TEXT SEARCHABLE DOCUMENT

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON D.C., 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

PC Code: 109801
DP Barcode: 291976, 343734
Date: January 31, 2008

MEMORANDUM

SUBJECT: Review of Surface Water Monitoring for Residues of Iprodione in High Use Areas in the United States: Interim Report (MRID 47170301).

TO: James Parker, Chemical Review Manager
Laura Parsons, Team Leader
Special Review and Re-Registration Division

CC: Carl Grable, Risk Manager Reviewer
Mary Waller, Risk Manager
Fungicide Branch, Registration Division

FROM: Marietta Echeverria, Environmental Scientist
Environmental Risk Branch IV
Environmental Fate and Effects Division

THROUGH: Elizabeth Behl, Branch Chief
Environmental Risk Branch IV
Environmental Fate and Effects Division

OPP has completed its review of the first year of monitoring data cited in the document "Interim Report: *Surface Water Monitoring for Residues of Iprodione in High Use Areas in the United Stated"* (MRID 47170301) submitted in response to the DCI issued for the fungicide iprodione.

The following are outstanding data requirements which need to be reviewed to fully accept the current submission:

- The analytical method of analysis entitled "Method of analysis for the determination of residues of iprodione and its metabolites, isoiprodione and 3,5 – dichloroaniline plus vinclozolin" (Appendix D) **and** an independent laboratory validation are required.
- The analytical method modification to detect N-3,5-dichlorophenyl formamide (3,5 DCPF) (Appendix B) **and** an independent laboratory validation are required.
- A storage stability study (report indicates that it is being conducted)

2076514

- More detailed usage data including how much was used, when and where, the percent of acres of golf courses (potential use sites) in the watersheds and the actual percent of sites treated have not been reported.

1. SUMMARY

Bayer Crop Science has commissioned a surface water monitoring study designed to determine the potential for iprodione residues to reach public water supplies following the use of iprodione on golf courses and plant nurseries. This submission reports on the first year of the three year monitoring study.

The study sites were selected based primarily on product sales and watershed size. High use regions (based on sales) were identified and community water systems (CWS) with among the highest use intensity (amount of iprodione applied per total watershed area) were selected. The three water treatment facilities that were selected for monitoring are in Bradenton FL, Aurora, IL and Rahway, NJ.

Sampling began in January 2006 and is scheduled to continue through 2008. This interim submission reports the first year of sampling. Paired raw and finished water samples were taken weekly and analyzed for iprodione, its degradates, isoiprodione and 3,5-dichloroaniline (3,5 DCA), and vinclozolin, which also degrades to 3,5 DCA.

Iprodione was detected at the Rahway, NJ site above the method detection limit (MDL) on 5 sampling occasions (MDL = 0.025 ppb for all analytes). Iprodione was detected at a maximum concentration of 0.565 (raw) and 0.124 (finished) ppb on March 5, 2007. Viclozolin was also detected at the Rahway, NJ site above MDL on 5 sampling occasions. Vinclozolin was detected at a maximum concentration of 0.216 ppb in the raw water and was not detected in the finished sample on September 6, 2006.

3,5 DCA was not detected above the MDL in any sample, however, the study authors reported unacceptably low recoveries of 3,5 DCA in the field spike samples. This was due, they propose, to the conversion of 3,5 DCA to N-3,5-dichlorophenyl formamide (3,5 DCPF) in the presence of formic acid, which was added to the samples to stabilize the other analytes. This conversion was accelerated when the samples were frozen. This discovery precipitated an amendment to the protocol that called for the samples to be refrigerated after collection and not frozen for samples collected starting August 15, 2006 and the addition of 3,5 DCFP to the analytical method for frozen samples. Approximately the first eight months of sampling was compromised (January – August, 2006). The recoveries of 3,5 DCA in the frozen samples were low ranging from on average 3 to 27%. Combining 3,5 DCA with the 3,5 DCFP improved the recoveries to an average ranging from 62 to 88% (Rahway, NJ site only reported). In the refrigerated samples the recovery of 3,5 DCA ranged on average from 85 to 90% for the Aurora, IL and Bradenton, FL sites (no field spikes for refrigerated samples at the Rahway, NJ sites).

Proprietary usage data, based on sales of non-agricultural products, suggests that use intensity (lbs ai of iprodione/ acre of total watershed) for 2006 decreased by 35, 41 and 50% for the FL, IL and NJ sites, respectively, compared to 2004, the year of data used to select the sites. Actual use information (how much was used, when and where), the percent of acres of golf courses (potential use sites) in the watersheds and the actual percent of sites treated have not been reported.

2. STUDY DESIGN

Bayer Crop Science has commissioned a surface water monitoring study designed to determine the potential for iprodione residues to reach public water supplies following the use of iprodione on golf courses and plant nurseries. The surface water monitoring study was commissioned in response to a Data-Call-in (DCI) issued by EPA in February, 2001.

The study sites were selected based on use intensity. States with the highest use based on sales in 2004 (>10,000 lbs ai) were identified and three regions were selected based on usage and the desire for geographical diversity. The three regions were Pennsylvania/New Jersey, Michigan/Illinois and Florida. Within those three regions a GIS analysis was conducted to identify the community water systems (CWS) with the highest use intensity (amount of iprodione applied per total watershed area). With few exceptions, the CWS with the highest use intensity in the region was selected as the monitoring site. The three treatment facilities are the City of Bradenton Water Treatment Plant (Bradenton, FL), Aurora City Water Treatment Plant (Aurora, IL) andRahway City Water Treatment Plant (Rahway, NJ). For more information on site selection see DP 294254 (USEPA, 2006).

At each site, paired raw and finished water samples are being collected weekly at the intake of the CWS. Sampling is scheduled for three years, beginning in January 2006. Samples are being analyzed for iprodione, its degradates, isoiprodione and 3,5-dichloroaniline (3,5 DCA), and vinclozolin, which also degrades to 3,5 DCA. According to the protocol, although duplicate samples are collected at each site, only a single sample of each sample type will be analyzed. Only at the direction of the Study Director are replicate samples analyzed. Also, the finished water samples are only analyzed based on the residue analysis of the corresponding pre-treatment sample. Therefore, although paired samples are being taken, the majority of the analysis is limited to the raw samples. It is worth noting that some monitoring studies have reported residues detected in finished water samples even when they were not detected in raw samples. This may be due, in part, to difficulty in pairing samples precisely.

3. ANALYSIS

3.1. Methods

About 100 mL of water samples are collected and stabilized with sodium thoisulfate and formic acid. Samples collected from the beginning of the study (January 2006) to August 15, 2006 were stored frozen before being shipped for analysis. Upon receipt, samples were frozen until analysis. Samples collected after August 15, 2006 were shipped in a cooler and upon receipt stored in the refrigerator and analyzed with 30 days (with minimal exceptions).

Stability of the analytes in raw and finished water under the frozen conditions of packaging and shipping was tested for three sites. Stability of the analytes under refrigerated conditions of packaging and shipping was tested for Aurora and Bradenton sites. Field spikes were prepared by fortifying a mixture of iprodione, isoiprodione, 3,5-

DCA and vinclozolin to three 100 mL of finished water at 0.25 ppb and three 100 mL at 0.5 ppb of each analyte. Six raw water samples were fortified at 0.25 ppb and 0.50 ppb in the same way. A study to determine the freezer storage stability of the analytes in raw and finished water is ongoing.

Sample analysis was conducted using the method of analysis entitled "Method of analysis for the determination of residues of iprodione and its metabolites, isoiprodione and 3,5 –dichloroaniline plus vinclozolin". The method was modified to detect N-3,5-dichlorophenyl formamide (3,5 DCPF). These methods and corresponding independent laboratory validation studies (not submitted) will need to be reviewed by the Agency.

3.2. Recoveries

Field spikes were conducted at the three sites for frozen samples. Control raw and finished samples were spiked in the field with 0.25 and 0.5 ppb of iprodione, isoiprodione, 3,5-DCA and vinclozolin each. The average recoveries of iprodione and vinclozolin were between 70-120% for all sample types and spike levels. For isoiprodione recoveries were between 70-120% at the Bradenton, Fl and Rahway, NJ sites. The average recovery of isoiprodione collected from the Aurora, IL site were 84 ±1.5% and 74 ± 0.6% when fortified at 0.25 ppb and 77 ±1.5% and 69 ±0.6% when fortified at 0.5 ppb.

The study authors reported unacceptably low recoveries of 3,5 DCA in the field spike samples for frozen samples. This was due, they propose, to the conversion of 3,5-DCA to N-3,5-dichlorophenyl formamide (3,5 DCPF) in the presence of formic acid, which was added to the samples to stabilize the other analytes. This conversion was accelerated when the samples were frozen. This discovery precipitated an amendment to the protocol that called for the samples to be refrigerated after collection and not frozen for samples collected starting August 15, 2006 and the addition of 3,5-DCFP to the analytical method for frozen samples. The recoveries of 3,5-DCA in the frozen samples were low ranging from on average 3 to 27%. Combining 3,5 DCA with the 3,5 DCFP improved the recoveries to 88 ± 20% and 71 ±1 1% when fortified at 0.25 ppb and 71 ± 3.4% and 62 ± 2.3% when fortified at 0.5 ppb (Rahway, NJ site only reported). The study authors did not indicate whether the sampling would be continued for more than three years given the issues with the first eight months of analyses.

Field spikes for refrigerated samples were conducted at the Aurora, IL and Bradenton, FL sites. Control raw and finished samples were spiked in the field with 0.25 and 0.5 ppb of iprodione, isoiprodione, 3,5-DCA and vinclozolin each. The average recoveries for iprodione, 3,5-DCA and vinclozolin ranged from 70 to 110% for all sample types and spike levels. Recoveries of isoiprodione from Bradenton, FL ranged from 70 to 110%, but the recoveries from Aurora, IL spikes were 68 ± 3.2% and 56 ± 1.5% fortified at 0.25 ppb for raw and finished water, respectively, and 67 ± 1.0% and 60 ± 0.6 fortified at 0.5 ppb for raw and finished water, respectively.

3.3. Iprodione Usage during First Year of Study

Usage data for the first year of monitoring data (2006) was estimated based on iprodione sales information summarized at the zip code level. The estimated use

information is for non-agricultural products only which are used almost exclusively on golf courses and nurseries. The proprietary usage data (based on sales) suggests that use intensity (lbs ai of iprodione/ acre of total watershed) for 2006 decreased by 35, 41 and 50% for the FL, IL and NJ sites, respectively, compared to 2004, the year of data used to select the sites. Estimated use intensity for 2006 was over an order of magnitude greater for Rahway, NJ compared to the other two sites which were characterized by similar estimates of use intensity. Iprodione use is likely a function of fungal pressure which can vary from year to year. Longer term trends can not be inferred from the three years worth of data. However, the significant decrease in use intensity compared to the time of site selection is a cause of concern. It is not clear if these sites still represent the watersheds of highest use intensity in the three regions.

Actual use information (how much was used, when and where), the percent of acres of golf courses (potential use sites) in the watersheds and the actual percent of sites treated have not been reported. This type of information would provide necessary context needed to interpret the monitoring results. It would also allow meaningful comparison of monitoring results with modeled results.

3.4. Weather Data

Average daily maximum and minimum temperature and precipitation data was reported for the three sites (appendix E). The data were also summarized on a monthly basis and compared to 30-year averages. On an annual basis, precipitation during 2006 at the 3 sites was within -2 to +15% of the 30-year average. On a monthly basis, the precipitation ranged from -160 to +66% of the 30-year average monthly values. Without temporally explicit usage information it is not possible to correlate precipitation with applications of iprodione.

4. ANALYTICAL RESULTS

Water from three community water treatment facilities located in Bradenton, FL, Aurora, IL and Rahway, NJ is being monitored for iprodione residues. Both raw and finished drinking water samples were collected at weekly intervals. Finished water samples were only analyzed when residues were detected in the corresponding pre-treatment samples. Therefore, although paired samples were taken, the majority of the analysis is limited to the raw samples.

Iprodione residues were not detected in raw water samples at the Bradenton, FL and Aurora IL sites at any sampling point during the first year of monitoring. Finished water samples were not analyzed.

Iprodione was detected at the Rahway, NJ site above the method detection limit (MDL) on 5 sampling occasions. Iprodione was detected at a maximum concentration of 0.565 (raw) and 0.124 (finished) ppb on March 5, 2007. Viclozolin was also detected at the Rahway, NJ site above MDL on 5 sampling occasions. Vinclozolin was detected at a maximum concentration of 0.216 ppb in the raw water and was not detected in the finished sample on September 6, 2006. 3,5-DCA and isoiprodione were not detected at any site at any sampling occasion. Samples with iprodione or vinclozolin above the MDL are summarized in Table 1.

Table 1. Results of samples at the Rahway, NJ site that had levels of iprodione or vinclozolin above MDL[1].			
Sample Date	**Water Type**	**Iprodione (ppb)**	**Vinclozolin (ppb)**
06/07/06	Raw	0.034 (<LOQ[2])	ND[3]
06/28/06	Raw	ND	0.029 (<LOQ)
09/06/06	Raw	ND	0.216
09/12/06	Raw	ND	0.037 (<LOQ)
09/19/06	Raw	ND	0.048 (<LOQ)
10/10/06	Raw	0.062	ND
10/24/06	Raw	0.038 (<LOQ)	ND
10/31/06	Raw	0.031 (<LOQ)	ND
03/05/07	Raw	0.565	ND
03/05/07	Finished	0.124	ND

[1] Method detection limit (MDL) = 0.025 ppb
[2] Limit of quantitation (LOQ) = 0.05 ppb
[3] ND = non-detect
Note: If more than one sample was analyzed or processed for a sampling date, an average is shown.

5. CONCLUSIONS AND UNCERTAINTIES

Iprodione residues were not detected in raw water samples at the Bradenton, FL and Aurora IL sites at any sampling point during the first year of monitoring. Iprodione was detected at the Rahway, NJ site above the method detection limit (MDL) on 5 sampling occasions at a maximum concentration of 0.565 (raw) and 0.124 (finished) ppb. Viclozolin was also detected at the Rahway, NJ site above MDL on 5 sampling occasions at a maximum concentration of 0.216 ppb. 3,5-DCA and isoiprodione were not detected at any site at any sampling occasion.

Usage data (based on sales) suggests that use intensity (lbs ai of iprodione/ acre of total watershed) for 2006 decreased by 35, 41 and 50% for the FL, IL and NJ sites, respectively, compared to 2004, the year of data used to select the sites. The significant decrease in use intensity compared to the time of site selection is a cause of concern. It is not clear if these sites still represent the watersheds of highest use intensity in the three regions. Ideally the monitoring study would capture years of higher use intensity at the study sites.

Actual use information (how much was used, when and where), the percent of acres of golf courses (potential use sites) in the watersheds and the actual percent of sites treated have not been reported. This type of information would provide necessary context needed to interpret the monitoring results. It would also allow meaningful comparison of monitoring results with modeled results.

The study authors reported unacceptably low recoveries of 3,5 DCA in the field spike samples for frozen samples. This discovery precipitated an amendment to the protocol that called for the samples to be refrigerated after collection and not frozen for samples collected starting August 15, 2006 and the addition of 3,5-DCFP to the analytical method for frozen samples. The analytical method and independent laboratory validation have not been submitted or reviewed. The study authors did not indicate whether the

sampling would be continued for more than three years given the issues with the first eight months of analyses.

REFERENCES

USEPA. 2006. Iprodione Monitoring Site Selection. DP 294254.