kg ai ha^{-1} postemergence. Muck Research Station, Kettleby, 1985 (Experiment #4).

Sampling Date	Pre & Post Application (days)	Onions[1]		Soil	
		Propachlor	Bound Metabolite[2]	Propachlor	Bound Metabolite[2]
10 July	-2	<0.01	<0.01	<0.01	0.35+0.06
12 July	0	26+4.6	2.1+0.95	62+31	0.53+0.18
22 July	10	<0.01	0.63+0.21	1.8+1.5	4.6+2.9
21 Aug.	40	<0.01	0.61+0.11	<0.01	NA
20 Sept.[3]	70	<0.01	0.21+0.09	<0.01	6.7+1.5
19 Oct.[4]	130	<0.01	0.07+0.03	NS	NS
28 Nov.[4]	143	<0.01	0.08+0.04	NS	NS

[1]Seeded 26 April with Autumn Keeper; [2]No free N-isopropylaniline was detected <0.01 mg kg^{-1}; [3]Harvest date; [4]Storage onions; NA: not analyzed; NS; not sampled.

Table 5. Residue (mg kg^{-1}) analyses of onions and soils from 12 farm fields where propachlor was used under research permit during 1985.

Farm number	Propachlor rates (kg ha^{-1})	Application dates	Sampling date	Post application (days)	Onion[1] bound metabolite	Soil[2] Propachlor	Soil[2] Bound metabolite
1	6.0, 4.1	6 May, 21 June	10 July	19	0.03	0.85	0.19
			12 Dec	174	0.02	<0.1	1.9
2	6.0	8 May	10 July	63	<0.01	0.31	0.93
3	6.0, 4.1	8 May, 17 June	20 Sept	95	0.08	<0.1	8.0
4	6.0, 4.1	10 May, 21 June	10 July	19	0.02	2.2	0.4
			25 Nov	157	0.01	<0.1	4.2
5	4.1	23 June	20 Sept	89	0.04	<0.1	6.5
6	6.0, 4.1	13 May, 13 June	20 Sept	99	0.04	<0.1	6.5
7	6.0, 4.1	10 May, 20 June	20 Sept	92	0.05	<0.1	7.9
8	3.0	7 June	17 Dec	193	0.07	<0.1	0.2
9	4.1	3 July	17 Dec	167	0.04	<0.1	0.5
10	6.0	10 May	1 Nov	175	<0.01	<0.1	1.4
11	6.0, 4.1	10 May, 20 June	6 Nov	139	0.01	<0.1	0.1
12	3.5	10 July	2 Jan 86	176	0.04	<0.1	0.7

[1]No residues of propachlor or free N-isopropylaniline found in onions <0.01 mg kg^{-1}; [2]No residues of propachlor or free N-isopropylaniline found in soil <0.01 mg kg^{-1}.

In Experiment 4, propachlor was observed in onions and soil samples immediately after application at levels of 26 and 62 mg kg^{-1}, respectively, (Table 4). Propachlor rapidly dissipated from onions and was not detected (<0.01 mg kg^{-1}) only 10 days later. A level of 1.8 mg kg^{-1} propachlor was observed in soil at Day 10 and no residues were observed (<0.1 mg kg^{-1}) at Day 40. No free N-isopropylaniline was observed in onion or soil samples as described previously (Frank et al. 1977). The bound residues of N-isopropylaniline were 2.1 mg kg^{-1} at Day 0 and declined to 0.21 mg kg^{-1} at day 70. Storage onions at Days 130 and 143 showed residues less than the allowable (0.1 mg kg^{-1}) negligible residue limit, and levels were 0.07 and 0.08 mg kg^{-1} respectively. Soil residues of bound N-isopropylaniline at 0.35 mg kg^{-1} were observed prior to treatment with propachlor. Levels of N-isopropylaniline increased from 0.53 mg kg^{-1} at day 0 to 6.70 mg kg^{-1} at day 70.

Samples of onions and soils also were analyzed from farmers' fields where propachlor was used under Research Permits (Table 5). No free propachlor was found in onions at various time intervals after propachlor application. Propachlor was identified in some soils at 19 and 63 days at levels ranging from 2.2 to 0.31 mg kg^{-1}. No free N-isopropylaniline was found in anyll onions or soils analyzed. The residues of N-isopropylaniline identified in onions were all less than the negligible residue (<0.1 mg kg^{-1}) tolerance allowed under the Canadian Food and Drug Act. Residues of N-isopropylaniline in soil were somewhat more variable and residues ranged from <0.1 to 8.0 mg kg^{-1}.

The results of these studies indicate that when propachlor is applied as a preemergent herbicide, no residues were detected in harvest (bulb) onions under Ontario conditions. Free propachlor and N-isopropylaniline were not detected <0.01 mg kg^{-1} and residues of bound metabolite (released by hydrolysis) were not detected, 0.01 mg kg^{-1}. Propachlor could be considered as a substitute for allidochlor for use in onions when used at the pre-emergence stage.

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