Pesticides On Used Agricultural Plastics

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Abstract: This paper summarizes the results of a 2 1/2 year project, funded by the Pennsylvania Department of Agriculture, which investigated the levels of pesticide residues present on used agricultural plastics. The paper briefly describes the on-farm sampling procedures for both film plastics and rigid plastics from different agricultural enterprises. It also describes the laboratory test procedures used to quantify pesticide residues. Lastly, it lists the types and quantities of pesticide residues that were found on the different types of plastics. The paper concludes with recommendations for providing a cleaner product to recycle.

Keywords: Pesticides, Agricultural pesticides, Contamination, Plastic-film, Extraction

Introduction

Many recyclers and resource recovery facilities are reluctant to use agricultural plastics. This project, funded by the Pennsylvania Department of Agriculture, investigated the levels of pesticides present at the time of plastic disposal. The goal has been to work with a statewide group of farmers to determine the extent and concentration of pesticide contaminants on commonly used agricultural plastics. In addition, the intent of the project team was to determine the extent of dirt and debris on these wastes.

Methods and Materials

Plastic Products. Three broad categories of film plastic products were sampled: mulch films, greenhouse films, and forage films including silage bags and wraps. Several types of rigid plastic products were included at one point in the study, namely nursery trays, flats, pots, and inserts.

Seasonal Sampling. Collection of different products described herein occurred in two timeframes:

Phase 1. Summer through fall, 1995 -- film plastics only
Phase 2. Spring, 1996 -- rigid plastic products and a few films

Experimental Control Sampling. In Phase 1, an experimental control sample one square meter in size was obtained for each film plastic sample. This sample was for a reference to detect background interferences during the chemical analysis of field samples, and hence had to remain untouched and free of all contamination. During Phase 2, it was determined that obtaining a untouched control sample for each rigid plastic item would be difficult since many of the items were reused many times for several years. Several unused items were granulated and mixed together to form a composite sample.

Field Sampling. All plastics from the field were sampled by the county agents *only when the farmer was disposing of the item.* This was done in an effort to have the samples representative of what a processor of recycled material would be receiving at the dock.

Film samples were obtained by cutting square pieces 10 cm x 10 cm, then placing them in a plastic sample bag. To help prevent cross-contamination, polyethylene gloves were worn and sampling tools were decontaminated by washing with distilled water and ethyl alcohol. Tools were washed and a new pair of gloves were used before sampling began in another area. Besides taking samples for pesticide residue analysis, replicates were taken to determine the amount of dirt and debris contained on the plastic. Only the soil and debris from the 10 cm x 10 cm area was retained. Samples were put in cold storage at -23° C until they could be delivered to the pesticide testing laboratory.

For soiled rigid plastics, at least four identical items comprised a sample lot. Depending on size, some sub-sampling was required. The items were cut into 1-10 sq cm pieces to fit into the collection bags, and to provide at least 50g of sample for the lab analyses.

Spray Records. Cooperating farmers kept spray records for each crop. These records were used to narrow the number of analyses performed. For economic reasons, not all pesticides known to have been applied were searched for. To shorten the list of pesticides to search for, a simple mathematical weighting system was developed which factored in three criteria: Dermal LD50 toxicity, number of applications, and the application rate. In the case of the rigid plastics, not all spray records were available, making it necessary to use special analytical chemistry screening processes.

Laboratory Procedures. There were many quality assurance and quality control requirements deemed to be necessary. Efforts were made to conform to EPA quality assurance and control standards. Prior to analyzing samples, the laboratory had to generate acceptable accuracy and precision data for each analyte (pesticide). The following procedures were the most noteworthy:

1. Quad-spiked samples were to be analyzed as directed in SW-846 standards and had to meet acceptable accuracy and precision requirements for each particular compound.

2. For each analytical batch of up to 20 samples, a reagent blank, a duplicate sample, a matrix spike, and a duplicate matrix spike were to be analyzed for each analyte. The blank and spiked samples were carried through all stages of the sample preparation and measurement steps.

3. Criteria for quality control spiking and use of surrogate compounds were to be established prior to analyses of field samples.

In phase 1, a total of 48 pesticides were applied by 9 cooperating farmers. This list was reduced to eighteen pesticides and metabolites to search for. In phase 2, 37 samples from 8 farmers were analyzed by a screening process which searched for many common pesticides contained in a database library.

Results and Discussion

Results of phases 1 and 2 are shown in Tables 1 and 2, repectively. Table 3 is a comparison of EPA residue tolerances for pesticides on various crops as they leave the farm gate versus limits found on the various plastic products. Table 4 is a summary of dirt and debris and moisture found on various plastic products.

Table 1. Phase 1 pesticides that were searched for on the sample. Within each row corresponding to a specific pesticide is the number of times residues of that pesticide were detected on those samples that received some degree of overspray from, or contact with, that same pesticide.

Pesticide Name	Mulch film # detections / # samples	Range of residue on mulch, ppm	Greenhouse film # detections / # samples	Range of residue on greenhouse film, ppm	Forage film # detections / # samples*
Etradiazole	nd	nd	0/1	nd	--
Chlorothalonil	2/9	3-343	0/1	nd	--
Dicofol	3/3	1.9-34	nd	nd	--
Captan	nd	nd	0/1	nd	--
Endosulfan I	2/5	1-10.7	nd	nd	--
Endosulfan II	3/5	1.5-9.3	nd	nd	--
Endosulfan Sulfate	3/5	0.5-1.0	nd	nd	--
Bifenthrin	nd	nd	1/2	2.9	--
Esfenvalerate	5/7	2.2-22.2	nd	nd	--
Benomyl	0/8	nd	nd	nd	--
Acephate	nd	nd	0/2	nd	--
Dimethoate	0/1	nd	nd	nd	--
Diazinon	0/1	nd	nd	nd	--
Oxamyl	0/2	nd	nd	nd	--
Methomyl	1/2	3.3	nd	nd	--
Carbofuran	0/1	nd	nd	nd	--
Carbaryl	0/3	nd	nd	nd	--
Copper Sulfate	5/5	9-135**	nd	nd	--
Copper Oxychloride Sulfate	3/3	10-106**	nd	nd	--
Mancozeb	2/2	843-1106**	nd	nd	--

* No forage films were in contact with pesticides, and thus were not tested.
** High levels of elemental copper, manganese and zinc believed to be from soil on film.
nd = Not detected; below detection limits.
-- = Not tested; no contact with pesticides.

Table 2. Phase 2 test results listing pesticide residue values for each detection, shown by category of items. The number (n) of each sample per category is listed. The top portion of the table lists those pesticides screened for using the HPLC method; the bottom shows results from the GC / MS SIM method.

	Individual residue values for each detection, ppm						
Pesticide Name	**Mulch Film (n=1)**	**Winter Cover Film (n=1)**	**Greenhouse Film (n=1)**	**Pots (n=12)**	**Trays / Flats (n=21)**	**Tray Insert (n=1)**	**Range of residues, ppm**
HPLC Analyses*							
Dichlorvos	nd	nd	nd	nd	0.2	nd	0.2
Etridiazole	nd	nd	nd	nd	0.3, 1.6, 0.7	nd	0.3-1.6
Acephate	nd	nd	nd	0.3		nd	0.3
Diazinon	nd	nd	nd	nd	1.7, 0.4, 0.3	nd	0.3-1.7
Metalaxyl	nd	nd	nd	nd	0.4	nd	0.4
Chlorpyrifos	nd	nd	nd	0.7, 1.4	1.3, 1.6, 3.3	nd	0.7-3.3
Malathion	nd	nd	nd	nd	0.3, 0.9	nd	0.3-0.9
Bifenthrin	nd	nd	0.7	nd	0.2	nd	0.2-0.7
EPN	nd	nd	nd	nd	0.3	nd	0.3
trans-Permethrin	nd	nd	nd	nd	0.4	nd	0.4
PCNB	nd	nd	nd	nd	<0.4, 4.5	nd	<0.4-4.5
Chlorothalonil	nd	nd	nd	0.4, 8.6	1.5, 1.4, 3.9	0.3	0.3-8.6
Endosulfan I	nd	nd	nd	nd	0.4	nd	0.4
Endosulfan II	nd	nd	nd	nd	0.6	nd	0.6
GC / MS SIM Analyses*							
Aldicarb Sulfone	nd	nd	nd	0.06	0.09, 0.09	nd	0.06-0.09
Oxamyl	nd	nd	nd	0.08	0.13, 0.12	nd	0.08-0.13
Methomyl	nd	nd	nd	nd	2.2	nd	2.2
Carbaryl	nd	nd	nd	nd	0.08	nd	0.08

nd = Not detected; below detection limits.

*The following pesticides were also screened by HPLC analysis but were without any hits: Methamidophos, Demeton-S, HCB, Phorate, Trifluralin, Sulfotep, Terbufos, Prometon, Disulfoton, Simazine, Atrazine, Heptachlor, Dimethoate, Chlorpyrifos-methyl, Monocrotofos, Metribuzin, Methyl parathion, Fenthion, Isofenfos, Chlorfenvinphos, Captan, Bromacil, Cyanazine, Carbofenthion, Resmethrin, Mirex, Fensulfothion, Azinphos-methyl, cis-Permethrin, Coumaphos, a-BHC, Dicrotophos, gamma-BHC, Aldrin, Alachlor, beta-BHC, Dicofol, Metolashlor, delta-BHC, Heptachlor Epoxide, Parathion, trans-Chlordane, cis-Chlordane, pp-DDE, Dieldrin, Endrin, OP-DDT, PP-DDD, PP-DDT, Endosulfan Sulfate, Methoxychlor.

**The following pesticides were also screened by GC / MS SIM analysis but were without any hits: Aldicarb Sulfoxide, 3-OH Carbofuran, Aldicarb, Baygon, Carbofuran, Barbaryl, Methiocarb.

Table 3: Allowable EPA pesticide residue tolerance limits on crops leaving the farm gate versus pesticide residues on agricultural plastics.

	Allowable EPA pesticide residue tolerance limits for various crops, ppm								
Pesticide	Tomato	Pepper	Cu-cumber	Musk-melon	Broccoli	Cauli-flower	Squash	Pumpkin	Range Found on Plastics, ppm
Carbaryl	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	0.07 - 0.46
Chlorothalonil	5.0		5.0	5.0	5.0	5.0	5.0	5.0	0.3 - 8.6
Dachtal	1.0	2.0	1.0	1.0			1.0		0.01 - 28
Dicofol	5.0	5.0	5.0	5.0			5.0	5.0	0.02 - 35
Endosulfan I	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0.1 - 4.0
Endosulfan II									0.1 - 19
Esfenvalerate	1.0	1.0	0.5	1.0	2.0	0.5	0.5	1.0	2.2 - 22.2
Azinphos-methyl	2.0	0.3	2.0	2.0	2.0	2.0			0.05 - 0.2
Acephate	5.0	4.0		5.0		2.0			0.3
Chlorpyrifos	0.5	1.0	0.05		1.0	1.0		0.05	0.3 - 3.3
Diazinon	0.75	0.5	0.75	0.75	0.7	0.7	0.5		0.3 - 1.7
Etridiazole	0.15								0.3 - 1.6
Malathion	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	0.07 - 0.9
Metalaxyl			1.0		2.0	1.0			0.01 - 0.4
Methomyl	1.0	2.0	0.2		3.0	2.0			2.2 - 3.3
Oxamyl	2.0	3.0	2.0	2.0			2.0	2.0	0.08 - 0.13
PCNB	0.1	0.1			0.1	0.1			4.5
Dimethoate	2.0	2.0		1.0	2.0	2.0			0.01
Permethrin	2.0	1.0			1.0	1.0			0.01 - 41
Captan	25.0	25.0	25.0	25.0	2.0	2.0	25.0	25.0	0.04 - 90

Table 4. Debris and moisture information for various plastic products from the field.

Plastic Product	**Debris Range, %**	**Avg. Debris, %**	**Moisture Range, %**	**Avg. Moisture, %**
Mulch films (n=11)	6.1-71.2	28.1	0-13.2	2.3
Greenhouse films (n=2)	0	0	0.5-1.1	0.8
Forage films (n=8)	0-19.8	6.0	0.5-24.7	10.4
Nursery trays / flats (n=19)	0-11.7	2.5	--	--
Tray inserts (n=5)	0-0.4	0.2	--	--
Nursery pots (n=10)	0-1.7	0.9	--	--

Conclusions

This project has revealed that pesticide residues do in fact remain on both film and rigid agricultural plastics. Typical concentrations were less than 10 parts per million on a weight basis, which is not considered to be of concern when handling or preparing for most recycling or resource recovery purposes. However, routing these wastes into certain sensitive recycling streams, such as personal care products, should be avoided. One sample had pesticide concentrations that cause concern (343 ppm), but it was unusual in that it had been sampled less than 6 days after pesticide application by the farmer. Normally, agricultural plastics would undergo a weathering process before being recycled or sent to a waste-to-energy facility, allowing some of the pesticides to wash off. Additionally, the weathering period would provide time for natural pesticide degradation. Our data suggests a period of four weeks or more weathering is best.

On a wet weight basis, the average dirt and debris on the field samples was: mulches, 28.1%; greenhouse films, 0%; and forage films 6%. Since most recyclers want a maximum of 4%, it is felt that mulches will remain a disposal problem for growers in the forseeable future. Greenhouse films are easily marketed because of their physical cleanliness and site concentration. Forage films are free of pesticides, but may have some problems meeting recovery specifications for cleanliness, especially in the case of laminations.

The fate of the pesticide residues over time, and after washing for recycling, remains a concern that may need to be addressed in a future project. Determining the residues that could potentially be carried through processing and into a product made from used agricultural plastics remains as a challenge for further research. Pesticide residues allowable at the farm gate are established by the Environmental Protection Agency (EPA) and are enforced by the Food and Drug Administration (FDA). In this project, it was decided that the most reasonable approach was to relate pesticide residues found on plastic to those residues allowed on agricultural fruits and vegetables leaving the farm gate. This approach does not answer the question "Will I get pesticides on me if I touch it?", but it is an assurance that says plastics typically are no more contaminated than the food one eats.

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