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ABSTRACT

This study is scientifically valid and generally meets Subdivision N Guidelines for the fulfillment of EPA data requirements on small-scale prospective groundwater studies and is therefore classified as acceptable. Laboratory studies indicated that metolachlor and its degradates were likely to be persistent and mobile in soil and were therefore considered to have the potential to leach to groundwater. A small-scale prospective groundwater study was completed by the registrant on s-metolachlor (CGA 77102) in order to evaluate the mobility of s-metolachlor in a vulnerable area used for corn production. The site selection process was documented in a separate study (*A Small-Scale Prospective Ground Water Monitoring Study for Herbicide S-Metolachlor (CGA-77102) at a Worst-Case Vulnerable Site in the Midwestern United States, Part A - Preliminary Site Selection*) attached to this study as Part A of Appendix I.

In addition, the registrant and EFED previously agreed that the submission of the PGW study could be used to meet the upgrade requirement for previously reviewed field dissipation studies on row crops (this agreement is documented most recently in a memorandum from EFED to Joanne Miller of Registration Division dated August 17, 2000). EFED has evaluated the analytical results of soil samples collected as part of this study in the context of this requirement. EFED has estimated a half life for soil dissipation from the study of 9.8 days ($r^2 = 0.96$). This value is at the low end of the range of half-lives estimated previously (terrestrial field dissipation half-lives ranged from 7 days to 292 days). However, the dissipation half live estimated from this PGW study data is clearly influenced by the movement of s-metolachlor vertically through the soil profile. A more thourough discussion of this evaluation is presented in the results section

The study was initiated at a site in Sherburne County, Minnesota which was selected based on surface topography (less than 2 to 3 percent slope), soil type vulnerable to leaching (Zimmerman loamy fine sand), low organic matter content (0.1 to 0.9 percent), no subsurface restrictive layers, and shallow depth to groundwater (approximately 20 to 24 feet). The detailed site characterization was documented in a separate study (*A Small-Scale Prospective Ground Water Monitoring Study for Herbicide S-Metolachlor (CGA-77102) at a Worst-Case Vulnerable Site in the Midwestern United States, Part B - Detailed Site Characterization Preliminary Interim Report*) attached to this study as Part B of Appendix I.

The site was instrumented with a network of observation wells, clustered groundwater monitoring wells (shallow well intersecting the water table and a deeper well), and clustered suction lysimeters (each cluster consisted of porous cup lysimeters at 3, 6, 9, and 13 feet below grade). The site was instrumented with eight well/lysimeter clusters. A single upgradient groundwater monitoring well (intercepting the water table) was installed at the Minnesota site. S-metolachlor was applied at the Minnesota site at a target rate of 2.67 lbs a.i./A in a single application and was ground applied with a boom sprayer on May 29, 1996.

The data from the small-scale prospective groundwater study indicate that s-metolachlor moved rapidly into pore water at the site but was only detected in a single shallow groundwater sample at 0.10 ppb (the limit of quantitation is 0.10 ppb) at 27 months after application and in a deep groundwater sample (also at 0.10 ppb) at 7 months after application. However, the degradates, metolachlor ESA and metolachlor OA, were both more mobile in the subsurface than the parent compound and both degradates migrated to groundwater. It is important to note that s-metolachlor was detected in the deepest lysimeter (13 feet below grade) at a maximum concentration of 0.5 ppb at 3 months after application. The data suggest that both degradates are very mobile and persistent in ground water and are likely to be found at concentrations exceeding the parent compound. This data suggests that the occurrence of metolachlor ESA and metolachlor OA are more likely to impact groundwater supplies than s-metolachlor.

MATERIALS AND METHODS

Site Instrumentation

The test plot is approximately 300 feet by 300 feet with a 50 foot buffer strip surrounding the plot. A control plot measuring 60 feet by 60 feet is located no closer than 75 feet of the test plot. The site was instrumented with eight lysimeter/well clusters with a ninth cluster located within the control plot. Each cluster in the test plot consisted of four lysimeters at 3, 6, 9, and 13 feet below ground surface (bgs). The control plot cluster consisted of two lysimeters and one well. Finally, a weather station and removable irrigation system were installed at the site. The irrigation well was installed away from the site and piped to the site to avoid cross-contamination from the test substance application.

Site Characterization

Preliminary site characterization identified that the site is dominated by Zimmerman (Alfic Udipsamment) loamy fine sand with low organic matter (0.1 to 0.9%). Detailed site characterization confirmed that the trial site is composed of predominantly fine grained sand to a depth of between 14 to 17 feet below grade with an underlying layer of sand and gravel. Installation of observation wells confirmed that the depth to the top of the water table at the site varied from 20 to 24 feet below grade. Data collected from the saturated zone indicate the groundwater flow direction below the site is to the south and southeast with a hydraulic gradient ranging from 0.0002 to 0.0009 foot per foot. Slug tests conducted at the site indicate hydraulic conductivities in the saturated zone ranged from 490 to 2,150 feet per day in the shallow wells.

Test Substance Application

S-metolachlor was applied at 2.67 lbs ai/acre using a Willmar Air Ride 745 variable rate sprayer with a 60 foot boom with 36 nozzles held at 3 feet above the ground surface. Plastic covers were applied to each monitoring well and lysimeter to prevent pesticide entering directly into the subsurface. In addition to s-metolachlor, a tracer of potassium bromide (KBr) was applied to the site at approximately 99.8 lbs/acre.

The application rate was confirmed using three techniques. Twenty application pans consisting of 9 inch by 13 inch by 2.25 inch tall aluminum pans were placed randomly across the site. Second, a total of six tank mix samples were collected pre and post application. Third, soil samples were collected immediately after application of s-metolachlor from 0 to 6 inches bgs.

Analytical Methods

Pore water and groundwater samples were analyzed for bromide ion using Syngenta Method AG-656. The limit of detection for bromide ion was 0.2 ppm. Syngenta Method AG-682 was used to analyze water samples (soil pore water and groundwater) for s-metolachlor (CGA-77102), metolachlor ESA (CGA-354743), metolachlor OA (CGA-51202), CGA-37735, CGA-67125, and CGA-41638. The limit of quantitation for all analytes was 0.1 ppb. Soil samples were analyzed using Syngenta Method AG-640. The limit of quantitation for soil samples was 10.0 ppb.

Transit and Storage Stability

In order to evaluate the stability of each analyte during transport and storage, duplicate control (upgradient) samples were fortified in the field and shipped to the analytical laboratory and stored in a refrigerator. The samples were stored in the refrigerator for 1239 days. The samples were subsequently analyzed for s-metolachlor and the five targeted degradates. The recoveries ranged as follows: 85% to 97% for s-metolachlor, 95% to 102% for metolachlor OA,89% to 104% for metolachlor ESA, 69% to 93% for CGA-37735, 67% to 87% for CGA-41638, and 84% to 113% for CGA-67125. The results are tabulated in Table 11 of Appendix VI (page 453 of 670 in study). The maximum storage time appears to be 172 days for water samples (lysimeter and well samples). No storage stability data was reported for the soil samples collected as part of the assessment.

RESULTS/DISCUSSION

Precipitation and Irrigation

The test plot was instrumented with a sprinkler irrigation system shortly after application of s-metolachlor. The first irrigation event occurred on May 30, 1996 one day after application. The system was removed annually in the fall and reinstalled in the spring. The target cumulative total water input for the study (rainfall plus irrigation) was 120 percent of the 30-year monthly average. The 30-year monthly average was calculated using data from the three nearest NOAA weather stations. Between May 1996 and August 1999 at total of 27.58 inches of irrigation water was applied which when combined with the 67.63 inches of natural precipitation from June 1996 through September 1999 exceeded the target total water input. However, in 2000 the total water input did not exceed the 120 percent target likely due to the removal of the irrigation system. Pan evaporation data was not reported in this study to provide a site water balance. However, the movement of the bromide tracer through the soil profile and into groundwater indicates sufficient water was applied. Table 8 (page 60) summarizes the monthly water totals at the site from 1996 through 1999. Table 9 (page 61) presents the 2000 data estimated from the NOAA stations. Monthly precipitation data tabulated from the on-site weather station are summarized in Appendix VI.

Site Agronomics

The test site had been cropped with both corn and soybeans prior to 1989 but remained idle subsequently. No chemicals were applied to the site prior to 1995. The site was prepared for cultivation using standard local practices. The site was limed on May 9, 1996 (20 days prior to application) and both the control and test plots were tilled on May 22, 1996. Fertilizer was spread on June 13, 1996, were cultivated on July 4, 1996, and received a final fertilizer application on July 12, 1996. Weed control around well heads and lysimeters was performed manually and no chemicals were used to control weeds at the site. The site was seeded on June 4, 1997.

Analytical Results

Test substance application was verified through the analysis of 20 application devices (aluminum pans) placed across the test site and analyzed for s-metolachlor. The mean application rate was 88% of theoretical while the average procedural recovery (and standard deviation) was 101 % (11) for the four control pans fortified in the field. Analysis of tank mix samples (pre and post application) was 94.3% of theoretical.

No residues of CGA-37735, CGA-67125, and CGA-41636 were found in any samples and are not discussed further.

In general, s-metolachlor was not detected in any of the groundwater wells (s-metolachlor was detected once in ground water. Although a single detection does not indicate massive movement into ground water, it does suggest s-metolachlor can move through the soil into ground water). Metolachlor ESA was detected at a maximum concentration of 15.6 ppb in shallow groundwater and metolachlor OA was detected at a maximum concentration of 5.3 ppb in shallow groundwater at the Minnesota site. The analytical results of the study are presented in Appendix VI, Part D: Analytical Phase dated October 19, 2001 (Syngenta Report Number 656-95 Part D). The following discussion presents a more detailed summary of the findings.

Bromide tracer in suction lysimeter samples (soil pore water) reached a maximum at the 3 foot depth of 8.2 ppm at Event 5 (2 months post-treatment), at the 6 foot depth of 16.9 ppm on Event 6 (3 months post-treatment), at the 9 foot depth of 10.6 ppm at Event 8 (5 months post-treatment), and at the 13 foot depth of 7.9 ppm at Event 13 (10 months post-treatment). All bromide decreased to background concentrations (0.2 ppm) by Event 28 (26 months post-treatment). S-metolachlor was not detected at the 3 foot depth above the LOQ, reached a maximum concentration at the 6 foot depth of 0.6 ppb at Event 6 (3 months post-treatment), reached a maximum concentration at the 9 foot depth of 0.2 ppb at Event 7 (4 months post-treatment), and reached a maximum concentration at the 13 foot depth of 0.1 ppb at Event 5 (2 months post-treatment). S-metolachlor decreased to non detect (0.1 ppb) by Event 18 (15 months post-treatment). Metolachlor ESA reached a maximum concentration at the 3 foot depth of 16.3 ppb at Event 7 (4 months post-treatment), reached a maximum concentration at the 6 foot depth of 102.5 ppb at Event 8 (5 months post-treatment), reached a maximum concentration at the 9 foot depth of 48.9 ppb at Event 13 (10 months post-treatment), and reached a maximum concentration at the 13 foot depth of 40.6 ppb at Event 17 (14 months post-treatment). Metolachlor ESA decreased to concentrations just above the detection limit (0.1 ppb) as of Event 32 (36 months post-treatment). Metolachlor OA reached a maximum concentration at the 3 foot depth of 5.2 ppb at Event 5 (2 months post-treatment), reached a maximum concentration at the 6 foot depth of 61.5 ppb at Event 6 (3 months post-treatment), reached a maximum concentration at the 9 foot depth of 19.4 ppb at Event 14 (11 months post-treatment), and reached a maximum concentration at the 13 foot depth of 15.1 ppb at Event 17 (14 months post-treatment). Metolachlor OA has decreased to concentrations just above the detection limit (0.1 ppb) by Event 29 (27 months post-treatment).

Bromide was first detected in the shallow groundwater wells at 0.3 ppm at Event 7 (4 months post-treatment) and reached a maximum concentration of 2.9 ppm at Event 22 (19 months post-

treatment). S-metolachlor was detected once at 0.1 ppb at Event 29 (27 months post-treatment) in the shallow groundwater wells at the site. Metolachlor ESA was first detected in the shallow groundwater wells at 0.2 ppb at Event 8 (5 months post-treatment) and reached a maximum concentration of 15.6 ppb at Event 22 (19 months post-treatment). Metolachlor OA was first detected in the shallow groundwater wells at 0.2 ppb at Event 8 (5 months post-treatment) and reached a maximum concentrations of 5.3 ppb at Event 17 (14 months post-treatment). Lower concentrations were detected in the deeper wells.

The data from the small-scale prospective groundwater study indicate that s-metolachlor moved rapidly in soil pore water at the site but was only detected in a single shallow groundwater sample at 0.10 ppb (the limit of quantitation is 0.10 ppb) at 27 months after application and in a deep groundwater sample (also at 0.10 ppb) at 7 months after application. However, the degradates, metolachlor ESA and metolachlor OA, were both more mobile in the subsurface than the parent compound and both degradates migrated to groundwater. It is important to note that s-metolachlor was detected in the deepest lysimeter (13 feet below grade) at a maximum concentration of 0.5 ppb at 3 months after application. The data suggest that both degradates are very mobile and persistent in drinking water ground water and are likely to be found at concentrations exceeding the parent compound. This data suggests that the occurrence of metolachlor ESA and metolachlor OA are more likely to impact groundwater supplies than s-metolachlor.

The registrant and EFED previously agreed that the submission of the PGW study could be used to meet the upgrade requirement for previously reviewed (supplemental) field dissipation studies on row crops (this agreement is documented most recently in a memorandum from EFED to Joanne Miller of Registration Division dated August 17, 2000). EFED has evaluated the analytical results of soil samples collected as part of this study in the context of this requirement. The registrant collected soil data from the upper 24 inches of the site through day 28 (Event 4). S-metolachlor was detected in soil at a maximum concentration of 1.3 ppm on day 0 in the 0-6 inch samples, 0.09 ppm on day 3 in the 6 to 12 inch samples, and 0.03 ppm in the 12 to 24 inch sample on day 28. EFED has estimated a half life for soil dissipation from the study of 9.8 days (rate constant = -0.0704 with a standard error of 0.007932, $r^2 = 0.96$, and a p-value for the F-test of 0.003) using linear regression on log transformed data (sum of mean concentrations for each depth). This value is at the low end of the range of half-lives estimated previously (terrestrial field dissipation half-lives ranged from 7 days to 292 days). However, the dissipation half live estimated from this PGW study data is clearly influenced by the movement of s-metolachlor vertically through the soil profile.

DEFICIENCIES/DEVIATIONS

1. The study authors note that the irrigation system was removed from the site annually in the fall and reinstalled in the spring. In 1999 and 2000 the irrigation system was not reinstalled for the growing seasons. No explanation for this is given. This fact should not materially affect the results of this study.

2. The study authors note that the weather station installed at the initiation of the study was removed from the site in 2000 at the direction of the study director. No explanation for

this is given. Also, the study author reports that weather data from this period was supplemented with NOAA data from three nearby by stations (averaged across all three). However, the report notes this information was not used. This fact should not materially affect the results of this study.

3. Procedural recovery values for s-metolachlor and the five degradates were reported in Table 9 of Appendix VI (page 444 of 670). However, analytical results of water samples were not corrected for recoveries. Procedural recoveries (plus standard deviations) were between 82.9% (9.8) and 96.8% (16.2) for s-metolachlor, between 87.5% (8.9) and 94.5% (9.2) for metolachlor ESA, and between 92.2% (7.0) and 99.0% (11.0) for metolachlor OA.

4. Storage stability data was reported for the water samples analyzed. The data indicate that in water s-metolachlor, metolachlor ESA, and metolachlor OA are stable (>90% recovery) up to 1239 days. No soil data was reported with this study. However, the registrant subsequently submitted soil storage stability data from a turf field dissipation study (MRID 45848001) which indicates that s-metolachlor is stable in frozen storage for up to 370 days but showed a decline in recoveries at 546 days and 756 days (postulated by the registrant to be due to unspecified method problems). Soil samples from the PGW study were stored between 84 days and 182 days.