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Analysis of Pesticide Detections in California Surface Waters, 1991-2010: Identification of detections exceeding US EPA Aquatic Life Benchmarks

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Abstract

Data from the California Department of Pesticide Regulation (CDPR) surface water monitoring database were analyzed in order to identify pesticide active ingredients (AI) which have been frequently detected in California surface water at concentrations exceeding US EPA Aquatic Life Benchmarks. Monitoring data was from surface water samples collected between 1991 and 2010; over 50,000 chemical analysis results were included in the analysis. The ten AIs which most frequently exceeded the benchmarks were identified; seven were insecticides and three were herbicides. Five insecticides had agricultural use and benchmark exceedances in agricultural areas: diazinon, chlorpyrifos, malathion, dimethoate, and methomyl. Two additional insecticides, bifenthrin and fipronil, had recent benchmark exceedances primarily in urban areas. Of the three herbicides identified, diuron's benchmark exceedances were primarily from agricultural areas; the recent 2,4-D exceedances were all in samples from urban areas. Thiobencarb had few recent benchmark exceedances.

I. INTRODUCTION

Over 300 pesticide active ingredients are registered for use in urban or agricultural areas of California (CDPR 2011b); off-site movement of pesticides into California surface water has been well documented (CDPR 2011a). CDPR is currently developing regulations to minimize such off-site movement (CDPR 2011c, CDPR 2011d). An important part of this effort is the identification of pesticides which have contaminated surface waters at concentrations that may affect aquatic life. CDPR's surface water database contains surface water monitoring data for over 300 pesticide analytes from all major agricultural and urban areas of the state. Data from this database were analyzed in order to identify pesticide active ingredients (AI) which have been frequently detected in California surface water at concentrations exceeding US EPA Aquatic Life Benchmarks.

II. OBJECTIVE

The objective of this analysis was to identify pesticide active ingredients which have been frequently detected in California surface water at concentrations that exceed US EPA Aquatic Life Benchmarks. Results may be used in the development of regulations designed to prevent surface water contamination by pesticides.

III. MATERIALS AND METHODS

Aquatic Life Benchmarks

Pesticide Aquatic Life Benchmarks were obtained from the US EPA Office of Pesticide Programs' web page (US EPA 2011). For each AI, the lowest available benchmark was used for comparison to detected concentrations (Table 1). For 2,4-D, aquatic life benchmarks have not been developed; a concentration of 0.56 ug/L was used for 2,4-D. This value was derived from the lowest Office of Pesticide Programs database value, multiplied by a safety factor (Pepple 2010).

Surface water monitoring data

Pesticide surface water monitoring data were acquired from the CDPR surface water monitoring database (CDPR 2011a). All surface water monitoring data available as of September 2011 were included in the analysis. Sediment data were not included in this analysis due to the relatively small amount of sediment data available. Monitoring data from 1991 to 2010, with over 13,000 samples collected from over 900 sample sites, were included in the initial dataset. For each AI in the database, the total number of samples, detections, and detected concentrations greater than the selected US EPA Aquatic Life Benchmark were determined. From these data, the frequency of detection and the frequency of benchmark exceedance were calculated. The ten AIs with the highest exceedance frequencies were identified for further analysis (Table 2, Figure 1). For these ten AIs, the detection and exceedance frequencies by year (1991 through 2010) were also determined.

Pesticide use data

Using CDPR's Pesticide Use Reporting (PUR) database, the total reported agricultural use for the ten AIs was determined for the most recent three years of available data (2008-2010) (CDPR 2011b) (Table 2).

IV. RESULTS AND DISCUSSION

The ten AIs with the highest overall exceedance frequencies are presented in Table 2. The group includes seven insecticides and three herbicides. The insecticides include four organophosphate, one carbamate, one pyrethroid, and one pyrazole insecticide.

For the ten AIs, average annual reported agricultural use (2008 through 2010) ranged from less than 100 pounds of AI (fipronil) to over one million pounds (chlorpyrifos). Fipronil does have significant urban/nonagricultural use; however, only agricultural use was included in this analysis. Malathion had the second highest agricultural use, at nearly 500,000 pounds applied.

For the entire period between 1991 and 2010, the overall exceedance frequencies ranged from 2% (methomyl) to over 11% (diazinon and fipronil) (Table 2). Over the 20 year period examined, pesticide use patterns have changed significantly for many of the AIs. As such, the detection and exceedance data are further examined below on a year-by-year basis; monitoring results from the more recent years may be more representative of current risk of off-site movement than the earlier data.

Detection and exceedance frequency data are shown by year for the ten AIs in Figures 2 through 11. Details for each AI are presented below.

<u>Fipronil</u>

Fipronil had the highest overall exceedance frequency of all AIs in the database (11.4%) (Table 2, Figure 1). This was based on fewer than 500 samples analyzed over a six-year period (2005 through 2010) (Figure 2). No fipronil data from 2004 or earlier were available. Fipronil reported use is nearly all nonagricultural; fipronil exceedances in the database were all from samples collected in urban areas (DPR 2011a).

<u>Diazinon</u>

Nearly 12,000 diazinon samples were analyzed between 1991 and 2010 (Table 2, Figure 1); samples were collected and exceedances occurred in each of the 20 years (Figure 3). Of those, diazinon was detected in 4,469 samples (38%); 1,325 samples exceeded the benchmark of 0.11 ug/L. Over the 20-year period, exceedance frequency by year has ranged from less than 1% to nearly 28%; in the most recent year with monitoring data (2010), exceedance frequency was 23% (Figure 3). Agricultural use of diazinon is decreasing; statewide use in 2010 was ca. 50 % lower than in 2008 (Figure 12).

<u>Chlorpyrifos</u>

Over 11,000 chlorpyrifos samples were analyzed over the 20-year period, with samples collected every year (Figure 4). Exceedances occurred in all 20 years. Chlorpyrifos was detected in 2,413 samples (21%) and the benchmark of 0.04 ug/L was exceeded in 840 (7%) (Table 2, Figure 1). Exceedance frequencies by year ranged from less than 1% to 26%. The most recent year with monitoring data was 2010; the benchmark was exceeded in 26 of 99 samples (26%) (Figure 4). Chlorpyrifos use over 2008 through 2010 was consistently high; use was over one million pounds AI each of the 3 years (Figure 12).

Bifenthrin

A total of 1,581 samples were analyzed for bifenthrin between 1999 and 2009 (Table 2, Figure 1); no data were available prior to 1999 or for 2010 (Figure 5). A total of 105 samples had detections for bifenthrin; all 105 of those exceeded the benchmark of 0.0013 ug/L. By year, exceedance frequencies ranged from less than 1% to 50%. The most recent year with monitoring data was 2009; 90 samples were collected, and there were 45 exceedances (50%) (Figure 5). Those samples were all collected from nonagricultural (urban) areas. Bifenthrin has significant use in both agricultural and nonagricultural areas; agricultural use of bifenthrin increased substantially in 2010 (Figure 12). Note that bifenthrin is hydrophobic (Laskowski 2002) and sediment monitoring data were not included in this analysis.

Diuron

A total of 3,388 samples were analyzed for diuron between 1992 and 2010 (Table 2, Figure 1). No diuron data were available for 1991 (Figure 6). Overall, diuron was detected in 1,183 samples (35%). Exceedance frequency was 6% overall. By year, exceedance frequency ranged from 0% to 48%. The highest exceedance frequency occurred in 1992. The exceedance frequency over the most recent five years with data (2006-2010) was 7%. The most recent year with data was 2010, when 34 samples were analyzed; there were no exeedances of the benchmark in those samples. Diuron has significant agricultural and nonagricultural use; agricultural use has decreased by about 20% between 2008 and 2010 (Figure 13).

2,4-D

Over the 20 year period, 1,081 samples were analyzed for 2,4-D (Table 2, Figure 1). Samples were available for every year except 1995 and 2003 (Figure 7). There were 224 detections (21%) and 50 exceedances (5%) of the 0.56 ug/L derived benchmark (Pepple 2010). There were no exceedances of 34 samples in 2010; however, the exceedance frequency was 16% in both 2008 and 2009, when 112 and 73 samples were analyzed, respectively. These samples were collected in urban areas. Current agricultural use of 2,4-D is quite low; from 2008 to 2010, about 10,000 pounds AI were applied in agricultural settings each year (Figure 13). 2,4-D is also available for nonagricultural use, including as consumer products available for use by homeowners (Osienski *et al.* 2010).

Malathion

Malathion data were available for all 20 years between 1991 and 2010; a total of 9,761 samples were analyzed. Of those, there were 433 detections (4%) and 308 exceedances (3%) of the 0.035 ug/L benchmark (Table 2, Figure 1). Exceedance frequencies by year ranged from less than 1% to 23% (Figure 8). In the most recent year with data (2010), there were 23 detections and exceedances out of 99 samples (23%); those samples were all collected from agricultural areas. Use of malathion is increasing; statewide agricultural use of malathion increased by 11% between 2008 and 2010 (Figure 12).

Thiobencarb

Thiobencarb monitoring data were available for all 20 years between 1991 and 2010. Of a total of 6,192 samples, there were 531 detections and 187 exceedances (3%) of the 1.0 ug/L benchmark (Table 2, Figure 1). Most exceedances were prior to 2003 (Figure 9). Exceedance frequency for the last five years of data (2006 - 2010) was less than 1% (10 of 2157 samples).

Thiobencarb is used primarily on rice (CDPR 2011b) and is currently regulated through the use of restricted materials permits in order to protect water quality.

Dimethoate

Dimethoate monitoring data were available for each year from 1991 through 2010. Overall, the 0.5 ug/L benchmark was exceeded in 3% of samples (155 of 5,945) (Table 2, Figure 1). Most exceedances have occurred since 2003 (Figure 10). In the most recent year with data available, 2010, the exceedance frequency was 7% (7 of 99 samples). Statewide agricultural use of dimethoate decreased from 2008 to 2010 by about 28% (Figure 12).

Methomyl

Methomyl monitoring data were available for each year from 1991 through 2010. The overall exceedance frequency of the 0.7 ug/L benchmark was 2% (66 of 3,390 samples) (Table 2, Figure 1). Nearly all exceedances have occurred since 2006 (Figure 11). In 2010, the exceedance frequency was 10% (9 of 87 samples). Methomyl use in agricultural settings has remained fairly steady at approximately 225,000 pounds AI per year in 2008 to 2010 (Figure 12).

V. CONCLUSIONS

Ten pesticide AIs were assessed in terms of the frequency of detection in California surface water at concentrations exceeding US EPA Aquatic Life Benchmarks (benchmarks).

Of seven insecticdes identified in the analysis, five have significant recent agricultural use and recent benchmark exceedances in agricultural areas (diazinon, chlorpyrifos, malathion, dimethoate and methomyl). One insecticide with both urban and agricultural use, bifenthrin, had recent exceedances primarily in samples collected from urban areas. These exceedances likely resulted from urban use. Fipronil also had frequent benchmark exceedances from samples collected in urban areas; fipronil use in California is primarily in urban areas.

Of three herbicides identified in the analysis, one (thiobencarb) has had few recent exceedances. Another herbicide, 2,4-D, has had recent benchmark exceedances, has low agricultural use but has some reported nonagricultural use and is available to consumers for home use. Diuron, which has had recent benchmark exceedances, has significant agricultural and nonagricultural uses.

VI. REFERENCES

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http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm

CDPR 2011b. California Pesticide Information Portal, Pesticide Use Report (PUR) data.
http://calpip.cdpr.ca.gov/main.cfm.

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http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm
Accessed October 2011.

Table 1. Selected US EPA Aquatic Life Benchmarks.

Chemical	Benchmark (ug/L)	Type
2,4-D	0.56	note 1
bifenthrin	0.0013	CI
chlorpyrifos	0.04	CI
diazinon	0.11	AI
dimethoate	0.5	CI
diuron	2.4	ANV
fipronil	0.011	CI
malathion	0.035	CI
methomyl	0.7	CI
thiobencarb	1	CI

note 1: No US EPA Benchmark available. Concentration is from Pepple 2009.
All values are in ug/L.
AI= acute invertebrate; CI = chronic invertebrate; ANV = acute nonvascular plant.

Table 2. Summary of pesticide use, detection and exceedance data, 1991 - 2010.

		Ag	Count			Frequency (%)	
Chemical	**Class**	**Use**	**Samples**	**Detections**	**Exceedances**	**Detection**	**Exceedance**
fipronil	I	97	466	53	53	11.4	**11.4**
diazinon	I (OP)	174,849	11,886	4,469	1,325	37.6	**11.1**
chlorpyrifos	I (OP)	1,294,156	11,301	2,413	840	21.4	**7.4**
bifenthrin	I (PY)	152,875	1,581	105	105	6.6	**6.6**
diuron	H	363,087	3,388	1,183	210	34.9	**6.2**
2,4-D	H	10,642	1,081	224	50	20.7	**4.6**
malathion	I (OP)	491,780	9,761	433	308	4.4	**3.2**
thiobencarb	H (CB)	280,847	6,192	531	187	8.6	**3.0**
dimethoate	I (OP)	250,951	5,945	532	155	8.9	**2.6**
methomyl	I (CB)	234,475	3,390	369	66	10.9	**1.9**

Class: I = insecticide; H = herbicide. OP = organophosphate; PY = pyrethroid; CB = carbamate.
Ag Use is average of agricultural use, pounds of active ingredient, 2008-2010

Figure 1. Overall pesticide detection and benchmark exceedance frequencies, 1991 - 2010.

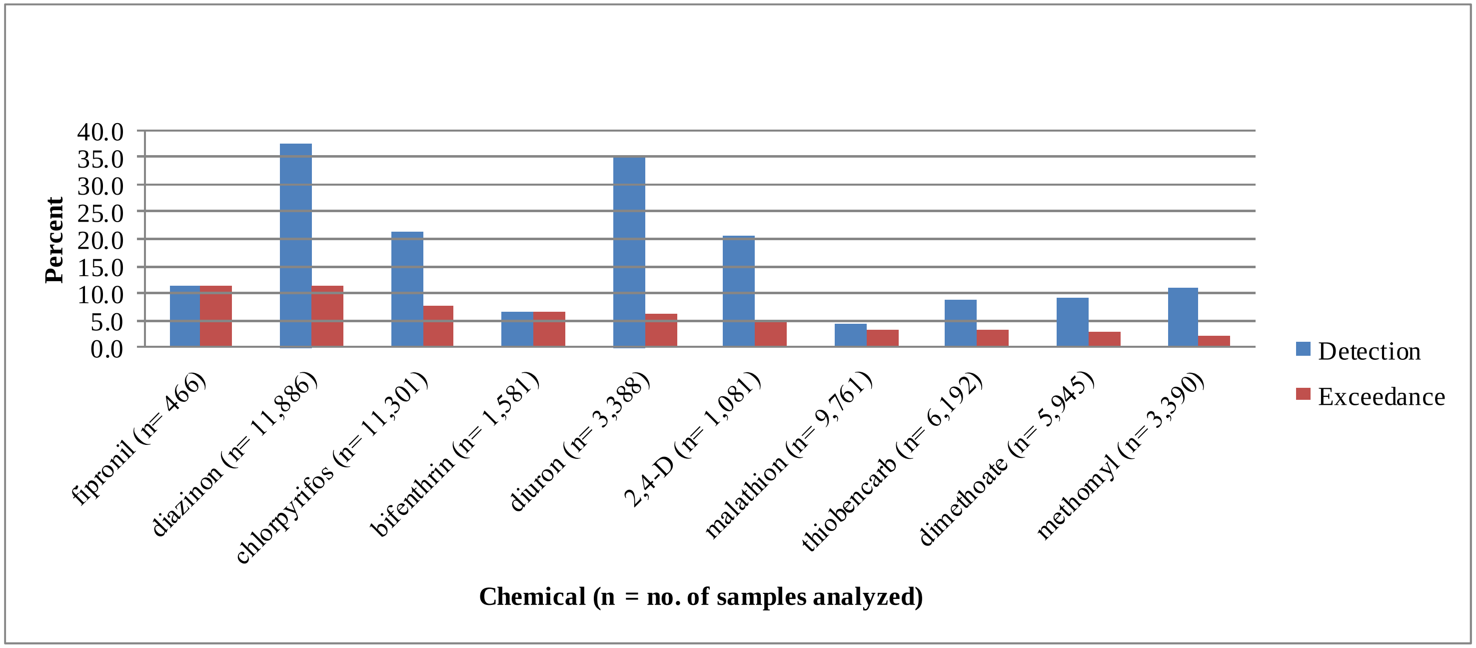
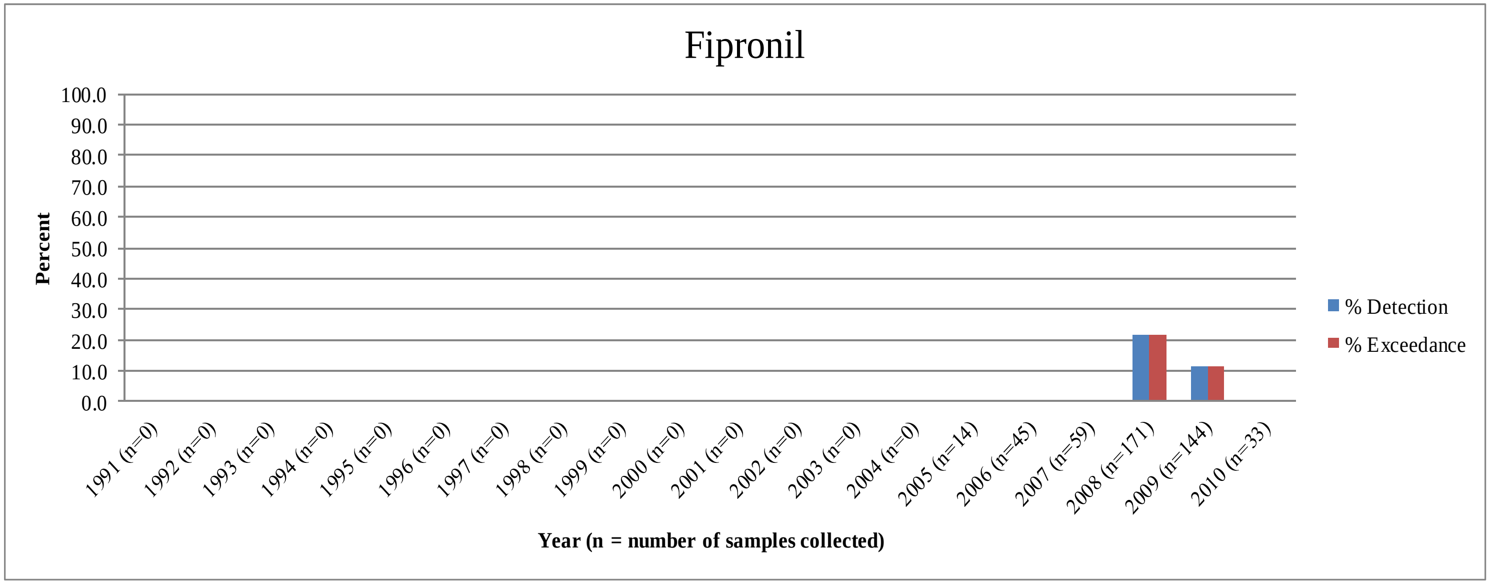


Figure 2. Fipronil detection and benchmark exceedance frequencies, 1991 - 2010.



No fipronil data prior to 2005.

Figure 3. Diazinon detection and benchmark exceedance frequencies, 1991 - 2010.

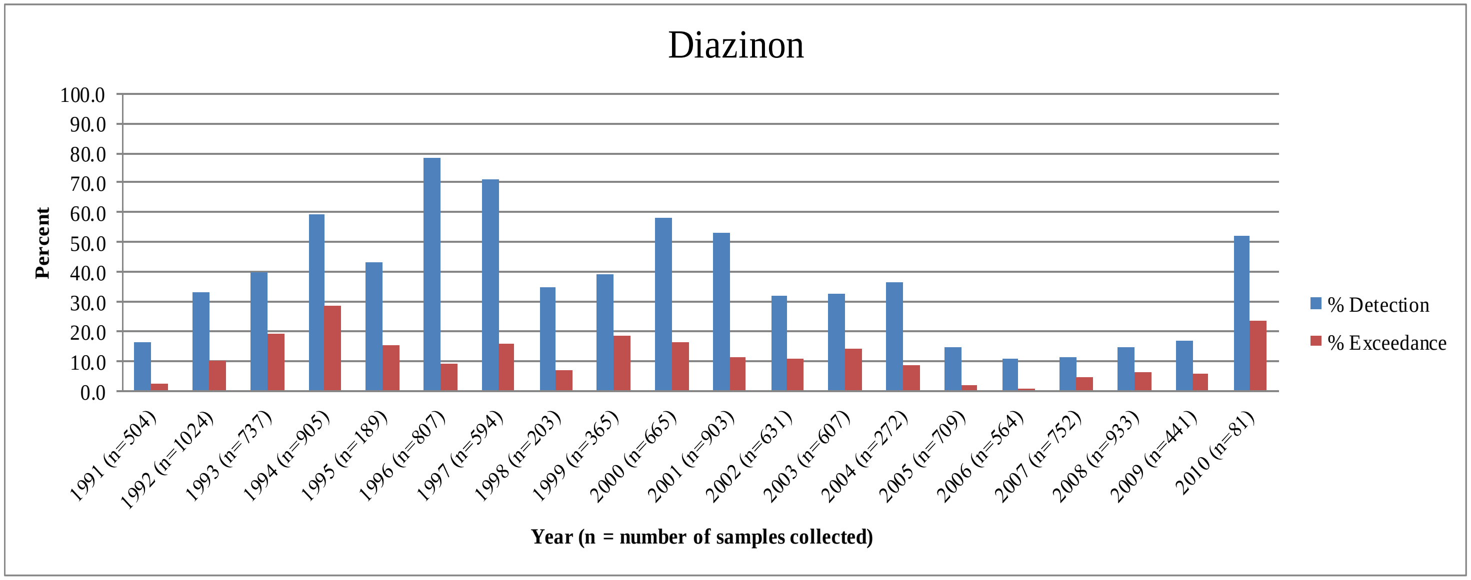


Figure 4. Chlorpyrifos detection and benchmark exceedance frequencies, 1991 - 2010.

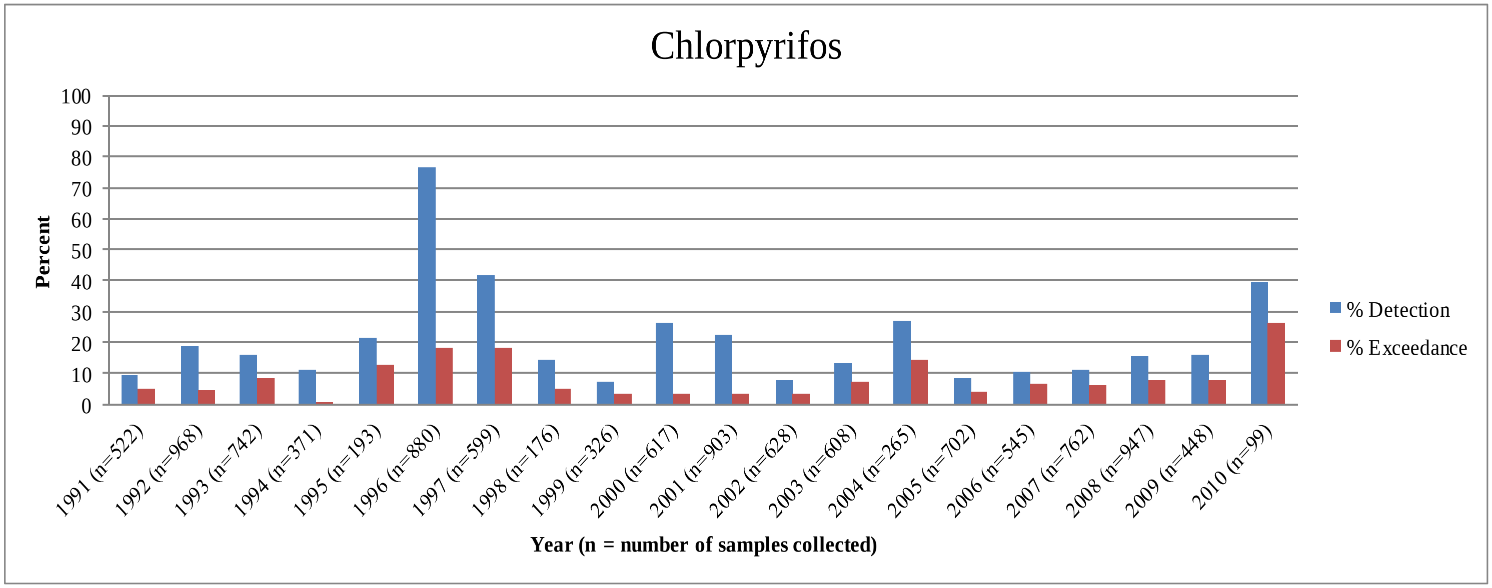
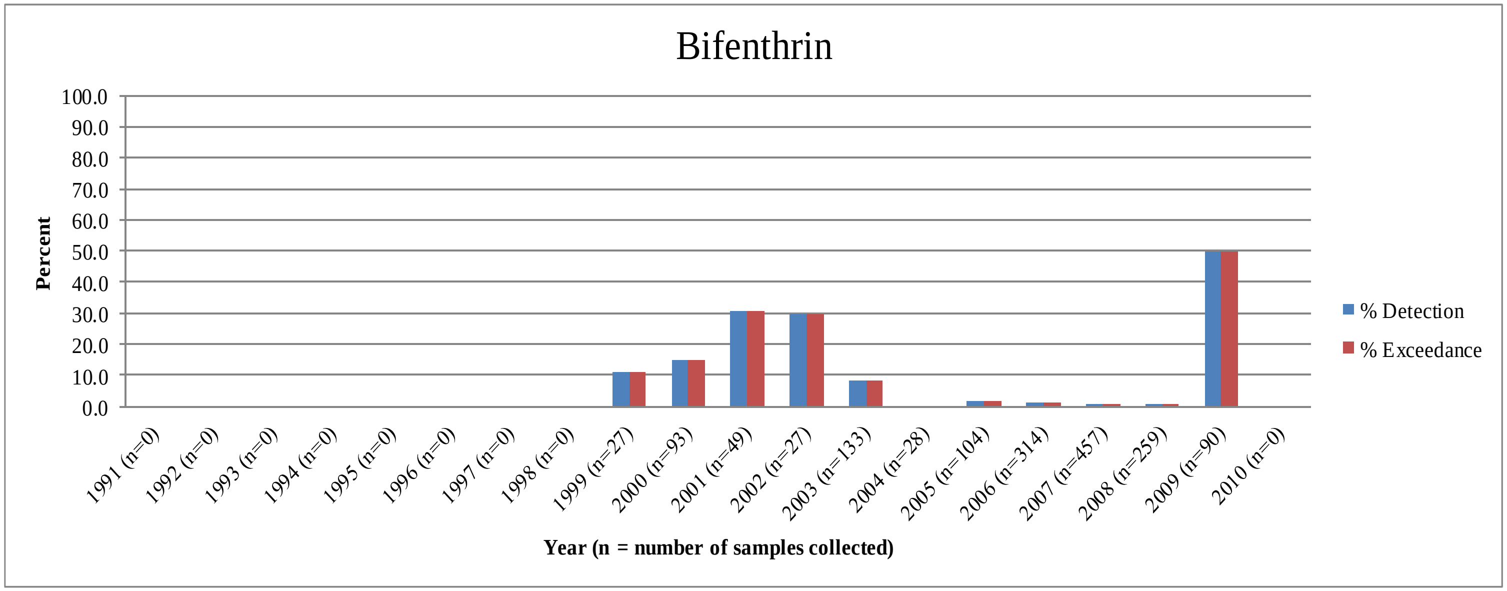


Figure 5. Bifenthrin detection and benchmark exceedance frequencies, 1991 - 2010.



No bifenthrin data until 1999.

Figure 6. Diuron detection and benchmark exceedance frequencies, 1991 - 2010.

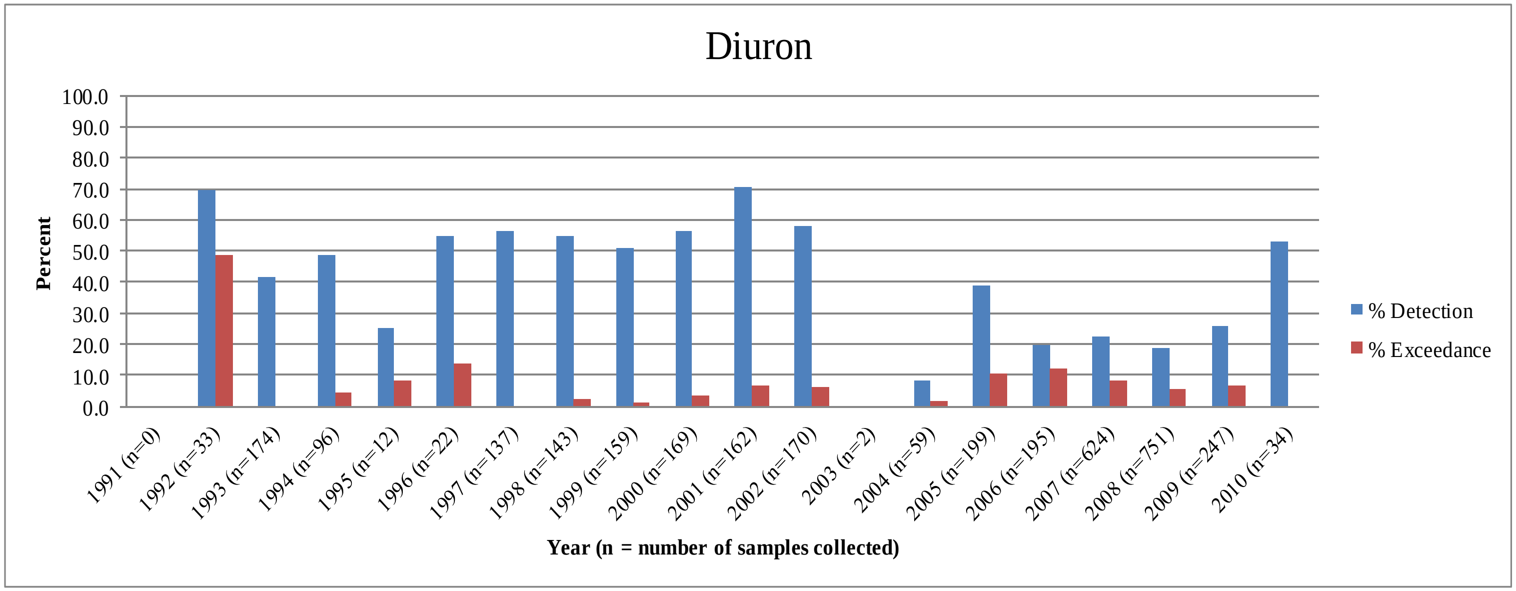


Figure 7. 2,4-D detection and benchmark exceedance frequencies, 1991 - 2010.

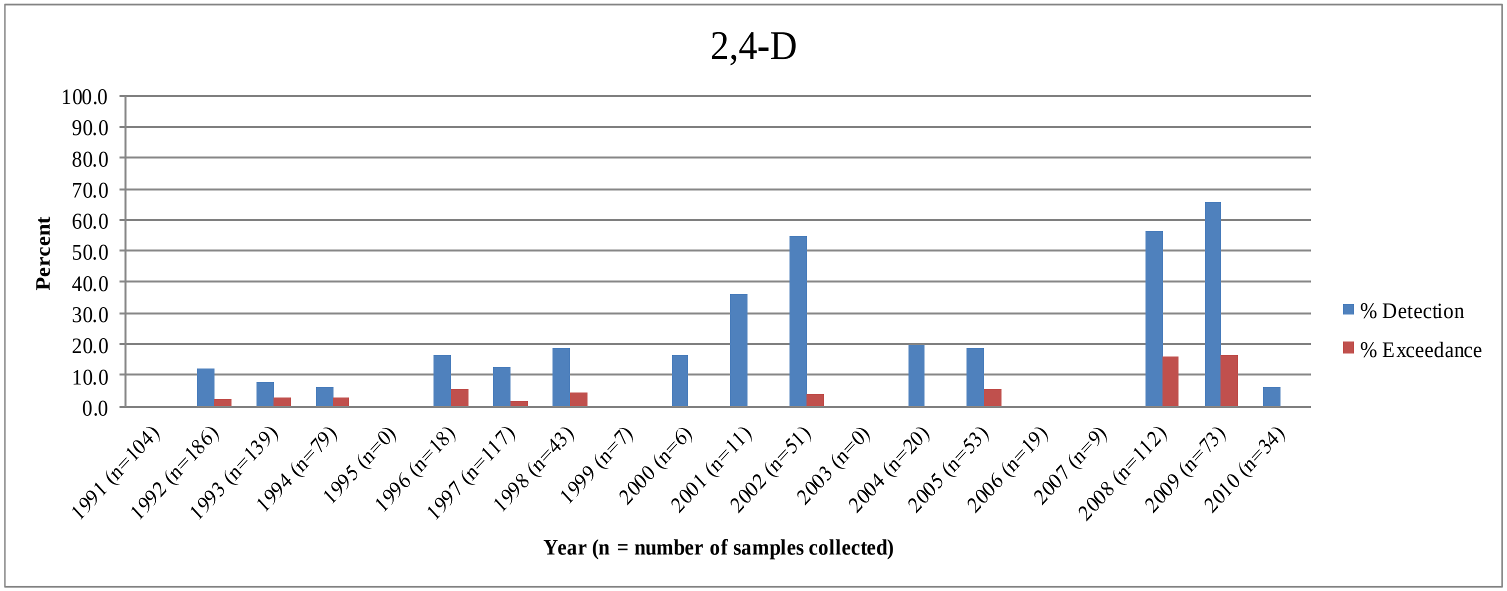


Figure 8. Malathion detection and benchmark exceedance frequencies, 1991 - 2010.

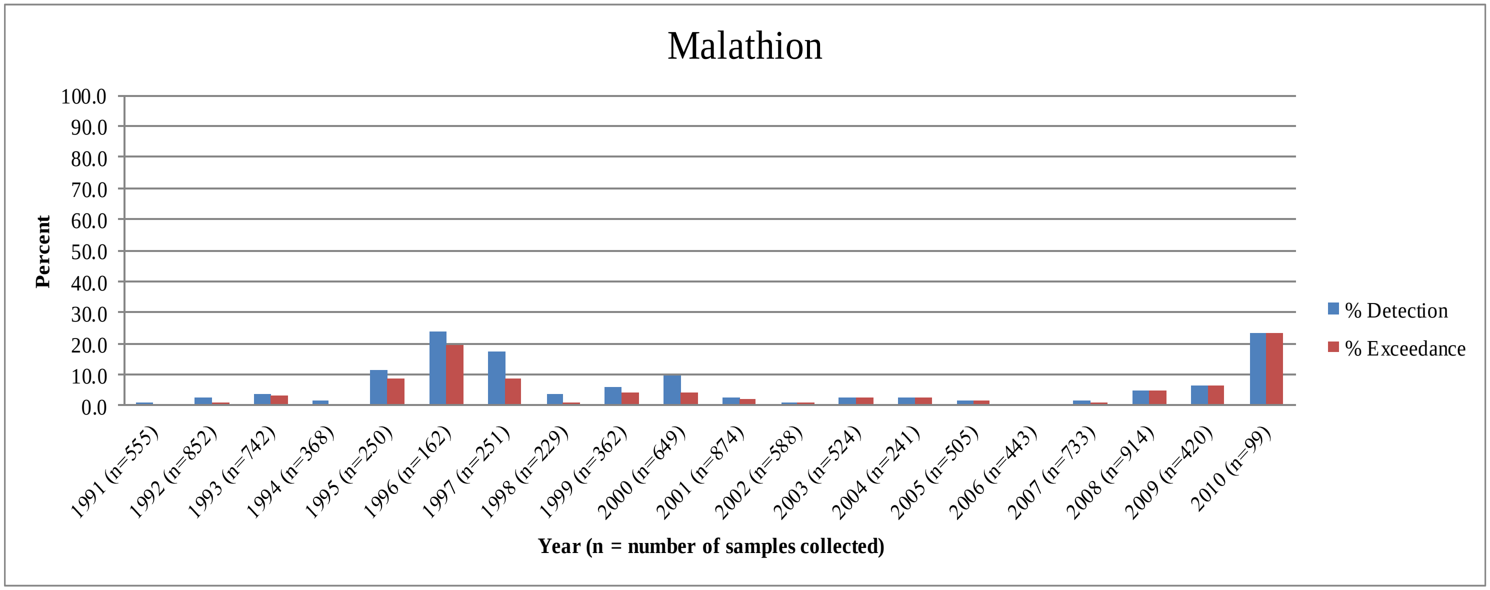


Figure 9. Thiobencarb detection and benchmark exceedance frequencies, 1991 - 2010.

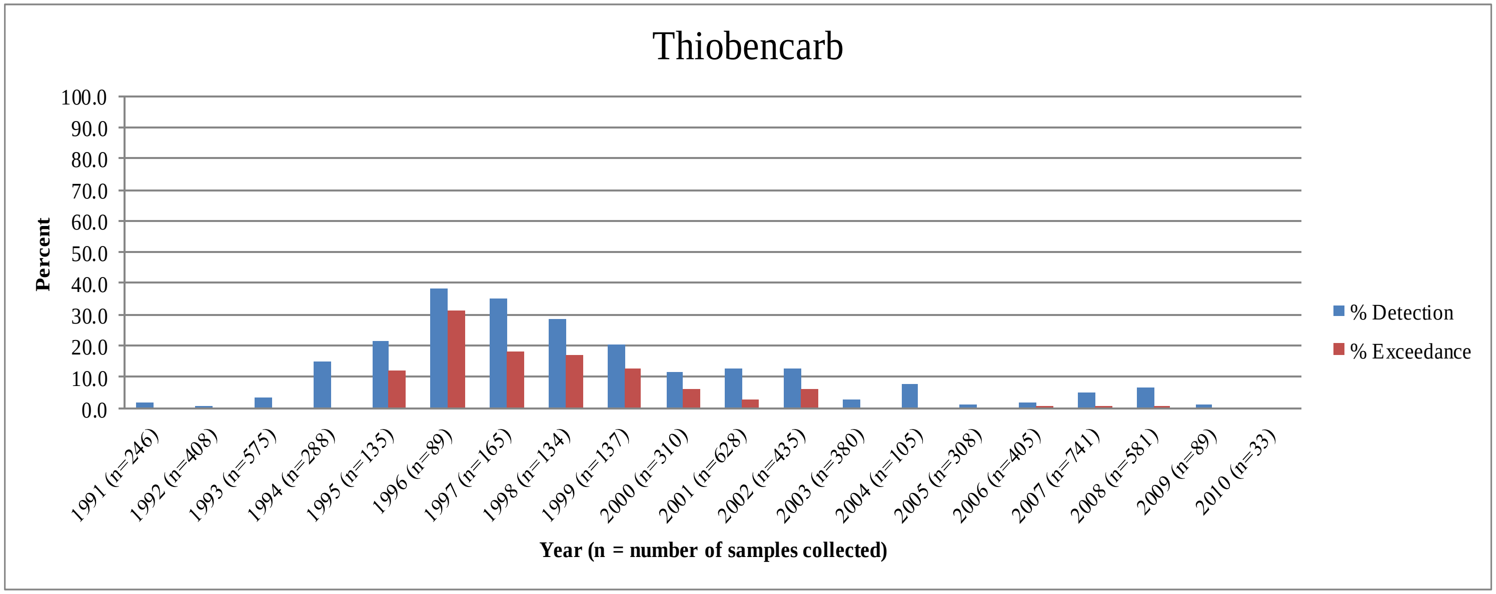


Figure 10. Dimethoate detection and benchmark exceedance frequencies, 1991 - 2010.

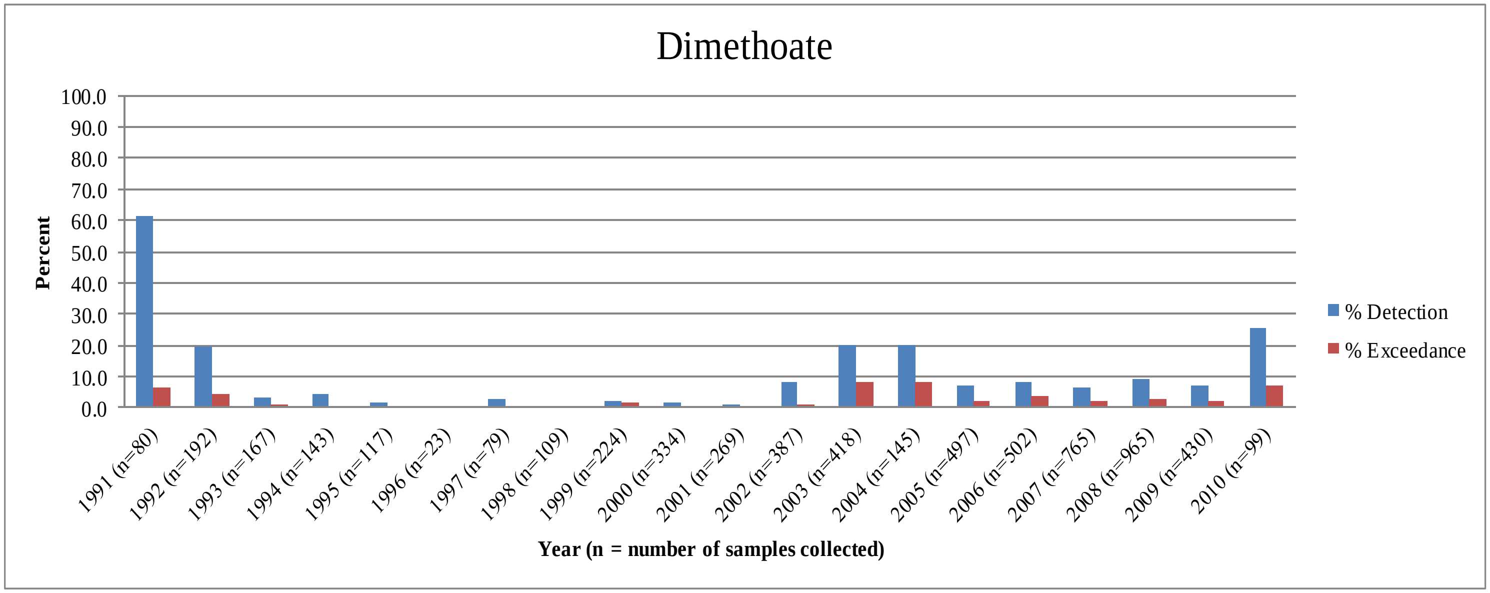


Figure 11. Methomyl detection and benchmark exceedance frequencies, 1991 - 2010.

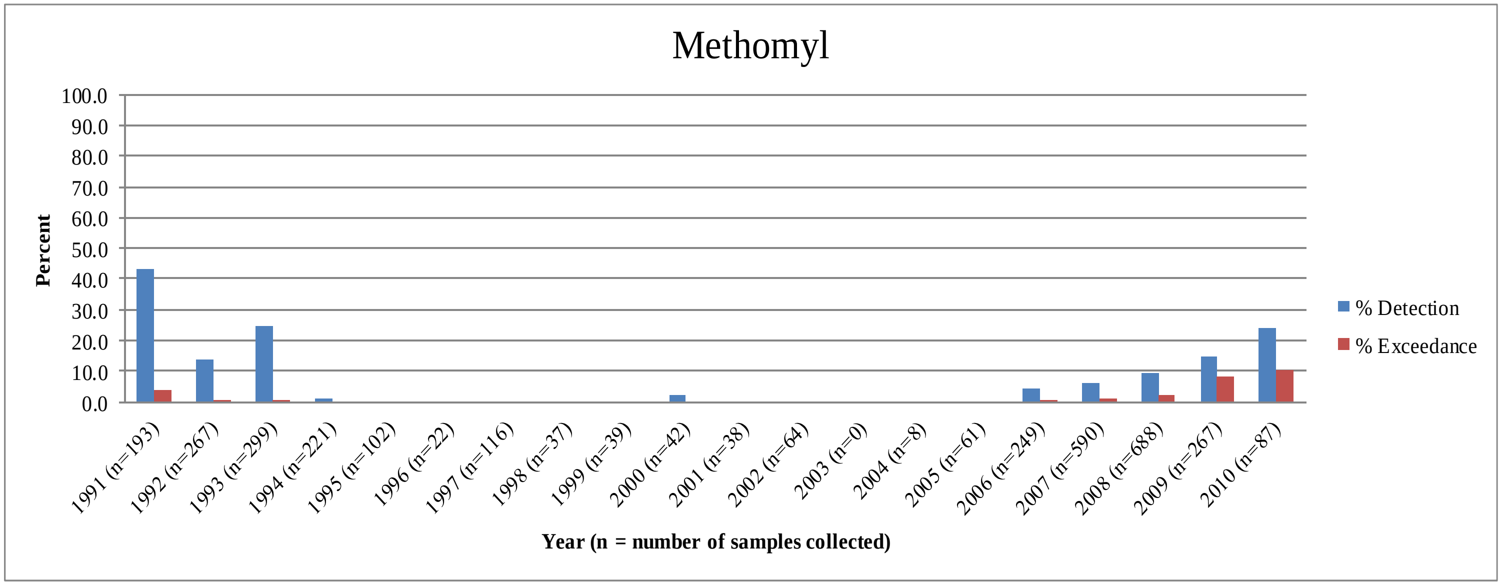


Figure 12. Agricultural use of selected insecticides, 2008 - 2010.

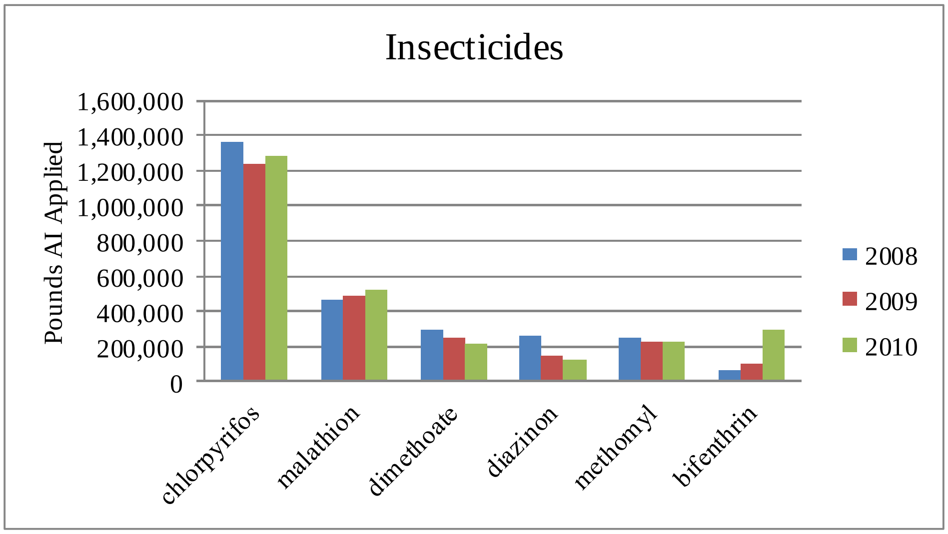


Figure 13. Agricultural use of selected herbicides, 2008 - 2010.