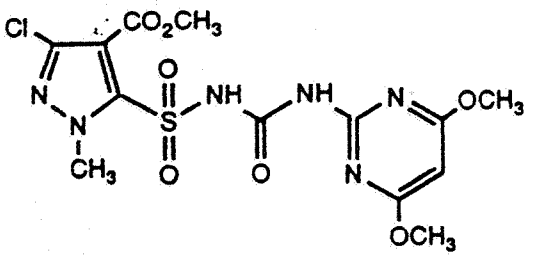
1. CHEMICAL:
Common Name: Mon 12000

Chemical Name: 3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid

Type of product: Herbicide

Chemical Structure:



Physical/Chemical Properties
molecular weight: 434.8
Color: Light white powder
Aqueous solubility: pH 5@ 20C= 15 ppm
pH 7@ 20C= 1630 ppm
pH 9@ 20C= 7470 ppm
Vapor pressure: 3.5 X 10^{-12} mmHg (25C)
Dissociation constant: Ka= 3.61 X 10^{-4} (22.4C); pka= 3.5
Octanol/Water Partition Coefficient (23 C± 2)
pH 5 log Kow = 1.67
pH 7 log Kow = -0.0186
pH 9 log Kow = -0.542
Density: 1.618 gmL^{-1} (25C)
pH (25C; 1% w/v slurry): 4.11

REVIEWED BY:

Kevin L. Poff, Chemist
Environmental Chemistry Review Section #3 Date:
Environmental Fate and Groundwater Branch/EFED

APPROVED BY:

Akiva Abramovitch, Ph.D., Chemist
Environmental Chemistry Review Section #3 Date:
Environmental Fate and Groundwater Branch/EFED

GENERAL ENVIRONMENTAL FATE ASSESSMENT

The laboratory data as well as the terrestrial field/lysimeter data indicate that degradation half-lives of MON 12000 is temperature as well as pH dependent. MON 12000 applied in a cooler, milder climate under acidic soil conditions could persist at undetectable limits for some time. If the organic matter content of the soil is low, or the soil is permeable, a heavy rainfall event could cause parent MON 12000 to move to ground water particularly to a shallow aquifer. Likewise, in poorly drainable soils heavy rainfall events after MON 12000 application may cause

transport to surface waters by dissolved run-off. Aerobic soil metabolism and hydrolysis data indicate that under certain conditions MON 12000 degrades fairly rapidly in the soil and water and therefore the potential for leaching of parent MON 12000 under normal use conditions would be somewhat reduced. If the compound were to reach ground or surface waters, it is likely that it would not persist for a long time because MON 12000 hydrolyzes with a half-life of less than 28 days at pH 5-9. The aerobic soil metabolism and hydrolysis of MON 12000 results in 2 major degradates, aminopyrimidine and the 3-chlorosulfonamide ester. These degradates can be considered resistant to further degradation in soil and water. These would be present in the field at less than ppm concentrations but may have a high potential to move to ground water because of their persistence and mobility characteristics.

The registrant has commented (MRID #42976301, page 2) that the major degradates from abiotic hydrolysis, 3-chlorosulfonamide ester, 3-chlorosulfonamide acid, rearrangement ester, or aminopyrimidine have not demonstrated herbicidal activity. In addition, ecotoxicological data summaries have been submitted to the branch (see attached) verifying the fact.

In general, analytical methods were capable of detecting less than 5% of herbicide levels in soil on the day of application with the lower limit of detection (LLOD) at 2 ppb and capabilities for measuring 0.5 ppb in water. A lower limit of method validation (LLMV) of 5 ppb was established for 3-chlorosulfonamide ester and aminopyrimidine. In the radiolabelled field studies the LLMV was 3 ppb for MON 12000 and its metabolites.

a. Abiotic hydrolysis is an important degradation process. Hydrolysis rate is pH-dependent (pH 5, 24-28.9 days; pH 7, 13.9-14.9 days; pH 9, 17.6-19.5 hours). However, the mechanism of degradation differs considerably at pH 5 and pH 9. At pH 5, cleavage of the sulfonylurea bridge is the mode of degradation which leads to the formation of degradates containing a single ring (3-chlorosulfonamide ester, and aminopyrimidine). At pH 9, elimination of -SO_2 and -CONH- from the bridge followed by re-bridging via the remaining -NH- group is the major degradation mechanism leading to the formation of the major degradate "rearrangement ester." At pH 7 both mechanisms appear to operate. The formation of the "rearrangement ester" appears to be more favored under homogeneous media conditions (aqueous solutions) than in heterogeneous media (soils), which may explain in part why only small amounts of the "rearrangement ester" are found in alkaline soils.

b. Photodegradation in water and on soil do not contribute significantly to the degradation of NON 12000.

c. Biodegradation under aerobic conditions is an important degradation process for MON 12000. Half-lives in a Sable silty clay loam soil and in Sarpy sandy loam soils were reported as 13.7-18.3 days and 8.3-13.6 days, respectively. Extensive mineralization was found in the alkaline (pH 8.0) Sarpy soil. In

both soils, the bridge-cleavage degradates 3-chlorosulfonamide ester and acid (particularly in the acidic pH 5.8 Sable soil) and the aminopyrimidine degradates were found, but were present at a higher and significant concentration in the Sable soil. The amount of 3-chlorosulfonamide acid and aminopyrimidine increased with time in the acidic Sable soil. A distinct "MON 12000 Guanidine" degradate was identified in the Sarpy soil.

Soil data from the rotational crop (MRID #'s 421494412, #42396204) study (165-1) indicated a half-life of 23 days in Elder sandy loam soil.

d. Parent MON 12000 and the degradates 3-chlorosulfonamide acid and 3-chlorosulfonamide ester were very mobile in the soils studied. MON 12000 gave (K_d)'s ranging from 0.32 (Spinks loamy sand) to 3.56 (Sable silty clay loam); K_{oc} values were less than 200. (K_d) values for 3-chlorosulfonamide acid ranged from 0.02 (Drummer silt loam) to 0.22 (Sable silty clay loam), however due to the extremely low adsorption tendency the data were not statistically reliable. K_{oc} values were less than 10. (K_d) values for 3-chlorosulfonamide ester were 0.70 (Spinks loamy sand), 0.80 (Sarpy sandy loam), and 2.98 (Drummer silt loam). The K_{oc} values were below 350. Although aminopyrimidine is less mobile, its mobility is dependent on the type of soil. (K_d) values for aminopyrimidine gave an indication that it was the least mobile of the degradates and were 32.23 (Sable soil), 11.54 (Drummer soil), 1.92 (Sarpy soil), 2.59 (Spinks soil). The K_{oc} values in the above soils were 9279, 1042, 399 and 260 respectively. Refer to the specific DER (MRID #42139411, EFGWB #92-0437,-1202, 2/25/93) for results.

e. Terrestrial Field Dissipation Studies indicate Parent MON 12000 and its degradates are relatively mobile. However, the studies also indicate MON 12000 and its degradates have low to moderate persistence in water and soils reducing the potential for MON 12000 to migrate to ground water under normal use conditions.

f. The EFGWB believes that parent MON 12000 does not have the potential to accumulate in fish (high water solubility/rapid degradation in water; low octanol/water partition coefficient). The major degradates 3-chlorosulfonamide acid, 3-chlorosulfonamide ester and aminopyrimidine are not likely to concentrate in fish due to their high solubility in water (2.3×10^5 ppm, 860 ppm and 6.5×10^3 ppm, respectively). The estimated octanol/water partition coefficient for aminopyrimidine (25C) is $\log P_{o/w} = 0.95$.

g. Based on the low vapor pressure of parent MON 12000 (3.5×10^{-12} mmHg @ 25C), direct volatilization from soils will not be an important dissipation mechanism.

GROUND WATER ASSESSMENT

In radiolabelled "pipe" studies conducted in the field, halosulfuron half-lives were recalculated because the registrant's calculations of half-lives were inadequately justified. First

order half-lives for halosulfuron dissipation in the summer and early fall were similar for each of four treatments at each site and analysis of variance revealed that there was no significant difference between treatments. Halosulfuron had an overall half-life of 56 days at the Iowa site (range of 44 to 81 days) and 22 days at the North Carolina site (range of 15 to 22 days). The registrant calculated half-lives were 7 to 86 days at Iowa and 4 to 12 days at North Carolina. A full statistical analysis and justification for our recalculation of these half-lives is contained in a separate EFGWB review of modeling of halosulfuron leaching potential by the registrant (DP Barcode 196912).

The persistence and mobility of halosulfuron appears to vary greatly over the use area. Field dissipation half-lives based on loss of the pesticide from the upper six inches of soil varied from 4 to 81 days at nine sites (six bare-ground and three turf sites) and aerobic soil degradation half-lives were 11 and 16 days in two soils in laboratory studies (Tables 3 and 4). The median soil half-life was 20 days. Soil organic carbon partition coefficients for halosulfuron parent were 31 to 199 in four soils, the median value was 104. If the median mobility and persistence values in these studies are representative of the behavior of halosulfuron in the majority of the prospective use area, then halosulfuron would only have a very modest leaching potential in the majority of the use area. However, halosulfuron clearly can be extremely mobile and persist for several months in at least some soils under some weather conditions. Furthermore, field dissipation half-lives may underestimate persistence of pesticides because some loss or apparent loss of pesticide from the treated zone of soil may be by mechanisms other than degradation (leaching, volatilization, sorption, runoff, and lateral movement).

The presence of an abiotic hydrolysis mechanism over the entire range of environmental hydronium ion concentrations (pH 5 to 9) suggests that halosulfuron, even if it does leach to ground water may rapidly degrade there. However, the available data show halosulfuron to be much more persistent in a variety of soils than it was in sterile aqueous solution. It is entirely possible that in many ground-water matrices halosulfuron may be more persistent than predicted from the sterile hydrolysis study. Therefore, while the possibility of rapid hydrolysis in ground water exists, we cannot assume this to be the case without further evidence.

The submitted data do not clearly demonstrate any relationship between gross soil properties (pH and percent organic matter) and the persistence of halosulfuron. Therefore, other than a general assumption that leaching to ground water is more likely to occur in soils where the sorptive capacity is low and there is a shallow depth to ground water, we have no basis to identify what the problem areas for halosulfuron use might be.

The major environmental concern appears to be for effects of halosulfuron parent on non-target plants. For example, a 25% weight reduction in lettuce seedling dry weight (EC25) results

after an application of only 0.00002 lb ai/A of halosulfuron, such an exposure level could be achieved by irrigation with ground water containing only 0.03 ppb of halosulfuron (see separate EFGWB review of the registrant's modeling of halosulfuron leaching potential, DP Barcode 196912). Even if only a small fraction of halosulfuron from normal applications leaches to ground water, it is possible that residues in ground water could reach potentially phytotoxic levels. The registrant contends that halosulfuron leaching potential will be insignificant over the entire use area. Therefore, the following is recommended:

> A small-scale prospective ground-water monitoring study at a site with highly vulnerable ground water. This site should have permeable soils and shallow ground water (<20 foot depth). A site must be selected where halosulfuron has a half-life of greater than 40 days under the conditions of an aerobic soil metabolism study and a Koc of less than 100. Preliminary soil metabolism studies and adsorption / desorption studies on candidate soils may be necessary to confirm this. The soil organic matter content should be less than 2% and preferably less than 1%. Soil texture should be sand, loamy sand, or sandy loam with less than 15% clay throughout the profile. The registrant should discuss the protocol and site selection with the Agency before initiating this study.

Since there appears to be little <u>immediate</u> risk of adverse effects from ground-water residues, we suggest that it is not necessary to delay registration pending the results of this study.

<u>SURFACE WATER ASSESSMENT</u>

Substantial fractions of applied MON 12000 could be available for runoff for several days to weeks after application (aerobic soil metabolism half-lives of 8.3 to 18.3 days; terrestrial field dissipation half-lives of 6-34 days). Although the ionic nature of MON 12000 makes its soil/water partitioning pH dependent, its generally low soil/water partitioning (K_{oc}s < 200) indicates that runoff will occur primarily by dissolution into runoff water.

Although it is not susceptible to volatilization from water (1.34×10^{-10} atm*l/mol at pH 5 to 2.68×10^{-13} atm*L/mol) or to direct photolysis in water, the pH dependent intermediate to high susceptibility of MON 12000 to abiotic hydrolysis (24-28.9 days at pH 5 to 17.6-19.5 hours at pH 9) and to aerobic degradation in soil coupled with its intermediate suscetibility to anaerobic aquatic degradation (half-lives of 18.8 to 27.2 days) indicates that it will at most be only moderately persistent even in acidic surface waters with long hydrological residence times. In surface waters with shorter hydrological residence times (where flow can also contribute to its dissipation from the system), and in neutral to alkaline waters, its persistence will be relatively low. Its low soil/water partitioning indicates that most of it will remain dissolved in the water column. Its low pH dependent octanol/water

partition coefficients (log K_{ow} = -0.542 at pH 9 to 1.67 at pH 5) indicate that its bioconcentration potential is negligible.

In response to a request from EEB, EFGWB generated conservative EEECs in a 1 ha, 6 meter deep pond receiving drainage from an adjacent 10 ha field for MON 12000 applications to corn, sorghum, and turf. One in 10 year maximum EECs varied from a 90 day average of 0.26 ug/L for application to sorghum to an intial EEC of 7.95 ug/L for application to corn (see EFGWB action 204189 dated 8/3/94 for a complte table and graphical distributions of the EECs).

If a decision is made to generate a labeling surface water advisory for MON 12000, EFGWB recommends the following wording:

Under some conditions, MON 12000 may also have a high potential for runoff into surface water (primarily via dissolution in runoff water), for several weeks post-application. These include poorly draining or wet soils with readily visible slopes toward adjacent surface waters, frequently flooded areas, areas over-laying extremely shallow ground water, areas with in-field canals or ditches that drain to surface water, areas not separated from adjacent surface waters with vegetated filter strips, and areas over-laying tile drainage systems that drain to surface water.

RECOMMENDATIONS:

1) Inform the registrant of the status of data requirements in attached TABLE A, ie., that studies MRID #42661409 (aqueous photolysis; 161-2), MRID #42661410 (soil photolysis, 161-3), MRID #42661411 (anaerobic aquatic metabolism 162-3) are acceptable and completely satisfy those data requirements. Lysimeter studies MRID #42661414 and MRID #42976303 are acceptable and may be used as supplemental data to the terrestrial field (164-1) studies. In addition, the Terrestrial Field Dissipation studies MRID #42976302, MRID #42661413 and MRID #42976304 are acceptable and satisfy the terrestrial field dissipation data requirement for MON 12000. Generally the EFGWB requires two field sites per formulation, however the information gained by additional studies with the granular formulation would not likely further clarify the environmental fate of MON 12000 and its degradates. The Laboratory Volatility (163-2) and Bioaccumulation in Fish (165-4) data requirements were waived in a previous review for a EUP (EFGWB #92-0437,-1202, 2/25/93).

The Ground Water Technology Section of the EFGWB recommends that the label for MON 12000 should be modified to contain a ground-water advisory using the following language:

"This chemical demonstrates the properties and characteristics associated with chemicals detected in ground water. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination."

In addition, the Ground Water Technology Section is recommending that the registrant complete a small-scale prospective (166-1) ground water monitoring study because of the mobility/persistency characteristics (see ground water assessment above) of parent MON 12000. A small-scale prospective ground-water monitoring study at a site with highly vulnerable ground water. This site should have permeable soils and shallow ground water (<20 foot depth). A site must be selected where halosulfuron has a half-life of greater than 40 days under the conditions of an aerobic soil metabolism study and a Koc of less than 100. Preliminary soil metabolism studies and adsorption / desorption studies on candidate soils may be necessary to confirm this. The soil organic matter content should be less than 2% and preferably less than 1%. Soil texture should be sand, loamy sand, or sandy loam with less than 15% clay throughout the profile. The registrant should discuss the protocol and site selection with the Agency before initiating this study.

Since there appears to be little immediate risk of adverse effects from ground-water residues, we suggest that it is not necessary to delay registration pending the results of this study.

2) The registrant should address the EFGWB's concerns/comments expressed in a previous (February 25, 1993) EUP review for MON 12000 (see also the attached TABLE A). Specifically, concerns/comments expressed in the specific DER's and TABLE A sections for the 161-1, 162-1 studies (see attached TABLE A). At the time of the EUP review the EFGWB also requested the registrant to submit batch-equilibrium adsorption/desorption data for the degradate MON 12000-guanidine. The submitted field data adequately defined the mobility of MON-12000 guanidine, therefore the batch-equilibrium adsorption/ desorption (163-1) study is no longer required.

3) RD and HED should be made aware that MON 12000 and its hydrolysis products 3-chlorosulfonamide ester, 3-chlorosulfonamide acid, and aminopyrimidine are mobile under certain conditions (cooler, milder) in some soils (low organic matter) and thus have the potential to leach to ground water and/or be transported to surface waters by dissolved run-off. Also, these degradates appear to be persistent and may be of toxicological and ecotoxicological concerns. To the best to our knowledge only phytotoxicity data are available on the degradates at this time.

The EFGWB has reviewed the Environmental Chemistry Method Evaluation by Bay St. Louis on MON 12000 (see attached) in water using the Monsanto Company analytical method, "Analytical Method for the Determination of MON 12000 in Water Matrices". The conclusions are that the method performed well and supports the registrants claim that MON 12000 can be quantified in water at levels at or above 0.5 ppb. The methods estimated Method Detection Limit (MDL) was 0.15 ppb and Limit of Quantitation (LOQ) was 0.5 ppb.

SUMMARY OF ENVIRONMENTAL FATE DATA

The hydrolysis of MON 12000 (Halosulfuron) is pH dependent. At pH 5 Halosulfuron degraded with a half-life of 28.9 and 24.8 days for the pyrimidine- and pyrazole- labeled compound, respectively. The degradates are formed from the cleavage of the sulfonylurea bridge and include 3-chlorosulfonamide ester, aminopyrimidine, and small amounts of 3-chlorosulfonamide acid. At pH 7 the degradation half-life decreased to 13.9 and 14.9 days for the pyrimidine- and pyrazole- label respectively. The degradates formed from the elimination of $-SO_2$ and -CONH- from the sulfonylurea bridge followed by rebridging to the remaining -NH- group to form the "rearrangement ester" degradate, and 3-chlorosulfonamide ester; amionpyrimidine was also observed at pH 7. At pH 9 the half-life decreased to 17.6 and 19.5 hours for the pyrimidine- and pyrazole- labels respectively. The main degradate is the rearrangement ester with small amounts of 3-chlorosulfonamide ester also observed.

Photolysis was not a major degradation pathway for parent Halosulfuron. Hydrolysis controlled the degradation process. Aqueous photolysis at pH 5 yielded half-lives of 23.8 days and 29.5 days for the irradiated and dark controls respectively. The major degradates identified in both solutions were 3-chlorosulfonamide ester and aminopyrimidine. Halosulfuron irradiated on a Sable silt loam yielded a half-life of 16.2 days as compared to 8 days in the dark control. The degradates in the irradiated and dark control were hydrolysis products 3-chlorosulfonamide ester and aminopyrimidine.

Aerobic soil metabolism studies indicated Halosulfuron degrades at variable rates depending upon soil types. The metabolites/degradates that were observed in two separate soils during the 1-year study were 3-chlorosulfonamide ester, 3-chlorosulfonamide acid, aminopyrimidine, MON 12000 acid, MON 12000 guanidine, MON 12000 rearrangement ester, and $^{14}CO_2$ (as well as the rearrangement acid and MON 12000 desmethyl; which were <10% of applied). In a Sable soil (silty clay loam; pH 5.8) the half-life of parent was 13.7 and 18.3 days (pyrazole and pyrimidine labels respectively) and 8.3 to 13.6 days (pyrazole and pyrimidine labels respectively) in Sarpy soil (sandy loam; pH 8.0). In the Sable soil the sulfonylurea bridge was cleaved generating aminopyrimidine which reached a maximum concentration of 27% of applied by day 364 and 3-chlorosulfonamide ester which reached a maximum of 29% of applied by day 56 then decreased to 12.7% of applied by day 364. 3-chlorosulfonamide ester was then hydrolyzed to 3-chlorosulfonamide acid which reached a maximum concentration of 32.1% by day 364. $^{14}CO_2$ accounted for 9.21% and 6.52% of applied for the pyrazole and pyrimidine labeled MON 12000 in the sable soil. The amount of unextractable residues increased with time and were the highest after 1 year for the sable soil (54.6%, pyrimidine label). In the Sarpy soil the major degradates were the bridge-cleavage products aminopyrimidine, 3-chlorosulfonamide ester, 3-chlorosulfonamide acid as in the acidic Sable soil; MON 12000 acid

(formed from hydrolysis of the methyl ester of MON 12000) and the rearrangement ester/acid which all reached a maximum and then declined. MON 12000 guanidine reaches a maximum of 15% of applied by day 168 and then decreased to 12.6% of applied by day 364.

Anaerobic aquatic metabolism showed that hydrolysis appears to predominate the route of degradation under aquatic conditions given the half-lives and the nature of the degradates. The majority of the radioactivity was associated with the pond water. Reported half-lives ranged 18.8 to 27.2 days in a clay loam soil (pH 7). 3-chlorosulfonamide ester was the major degradate in the pyrazole labeled MON 12000 at 2.4% of applied at day 0, increased to 26.8% at day 14, was at 49.9% month 1, then reached a maximum of 91.5% at month 6 and remained relatively constant through month 12. The rearrangement ester was present at a maximum average of 1.5% at month 4 and was detected sporadically through month 12. Aminopyrimidine was the major degradate in the pyrimidine labeled MON 12000 at 0.6% (individual sample) of applied at day 0, increased to 10.3% at day 14, was at 39.1% at month 1, then reached a maximum of 77.8% at month 4, then decreased to 46.3% at month 12. MON 12000 acid was detected only twice in separate samples at month 1 and month 6 at 4.2 and 12.0% respectively. The rearrangement ester was detected at a maximum average of 7.1% at month 3 and decreased to an average of 1.4% of applied by month 12.

Batch equilibrium studies give a strong indication that parent MON 12000, and its degradates 3-chlorosulfonamide acid, 3-chlorosulfonamide ester were very mobile. Freundlich adsorption coefficients (K_d) values for MON 12000 ranged from 0.32 (Spinks loamy sand) to 3.56 (Sable silty clay loam); K_{oc} values were less than 200. (K_d) values for 3-chlorosulfonamide acid ranged from 0.02 (Drummer sit loam) to 0.22 (Sable silty clay loam), however due to the extremely low adsorption tendency the data were not statistically reliable. K_{oc} values were less than 10. (K_d) values for 3-chlorosulfonamide ester were 0.70 (Spinks loamy sand), 0.80 (Sarpy sandy loam), and 2.98 (Drummer silt loam). The K_{oc} values were below 350. (K_d) values for aminopyrimidine gave an indication that it was the least mobile of the degradates and were 32.23 (Sable soil), 11.54 (Drummer soil), 1.92 (Sarpy soil), 2.59 (Spinks soil). As it is the case with parent MON 12000, 1/n also deviated from 1 for all degradates, which is indicative of a non-linear adsorption process. The K_{oc} values in the above soils were 9279, 1042, 399 and 260 respectively. However, the terrestrial field dissipation (164-1) studies give an indication that MON 12000 when applied as a wettable powder in 6 separate field situations (sites) does not have a high potential to leach because of its fairly rapid degradation rates through hydrolysis and aerobic soil metabolism. MON 12000 leached below the 6 inch soil layer, but at concentrations < 8 ppb at all sampling depths and intervals. In addition, the major degradates from the aerobic soil metabolism aminopyrimidine and 3-chlorosulfonamide ester were present at < 5 ppb at all soil depths and intervals throughout the field studies duration.

MON 12000 applied once at approximately 0.125 lb ai/A, dissipated with half-lives of 6-34 days from plots of loam soil in Illinois and clay loam soil in Texas. MON 12000 was ≤0.004 ppm below the 6-inch soil depth at all test sites at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the study. MON 12000 applied twice, at approximately 0.125 lb ai/A and 0.094 lb ai/A dissipated with half-lives of 18-60 days from the upper 6 inches of plots of sandy clay loam soil in California and loam soil in Iowa respectively. The longer dissipation rates in Iowa can be attributed to a cooler, milder climate. MON 12000 was ≤0.004 ppm below the 6-inch soil depth at all test sites at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the study. In addition, MON 12000 dissipated with observed half-lives of <1 month from the upper 6 inches of turf-covered plots of sandy loam, loamy sand, and silt loam soils in California, Georgia, and Missouri that were treated with MON 12000 three times, at approximately 0.063-0.125 lb ai/A/application. MON 12000 was ≤0.008 ppm below the 6-inch soil depth at all test sites at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the study.

The lysimeter studies appeared to be in agreement with the terrestrial field data. MON 12000 (pyrazole and pyrimidine labelled) dissipated with observed half-lives of 3.7-10 days from the upper 6 inches of in-situ sandy loam soil columns in North Carolina and 13.6-56.3 days from the upper 6 inches of loam soil columns in Iowa. The degradates detected in the soils at both sites were aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine), 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], 3-chlorosulfonamide ester, the "rearrangement ester", the "rearrangement acid", MON 12000 acid, MON 12000 desmethyl, and MON 12000 guanidine. MON 12000 was detected at a maximum of 5.0 ppb (8% of applied) in the 6-12 inch soil layer and none above 3 ppb was observed below 12 inches for any of the eight treatments. At both locations no metabolite residues above 5 ppb were observed below the top six inches of soil over the course of the year.

In two other lysimeter studies MON 12000 dissipated with observed half-lives of 1-2 weeks from the upper 6 inches of in-situ sandy loam soil columns in North Carolina and 1-2.5 months from the upper 6 inches of loam soil columns in Iowa. The longer half-life at the Iowa site can be attributed to the milder climate. The degradates detected in the soils at both sites were aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine), 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], 3-chlorosulfonamide ester, the "rearrangement ester", the "rearrangement acid", MON 12000 acid, MON 12000 desmethyl, and MON 12000 guanidine. Neither MON 12000 nor any [^{14}C]degradate was detected at >5 ppb below the 6-inch soil depth at either site.

Based on a personal communication with Dr. Michael Barrett of the Ground Water Technology Section of the EFGWB a recalculation of

the lysimeter dissipation data gave half-lives of 44-81 days in Iowa and 15-22 days in North Carolina.

DISCUSSION:

Aqueous Photolysis: DER 1

1. Study MRID #42661409 is acceptable and satisfies the photolysis in water (161-2) data requirement for MON 12000.

2. Hydrolysis predominated the degradation process. A mixture of ^{14}C-pyrimidine and ^{14}C-pyrazole labeled MON 12000 (3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl] amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid) degraded with a half-life of 23.8 days (assuming pseudo first order kinetics) in aqueous pH 5 sodium acetate buffer irradiated with natural sunlight for 30 days. In contrast, MON 12000 degraded with a calculated half-life of 29.5 days when incubated in the dark under similar conditions. The major degradates identified in the irradiated and the dark controls were 3-chlorosulfonamide ester and aminopyrimidine. By day 30 in the irradiated solutions 3-chlorosulfonamide ester reached a maximum (average of two replicates) of 30.5% and aminopyrimidine accounted for an average of 28.3% of applied. At day 30 the rearrangement ester accounted for an average of 0.6% of applied.

Soil Photolysis: DER 2

1. Study MRID #42661410 is acceptable and satisfies the soil photolysis (161-3) data requirement for MON 12000.

2. Degradation in soils exposed to sunlight and non-exposed was essentially identical. A mixture of pyrazole-^{14}C and pyrimidine-^{14}C and unlabeled MON 12000 degraded with a registrant calculated (assuming pseudo first order reaction kinetics) half-life of 16.2 days on a Sable silt loam soil (pH 5, 2.39% OC) that was irradiated with sunlight outdoors for 30 days. The dark control yielded a half-life of 8.1 days. It appeared that photodegradation was not a major degradative pathway. One major product, 3-chlorosulfonamide ester accounted for 24.7 and 37.4% of the applied radiocarbon in the Day 30 irradiated and dark control samples respectively. Aminopyrimidine accounted for 24.8 and 35.7% of the applied radiocarbon in the Day 30 irradiated and dark control samples respectively. No other degradates accounted for greater than 3.9% of the applied. No radiocarbon greater than 0.1% and 0.4% of the applied radiocarbon was detected in the ethylene glycol and sodium hydroxide traps, respectively, for any sample over the 30 day period.

Anaerobic Aquatic Metabolism: DER 3

1. Study MRID #42661411 is acceptable and satisfies the anaerobic aquatic metabolism (162-3) study data requirement for MON 12000.

2. Pyrazole and pyrimidine-^{14}C-MON 12000 degraded with a registrant

calculated (assuming pseudo first order kinetics) half-life of 27.2 days and 18.8 days respectively in a clay loam soil (pH 7, 0.15% OC, CEC = 16 meq/100g) that was incubated anaerobically (flooding plus nitrogen) at approximately 25C in the dark for 12 months. It appears that hydrolysis (pH range 7 - 8) is the major route of degradation in this aquatic study. The majority of the radioactivity was associated with the pond water (the major component of the water was aminopyrimidine at 46.3% of applied at month 12). The degradates observed were 3-chlorosulfonamide ester, the rearrangement ester, aminopyrimidine, and MON 12000 acid. Pyrazole labeled MON 12000 decreased from an average (2 replicates) of 95.2% at day 0 to 68.3% at day 14, 46.1% at month 1, 3.8% at month 4, then was not detected by month 6. 3-chlorosulfonamide ester was the major radiolabelled degradate in the pyrazole labeled MON 12000 at 2.4% of applied at day 0, increased to 26.8% at day 14, was at 49.9% month 1, then reached a maximum of 91.5% at month 6 and remained relatively constant through month 12. The rearrangement ester was present at a maximum average of 1.5% at month 4 and was detected sporadically through month 12. Pyrimidine labeled MON 12000 decreased from an average of 98.9% at day 0 to 76.8% at day 14, 51.4% at month 1, 0.8% at month 4, then was not detected by month 6. Aminopyrimidine was the major radiolabelled degradate in the pyrimidine labeled MON 12000 at 0.6% (individual sample) of applied at day 0, increased to 10.3% at day 14, was at 39.1% at month 1, then reached a maximum of 77.8% at month 4, then decreased to 46.3% at month 12. MON 12000 acid was detected only twice in separate samples at month 1 and month 6 at 4.2 and 12.0% respectively. The rearrangement ester was detected at a maximum average of 7.1% at month 3 and decreased to an average of 1.4% of applied by month 12. Unknowns were detected at a maximum of 20.7% (individual sample) at month 2 and were present at variable concentration through month 12 ranging from 18.7 to 2.3%.

Terrestrial Field Dissipation DER 4 (Radiolabelled Study)

1. Study MRID #42661414 is acceptable and may be used as supplemental information to satisfy the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

2. MON 12000 [Halosulfuron] dissipated with observed half-lives of 3.7-10 days from the upper 6 inches of in-situ sandy loam (69.5% sand, 25.2% silt, 5.3% clay, 1.2% organic matter, pH 6.0, CEC 7.8 meq/100 g) soil columns in North Carolina and 13.6-56.3 days from the upper 6 inches of loam (43.5% sand, 39.2% silt, 17.3% clay, 2.3% organic matter, pH 5.9, CEC 18.1 meq/100 g) soil columns in Iowa; the columns had been treated at a nominal rate range of 0.12-0.21 lb/A (20-39 g/ha) with either pyrazole ring- or pyrimidine ring-labeled [^{14}C]MON 12000 formulated alone (51% wettable powder) or with the herbicide safener MON 13900 (15% wettable powder). The degradates detected in the soils at both sites were aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine), 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], 3-chlorosulfonamide ester, the "rearrangement ester", the "rearrangement acid", MON 12000 acid, MON 12000 desmethyl, and MON

12000 guanidine. MON 12000 was detected at a maximum of 5.0 ppb (8% of applied) in the 6-12 inch soil layer and none above 3 ppb was observed below 12 inches for any of the eight treatments. At both locations no metabolite residues above 5 ppb were observed below the top six inches of soil over the course of the year. The test plots were irrigated throughout the study with a hand-held sprinkler to maintain a minimum of approximately 120% of total water for the monthly 10-year rainfall averages. During the North Carolina studies, rainfall plus irrigation totaled 3.14 inches at 15 days posttreatment, 4.06 inches at 30 days, 18.62 inches at 61 days, 60.64 inches at 366 days, and 96.78 inches at 559 days. During the Iowa studies, rainfall plus irrigation totaled 7.30 inches at 31 days posttreatment, 10.38 inches at 62 days, 18.58 inches at 123 days, 43.00 inches at 366 days, and 63.85 inches at 567 days. In leachate samples collect from 36 inch deep lysimeters at 18.5 months posttreatment from 14 of 16 (2 lysimeters were poorly constructed) treated lysimeters no cumulative residues above 0.08% or 1.2% of the applied radioactivity were found.

Terrestrial Field Dissipation DER 5 (Radiolabelled Study)

1. Study MRID #42976303 is acceptable and may be used as supplemental information to satisfy the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

2. MON 12000 [3-chloro-5-([[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester] dissipated with observed half-lives of 1-2 weeks from the upper 6 inches of in-situ sandy loam (69.5% sand, 25.2% silt, 5.3% clay, 1.2% organic matter, pH 6.0, CEC 7.8 meq/100 g) soil columns in North Carolina and 1-2.5 months from the upper 6 inches of loam (43.5% sand, 39.2% silt, 17.3% clay, 2.3% organic matter, pH 5.9, CEC 18.1 meq/100 g) soil columns in Iowa; the columns had been treated at a nominal rate of 0.23 lb ai/A with either pyrazole ring- or pyrimidine ring-labeled [^{14}C]MON 12000 formulated alone (51% wettable powder) or with the herbicide safener MON 13900 (15% wettable powder). The degradates detected in the soils at both sites were aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine), 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], 3-chlorosulfonamide ester, the "rearrangement ester", the "rearrangement acid", MON 12000 acid, MON 12000 desmethyl, and MON 12000 guanidine. Neither MON 12000 nor any [^{14}C]degradate was detected at >5 ppb below the 6-inch soil depth at either site. The test plots were irrigated throughout the study with a hand-held sprinkler to maintain a minimum of approximately 120% of total water for the monthly 10-year rainfall averages. During the North Carolina studies, rainfall plus irrigation totaled 3.14 inches at 15 days posttreatment, 4.06 inches at 30 days, 18.62 inches at 61 days, 60.64 inches at 366 days, and 96.78 inches at 559 days. During the Iowa studies, rainfall plus irrigation totaled 7.30 inches at 31 days posttreatment, 10.38 inches at 62 days, 18.58 inches at 123 days, 43.00 inches at 366 days, and 63.85 inches at 567 days. No MON 12000 residues above 3 ppb are observed below the top twelve inches

of soil in this study. At 18.5 months posttreatment, cumulative [^{14}C]residues in leachate samples collected from 36-inch deep lysimeters located at the North Carolina and Iowa sites were 0.047-0.434% and 0.078-1.627% of the applied, respectively.

Terrestrial Field Dissipation DER 6 (Cold Study)

1. Study MRID #42976302 is acceptable and contributes towards satisfying the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

2. MON 12000 [Halosulfuron, 25% WP] dissipated with half-lives of 18-60 days from the upper 6 inches of plots of sandy clay loam (San Ysidoro series, 56% sand, 22% silt, 22% clay, 1.2% organic matter, pH 6.0, CEC 13.2 meq/100 g) soil in California and loam (Harp series, 38% sand, 38% silt, 24% clay, 4.5% organic matter, pH 6.5, CEC 17.3 meq/100 g) soil in Iowa that were treated with MON 12000 twice, at approximately 0.125 lb ai/A (23 g/ha) and 0.094 lb ai/A (17 g/ha), in Spring 1990. Also, MON 12000 dissipated with half-lives of 6-34 days from plots of loam (Harpster series, 24% sand, 50% silt, 26% clay, 4.8% organic matter, pH 7.7, CEC 22.7 meq/100 g) soil in Illinois and clay loam (Uvalde series, 30% sand, 34% silt, 36% clay, 2.1% organic matter, pH 8.3, CEC 21.3 meq/100 g) soil in Texas that were treated with MON 12000 once, at approximately 0.125 lb ai/A, in Spring 1990. MON 12000 was <0.004 ppm below the 6-inch soil depth at all test sites at all sampling intervals No MON 12000 residues were observed at or above 2 ppb detection limit 123 days after the last treatment. No MON 12000 soil metabolites were observed at or above the lower limit of method validation (G.C.), 5 ppb, in any of the samples at any interval or depth. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the four studies duration. During the California study, rainfall plus irrigation was 20.35 inches throughout the entire 18-month period. During the Iowa study, rainfall plus irrigation was 73.17 inches throughout the entire 18-month period. During the Illinois and Texas studies rainfall plus irrigation was 69.91 inches, and 58.23 inches respectively throughout the entire 18-month period.

Terrestrial Field Dissipation DER 7 (Cold Study) - Turf

1. Study MRID #42661413 and MRID #42976304 is acceptable and contributes in satisfying the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

2. MON 12000 [3-chloro-5-([[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester; 25% WP] dissipated with observed half-lives of <1 month from the upper 6 inches of turf-covered plots of sandy loam (Hanford series, 66% sand, 20% silt, 14% clay, 0.5% organic matter, pH 6.8, CEC 10.0 meq/100 g), loamy sand (Dothan series, 80% sand, 12% silt, 8% clay, 1.5% organic matter, pH 6.0, CEC 2.7 meq/100 g), and silt loam (Mexico series, 20% sand, 54% silt, 26% clay, 2.0% organic matter, pH 7.2, CEC 12.4 meq/100 g) soils in California,

Georgia, and Missouri that were treated with MON 12000 three times, at approximately 0.063-0.125 lb ai/A/application, in Spring and Summer 1990. MON 12000 was ≤0.008 ppm below the 6-inch soil depth at all test sites at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged < 5 ppb (lower limit of method validation) at all soil depths throughout the study. In California, rainfall plus irrigation was 39.90 inches through the entire 7-month study. In Georgia and Missouri rainfall plus irrigation was 40.44 inches throughout the entire 4-month study and 30.30 inches throughout the entire 4-month study respectively.

Ancillary Study - Freezer Storage Stability DER 8

1. Freezer storage stability studies are not specifically required by Subdivision N guidelines.

2. MON 12000 [Halosulfuron] and its degradate, 3-chlorosulfonamide acid[5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid] were stable in loam soil that was fortified at 0.02 ppm and stored frozen at <0 F for up to 12 months. In contrast, the degradate aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine) was unstable during 12 months of storage in loam soil fortified at 0.02 ppm and stored at <0 F; aminopyrimidine averaged 101% of the applied immediately posttreatment, 69.1% after 2 months of frozen storage, and 29.6-32.6% after 8 and 12 months.

3. This study is scientifically sound and provides information on the freezer storage stability of MON 12000 and its degradates aminopyrimidine and 3-chlorosulfonamide acid in soil stored at <0 F.

4. No additional information on the stability of MON 12000, aminopyrimidine, and 3-chlorosulfonamide acid in soil during frozen storage for 12 months is required at this time.

BACKGROUND :

MON 12000 is a sulfonyl urea herbicide with proposed use rates of 0.016 lb (3 g/ha) to 0.125 lb/acre (23 g/ha). The current proposed uses are corn, turf and sorghum. In corn a single preemergent, a single postemergent application or a sequential application (pre plus post, early post plus late post). Certain applications of MON 12000 are intended for use in conjunction with the herbicide safener MON 13900, which is intended to counteract the phytotoxic effects of the sulfonylurea herbicide on corn germination. The maximum expected use rate in a season would be 0.23 lbs/acre.

Products containing the active include:
-Battalion (15% of the ai and the safener formulated as a water soluble granular for use on field corn at maximum preemergence or preplant incorporated rates of 0.1215 lb ai/a. Expected use rates ar 0.016 to 0.094 lbs ai/a.

-Permit (72% of the ai formulated as a water soluble granular for postemergence applications from the two leaf stage to layby in corn and milo at maximum use rates of 0.094 lbs ai/a. Expected use rates are 0.016 to 0.062 lbs ai/a.

-Manage (50% of the ai formulated as a wettable powder for turf applications with a maximum use rate for sequential applications of 0.063 lbs ai/a and expected sequential use rates of 0.031 lbs ai/a.

References:

(161-2) MRID No: 42661409
A. Kesterson and B. Lawrence. January 20, 1993. Solution Photolysis of ^{14}C-MON 12000 in Natural Sunlight. Performed by PTRL East Inc. 3945 Simpson Lane Richmond, KY 40475. Submitted by The Agricultural Group of Monsanto Company, New Products Division 700 Chesterfield Parkway North St. Louis, MO 63198.

(161-3) MRID No: 42661410
A. Kesterson and B. Lawrence. July, 1992. Soil Surface Photolysis of [^{14}C] MON 12000 in Natural Sunlight.
Performed by PTRL East Inc. 3945 Simpson Lane Richmond, KY 40475. Submitted by The Agricultural Group of Monsanto Company, New Products Division 700 Chesterfield Parkway North St. Louis, MO 63198.

(162-3) MRID No: 42661411
B. Lawarence, S.G. Mobley, J. Lambert and A. Kesterson. January 25, 1993. Anaerobic Aquatic Metabolism of [^{14}] /MON 12000. Performed by PTRL East Inc. 3945 Simpson Lane Richmond, KY 40475. Submitted by The Agricultural Group of Monsanto Company, New Products Division 700 Chesterfield Parkway North St. Louis, MO 63198.

(164-1) MRID No: 42661414
R.H. White and M.A.- Schlicher. January 1993. Dissipation of Radiolabelled MON 12000 and MON 12000 Metabolites in Field Soil. Performed by Hazleton Laboratories, Inc. 3301 Kinsman Blvd. Madison, Wisconsin 53704; Monsanto Company. The Agricultural Group 700 Chesterfield Parkway North St. Louis, MO 63198; American Agricultural Services, Inc. P.O. Box 1293, Cary, North Carolina 27512. Project No. MSL 12463/ American Ag No. 91-42-R-3

(164-1) MRID No: 42976303
White, R.H., and M.A. Schlicher. 1993. Dissipation of radiolabelled MON 12000 and MON 12000 metabolites in field soil. Monsanto Study No. MSL 12891; Hazelton Project No. HWI 6103-157; A.A.S.I. Project No. 0642-91-3. Unpublished study performed by Monsanto Company, St. Louis, MO; Hazelton Wisconsin, Inc., Madison, WI; and American Agricultural Services, Inc., Cary, NC. Unpublished study submitted by Monsanto Company, St. Louis, MO.

(164-1) MRID No: 42661412
Beasley, R.K. 1993a. Dissipation of MON 12000 and MON 12000

metabolites in field soil. Monsanto Study No. MSL 12356; Harris Study No. 9200520; Stewart Study No. 90-42-R-2. Unpublished study performed by Harris Laboratories, Inc., Lincoln, NE; Monsanto Company, St. Louis, MO; and Stewart Agricultural Research Services, Inc., Macon, MO. Submitted by Monsanto Company, St. Louis, MO.

(164-1) MRID No: 42976302
Beasley, R.K. 1993b. Dissipation of MON 12000 and MON 12000 metabolites in field soil. Monsanto Study No. MSL 12892; Harris Study Nos. 9200520, 9200536, and 15628; Stewart Study No. 90-42-R-2. Unpublished study performed by Harris Laboratories, Inc., Lincoln, NE; Monsanto Company, St. Louis, MO; and Stewart Agricultural Research Services, Inc., Macon, MO. Submitted by Monsanto Company, St. Louis, MO.

(164-1) MRID No: 42661413
Beasley, R.K. 1993c. Dissipation of MON 12000 and MON 12000 metabolites in turf soil. Monsanto Study No. MSL 12357; Hazleton Study No. 6103-156; Stewart Study No. 90-42-R-4. Unpublished study performed by Hazelton Wisconsin, Inc., Madison, WI; Monsanto Company, St. Louis, MO; and Stewart Agricultural Research Services, Inc., Macon, MO. Unpublished study submitted by Monsanto Company, St. Louis, MO.

(164-1) MRID No: 42976304
Beasley, R.K. 1993d. Dissipation of MON 12000 and MON 12000 metabolites in turf soil. Monsanto Study No. MSL 12893; Hazleton Study No. HWI-6103-156; Stewart Study No. 90-42-R-4. Unpublished study performed by Monsanto Company, St. Louis, MO; Stewart Agricultural Research Services, Inc., Macon, MO, Hazelton Wisconsin, Inc, Madison, WI; and Harris Laboratories, Inc., Lincoln, NE. Unpublished study submitted by Monsanto Company, St. Louis, MO.

(164-1) MRID No:42661415
Beasley, R.K. 1993e. Storage stability of MON 12000 and its metabolites in or on soil. Laboratory Project No. MSL 12358. Unpublished study performed and submitted by Monsanto Company, St. Louis, MO.

DATA EVALUATION RECORD
DER 1

SHAUGHNESSY No. 128721
COMMON NAME: MON 12000
CHEMICAL NAME: 3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid
FORMULATION: Active Ingredient
DATA REQUIREMENT: 161-2

MRID No: 42661409 A. Kesterson and B. Lawrence. January 20, 1993. Solution Photolysis of ^{14}C-MON 12000 in Natural Sunlight. Performed by PTRL East Inc. 3945 Simpson Lane Richmond, KY 40475. Submitted by The Agricultural Group of Monsanto Company, New Products Division 700 Chesterfield Parkway North St. Louis, MO 63198

REVIEWED BY: Kevin L. Poff
Chemist EFGWB/EFED
Signature:
Date:

APPROVED BY: Akiva Abramovitch, Ph.D.
Chemist EFGWB/EFED
Signature:
Date:

CONCLUSIONS:

1. Study MRID #42661409 is acceptable and satisfies the photolysis in water (161-2) data requirement for MON 12000.

2. A mixture of ^{14}C-pyrimidine and ^{14}C-pyrazole labeled MON 12000 (3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid) degraded with a half-life of 23.8 days (assuming pseudo first order kinetics) in aqueous pH 5 sodium acetate buffer irradiated with natural sunlight for 30 days. Hydrolysis predominated the degradation processes. In contrast, MON 12000 degraded with a calculated half-life of 29.5 days when incubated in the dark under similar conditions. The major degradates identified in the irradiated and the dark controls were 3-chlorosulfonamide ester and aminopyrimidine. By day 30 in the irradiated solutions 3-chlorosulfonamide ester reached a maximum (average of two replicates) of 30.5% and aminopyrimidine accounted for an average of 28.3% of applied. At day 30 the rearrangement ester accounted for an average of 0.6% of applied.

MATERIALS AND METHODS:

Two stock solutions of pyrazole-^{14}C-MON 12000 and pyrimidine-^{14}C-MON 12000 were prepared in acetonitrile then added to the appropriate test solutions at pH 5 or 9. Aliquots (10ml) of the sterile (milipore filtered, 0.22um) aqueous sodium acetate buffer and aqueous sodium borate buffer adjusted to pH 5 and 9 were transferred to quartz tubes with the final concentration of the pyrazole-^{14}C-MON 12000 (specific activity 27.70 mCi/mMole, radiochemical purity 99.0%) and pyrimidine-^{14}C-MON 12000 (specific activity - 31.01 mCi/mMole, radiochemical purity 98.5%) at 5.2 ppm. The quartz tube were immersed in a plexiglass tank (12 X 72 inches) that contained 4 inches of deionized water (no attenuation of sunlight thru this depth) and exposed to direct sunlight in Richmond Kentucky (latitude 37.5200, longitude 84.2004; November 5, 1991-December 5, 1991). The temperature of the water bath was set at 25.3C. Temperature was monitored at 5 second intervals. Sunlight irradiance was measured and recorded at 10 minute intervals with an International Light Radiometer, the probe was calibrate April 8, 1991; cumulative energy was calculated as peak area accumulated. Samples were irradiated in duplicate. Two sets of dark controls were wrapped in aluminum foil and placed in the waterbath with the irradiated samples. Duplicate tubes were taken from the irradiated and the dark control at 0, 2, 10, 20 and 30 days; an aliquot was taken for immediate radioassay, for pH determination and for storage at -20C until analysis by HPLC and/or TLC. Gas dispersion traps were removed on Days 2, 10, 20 and 30. The test solutions were stored at -20C until analysis by HPLC and/or TLC. Detection Limit was 2X's background (approx. 0.01 ppm).

Acetonitrile (10-15%) was added to some samples to solubilize the ^{14}C-material after storage at -20C. The samples were also fortified with the unlabeled reference compounds MON 12000, the rearrangement ester, 3-chlorosulfonamide ester, aminopyrimidine, MON 12000 acid, desmethyl MON 12000 and the rearrangement acid (sodium salt) and injected onto an HPLC, eluted with a linear gradient system with a reverse phase column, UV and a radiomatic detector. TLC was used to confirm the HPLC characterization of MON 12000 and its degradates using ethyl acetate:acetic acid and benzene:ethyl acetate and visualized with UV light.

RESULTS:

A mixture of ^{14}C-pyrimidine and ^{14}C-pyrazole labeled 3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid at 5.2 ppm photodegraded with a registrant calculated (assuming pseudo first order kinetics) half-life of 23.8 days in sterile aqueous pH 5 sodium acetate buffer irradiated with natural sunlight for 30 days. In contrast, MON 12000 degraded with a calculated half-life of 29.5 days when incubated in the dark under similar conditions. The major degradates identified in the irradiated and the dark controls were 3-chlorosulfonamide ester and aminopyrimidine.

In the irradiated solutions at day 20, 3-chlorosulfonamide ester accounted for 22.6% of the applied radiocarbon and aminopyrimidine accounted for 21.2%. By day 30 in the irradiated solutions 3-chlorosulfonamide ester reached a maximum (average of two replicates) of 30.5% and aminopyrimidine accounted for an average of 28.3% of applied. At day 30 the rearrangement ester accounted for an average of 0.6% of applied. Unknowns with a retention time of 30-35 minutes accounted for 0.9% and 0.7% of applied in both the irradiated and the dark control respectively beginning at day 20 and remained at 0.7% at day 30 sampling. Other unknowns found at day 20 and 30 accounted for an average of 0.8 and 0.6% of applied respectively.
In the dark controls 3-chlorosulfonamide ester accounted for 21.9% of applied and aminopyrimidine accounted for 20.4% of applied. In the irradiated samples MON 12000 accounted for 41.3% of applied at day 30. No other products accounted for greater than 1% of the applied radiocarbon in any sample throughout the studies duration. It appears that both degradates are stable to conditions present during the study.
At pH 9 the half-lives were 0.6 day for both the irradiated and the dark control samples. The rearrangement ester accounted for 50.4 and 50.7% of the applied radiocarbon in the day 30 irradiated and dark control samples respectively. The rearrangement acid accounted for 45.6 and 47.1% the applied radiocarbon at day 30 in the irradiated and dark control samples respectively.

DISCUSSION:

1. The concentration of the cosolvent was not reported.

2. No confirmation of degradate identity was completed, however, since photodegradation is not a major dissipation/degradation process TLC/HPLC data comparison was adequate.

3. The tubes containing the day 30 dark control samples were broken prior to sampling.

4. Immediately following sampling the samples were stored at -20C until HPLC and/or TLC analysis, typically 3-5 days. The longest time of storage was up to 23 days. The Day 10 samples from a previous study were stored frozen for approx. 1.5 years and reanalyzed showing stability of MON 12000 and its degradates through frozen storage.

5. An absorption spectrum of the pesticide in the test solution was not provided. However, an absorption spectrum of MON 12000 at pH 5, 7, and 9 was provided (MRID #42976307); the spectrum indicates that MON 12000 absorbs light primarily at wavelengths <290 nm.

6. The solubility of MON 12000 in water at 20C at pH 5 and 7 has been determined to be 15 ppm and 1630 ppm respectively. At pH 9, the solubility in water at 20C was 7410 ppm at 24 hours, 3790 ppm at 48 hours and 2610 ppm at 72 hours; the authors note that the change in solubility is indicative of the compounds instability.

DATA EVALUATION RECORD
DER 2

SHAUGHNESSY No. 128721
COMMON NAME: MON 12000
CHEMICAL NAME: 3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid
FORMULATION: Active Ingredient
DATA REQUIREMENT: 161-3

MRID No: 42661410 A. Kesterson and B. Lawrence. July, 1992. Soil Surface Photolysis of [^{14}C] MON 12000 in Natural Sunlight. Performed by PTRL East Inc. 3945 Simpson Lane Richmond, KY 40475. Submitted by The Agricultural Group of Monsanto Company, New Products Division 700 Chesterfield Parkway North St. Louis, MO 63198.

REVIEWED BY: Kevin L. Poff
Chemist EFGWB/EFED
Signature:
Date:

APPROVED BY: Akiva Abramovitch, Ph.D.
Chemist EFGWB/EFED
Signature:
Date:

CONCLUSIONS:

1. Study MRID #42661410 is acceptable and satisfies the soil photolysis (161-3) data requirement for MON 12000.

2. A mixture of pyrazole-^{14}C and pyrimidine-^{14}C and unlabeled MON 12000 degraded with a registrant calculated (assuming pseudo first order reaction kinetics) half-life of 16.2 days on a Sable silt loam soil (pH 5, 2.39% OC) that was irradiated with sunlight outdoors for 30 days. The dark control yielded a half-life of 8.1 days. It appeared that photodegradation was not a major degradative pathway. One major product, 3-chlorosulfonamide ester accounted for 24.7 and 37.4% of the applied radiocarbon in the Day 30 irradiated and dark control samples respectively. Aminopyrimidine accounted for 24.8 and 35.7% of the applied radiocarbon in the Day 30 irradiated and dark control samples respectively. No other degradates accounted for greater than 3.9% of the applied. No radiocarbon greater than 0.1% and 0.4% of the applied radiocarbon was detected in the ethylene glycol and sodium hydroxide traps, respectively, for any sample over the 30 day period.

MATERIALS AND METHODS:

Samples (approximately 3.1g) of sieved (2mm), air dried sable silt loam soil (16% sand, 52% silt, 32% clay, 2.39% OC, CEC 25.4 meq/100g, pH 5) with 3.0 ml HPLC grade water were placed on test plates and treated at 0.5 lb/acre (35.2 ppm) with pyrazole-^{14}C-MON 12000, pyrimidine-^{14}C-MON 12000 and unlabeled MON 12000. The soil was then brought up to 75% of the field capacity. The soil layered petri dishes were then placed in a quartz covered stainless steel temperature control chamber and maintained at 23 $\pm$ 0.6C. An identical set of samples were incubated at 25.3C for the dark controls. During the study, (5/10/91-6/9/91) the radiant energy received by the irradiated soil totaled 150.0 watt-min/m^2 total radiant energy received by the irradiated soil was continuously monitored and averaged and recorded using a radiometer. The study took place in Richmond, Kentucky (latitude 37" 52'00";longitude 84" 20'04"). Duplicate irradiated and dark control soil samples were collected at 0, 1, 12, 20 and 30 days posttreatment. Gas dispersion traps ethylene glycol, 10% NaOH) were sampled on days 1, 12, 20, and 30 days and replaced with fresh traps on days 1, 12 and day 20. All plates were covered with parafilm and aluminum foil and immediately placed in the freezer (approx. -20C) until their extraction on that same day.

Soil samples were extracted three times with an acetonitrile:water (7:3) using a wrist action shaker; after each extraction, the extracts were separated from the soil by centrifugation. The extracts from each sample were combined, and aliquots were analyzed for total radioactivity using LSC. Additional extracts were performed with NH_4OH to remove residual radiocarbon from day 1-30 soil samples. The additional extracts were partitioned in methylene chloride. The organic phases contained $\leq$6% of the applied radiocarbon and were not analyzed. All samples were analyzed by liquid chromatograph with a C-18 column and a Radiomatic Beta Flow-One detector and a variable wavelength UV/vis detector (240 nm). TLC was used to confirm the HPLC characterization of pyrazole and pyrimidine-^{14}C-MON 12000. Detection Limit was 2X's background.

RESULTS:

A mixture of pyrazole-^{14}C (specific activity 25.2 mCi/mMole; radiochemical purity 99.9%) and pyrimidine-^{14}C (specific activity 23.0 mCi/mMole; radiochemical purity 99.2%) and unlabelled MON 12000 at 0.5 lb/acre (35.2 ppm) degraded with a registrant calculated (assuming pseudo first order reaction kinetics) half-life of 16.2 days on a sable silt loam soil that was irradiated with sunlight outdoors 23 $\pm$ 0.6C. The mean total energy per study day was 6.2 $\pm$ 2.1 W(min)/cm^2 per full study day. The total cumulative light energy for the study was 150.0 W(min)/cm^2. The dark control yielded a half-life of 8.1 days. One major product, 3-chlorosulfonamide ester accounted for 24.7 and 37.4% of the applied radiocarbon in the Day 30 irradiated and dark control samples respectively. Aminopyrimidine accounted for 24.8 and 35.7%

of the applied radiocarbon in the Day 30 irradiated and dark control samples respectively. There were several "other" unidentified products which were detected but none which accounted for greater than 3.9% of the applied. No radiocarbon greater than 0.1% and 0.4% of the applied radiocarbon was detected in the ethylene glycol and sodium hydroxide traps, respectively, for any sample over the 30 day period. After 30 days of irradiation [^{14}C] residues that were removed by harsher methods comprised up to 6.3% of applied and 5.5% of applied for the dark control respectively. Unextracted residues comprised 3.5 and 2.4% of the applied radiocarbon for the Day 30 irradiated and dark control samples respectively. Total radiocarbon recoveries in the irradiated and dark controls ranged from 96.5 to 107.4%. The mean ± S.D. total radiocarbon recovery was 102.4 ± 3.4% and 102.9 ± 2.7% for the irradiated and dark control samples respectively. The mean ± S.D. total radiocarbon recovery for all study samples was 102.6 ± 3.0%.

DISCUSSION:

1. The study authors concluded that MON 12000 did not significantly photodegrade on soil given as indicated by the degradation half-lives of 16.2 and 8.1 days in the irradiated and dark control soils, respectively.

2. The degradates 3-chlorosulfonamide ester and aminopyrimidine reached a maximum (mean of duplicates) of 24.7 and 24.8% of applied radiocarbon on the irradiated soils which could indicate the stability of those particular degradates to soil photolysis.

3. Storage stability was not a question being that samples were extracted and analyzed the same day of sampling.

4. No confirmation of degradate identity was completed, however, since photodegradation is not a major dissipation/degradation process TLC/HPLC data comparison was adequate.

5. For HPLC analysis of the soil extracts, radioactive peaks were reconstructed following LSC analysis of fractions collected at 0.5-minute intervals, as graphs with linear segments drawn from one dpm value to the next. It is preferred that either UV and/or in-line radioactivity detection be used in addition to fraction collection for HPLC analysis.

6. An absorption spectrum of the pesticide in the test solution was not provided. However, an absorption spectrum of MON 12000 at pH 5, 7, and 9 was provided (MRID #42976307); the spectrum indicates that MON 12000 absorbs light primarily at wavelengths <290 nm.

7. The authors reported the water solubility of MON 12000 to be 36 ppm at 25C (pH was not specified).

DATA EVALUATION RECORD
DER 3

SHAUGHNESSY No. 128721
COMMON NAME: MON 12000
CHEMICAL NAME: 3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid
FORMULATION: Active Ingredient
DATA REQUIREMENT: 162-3

MRID No: 42661411 B. Lawrence, S.G. Mobley, J. Lambert and A. Kesterson. January 25, 1993. Anaerobic Aquatic Metabolism of [^{14}] MON 12000. Performed by PTRL East Inc. 3945 Simpson Lane Richmond, KY 40475. Submitted by The Agricultural Group of Monsanto Company, New Products Division 700 Chesterfield Parkway North St. Louis, MO 63198.

REVIEWED BY: Kevin L. Poff
Chemist EFGWB/EFED
Signature:
Date:

APPROVED BY: Akiva Abramovitch, Ph.D.
Chemist EFGWB/EFED
Signature:
Date:

CONCLUSIONS:

1. Study MRID #42661411 is acceptable and satisfies the anaerobic aquatic metabolism (162-3) study data requirement for MON 12000.

2. Pyrazole and pyrimidine-^{14}C-MON 12000 degraded with a registrant calculated (assuming pseudo first order kinetics) half-life of 27.2 days and 18.8 days respectively in a clay loam soil (pH 7, 0.15% OC, CEC = 16 meq/100g) that was incubated anaerobically (flooding plus nitrogen) at approximately 25C in the dark for 12 months. It appears that hydrolysis (pH range 7 - 8) is the major route of degradation in this aquatic study. The majority of the radioactivity was associated with the pond water (the major component of the water was aminopyrimidine at 46.3% of applied at month 12). The degradates observed were 3-chlorosulfonamide ester, the rearrangement ester, aminopyrimidine, and MON 12000 acid. Pyrazole labeled MON 12000 decreased from an average (2 replicates) of 95.2% at day 0 to 68.3% at day 14, 46.1% at month 1, 3.8% at month 4, then was not detected by month 6. 3-chlorosulfonamide ester was the major radiolabelled degradate in the pyrazole labeled MON 12000 at 2.4% of applied at day 0, increased to 26.8% at day 14, was at 49.9% month 1, then reached a maximum of 91.5% at month 6 and remained relatively constant through month 12. The rearrangement ester was present at a maximum average of 1.5% at month 4 and was detected sporadically through month 12. Pyrimidine labeled MON 12000 decreased from an average of 98.9% at day 0 to

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76.8% at day 14, 51.4% at month 1, 0.8% at month 4, then was not detected by month 6. Aminopyrimidine was the major radiolabelled degradate in the pyrimidine labeled MON 12000 at 0.6% (individual sample) of applied at day 0, increased to 10.3% at day 14, was at 39.1% at month 1, then reached a maximum of 77.8% at month 4, then decreased to 46.3% at month 12. MON 12000 acid was detected only twice in separate samples at month 1 and month 6 at 4.2 and 12.0% respectively. The rearrangement ester was detected at a maximum average of 7.1% at month 3 and decreased to an average of 1.4% of applied by month 12. Unknowns were detected at a maximum of 20.7% (individual sample) at month 2 and were present at variable concentration through month 12 ranging from 18.7 to 2.3%.

MATERIALS AND METHODS:

Pond sediment (20 g dry weight) of clay loam (24% sand, 48% silt, 28% clay, organic carbon 0.15%, CEC 16 meq/100g, field capacity at 1/3 bar 34.1%, pH 7) were weighed into flasks in two separate experiments and treated with 0.10 ppm (based upon 20g dry weight of the sediment and 100 ml pond water) pyrazole (specific activity 25.2 mCi/mMole, 100.0% purity) and pyrimidine (specific activity, 99.2% purity)-^{14}C-MON 12000 dissolved in acetonitrile. The water used in the study was from the same pond as the sediment was obtained (Table 2). Twenty three flasks were treated with the pyrimidine and pyrazole labeled [^{14}C]MON 12000. Six additional flasks were treated at higher rates (10 ppm) for the identification of degradation products, but were not needed. Approximately 2 weeks before application 2.0g of glucose were added to the sediment to ensure microbial viability. The 500 ml biometer flask test system was equipped with a side arm containing 50 ml of 10% NaOH and a dichloromethane rinsed polyurethane foam plug to trap $^{14}CO_2$ and volatile organic compounds. Humidified nitrogen provided positive pressure to the system. The NaOH was radioassayed and if radiocarbon was detected $BaCl_2$ was added, centrifuged then the supernatant was reexamined to determine the amount of radiocarbon trapped in the precipitate. The foam plugs were changed monthly through Month 4 and thereafter when the flasks were sampled. The polyurethane foam plugs were extracted with chloroform and radioassayed directly.
The treated soil was incubated in the dark at 25.0 $\pm$ 0.27C for 12 months. Duplicate flasks were sampled on days 0, 2, 8 and 14 and Months 1, 2, 3, 4, 6, 9 and 12 of each of the two experiments with the pyrazole and pyrimidine labels. The pH and dissolved oxygen was measured with ColorpHast strips or Corning model 240 pH meter and a YSI Model 54A oxygen meter respectively.

After the water portion was separated from the sediment by centrifugation acetonitrile:water (7:3, v:v) was used to extract the pellet three separate times on a wrist action shaker. The extracts were pooled and stored at -20C. Month 1 through month 12 samples required additional extractions. Generally samples were extracted with acetonitrile on a wrist action shaker and stored at -20C. These sediments were further extracted with 0.1N NH_4OH partitioned with methylene chloride and ethyl acetate, then

analyzed by HPLC with a reverse phase column, linear gradient system of acetonitrile: acetic acid with UV/vis, Radiomatic Flo-one detectors. The aqueous samples were then partitioned with butanol but the radiocarbon in the organic layer was not concentrated enough to be analyzed by HPLC. In some cases the aqueous samples were acidified to pH 3-4 with con H to increase organic partitioning. The final aqueous fractions from organic partitioning contained particulate matter from the sediment that was filtered out and combusted to ensure recovery. The radiocarbon on the filter was considered material not extracted from the sediment. Two different one dimensional TLC systems with UV light were used to confirm the characterization of MON 12000, the aminopyrimidine, and the 3-chlorosulfonamide ester.

RESULTS:

Pyrazole and pyrimidine-^{14}C-MON 12000 degraded with a registrant calculated (assuming pseudo first order kinetics) half-life of 27.2 days and 18.8 days respectively in a in two separate experiments in a clay loam soil that was incubated anaerobically (flooding plus nitrogen) at approximately 25C in the dark for 12 months.

Pyrazole labeled MON 12000 decreased from an average (2 replicates) of 95.2% at day 0 to 68.3% at day 14, 46.1% at month 1, 3.8% at month 4, then was not detected by month 6. 3-chlorosulfonamide ester was the major degradate at 2.4% of applied at day 0, increased to 26.8% at day 14, was at 49.9% month 1, then reached a maximum of 91.5% at month 6 and remained constant through month 12. The rearrangement ester was present at a maximum average of 1.5% at month 4 and was detected sporadically through month 12. Unknowns reached a maximum of 6.1% (individual sample) at month 4 and were present at variable concentration through month 12 ranging from 0.4 to 3.7%. Table XIII depicts the retention times of the unknowns.

Pyrimidine labeled MON 12000 decreased from an average of 98.9% at day 0 to 76.8% at day 14, 51.4% at month 1, 0.8% at month 4, then was not detected by month 6. Aminopyrimidine was the major degradate at 0.6% (individual sample) of applied at day 0, increased to 10.3% at day 14, was at 39.1% at month 1, then reached a maximum of 77.8% at month 4, then decreased to 46.3% at month 12. MON 12000 acid was detected only twice in separate samples at month 1 and month 6 at 4.2 and 12.0% respectively. The rearrangement ester was detected at a maximum average of 7.1% at month 3 and decreased to an average of 1.4% of applied by month 12. Unknowns were detected at a maximum of 20.7% (individual sample; sum of total of all unknowns at that interval) at month 2 and were present at variable concentration through month 12 ranging from 2.3% to 18.7%. Table XIV depicts the retention times of the unknowns.

Detection limits were 2X's background; backgrounds were typically 30 to 50 dpm. Limits of quantitation were typically 0.001 ppm for combustions and 0.008 ppm for extracts.

Polyurethane plugs accumulated as little as 0.6% of applied in [^{14}C]volatiles for the pyrazole-labelled samples and 2.1% of applied for the pyrimidine-labelled samples. Mineralization was insignificant as $^{14}CO_2$ totaled a maximum of 1.4% of applied.

The majority of the radioactivity was associated with the pond water. At day 0 an average (two replicates) of 91% of applied was found in the water portion and then decreased slowly to 83.5% of applied by month 12. The acetonitrile water sediment extract at day 0 was 8.7% of applied, remained relatively constant and was at 12.45% of applied by month 12. The 0.1N NH_4OH sediment extract was at an average of 1.0% at month 3 and 1.05% at month 4; other samples did not require this method of extraction.

Unextracted residues accounted for 3.2% and 6.4% respectively in the pyrazole and pyrimidine month 12 samples. Sodium hydroxide extracts were performed to determine the nature of the bound residues in the soluble humic, fulvic acid and insoluble humin fractions. The majority of the radiocarbon was associated with the fulvic acid fraction.

The mean incubator temperature throughout the study was 25.0 ± 0.3C. The pH of all water/sediment samples in the study ranged from 4.4 to 5.7 for the pyrazole label and from 4.5 to 5.9 for the first nine months and 7.3 and 8.2 for two replicates at 12 months for the pyrimidine label.

The dissolved oxygen levels were monitored to assure anaerobic conditions and ranged from 0.4 to 5.5 mg/L for the pyrazole label and 0.3 to 4.4 mg/L for the pyrimidine label. The overall material balances were 99.5 ± 2.2% and 101.8 ± 3.9% for the pyrazole and pyrimidine labels respectively.

DISCUSSION:

1. Several unknown products were observed but none exhibited a specific pattern of appearance or decline; it was suggested that the peaks are most likely artifacts formed due to difficulties in extraction and chromatographic analysis of the pyrimidine-^{14}C-MON 12000 and pyrazole labeled residues. The study authors reported that the unidentified compounds consisted of a number of products, none at >3.7% (0.004 ppm) of the applied for the pyrazole label and 11.2% (0.01 ppm).

2. It was not possible to determine what percentage of a specific radiocarbon compound was associated with either pond water or sediment extracts because the contribution from each profile was summed to quantify that component and reported as % of applied residues found in sediment extracts and water (Tables XI and XII). For instance, the major degradate in the sediment and water of the pyrazole samples was the 3-chlorosulfonamide; 91.2% of the applied radiocarbon in the month 12 samples. However, a large percentage (>90%) of the total degradates were found in the water portion of the test system, therefore one could assume that the majority of

the individual components identified were in the water soluble fraction.

3. The degradation half-lives and the nature of the degradates indicates hydrolysis is the main degradation pathway under anaerobic aquatic conditions.

4. Immediately following sampling and extraction all samples were stored at approximately -20C until analysis by HPLC, typically 1 to 2 months, the longest time between sampling and analysis was 17 months. Samples were later reanalyzed by HPLC after storage at approximately -20C for approximately 2 years.

5. Generally methods other than TLC are used to confirm the identity of degradates.

6. The solubility of MON 12000 in water at 20C at pH 5 and 7 was reported to be 15 ppm and 1630 ppm respectively.

DATA EVALUATION RECORD
DER 4

SHAUGHNESSY No. 128721
COMMON NAME: MON 12000
CHEMICAL NAME: 3-chloro-5-[[[[4,6-dimethoxy-2-pyrimindylamino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4 carboxylic acid
FORMULATION: Active Ingredient
DATA REQUIREMENT: Supplemental to 164-1

MRID No: 42661414 R.H. White and M.A. Schlicher. January 1993. Dissipation of Radiolabeled MON 12000 and MON 12000 Metabolites in Field Soil. Performed by Hazleton Laboratories, Inc. 3301 Kinsman Blvd. Madison, Wisconsin 53704; Monsanto Company. The Agricultural Group 700 Chesterfield Parkwasy North St. Louis, MO 63198; American Agricultural Services, Inc. P.O. Box 1293, Cary, North Carolina 27512. Project No. MSL 12463/ American Ag No. 91-42-R-3

REVIEWED BY: Kevin L. Poff
Chemist EFGWB/EFED
Signature:
Date:

APPROVED BY: Akiva Abramovitch, Ph.D.
Chemist EFGWB/EFED
Signature:
Date:

CONCLUSIONS:

1. Study MRID #42661414 is acceptable and may be used as supplemental information to satisfy the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

2. MON 12000 [Halosulfuron] dissipated with observed half-lives of 3.7-10 days from the upper 6 inches of in-situ sandy loam (69.5% sand, 25.2% silt, 5.3% clay, 1.2% organic matter, pH 6.0, CEC 7.8 meq/100 g) soil columns in North Carolina and 13.6-56.3 days from the upper 6 inches of loam (43.5% sand, 39.2% silt, 17.3% clay, 2.3% organic matter, pH 5.9, CEC 18.1 meq/100 g) soil columns in Iowa; the columns had been treated at a nominal rate range of 0.12-0.21 lb/A (20-39 g/ha) with either pyrazole ring- or pyrimidine ring-labeled [^{14}C]MON 12000 formulated alone (51% wettable powder) or with the herbicide safener MON 13900 (15% wettable powder). The degradates detected in the soils at both sites were aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine), 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], 3-chlorosulfonamide ester, the "rearrangement ester", the "rearrangement acid", MON 12000 acid, MON 12000 desmethyl, and MON 12000 guanidine. MON 12000 was detected at a maximum of 5.0 ppb (8% of applied) in the 6-12 inch soil layer and none above 3 ppb was observed below 12 inches for any of the eight treatments. At both locations no metabolite residues above 5 ppb were observed below the top six inches of soil over the course of the year. The test plots were irrigated throughout the study with a hand-held sprinkler to maintain a minimum of approximately 120% of total water for the monthly 10-year rainfall averages. During the North Carolina studies, rainfall plus irrigation totaled 3.14 inches at 15 days posttreatment, 4.06 inches at 30 days, 18.62 inches at 61 days, 60.64 inches at 366 days, and 96.78 inches at 559 days. During the Iowa studies, rainfall plus irrigation totaled 7.30 inches at 31 days posttreatment, 10.38 inches at 62 days, 18.58 inches at 123 days, 43.00 inches at 366 days, and 63.85 inches at 567 days. In leachate samples collect from 36 inch deep lysimeters at 18.5 months posttreatment from 14 of 16 (2 lysimeters were poorly constructed) treated lysimeters no cumulative residues above 0.08% or 1.2% of the applied radioactivity were found.

MATERIALS AND METHODS:

^{14}C-MON 12000 pyrazole and pyrimidine labeled were formulated (wettable powders) with and without a herbicide safener (MON 13900) and were applied to four soil columns (8 inches diameter and 40 inches long) and four lysimeters (in duplicate in two separate bare ground sites in North Carolina and Iowa at rates of 0.23 to 0.72 lb/a. Bromide tracers were added to the lysimeters at rates equivalent to 100 lb/a. Application rates were confirmed by: sampling aliquots of the test substance based on the amount of radioactivity present and specific activities of the test substance as well as comparing the calculated amount of test substance present with the actual residues detected at day 0 sampling. Treated and control columns were sampled at -1, 0, 1, 3, 7, 14, 21, 30, 60, 120, 180, 360, and 540 days after test substance application. Leachate collection and analysis was provided through 1 year. The in-ground soil columns were prepared by slowly driving galvanized steel pipes (8 X 40 inches) 36 inches into cultivated bare ground. The columns were arranged into four rows of 14 columns allowing one row for each of the MON 12000 treatment. Column rows were placed six feet apart and individual columns within each row were separated by two feet. The soil columns were removed from the ground for processing; upon removal the columns were immediately processed or stored frozen until analysis. The columns were opened and segmented into six inch segments, bagged, labeled, frozen and shipped to the sponsor for analysis. For the lysimeter study a single row of ten columns was installed to provide duplicates for each of four treatments. A trench was dug to provide access to the bottom of each lysimeter. A collection vessel was placed at the bottom to allow for weekly leachate sampling.

Lucama, North Carolina

The test substance was applied June 25, 1991 to both the soil columns and the lysimeters in a sandy loam soil (1% OM, pH 6). Total MON 12000 residues from the day of application or day after for the four treatments (2, 3, 4, and 5) were 0.11, 0.19, 0.13 and 0.20 lb/a respectively. Residues levels were measured at 1, 3, 7, 14, 21, 30, 64, 122, 191 and 373 days after application. Residue values corresponded well with the calculated values from the assayed application samples. The columns and lysimeters were irrigated to maintain monthly precipitation at 120% of the 10 year average. The first rainfall after application occurred between July third and fifth with a total accumulation of 3.13 inches. In the first five weeks of the study 14.1 inches was approximately 3X's the typical rainfall for the region. Very heavy rainfalls occurred from July 24 to July 31, 1991 in which 10 inches of water fell resulting in flooded conditions in the lysimeter trenches. Therefore the leachate samples collected from July 24 to July 31 contained flood water in addition to the leachate. The point at which the maximum water holding capacity occurred and the first leachate and bromide appearance occurred was determined to be on July 29, 1991, 34 days after the application of the test substance.

Cedar Falls, Iowa

The test substance was applied July 24, 1991 to both the soil columns and the lysimeters in a loam soil (2.3% OM, pH 5.9). Total MON 12000 residues from the day of application or day after for the four treatments (2, 3, 4, and 5) were 0.09, 0.17, 0.16 and 0.19 lb/a respectively. Residue levels were measured at 1, 3, 7, 14, 21, 28, 59, 121, 183 and 370 days after application. Residue values corresponded well with the calculated values from the assayed application samples. The columns and lysimeters were irrigated to maintain monthly precipitation at 120% of the 10 year average. A total of one inch of rain fell with the first week of application and rainfall within the first month of the study was 7.30 inches which was two times the typical monthly rainfall amount. During periods of heavy rainfall standing water collected on top of the soil columns which was analyzed with the corresponding 0-6 inch soil column subsection. Water holding capacity for the Iowa site was not calculated because of column compaction and measurement of the rainfall at a regional site as opposed to the test site.

Analytical

Soil Residues

The stored soil samples that were subsampled into six inch increments as described above were extensively mixed and sampled (75 g) extracted with aqueous acetonitrile for periods of 14, 4, and 1 hours, centrifuged and decanted. The extracts were analyzed by LSC to determine total radioactivity present. The soil pellet was combusted to determine total residue, extracted plus bound. When two consecutive depth intervals contained less than 3 ppb of extractable residues all lower depth intervals for that time point were analyzed by combustion only. When total residues of greater than 3 ppb were found the extracts were combined and concentrated to remove the acetonitrile. The resulting aqueous solution was then extracted with dichloromethane to partition aminopyrimidine into the organic phase. The aqueous extracts were then concentrated, recombined with the organic extracts and again concentrated. The remaining soil was then dried and combusted to determine bound residues. When residues were greater than 3 ppb by LSC the concentrated extracts were profiled by HPLC/RAD. If individual components were present at greater than 0.26 ppb the component was then identified. The lowest limit of method validation was 4.3 ppb, samples with residues less than 3 ppb were not identified; all values greater than 0.26 ppb were reported for each component. Soxhlet extraction was conducted to determine the nature of the bound residues. After extraction with the solvents used in the standard analytical method there was an exhaustive extraction for 24 hours using 60% acetonitrile:water followed by a second ethyl acetate extraction for an additional 24 hours. The resulting extracts were concentrated and profiled by HPLC/RAD. Soxlet extraction of control samples resulted in hydrolysis of control MON 12000 so the data provided does not accurately reflect the concentration of parent compound.

Leachate

After leachate sampling, the volume, pH, bromide levels, and total radioactivity was measured. All samples with greater than 0.041% of the applied radioactivity as determined by LSC were solvent partitioned, concentrated to 10 ml and HPLC/RAD profiled. For leachate samples that were not profiled, the total residue, expressed as the percent of MON 12000 applied was determined by LSC. Individual components present at 0.004% of applied radioactivity were identified. As with the soil samples the MON 12000 pyrimidine leachate samples were preextracted with dichloromethane too prevent volatilization of aminopyrimidine. During concentration MON 12000 rearranged to the rearrangement ester due to basic tap water. This did not occur with the MON 12000 pyrimidine samples or with any of the soil samples due to the preextraction step. Residues are separately identified as rearrangement ester and MON 12000 in the raw data. In addition the high levels of salt present occasionally prevented accurate recovery determinations of the 3-chlorosulfonamide acid levels present in the fortified samples.

Analytical methods were validated by fortifying soil samples with radiolabelled solutions per component at 4.3 to 172 ppb.

RESULTS:

Average recoveries for fortifications with MON 12000, 3-chlorosulfonamide ester, 3- chlorosulfonamide acid, and aminopyrimidine were 95.3, 104.1, 96.4 and 80% respectively for the registrant and 80.7, 102.3, 89.7 and 87.0% respectively for the contract laboratory. Leachate fortifications recoveries were 90.6 and 110.2% for MON 12000 and chlorosulfonamide ester respectively.

Lucama, North Carolina

The half-life of ^{14}C-MON 12000 as a wettable powder (51% alone, 15% with the safener) applied on June 25, 1991 in four separate column/lysimeter treatments in duplicate was 10.0, 3.8, 3.7, and 5.5 days corresponding to treatments with MON-12000-Pd, MON 12000-Pz, MON-12000-Pz with safener and MON

12000-Pd with safener respectively. Application rates in the sandy loam (1% OM, pH 6) in the previously mentioned lysimeters respectively were at 0.11, 0.19, 0.13 and 0.20 lb/a (measured soil residues) corresponded to 61, 119, 100, and 125% of the normal application rate. Dissipation calculations were based on extractable MON 12000 levels present in the top six inches of soil because levels below six inches were always less than 5 ppb. It appears there was not a significant difference in the rate of dissipation between the columns with and without safener. MON 12000 leached into the 6- to 12- inch depth (sandy loam) with all four treatments. During the North Carolina studies, rainfall plus irrigation totaled 3.14 inches at 15 days posttreatment, 4.06 inches at 30 days, 18.62 inches at 61 days, 60.64 inches at 366 days, and 96.78 inches at 559 days. Throughout the study, the air temperatures ranged from 16 to 102 F; the soil temperatures ranged from 34 to 99 F at a 4-inch depth. The slope of the test plot was $\leq$2%, and the depth to the water table ranged from 6 to 72 inches throughout the study.

General; MON 12000-Pd with/out safener

MON 12000-Pd with and without safener dissipated with observed half-lives (using first order non-linear spatially variable models) of 5.5 and 10.0 days respectively from the upper 6 inches of soil. It appeared that there were no significant difference in degradate or dissipation patterns in the two separate treatments (with and without safener). The major metabolite was aminopyrimidine which was present at a maximum of 17.6 ppb by 7 DAT in the 0- to 6- inch soil depth. MON 12000 acid, rearrangement ester, and MON 12000 Desmethyl were also observed. Downward movement of aminopyrimidine in the 6- to 12- inch soil depth occurred in the two columns using the MON 12000-Pd label with and without safener. MON 12000 acid was detected at the 6- to 12- inch soil depth in the two treatments. MON 12000 Desmethyl was detected at the 6- to 12- inch soil depth in the treatment without safener. The rearrangement ester did not leach below the 0- to 6- inch soil depth in either treatment but the rearrangement acid was detected at the 6- to 12- inch depth in the treatment with safener.

MON 12000-Pd with safener

MON-12000-Pd with safener as a wettable powder dissipated from the upper 6- inches of sandy loam soil (1% OM, pH 6) with an observed half-life of 5.5 days. In the 0- to 6- inch soil depth parent MON 12000-Pd was at a maximum of 121.7 ppb at 0 DAT, decreased to 87.5 ppb by 7 DAT, 30.4 ppb at 14 DAT, 19.5 ppb at 21 DAT, increased to 24.6 ppb at 30 DAT, decreased to 7.0 ppb at 64 DAT, then decreased to 1.0 ppb by 373 DAT (final sampling interval). In the 0- to 6- inch soil depth, the degradate aminopyrimidine was at 11.6 ppb at 0 DAT, increased to 17.6 ppb at 7 DAT, then decreased to 1.5 ppb by 373 DAT. At lower soil depths aminopyrimidine was detected only three times in the 6- to 12- inch depth at 0.9, 1.5 and 1.7 ppb at 21, 30 and 64 DAT and was not detected at later sampling intervals. MON 12000 acid was detected at 3.2 ppb at 0 DAT, then remained relatively constant until it was not detected by 30 DAT. MON 12000 acid was detected three times at lower soil depths where in the 6- to 12- inch depth it was present at 1.5 ppb at 14 DAT, 1.1 ppb at 21 DAT, and 0.5 ppb by 30 DAT. The MON 12000 Desmethyl was present at 1.7 ppb at 0 DAT, remained relatively constant until it was not detected by 30 DAT. MON 12000 Desmethyl was detected only one time at deeper soil depths (6- to 12- inch) where by 14 DAT it was at 1.2 ppb. The rearrangement acid was detected intermittently at the 0- to 6- inch soil depth at low concentrations; 0.8 ppb at 7 DAT, 0.7 ppb at 30 DAT, and 0.4 ppb by 122 DAT and once at the 6- to 12- inch depth at 1.2 ppb by 14 DAT. The rearrangement ester was detected at 1.7 ppb 0 DAT, 4.9 ppb 1 DAT, then decreased to 0.4 ppb by 191 DAT. The rearrangement ester was not detected at lower sampling depths. (Table VIII)

MON 12000-Pd without safener

MON 12000-Pd without safener as a wettable powder dissipated from the upper 6- inches of sandy loam soil (1% OM, pH 6) with an observed half-life of 10.0

days. In the 0- to 6- inch soil depth parent MON 12000-Pd was a maximum of 53.4 ppb at 1 DAT, was at 25.5 ppb at 7 DAT, decreased further to 9.6 ppb at 30 DAT then to 0.4 ppb by 373 DAT. Parent MON 12000 was detected two times at the 6- to 12- inch soil depth, 1.5 ppb at 14 DAT, and 0.8 ppb by 122 DAT. In the 0- to 6- inch soil depth the degradate aminopyrimidine was at 3.0 ppb at 0 DAT, increased to 6.9 ppb by 7 DAT, was not detected until 191 DAT at 0.6 ppb and 0.3 ppb by 373 DAT. At lower sampling depths aminopyrimidine was detected once at 1.4 ppb by 122 DAT in the 6- to 12- inch soil layer. The MON 12000 acid degradate in the 0- to 6- inch soil depth was at 1.3 ppb on 0 DAT, increased to a maximum of 3.7 ppb by 21 DAT then was not detected by 64 DAT. At lower sampling depths MON 12000 acid was detected once at 0.9 ppb by 14 DAT in the 6- to 12- inch soil layer. The MON 12000 Desmethyl degradate was at a maximum of 1.2 ppb at 3 DAT then decreased to 0.5 ppb by 21 DAT then was not detected throughout the remaining sampling intervals. The rearrangement acid was detected only twice in the 0- to 6- inch soil depth at 1.7 ppb at 21 DAT and 0.4 ppb at 373 DAT. The rearrangement ester was detected four times and was at a maximum of 3.1 ppb at 21 DAT then decreased to 0.7 ppb at 191 DAT (Table VII).

MON 12000-Pd leachate

Of the four lysimeter treatments of ^{14}C-MON 12000-Pd the cumulative amounts of radioactivity collected over the course of the year were 0.083%, 0.420%, 2.714% and 0.034% of the MON 12000 applied for the duplicate treatments (7A, 7B, 10A, 10B) without and with safener respectively (Table XI). Column 10A with the highest amount had 70% of the cumulative radioactivity (86% which was parent) and 15.955 of the cumulative bromide come through in the first two leachate collections of 10 and 11 DAT indicating poor column construction (physical observation established the presence of distinct unnatural channels). From this column as well as for the samples at 34 and 100 DAT profiled for the MON 12000-Pd without safener treatment no parent residues above 0.08% of the applied MON 12000 radioactivity were observed. With the exception of the rearrangement ester at 10 DAT no metabolites were observed in any of the leachate samples profiled above a level of 0.13% (0.04 ppb) of the applied MON 12000 radioactivity. The metabolites quantified were: MON 12000 acid, rearrangement ester, rearrangement acid, and aminopyrimidine.

General; MON 12000-Pz with/out safener

MON 12000-Pz with and without safener dissipated with observed half-lives of 3.7 and 3.8 days respectively from the upper 6 inches of soil. It appeared that there was no significant difference in degradate or dissipation patterns in the two separate treatments (with and without safener). The major metabolite was 3-chlorosulfonamide ester which was present at a maximum of 24.2 ppb by 0 DAT in the 0- to 6- inch depth. Rearrangement acid, MON 12000 acid, 3-chlorosulfonamide acid, MON 12000 Desmethyl, rearrangement ester, and MON 12000 guanidine was also observed. Downward movement of 3-chlorosulfonamide ester in the 6- to 12- inch soil depth occurred in the two columns using the MON 12000-Pz label with and without safener. The hydrolysis product 3-chlorosulfonamide acid was detected in the 0- to 6- inch soil depth and was once detected in the 12- to 18- inch soil depth. MON 12000 acid was detected at the 6- to 12- inch soil depth in the two treatments and twice in the treatment without safener in the 12- to 18- inch soil depth. MON 12000 Desmethyl was generally detected in the 0- to 6- inch depth but was detected once at the 18- to 24- inch soil depth in the treatment without safener. The rearrangement ester leached to the 6- to 12- inch soil depth but the rearrangement acid was detected only once throughout all samples at the 6- to 12- inch soil depth.

MON 12000-Pz with safener

MON 12000-Pd with safener as a wettable powder dissipated from the upper 6- inches of sandy loam (1% OM, pH 6) with an observed half-life of 3.7 days. In the 0- to 6- inch soil depth parent MON 12000-Pd was at a maximum of 112.1

ppb at 1 DAT, decreased to 69.8 ppb at 7 DAT, 14.4 ppb at 14 DAT, 3.2 ppb at 64 DAT, and was at 0.7 ppb by 373 DAT. Parent MON 12000-Pd was detected in the 6- to 12- inch soil depth at a maximum of 1.8 ppb by 191 DAT and not detected again throughout the remaining sampling intervals. In the 0- to 6- inch soil depth, the degradate 3-chlorosulfonamide ester was present at 10.0 ppb at 0 DAT, reached a maximum of 18.3 ppb at 7 DAT, then decreased to 2.3 ppb by 373 DAT; the ester was detected at a maximum of 4.3 ppb at 191 DAT in the 6- to 12- inch soil depth and once more at 1.2 ppb at 191 DAT. The hydrolysis product 3-chlorosulfonamide acid was detected at a maximum of 2.5 ppb at 30 DAT, was not detected thereafter in the 0- to 6- inch soil depth but once in the 12- to 18- inch soil depth at 0.9 ppb. In the 0- to 6- inch soil depth MON 12000 acid was detected at 2.3 ppb at 0 DAT reached a maximum of 4.4 ppb by 30 DAT. MON 12000 acid was detected three times at lower soil depths where in the 6- to 12- inch soil depth it was present at 0.7, 0.4 and 0.6 ppb at 14, 21, and 30 DAT. MON 12000 Desmethyl was present at a maximum of 5.1 ppb at 7 DAT then decreased to 0.5 ppb in the 0- to 6- inch soil depths. The MON 12000 Desmethyl was detected only twice at the deeper soil depths where at 30 and 191 DAT it was present at 0.4 and 0.8 ppb. The rearrangement acid was not detected in any sampling. The rearrangement ester was at a maximum of 4.2 ppb at 0 DAT then decreased to 0.6 ppb by 373 DAT. The ester was detected once in the 6- to 12- inch soil depth at 0.6 ppb 122 DAT. MON 12000 Guanidine was detected at a maximum of 4.7 ppb in the 0- to 6- inch soil layer and was generally detected throughout all samples through the 12- to 18- inch soil depth at maximum concentrations of 4.7 ppb (0- to 6- inch soil depth), 2.0 ppb (6- to 12- inch soil depth), 2.9 ppb (12- to 18- inch soil depth) (Table X).

MON 12000-Pz without safener

MON 12000-Pz without safener as a wettable powder dissipated from the upper 6 inches of sandy loam soil (1% OM, pH 6) with an observed half-life of 3.8 days. In the 0- to 6- inch soil depth parent MON 12000-Pz was a maximum of 139.1 ppb at 0 DAT, was at 80.3 ppb at 7 DAT, decreased further to 21.0 ppb at 30 DAT, then to 0.8 ppb by 373 DAT. Parent MON 12000 was detected three times at the 6- to 12- inch soil depth, 3.0 ppb at 14 DAT, 1.6 ppb at 21 DAT, and 0.8 ppb at 64 DAT. In the 0- to 6- inch soil depth the degradate 3-chlorosulfonamide ester was at a maximum of 24.2 ppb at 0 DAT, decreased to 12.6 ppb by 14 DAT, was at 6.4 ppb at 30 DAT, then decreased slowly to 1.4 ppb at 373 DAT. The ester was detected three times at the 6- to 12- inch soil layer at 0.9 ppb, 0.6 ppb, 0.8 ppb at 21, 64, and 122 DAT. The hydrolysis product 3-chlorosulfonamide acid was detected in the 0- to 6- inch soil depth only four times at 1.7 ppb at 14 DAT, 4.8 ppb at 21 DAT, 2.4 ppb at 30 DAT, and 0.4 ppb at 122 DAT. MON 12000 acid in the 0- to 6- inch soil depth was at a maximum of 8.4 ppb at 30 DAT, was not detected in the remaining 0- to 6- inch soil sampling but was detected twice in the 6- to 12- inch soil depths at 0.6 ppb and 0.4 ppb at 14 and 21 DAT and was detected once in the 12- to 18- inch soil depth at 1.5 ppb at 21 DAT and once in the 18-24 inch soil depth at 1.2 ppb at 21 DAT. The MON 12000 Desmethyl degradate was at a maximum of 5.7 ppb at 7 DAT then was variable throughout sampling until it reached 0.3 ppb at 373 DAT. MON 12000 Desmethyl was detected twice at the 6- to 12- inch depth at 0.5 ppb at 21 and 64 DAT and was detected once at 0.9 ppb at 21 DAT in the 18- to 24- inch depth. The rearrangement acid was detected once in the 0- to 6- inch soil depth at 0.5 ppb at 64 DAT. The rearrangement ester was at a maximum of 7.0 ppb 30 DAT, then decreased to 0.4 ppb by 373 DAT. MON 12000 Guanidine reached a maximum of 10.9 ppb at 21 DAT and was last detected at 1.4 ppb at 122 DAT in the 0- to 6- inch soil depth. MON 12000 was detected in the 6-12 inch soil layer at all sampling times at a maximum of 1.6 ppb 21 DAT and was detected at all samples in the 12- to 18- inch depth at a maximum of 4.0 ppb and was detected in one of two samples at the 18- to 24- inch depth at 2.1 ppb at 191 DAT (Table IX).

MON 12000-Pz leachate

Of the four lysimeter treatments of ^{14}C-MON 12000-Pd the cumulative amounts

of radioactivity collected over the course of the year were 0.38%, 7.720%, 0.050%, 0.074% of the MON 12000 applied for the duplicate treatments (8A, 8B, 9A, and 9B) without and with safener respectively (Table XI). Collectively the total residues found equaled 7.72% of the applied radioactivity (8B, Table XIV). The early leachate samples collected on 10 and 11 DAT contained primarily MON 12000 or rearrangement ester (possibly from work-up) at levels of 0.64% of the MON 12000 application. Later leachate collections primarily contained MON 12000 guanidine at a cumulative level of 5.6% of the total applied radioactivity. This column was apparently compensated as 20% of the bromide, 29% of the total leachate and 12% of the total radioactivity collected at 10 and 11 DAT (physical inspection established the presence of column channels). Essentially all of the parent found in the leachate collections, 74% of the total amount present was observed at the 10 and 11 DAT sampling points. This occurred 24 days before the maximum moisture holding capacity of the column had been reached and before irrigation or rainfall. For the remaining three lysimeters, which accumulated only 0.03 to 0.07% of the applied radioactivity, detectable levels of radioactivity were found after the moisture capacity of the soil had been attained at 34 DAT.

Cedar Falls, Iowa

The half-life of ^{14}C-MON 12000 as a wettable powder (51% alone, 15% with safener) applied on July 24, 1991 in four separate column/lysimeter treatments in duplicate was 56.3, 27.1, 13.6, and 28.1 days corresponding to treatments with MON-12000-Pd, MON 12000-Pz, MON-12000-Pz with safener and MON 12000-Pd with safener respectively. Application rates for the previously mentioned lysimeters respectively in the loam soil (2.3% OM, pH 5.9) were 0.09, 0.17, 0.16, 0.19 lb/a (measured soil residues) which correspond to 43, 100, 133, and 100% of the actual MON 12000 application rates. Dissipation calculations were based on extractable MON 12000 levels present in the top six inches of soil. It appears there was not a significant difference in the rate of dissipation between the columns with and without safener. Parent MON 12000 leached into the 12- to 18- inch depth in two of the four treatments. During the Iowa studies, rainfall plus irrigation totaled 7.30 inches at 31 days posttreatment, 10.38 inches at 62 days, 18.58 inches at 123 days, 43.00 inches at 366 days, and 63.85 inches at 567 days. Throughout the study, the air temperatures ranged from -11 to 93 F; soil temperatures were not provided. The slope of the test plot was $\leq$2%, and the depth to the water table ranged from 18 to 87 inches throughout the study.

General; MON 12000-Pd with/out safener

MON 12000-Pd with and without safener dissipated with observed half-lives (using first order non-linear spatially variable models) of 28.1 and 56.3 days respectively from the upper 6 inches of soil. Taking into consideration the difference in application rate (higher without the safener) it appeared that there were no significant differences in the degradate or dissipation patterns in the two separate treatments (with and without safener). The major metabolite was the rearrangement ester which was present at a maximum of 28.0 ppb at 28 DAT in the 0- to 6- inch soil depth. The rearrangement acid, aminopyrimidine, where measured at concentrations close to the ester and MON 12000 acid and MON 12000 Desmethyl were also observed. The rearrangement ester and aminopyrimidine did not leach below the 0- to 6- inch soil depth either of the four treatments. The rearrangement acid was detected at two of the four treatments at the 6- to 12 inch soil depth and at the 12- to 18- inch soil depth in one of the four treatments. MON 12000 acid was detected twice at the 6- to 12- inch soil depth in the two Pd labelled treatments. MON 12000 Desmethyl was detected one time at the 6- to 12- inch soil depth but generally remained in the 0- to 6- inch layer.

MON 12000-Pd with safener

MON 12000 Pd with safener as a wettable powder dissipated from the upper 6- inches of loam soil (2.3% OM, pH 5.9) with an observed half-life of 28.1

days. In the 0- to 6- inch soil depth parent MON 12000-Pd was at a maximum of 94.2 ppb at 0 DAT, decreased to 44.0 ppb by 7 DAT, increased to 58.0 ppb at 14 DAT, decreased to 29.3 ppb at 21 DAT, increased to 59.7 ppb at 28 DAT, then decreased to 10.4 ppb by 370 DAT. In the 0- to 6- inch soil depth, the degradate rearrangement ester was at 1.8 ppb at 0 DAT, was at 18.5 ppb at 21 DAT, then decreased to 2.7 ppb by 370 DAT. The ester was not detected between 0 DAT and 21 DAT. The rearrangement acid was detected at 1.9 ppb at 21 DAT, increased to a maximum of 11.4 ppb at 121 DAT, then decreased to 7.6 ppb at 370 DAT. In the 0- to 6- inch soil depth aminopyrimidine was at 2.9 ppb at 0 DAT, increased to a maximum of 18.9 ppb at 28 DAT, then decreased to 5.4 ppb at 370 DAT. Aminopyrimidine was not detected below 6- inches. MON 12000 acid was at 0.5 ppb at 1 DAT, increased to a maximum of 6.5 ppb at 28 DAT, then decreased to 3.3 ppb by 370 DAT. MON 12000 acid was not detected below the 6- inch soil depth. The MON 12000 Desmethyl was present at 2.8 ppb at 0 DAT, increased to a maximum of 6.5 ppb at 28 DAT, then decreased to 2.4 ppb by 370 DAT and was detected once at 1.8 ppb in the 6- to 12- inch soil depth at 183 DAT.

MON 12000-Pd without safener

MON 12000-Pd without safener as a wettable powder dissipated from the upper 6- inches of loam soil (2.3% OM, pH 5.9) with an observed half-life of 56.3 days. In the 0- to 6- inch soil depth parent MON 12000-Pd was a maximum of 85.7 ppb at 14 DAT. Initial concentrations were variable at 41.3 ppb at 0 DAT, 64.2 ppb at 1 DAT, 23.0 ppb at 3 DAT, 78.0 ppb at 7 DAT. Parent MON 12000 was detected in the 6- to 12- inch soil depth at 0.8, 3.3, and 2.2 ppb at 59 DAT, 183 DAT, and 370 DAT respectively. Parent MON 12000 was detected once in the 12- to 18- inch soil depth at 2.6 ppb at 183 DAT. The rearrangement ester was not detected until 14 DAT at 3.9 ppb, reached a maximum of 28.0 ppb at 28 DAT, then decreased to 3.9 ppb by 370 DAT. The rearrangement acid was first detected at 0.8 ppb at 14 DAT, increased to 21.0 ppb by 59 DAT, then decreased to 7.2 ppb by 370 DAT. At lower sampling depths (6- to 12- inch) the rearrangement acid was detected at 1.4 ppb at 59 DAT, and 3.1 ppb at 370 DAT. In the 0- to 6- inch soil depth the degradate aminopyrimidine was at 2.3 ppb by 1 DAT, increased to a maximum of 6.1 ppb by 21 DAT, then decreased to 2.2 ppb by 370 DAT. The MON 12000 acid degradate in the 0- to 6- inch soil depth was at 0.7 ppb by 1 DAT, increased to a maximum of 5.2 ppb by 59 DAT, then decreased to 2.7 ppb by 370 DAT. MON 12000 acid was detected once at 1.8 ppb by 370 DAT in the 6- to 12- inch soil depth. The MON 12000 Desmethyl degradate was first detected at 0.7 ppb at 0 DAT, reached a maximum of 4.4 ppb by 14 DAT then decreased to 2.6 ppb by 370 DAT. The Desmethyl compound was not detected below the 6- inch soil depth.

MON 12000-Pd leachate

Of the four lysimeter treatments of ^{14}C-MON 12000-Pd the cumulative amounts of radioactivity collected over the course of the year were 0.082%, 0.074%, 0.072%, and 0.026% of the application rate for the duplicate treatments (7A, 7B, 10A, and 10B) without and with safener respectively (Table XIX). Because of no single collection of leachate resulted in residues over 0.041% of the applied radioactivity no leachate samples were HPLC profiled for this treatment. It appears column saturation points were generally achieved between day 222 and 273 after treatment.

General; MON 12000-Pz with/out safener

MON 12000-Pz with and without safener dissipated with observed half-lives of 13.6 and 27.1 days respectively from the upper 6 inches of soil. It appeared that there were no significant differences in the degradation half-lives or patterns of the two treatments with and without safener. Parent MON 12000 was detected in the 6- to 12- inch soil depths as well as once in the 12- to 18- inch soil depth. The major metabolite was 3-chlorosulfonamide ester which was present at a maximum of 19.0 ppb at 21 DAT in the 0- to 6- inch soil depth. Rearrangement acid, MON 12000 acid, 3-chlorosulfonamide acid, MON 12000

clay loam soil (56% sand, 22% silt, 22% clay, 1.2% organic matter, pH 6.0, CEC 13.2 meq/100 g) using a tractor-mounted sprayer. The application was made on May 22, 1990; the herbicide was immediately incorporated to a 2-inch depth using a rotovator, and then the plot was planted to field corn. The plot was retreated with only MON 12000 at 0.094 lb ai/A on June 26, when the corn was 25-30 inches tall. An untreated plot (30 x 110 feet), located 225 feet from the treated plot, was maintained as a control. The site was irrigated by furrow irrigation when necessary. The corn was harvested on October 26, 1990, and the stubble was disced into the soil. Soil samples were collected from each subplot of the treated plot and from the control plot prior to treatment; at 0, 1, 3, 12, 14, and 22 days after the first treatment; and at 0, 1, 3, 7, 14, and 23 days and approximately 1, 2, 4, 6, 9, 11, 15, and 18 months after the final treatment. The soil samples were stored frozen for up to approximately 34 months prior to extraction.

At the Colo, Iowa, site, MON 12000, tank-mixed with acetochlor and MON 13900, was broadcast at 0.124 lb ai/A onto a bareground plot (90 x 105 feet) of loam soil (38% sand, 38% silt, 24% clay, 4.5% organic matter, pH 6.5, CEC 17.3 meq/100 g) using a tractor-mounted sprayer. The application was made on June 4, 1990, and the herbicide was immediately incorporated to a 4-inch depth using a field cultivator. The plot was planted to field corn on June 10 (6 days after treatment). The plot was retreated with only MON 12000 at 0.093 lb ai/A on July 17, when the corn was 30 inches tall. An untreated plot (90 x 105 feet), located 200 feet from the treated plot, was maintained as a control. The site was not irrigated. The corn was harvested on October 24, 1990. Soil samples were collected from each subplot of the treated plot and from the control plot prior to treatment; at 0, 1, 5, 7, and 21 days after the first treatment; and at 0, 1, 4, 7, 16, and 21 days and approximately 1, 2, 4, 9, 12, and 16 months after the final treatment. The soil samples were stored frozen for up to approximately 31 months prior to extraction.

At the Genesco,-Illinois, site, a plot (60 x 90 feet) of loam soil (24% sand, 50% silt, 26% clay, 4.8% organic matter, pH 7.7, CEC 22.7 meq/100 g) was planted to field corn, then treated at 0.129 lb ai/A with MON 12000, tank-mixed with acetochlor and MON 13900, using a tractor-mounted sprayer; the planting and herbicide treatment occurred on June 1, 1990. An untreated plot (20 x 100 feet), located 217 feet upslope from the treated plot, was maintained as a control. The site was irrigated by sprinkler as needed. The corn was harvested on October 26, 1990. Soil samples were collected from each subplot of the treated plot and from the control plot prior to treatment, and at 0, 1, 3, 8, 14, 24, 34, 60, 122, 181, 368, and 549 days posttreatment. The soil samples were stored frozen for up to approximately 26 months prior to extraction.

At the Uvalde, Texas, site, a plot (80 x 140 feet) of clay loam soil (30% sand, 34% silt, 36% clay, 2.1% organic matter, pH 8.3, CEC 21.3 meq/100 g) was planted to field corn on April 10, 1990, and treated

at 0.125 lb ai/A with MON 12000, tank-mixed with acetochlor and MON 13900, using a high-clearance sprayer, on April 11. An untreated plot (80 x 140 feet), located 200 feet from the treated plot, was maintained as a control. The site was irrigated by furrow irrigation as needed. The corn was harvested on August 23, 1990. Soil samples were collected from each subplot of the treated plot and from the control plot prior to treatment, and at 0, 1, 3, 7, 14, 20, 29, 61, 119, 183, 365, and 537 days posttreatment. The soil samples were stored frozen for up to approximately 26 months prior to extraction.

Analytical methods: To analyze for MON 12000, subsamples (75 g) of the soil were mixed with portions of celite and sea sand, then extracted twice with acetonitrile:water (75:25, v:v) by shaking on a mechanical shaker for 15 minutes. After each extraction, the samples were centrifuged, and the extracts were filtered through glass wool. The extracts were combined and mixed with saturated aqueous sodium chloride:deionized water (6:250, v:v), and the solutions were partitioned twice against methylene chloride. After each partitioning, the organic phases were filtered through sodium sulfate and combined. The organic solutions were concentrated to dryness at room temperature on a rotary evaporator, and the resulting residues were redissolved in methylene chloride:methanol (85:15, v:v). The solutions were diluted with methylene chloride, then purified on Florisil SPE columns; the columns were rinsed sequentially with methylene chloride and methylene chloride:methanol (95:5, v:v), and eluted with methylene chloride:methanol (85:15, v:v). To convert MON 12000 to 3-chloro-5-[(4,6-dimethoxy-2-pyrimidinyl)amino]-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester (the "rearrangement ester"), aliquots of 0.5 M potassium carbonate solution were added to the column eluants, and the samples were stirred overnight. After stirring, the solutions were partitioned twice against methylene chloride; after each partitioning, the organic phases were filtered through sodium sulfate and combined. The organic solutions were concentrated to dryness at room temperature on a rotary evaporator. The residues were redissolved in isooctane:ethyl acetate (95:5, v:v), and the solutions were purified on silica SPE columns; the columns were rinsed twice with isooctane:ethyl acetate (95:5, v:v), and eluted with isooctane:ethyl acetate (70:30, v:v). The eluants were concentrated to dryness at room temperature, and the residues were dissolved in isooctane:ethyl acetate (95:5, v:v). Aliquots of the solution were analyzed by GC with nitrogen/phosphorous detection. The identification and quantitation of MON 12000 in the extracts were achieved by comparison to MON 12000 reference standards. The detection limit was 2 ppb. Average recoveries from soil samples collected at the test sites and fortified with MON 12000 at 0.001-0.10 ppm were 73.15-100.6% of the applied.

For analysis of the MON 12000 degradates aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine) and 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], subsamples (75 g) of the soil were mixed with portions of celite and sea sand, and extracted twice with acetonitrile:water (75:25, v:v) by

shaking on a mechanical shaker for 15 minutes. After each extraction, the samples were centrifuged, and the extracts were filtered through glass wool and combined. The combined extracts were concentrated at room temperature on a rotary evaporator to remove acetonitrile; the remaining aqueous solutions were diluted with deionized water, and the pH was adjusted to >10 with 2.5 N NaOH. The solutions were partitioned twice against methylene chloride; after each partitioning, the organic phases were filtered through sodium sulfate and combined.

The organic phases, containing aminopyrimidine, were diluted with isooctane and concentrated at "ice bath temperatures" using a "cold finger" rotary evaporator. The remaining solutions were purified on amino SPE columns, and the columns were eluted with ethyl acetate:isooctane (20:80, v:v). The eluant was concentrated at "ice bath temperatures". Aliquots of the concentrated solutions were analyzed by GC with nitrogen/phosphorous detection. The identification and quantitation of aminopyrimidine in the extracts were achieved by comparison to reference standards; aminopyrimidine was quantitated to a lower limit of 5 ppb. Average recoveries from soil samples fortified at 0.005-0.10 ppm were 76.86-101.6% of the applied.

The aqueous phases remaining from the methylene chloride partitionings, which contained any 3-chlorosulfonamide, were acidified to pH <2 with 2 N sulfuric acid, then partitioned twice against ethyl acetate; after each partitioning, the organic phases were filtered through sodium sulfate and combined. For derivatization of 3-chlorosulfonamide to its trimethyl derivative, the combined organic solutions were concentrated to dryness on a rotary evaporator, diluted with acetone, and treated sequentially with methanol, 0.1 N HCl, and TMS-diazomethane. The samples were mixed by swirling, stoppered loosely, and allowed to stand overnight at room temperature. When necessary, additional TMS-diazomethane was added, and the samples were allowed to stand for an additional hour. The derivatized-samples were concentrated to dryness, and the resulting residues were redissolved in ethyl acetate. The solutions were diluted with isooctane, and purified on silica SPE columns. The columns were eluted with ethyl acetate:isooctane (30:70, v:v), and the eluants were concentrated to dryness. The resulting residues were redissolved in ethyl acetate:isooctane (20:80, v:v), and aliquots of the solutions were analyzed by GC with electron-capture detection. The identification and quantitation of 3-chlorosulfonamide in the extracts were achieved by comparison to reference standards; 3-chlorosulfonamide was quantitated to a lower limit of 5 ppb. Average recoveries from soil samples fortified at 0.005-0.10 ppm were 75.70-100.0% of the applied.

DATA SUMMARY:

MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester; 25% WP] dissipated with registrant-calculated half-lives of 18-60 days from the upper 6 inches of plots of sandy clay loam soil in California and loam soil in Iowa that were treated with MON 12000 twice, at approximately 0.125 lb ai/A (pre-plant incorporated) and 0.094 lb ai/A (late postemergence), in Spring 1990. Also, MON 12000 dissipated with half-lives of 6-34 days from plots of loam soil in Illinois and clay loam soil in Texas that were treated with MON 12000 once, at approximately 0.125 lb ai/A (pre-emergence), in Spring 1990. MON 12000 was ≤0.004 ppm below the 6-inch soil depth at all test sites at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the study.

At the California site, MON 12000, applied as sequential preplant soil-incorporated and late postemergence (field corn) broadcast treatments on May 22 and June 26, 1990, dissipated with a registrant-calculated half-life of 60.5 days and an observed initial half-life of approximately 1 month from the a plot of sandy clay loam soil. In the 0- to 6-inch soil depth, MON 12000 averaged 0.035-0.043 ppm at 0 through 22 days after the first application, 0.023 ppm immediately after the second application, 0.012-0.013 ppm 14 days through 1 month, 0.007-0.009 at 2 through 6 months, and <0.002 ppm at 15 and 18 months (Table 6). In the 6- to 12-inch depth, MON 12000 was an average maximum of 0.004 ppm at 22 days after the first application, and averaged <0.002 ppm at 2 through 18 months. MON 12000 was not detected (<0.002 ppm) below 12 inches at any sampling interval. The soil samples collected from this test site were not analyzed for degradates.

During the study, rainfall plus irrigation totaled 2.43 inches between the two treatments (May 22-June 25, 1990), 4.20 inches at 58 days after the final treatment (August 23), 4.77 inches at 114 days (October 18), 17.98 inches at 367 days, and 20.35 inches throughout the entire 18-month period. Throughout the study, the air temperatures ranged from 17 to 107 F; the soil temperatures, measured at each sampling interval, ranged from 47 to 114 F at a 1-inch depth, and from 43 to 86 F at a 6-inch depth. The slope of the test plot was ≤2%, and the annual depth to the water table was 10-50 feet.

At the Iowa site, MON 12000, applied as sequential preplant soil-incorporated and late postemergence (field corn) broadcast treatments on June 4 and July 17, 1990, dissipated with a registrant-calculated half-life of 17.6 days from a plot of loam soil. In the 0- to 6-inch soil depth, MON 12000 averaged 0.017-0.023 ppm at 0 through 21 days after the first treatment, 0.035-0.038 ppm at 0 through 4 days after the second treatment, 0.027 ppm at 7 days, 0.015 ppm at 16 and 21 days, and 0.002 ppm at 12 and 18 months (Table 5). In the 6- to 12-inch depth, MON 12000 was an average maximum of 0.003 ppm at 16 days

after the second treatment, and averaged <0.002 ppm at 1 through 18 months. MON 12000 was not detected (<0.002 ppm) below 12 inches at any sampling interval. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all depths throughout the study.

During the study, rainfall plus irrigation totaled 14.94 inches between the two treatments (June 4-July 17, 1990), 22.68 inches at 17 days after the final treatment (August 3), 25.17 inches at 33 days (August 19), 60.04 inches at 370 days, and 73.17 inches throughout the entire 18-month period. Throughout the study, the air temperatures ranged from -14 to 99 F; the soil temperatures, measured at each sampling interval, ranged from 30 to 96 F at a 2-inch depth, and from 35 to 90 F at a 4-inch depth. The slope of the test plot was 2%, and the annual depth to the water table was 1-3 feet.

At the Illinois site, MON 12000, applied as a preemergence broadcast treatment on June 1, 1990, dissipated with a registrant-calculated half-life of 34.4 days from a plot of loam soil which had been planted to field corn. In the 0- to 6-inch soil depth, MON 12000 averaged 0.037-0.049 ppm at 0 through 14 days posttreatment, 0.022 ppm at 34 days, 0.013 ppm at 60 days, 0.003 ppm at 368 days, and <0.002 at 549 days (Table 4). In the 6- to 12-inch depth, MON 12000 was an average maximum of 0.004 ppm at 34 days posttreatment, and averaged <0.002 ppm at 122 through 549 days. At all sampling intervals, MON 12000 averaged ≤0.002 ppm below the 12-inch depth. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all depths throughout the study.

During the study, rainfall plus irrigation totaled 11.72 inches at 37 days posttreatment (July 8, 1990), 17.82 inches at 63 days (August 3), 50.39 inches at 374 days, and 69.91 inches throughout the entire 18-month period. Throughout the study, the air temperatures ranged from -5 to 95 F; the soil temperatures, measured at each sampling interval, ranged from 34 to 80 F at a 2-inch depth, and from 44 to 78 F at a 4- or-6-inch depth. The slope of the test plot was ≤2%, and the annual depth to the water table was 0.5-2.0 feet.

At the Texas site, MON 12000, applied as a preemergence broadcast treatment on April 11, 1990, dissipated with a registrant-calculated half-life of 6.3 days from a plot of clay loam soil which had been planted to field corn. In the 0- to 6-inch soil depth, MON 12000 averaged 0.036-0.038 ppm at 0 through 3 days posttreatment, 0.021 ppm at 14 days, 0.015 ppm at 20 days, 0.006 ppm at 29 days, and <0.002 ppm at 365 and 537 days (Table 3). In the 6- to 12- and 12- to 18-inch depths, MON 12000 averaged <0.002 ppm at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all depths throughout the study.

During the study, rainfall plus irrigation totaled 3.05 inches at 15 days posttreatment (April 26, 1990), 5.66 inches at 34 days (May 15), 37.13 inches at 359 days, and 58.23 inches throughout the entire 18-

Desmethyl, rearrangement ester, and MON 12000 guanidine was also observed. 3-chlorosulfonamide ester, MON 12000 Desmethyl remained in the 0- to 6- inch soil layer. MON 12000 Guanidine, MON 12000 acid leached to the 6- to 12- inch soil depth. The ester hydrolysis product 3-chlorosulfonamide acid and the rearrangement acid leached to the 12- to 18- inch soil depth.

MON 12000-Pz with safener

MON 12000 with safener as a wettable powder dissipated from the upper 6-inches of loam (2.3% OM, pH 5.9) soil with an observed half-life of 13.6 days. In the 0- to 6- inch soil depth parent MON 12000-Pz was variable at a maximum of 76.6 ppb at 1 DAT, decreased to 25.6 ppb at 7 DAT, increased to 50.9 ppb by 14 DAT, decreased to 33.0 ppb by 21 DAT, increased to 44.3 ppb by 28 DAT, decreased to 9.9 ppb by 121 DAT, then was at 16.5 ppb by 370 DAT. Parent MON 12000-Pz was detected in the all of the 6- to 12- inch soil samples and was at a maximum of 5.0 ppb at 59 DAT. In the 0- to 6- inch soil depth, the degradate 3-chlorosulfonamide ester was present at 3.4 ppb at 0 DAT, reached a maximum of 4.6 ppb by 183 DAT, then decreased to 2.8 ppb by 370 DAT. The ester hydrolysis product 3-chlorosulfonamide acid was detected four times at a maximum of 4.4 ppb at 370 DAT. In the 0- to 6- inch soil depth MON 12000 acid was detected at 1.6 ppb at 0 DAT, reached a maximum of 5.2 ppb by 28 DAT, then decreased to 3.8 ppb by 370 DAT. MON 12000 acid was detected once at lower soil depths (6-12 inch) where it was at 1.4 ppb by 370 DAT. MON 12000 Desmethyl was present in the 0- to 6- inch soil depth at a maximum of 4.3 ppb at 14 DAT, then decreased to 1.1 ppb by 370 DAT and was not detected lower. The rearrangement acid was detected four times at a maximum of 4.4 ppb by 370 DAT. The rearrangement ester was at a maximum of 4.6 ppb at 183 DAT, then decreased to 2.8 ppb by 370 DAT. MON 12000 Guanidine was detected at a maximum of 5.5 ppb in the 0- to 6- inch soil depth and was detected twice in the 6- to 12- inch soil depth at a maximum of 4.1 ppb (Table XVIII).

MON 12000-Pz without safener

MON 12000-Pz without safener as a wettable powder dissipated from the upper 6- inches of loam soil with an observed half-life of 27.1 days. In the 0- to 6- inch soil layer parent MON 12000-Pz was a maximum of 15.28 ppb at 1 DAT, decreased to 78.2 ppb at 7 DAT, was 64.4 ppb at 14 DAT, 43.2 ppb at 28 DAT, then decreased slowly to 5.0 ppb at 370 DAT. Parent MON 12000 was three times in the 6- to 12- inch soil layer, 3.6 ppb at 59 DAT, 1.4 ppb at 121, 2.4 ppb at 183 DAT and detected once in the 12- to 18- inch soil layer at 2.8 ppb at 21 DAT. In the 0- to 6- inch soil layer the degradate 3-chlorosulfonamide ester was present at 1.4 ppb at 0 DAT, increased to a maximum of 15.8 ppb at 14 DAT, then decreased slowly-to 3.5 ppb at 370 DAT. The ester was not detected at lower sampling depths. The ester hydrolysis product 3-chlorosulfonamide acid was detected in the 0- to 6- inch soil layer at 1.2 ppb at 1 DAT, reached a maximum of 8.2 ppb at 59 DAT, then decreased to 2.8 ppb by 370 DAT. 3-chlorosulfonamide acid was detected at all sampling intervals in the 6- to 12-inch soil layer and was at a maximum of 4.8 ppb at 370 DAT and was detected one time in the 12- to 18- inch soil layer at 1.8 ppb at 370 DAT. MON 12000 acid in the 0- to 6- inch soil depth was at 1.1 ppb at 0 DAT, reached a maximum of 6.0 ppb at 28 DAT, then decreased slowly to 3.5 ppb at 370 DAT. MON 12000 acid was not detected at lower depths. The MON 12000 Desmethyl degradate was at 1.0 ppb at 0 DAT, increased to a maximum of 4.0 ppb at 21 DAT, then decreased slowly to 1.8 ppb at 183 DAT and was not detected at further depths. The rearrangement acid was detected four times in the 0- to 6- inch soil depth at a maximum of 10.3 ppb at 121 DAT and was detected once in the 12- to 18 inch soil layer at 370 DAT. The rearrangement ester was at 0.9 ppb at 1 DAT, increased to 5.9 ppb at 183 DAT, then decreased to 1.8 ppb at 370 DAT. MON 12000 Guanidine was detected three times in the 0- to 6- inch soil layer at 3.6 ppb at 59 DAT, 2.4 ppb at 183 DAT, and 1.9 ppb at 370 DAT (Table XVII).

MON 12000-Pz leachate

Of the four lysimeter treatments of ^{14}C-MON 12000-Pd the cumulative amounts

of radioactivity collected over the course of the year were 0.290, 1.163, 0.207, and 0.256% of the applied MON 12000 for the duplicate treatments without and with safener, respectively (Table XIX). The leachate samples for treatments without safener were profiled for 273 and 357 DAT (8A, Table XX) and 118, 222, 329, 336, 343, 357, and 364 DAT (8B, Table XX). The leachate samples for treatments with safener were profiled for 28 and 329 DAT (9A and 9B, respectively, Table XXI). Mon 12000 Guanidine, 3-chlorosulfonamide acid, 3-chlorosulfonamide ester, and MON 12000 acid were observed in the leachate samples analyzed, all at levels less than 0.28% of the applied radioactivity. Mon 12000 parent was observed in a single leachate sample at 28 DAT from the MON 12000-Pz with safener treatment (9A), but only at 0.037% of the applied radioactivity. The relative amounts of leachate, radioactivity and bromide collected over the 12 month period are presented in Figures 32-35.

DISCUSSION:

1. Soil samples from a confined rotational crop (165-1) study (MRID #42396204) were stored approximately 26 months since their initial HPLC profile was generated, were reanalyzed to determine the stability of MON 12000 and the appropriate metabolites. Those analyses gave an indication that MON 12000 and the metabolites were stable under frozen storage conditions for that length of time. A specific storage stability study using the soil, leachate and field spiked samples from North Carolina is underway and will be provided as additional report.

2. The leachate samples were stored frozen for up to approximately 16 months prior to analysis. No storage stability data were presented for water samples for MON 12000 or its degradates. Therefore, the data reported for the actual leachate field samples should be considered only supplemental.

3. Due to the high silt and clay content of the Iowa soil, significant compaction occurred during insertion of the steel pipes, resulting in soil columns with typical lengths of $\leq$30 inches. Unsuccessful attempts were made to locate a test plot at the Iowa location in which soil compaction would be less severe. During the study, standing water ("supernatant") collected from the top of the soil columns was present at all sampling intervals except those through 7 days posttreatment. Additionally, the late application date and the early freezing temperatures that occurred in 1991 represent environmental conditions which are atypical of the corn growing season. According to the study authors, the late seasonal application, soil compaction, and standing water provide a worst-case scenario for the dissipation of MON 12000 in soil, and provide information about the anaerobic aquatic metabolism of MON 12000 in the field.

4. According to the study authors, the "leachate" samples collected at the North Carolina site on July 31 through August 5, 1991 consisted primarily of floodwater resulting from heavy rainfall.

5. Residues reported as "% of the applied" were calculated from the total MON 12000 residues of the 0- or 1-day sample results.

6. Data obtained from two of the lysimeters at the North Carolina site ("Lysimeter A" treated with MON 12000-Pd with safener, and "Lysimeter B" treated with MON 12000-Pz only) were considered to be invalid. According to the study authors, "the rapid appearance of leachate, bromide, and radioactivity, prior to soil column saturation, was inconsistent with the other lysimeters [page 36]" and suggested that the column constructions were faulty; visual examination after collection verified that the soil columns contained "unnatural channels".

7. For characterization of bound residues, select extracted soils were Soxhlet-extracted sequentially with acetonitrile:water (60:40, v:v) and ethyl acetate for 24 hours per extraction; the Soxhlet extractions allowed for significant reduction in radioactivity bound to the soil. The extracts were analyzed by HPLC as previously described, and were found to contain the same degradates

as were found in the original extracts. However, Soxhlet extraction of soil samples fortified with MON 12000 resulted in the hydrolysis of the parent to chlorosulfonamide ester and aminopyrimidine [page 29]. Therefore, the data provided from the Soxhlet extractions of the actual field samples is of limited value.

8. The "rearrangement ester" was unexpectedly generated from MON 12000-Pz-fortified tap water samples during the rotary-evaporation step due to an increased concentration of salts in solution. In addition, the salt content in the tap water also interfered with the quantitation of 3-chlorosulfonamide acid. Recoveries from leachate samples and bottled water samples after fortification with the various compounds were reasonable and suggest that reported results for parent and the various degradates in the field leachate samples are reasonable.

9. Although a few recoveries of aminopyrimidine from fortified soil and water samples were low, the majority were reasonable.

DATA EVALUATION RECORD

DER 5

CHEM 128721 MON 12000 §164-1

FORMULATION--06--WETTABLE POWDER (WP)

STUDY ID 42976303
White, R.H., and M.A. Schlicher. 1993. Dissipation of radiolabeled MON 12000 and MON 12000 metabolites in field soil. Monsanto Study No. MSL 12891; Hazelton Project No. HWI 6103-157; A.A.S.I. Project No. 0642-91-3. Unpublished study performed by Monsanto Company, St. Louis, MO; Hazelton Wisconsin, Inc., Madison, WI; and American Agricultural Services, Inc., Cary, NC. Unpublished study submitted by Monsanto Company, St. Louis, MO.

DIRECT REVIEW TIME = 84

REVIEWED BY: M. Anderson TITLE: Staff Scientist

EDITED BY: C. Cooke TITLE: Staff Scientist
K. Ferguson Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: K. Poff
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: K. Poff

CONCLUSIONS:

Terrestrial Field Dissipation

1. Study MRID #42976303 is acceptable and may be used as supplemental information to satisfy the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

2. MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester] dissipated with observed half-lives of 1-2 weeks from the upper 6 inches of in-situ sandy loam (69.5% sand, 25.2% silt, 5.3% clay, 1.2% organic matter, pH 6.0, CEC 7.8 meq/100 g) soil

columns in North Carolina and 1-2.5 months from the upper 6 inches of loam (43.5% sand, 39.2% silt, 17.3% clay, 2.3% organic matter, pH 5.9, CEC 18.1 meq/100 g) soil columns in Iowa; the columns had been treated at a nominal rate of 0.23 lb ai/A with either pyrazole ring- or pyrimidine ring-labeled [^{14}C]MON 12000 formulated alone (51% wettable powder) or with the herbicide safener MON 13900 (15% wettable powder). The degradates detected in the soils at both sites were aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine), 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], 3-chlorosulfonamide ester, the "rearrangement ester", the "rearrangement acid", MON 12000 acid, MON 12000 desmethyl, and MON 12000 guanidine. Neither MON 12000 nor any [^{14}C]degradate was detected at >5 ppb below the 6-inch soil depth at either site. The test plots were irrigated throughout the study with a hand-held sprinkler to maintain a minimum of approximately 120% of total water for the monthly 10-year rainfall averages. During the North Carolina studies, rainfall plus irrigation totaled 3.14 inches at 15 days posttreatment, 4.06 inches at 30 days, 18.62 inches at 61 days, 60.64 inches at 366 days, and 96.78 inches at 559 days. During the Iowa studies, rainfall plus irrigation totaled 7.30 inches at 31 days posttreatment, 10.38 inches at 62 days, 18.58 inches at 123 days, 43.00 inches at 366 days, and 63.85 inches at 567 days. No MON 12000 residues above 3 ppb are observed below the top twelve inches of soil in this study. At 18.5 months posttreatment, cumulative [^{14}C]residues in leachate samples collected from 36-inch deep lysimeters located at the North Carolina and Iowa sites were 0.047-0.434% and 0.078-1.627% of the applied, respectively.

METHODOLOGY:

Soil column studies: Fifty-six galvanized steel cylinders (8-inch diameter, 40-inch length) were inserted vertically, in four rows of 14 columns, to a depth of 36 inches into each of two fenced, disced, bareground plots of sandy loam soil (69.5% sand, 25.2% silt, 5.3% clay, 1.2% organic matter, pH 6.0, CEC 7.8 meq/100 g) and loam soil (43.5% sand, 39.2% silt, 17.3% clay, 2.3% organic matter, pH 5.9, CEC 18.1 meq/100 g) in Lucama, North Carolina, and Cedar Falls, Iowa, respectively. The rows were approximately 6 feet apart, and the individual soil columns within each row were 2 feet apart. The columns in North Carolina were treated on June 25, 1991 and the columns in Iowa were treated on July 24, 1991. At each site, two of the rows of soil columns were surface-treated by pipet at a nominal rate of 0.23 lb ai/A with either pyrazole ring-labeled [1-^{14}C]MON 12000 [[^{14}C]MON 12000 Pz; 3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl)amino]-sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester; radiochemical purity 95.3%, specific activity 31.4 mCi/mMol, Monsanto] or pyrimidine ring-labeled [2-^{14}C]MON 12000 (radiochemical purity 95.2%, specific activity 30.3 mCi/mMol, Monsanto); each were formulated as a 51% wettable powder. The two remaining rows were treated at the same nominal rate with either pyrazole ring-labeled [1-^{14}C]MON 12000 or pyrimidine ring-labeled [2-^{14}C]MON 12000 mixed with the herbicide safener MON 13900

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[3-dichloracetyl-5-(2-furanyl)-2,2-dimethyl-oxazolidine; at 0.72 lb ai/A] and formulated as a 15% wettable powder. A fifth row of 14 columns, separated from the treated plot by a 100-foot buffer zone, was maintained as an untreated control. Single soil columns per treatment were randomly collected prior to treatment, immediately posttreatment (within 24 hours of treatment), at 1, 3, 7, 14, and 21 days, and approximately 1, 2, 4, 6, 12, and 18.5 months posttreatment using a tractor-mounted hydraulic lift or an earth-digging crane. The soil columns were divided into 6-inch segments, and samples were stored frozen for up to approximately 15.5 months prior to analysis. The test plots were irrigated throughout the study with a hand-held sprinkler to maintain a minimum of approximately 120% of total water for the monthly 10-year rainfall averages.

The soil columns collected from the Iowa site typically contained ≤30 inches of soil due to soil compaction resulting from insertion of the steel pipes; additionally, standing water ("supernatant") collected from the top of the soil columns was present at all sampling intervals except those through 7 days posttreatment. The supernatants were collected and analyzed along with the corresponding 0- to 6-inch soil segment.

Lysimeter studies: Also at the North Carolina and Iowa sites, a single row of ten galvanized-steel lysimeters (8-inch diameter; 40-inch length) were inserted into the soil vertically to a depth of 36 inches; the lysimeters were positioned approximately 2 feet apart. A 4- to 5-foot deep access trench was excavated parallel to the lysimeters, and a hole was excavated from the access trench to the bottom of each lysimeter. To collect leachate, a polyethylene funnel (8-inch diameter) inserted into a glass collection flask was installed under each column. To prevent soil loss from the lysimeters, a screen consisting of glass wool and a perforated steel plate or wire screen was positioned between the top of the funnel and the lower end of the soil column. The soil in the lysimeters was surface-treated at a nominal rate of 0.23 lb ai/A on the same days and in the same manner as the soil columns; duplicate columns were prepared for each treatment type, and two of the lysimeters were reserved as untreated controls. In order to trace water movement through the soil columns, an aqueous sodium bromide solution (0.45 M) was applied to the soil in the lysimeters at a rate of 100 lb bromide/A. Leachate samples were collected at 1- to 16-day intervals, except when temperatures were below freezing; at approximately 18.5 months, the lysimeters were collected, and the soil columns were divided into 6-inch segments. The soil samples were stored frozen for up to approximately 4 months prior to analysis, and the leachate samples were stored frozen for up to 16 months.

Analytical methods: Each 6-inch soil segment (soil columns and lysimeters) was thoroughly mixed by hand prior to analysis; extraction procedures are outlined in Figure 4. Subsamples (75 g) of each segment were extracted once with acetonitrile:water (60:40, v:v)

by shaking on a horizontal shaker for 14 hours; the sample was centrifuged, and the supernatant was decanted and vacuum-filtered through three GF/C microfiber glass filters. Aliquots of the filtered extract were analyzed for total radioactivity by LSC. If the extract contained [^{14}C]residues totaling <1.4 ppb, further extractions were discontinued, and the corresponding soil pellet was air-dried and analyzed by LSC following combustion. If the extract contained [^{14}C]residues totaling ≥1.4 ppb, the soil pellet was re-extracted twice with acetonitrile:water (60:40 for 4 hours, and 80:20 for 1 hour, v:v) by shaking as described. The extracts were combined and concentrated by rotary evaporation on an ice water bath (≤10 C) to remove acetonitrile. To prevent volatilization of the MON-12000 degradate aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine), the remaining aqueous solution was partitioned three times against methylene chloride. The extracted aqueous solution was concentrated by rotary evaporation at 40-50 C, and this solution was combined with the methylene chloride extract containing aminopyrimidine. The combined solution was concentrated to dryness by rotary evaporation on an ice water bath (≤10 C). The residues were redissolved in acetonitrile:methanol:water (1:2:7, v:v:v); aliquots were filtered (0.2 um) and analyzed by LSC. If the extract contained [^{14}C]residues totaling <3.0 ppb, residues were not characterized, and the corresponding soil pellet was air-dried and analyzed by LSC following combustion. If the extract contained [^{14}C]residues totaling ≥3.0 ppb, aliquots of the extract were treated with trifluoroacetic acid (TFAA) at 0.1% by volume, and analyzed by HPLC using a Beckman Ultrasphere ODS column eluted with an aqueous TFAA (0.1% by volume):acetonitrile gradient (100:0 to 0:100 to 100:0, v:v)); the column was equipped with radioactive flow detection. Compound identifications were achieved by comparison to radiolabeled and unlabeled reference standards of MON 12000, 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], 3-chlorosulfonamide ester, aminopyrimidine, the "rearrangement ester", the "rearrangement acid", MON 12000 desmethyl, and MON 12000 guanidine (Figure 3); unlabeled standards were located by UV detection. The analytical detection limit was 0.3 ppb. Recoveries from soil samples fortified with MON 12000, 3-chlorosulfonamide ester, 3-chlorosulfonamide acid, and aminopyrimidine were 67.4-117.2, 81.3-133.3, 69.2-119.6, and 47.0-106.0%, respectively. Subsamples of the extracted soil were analyzed by LSC following combustion.

Aliquots of the standing water ("supernatant") associated with the various Iowa soil columns were analyzed by LSC. An additional aliquot (volume proportional to soil subsample) of each "supernatant" was analyzed along with the upper 6-inch soil segment of the corresponding soil column.

Aliquots of the lysimeter leachates were analyzed for pH and bromide concentration. Additional aliquots were analyzed for total radioactivity using LSC; the leachate samples containing >30,000 dpm (approximately 0.04% of the applied radioactivity) were prepared for characterization analysis according to the scheme outlined in Figure

5. Aliquots of the leachates from the columns that were treated with pyrazole ring-labeled [^{14}C]MON 12000 were concentrated to dryness by rotary evaporation and/or under vacuum. To prevent volatilization of aminopyrimidine, aliquots of the leachates from the columns that were treated with pyrimidine ring-labeled [^{14}C]MON 12000 were partitioned three times against methylene chloride, and the aqueous and organic solutions were individually concentrated to dryness by rotary evaporation and/or under vacuum. The residues remaining from both label treatments were redissolved in acetonitrile:methanol:water (10:20:70, v:v:v), and aliquots were analyzed by LSC; additional aliquots were treated with TFAA at 1% by volume, and analyzed by HPLC as previously described. The method detection limit was approximately 0.004% of the applied. Recoveries from bottled water samples fortified with MON 12000, 3-chlorosulfonamide ester, 3-chlorosulfonamide acid, and aminopyrimidine were 83.2-125.8, 101.0-114.5, 77.2-106.5, and 29.2-96.4%, respectively.

DATA SUMMARY:

[^{14}C]MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester] dissipated with observed half-lives of 1-2 weeks from the upper 6 inches of in-situ sandy loam soil columns in North Carolina and 1-2.5 months from the upper 6 inches of loam soil columns in Iowa; the columns had been treated at 0.09-0.20 lb ai/A with either pyrimidine ring-labeled [2-^{14}C]MON 12000 ([^{14}C]MON 12000 Pd; radiochemical purity 95.2%) or pyrazole ring-labeled [1-^{14}C]MON 12000 ([^{14}C]MON 12000 Pz; radiochemical purity 95.3%), formulated alone (51% wettable powder) or with the herbicide safener MON 13900 [3-dichloracetyl-5-(2-furanyl)-2,2-dimethyl-oxazolidine; 15% wettable powder]. MON 12000 leached to a depth of 12 inches in the North Carolina columns and to a depth of 18 inches in the Iowa columns. The degradates detected in the soils at both sites were

aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine),

3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid],

3-chlorosulfonamide ester,

the "rearrangement ester",

the "rearrangement acid",

MON 12000 acid,

MON 12000 desmethyl, and

MON 12000 guanidine.

In the 0- to 6-inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000 was 1.3 ppb; 3-chlorosulfonamide ester was 2.4 ppb; and 3-chlorosulfonamide acid, MON 12000 acid, MON 12000 desmethyl, the rearrangement acid, the rearrangement ester, and MON 12000 guanidine were not detected (<0.3 ppb; Lysimeter Replicate A, Table XV). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeter A were 0.254% of the applied at 18.5 months posttreatment (Figure 20). Results from Lysimeter B were considered invalid due to faulty soil column construction.

In sandy loam soil at the North Carolina site treated at 0.13 lb ai/A with pyrazole ring-labeled [1-^{14}C]MON 12000 formulated with the safener MON 13900, MON 12000 dissipated with a registrant-calculated half-life of 4.2 days from the upper 12 inches and an observed half-life of approximately 1-2 weeks from the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was 95.7-112.1 ppb at 0 and 1 day posttreatment, 61.3-69.8 ppb at 3 and 7 days, 12.9-26.1 ppb at 14 days through 1 month, and ≤1.0 ppb at 4 through 18.5 months (Table XIII). 3-Chlorosulfonamide acid was a maximum 2.5 ppb at 1 month posttreatment; 3-chlorosulfonamide ester was a maximum 18.3 ppb at 7 days; MON 12000 acid was a maximum 4.4 ppb at 1 month; MON 12000 desmethyl was a maximum 5.1 ppb at 7 days; the rearrangement ester was a maximum 4.2 ppb immediately posttreatment; and MON 12000 guanidine was a maximum 4.7 ppb at 21 days. The rearrangement acid was not detected (<0.3 ppb) at any depth or sampling interval.

In the 6- to 12-inch depth at 14 days through 12 months posttreatment (only intervals where total extracted residues exceeded 3.0 ppb), MON 12000 was 1.1-1.8 ppb at 14 days through 6 months; MON 12000 acid was ≤0.7 ppb; MON 12000 desmethyl was ≤0.8 ppb; the rearrangement ester was ≤0.6 ppb; MON 12000 guanidine was 0.4-2.0 ppb; and 3-chlorosulfonamide ester was a maximum 4.3 ppb at 122 days. In the 12- to 18-inch depth at 1 through 6 months, 3-chlorosulfonamide acid was detected once at 0.9 ppb at 1 month, and MON 12000 guanidine was 1.1-2.9 ppb. Residues were not characterized (<3.0 ppb) below 18 inches. One unidentified polar [^{14}C]metabolite was ≤5.6, ≤4.0, and ≤1.0 ppb in the 0- to 6-, 6- to 12-, and 12- to 18-inch soil depths, respectively, at 7 through 30 days posttreatment (page 39). Unextractable [^{14}C]residues were maximums of 33.2 ppb in the 0- to 6-inch depth at 1 month, 7.5 ppb in the 6- to 12-inch depth at 18.5 months, and ≤5.1 ppb at all other depths (Table I).

In the 0- to 6-inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000 was ≤1.5 ppb, 3-chlorosulfonamide acid was ≤0.7 ppb, 3-chlorosulfonamide ester was 2.8-2.9 ppb, and the rearrangement ester was ≤0.9 ppb; MON 12000 acid, MON 12000 desmethyl, the rearrangement acid, and MON 12000 guanidine were not detected (<0.3 ppb; Table XV). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeter B were 0.387% of the applied at 18.5 months posttreatment (Figure 23). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeter A were 0.050% of the applied at 18.5 months posttreatment (Figure 22).

During the North Carolina studies, rainfall plus irrigation totaled 3.14 inches at 15 days posttreatment, 4.06 inches at 30 days, 18.62 inches at 61 days, 60.64 inches at 366 days, and 96.78 inches at 559 days. Throughout the study, the air temperatures ranged from 16 to 102 F; the soil temperatures ranged from 34 to 99 F at a 4-inch depth. The slope of the test plot was ≤2%, and the depth to the water table ranged from 6 to 72 inches throughout the study.

In loam soil at the Iowa site treated at 0.09 lb ai/A with pyrimidine ring-labeled [2-^{14}C]MON 12000, MON 12000 dissipated with a registrant-calculated half-life of 54.8 days from the upper 12 inches and an observed half-life of approximately 2 months from the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was 23.0-78.0 ppb at 0 through 7 days, was a maximum 85.7 ppb at 14 days, and decreased to 41.4 ppb at 21 days, 23.4 ppb at 2 months, 10.1 ppb at 12 months, and 6.4 ppb at 18.5 months (Table XVII). Aminopyrimidine was a maximum 6.1 ppb at 21 days posttreatment; MON 12000 acid was a maximum 5.2 ppb at 2 months; MON 12000 desmethyl was a maximum 4.4 ppb at 14 days; the rearrangement acid was a maximum 21.0 ppb at 2 months; and the rearrangement ester was a maximum 28.0 ppb at 1 month. In the 6- to 12-inch depth at 2 through 18.5 months posttreatment (only intervals where total extracted residues exceeded 3.0 ppb), MON 12000 was a maximum 3.3 ppb at 6 months; MON 12000 acid was detected once at 1.8 ppb at 12 months; and the rearrangement acid was ≤3.1 ppb. In the 12- to 18-inch depth, MON 12000 was 2.6 ppb at 6 months. Residues were not characterized (<3.0 ppb) below 18 inches. Unextractable [^{14}C]residues were maximums of 49.5 ppb in the 0- to 6-inch depth at 12 months, 5.4 ppb in the 6- to 12-inch depth at 12 months, and ≤1.1 ppb at all other depths (Table II).

In the 0- to 6-inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000 was 3.1-6.3 ppb, aminopyrimidine was 4.8-11.1 ppb, MON 12000 desmethyl was ≤3.3 ppb, and the rearrangement acid was ≤0.9 ppb; MON 12000 acid and the rearrangement ester were not detected (<0.3 ppb; Table XXII). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeters A and B were 0.078-0.093% of the applied at 18.5 months posttreatment (Figures 32 and 33).

In loam soil at the Iowa site treated at 0.19 lb ai/A with pyrimidine ring-labeled [2-^{14}C]MON 12000 formulated with the safener MON 13900, MON 12000 dissipated with a registrant-calculated half-life of 85.5 days from the upper 12 inches and an observed half-life of 2.5 months from the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was 94.2 ppb immediately posttreatment, 74.6 ppb at 1 day, 29.3-59.7 ppb at 3 days through 1 month, 22.1-31.0 ppb at 2 and 4 months, and 10.4 ppb at 12 months (Table XVIII). Aminopyrimidine was a maximum 18.9 ppb at 28 days posttreatment; MON 12000 acid was a maximum 6.5 ppb at 28 days; MON 12000 desmethyl was a maximum 6.5 ppb at 28 days; the rearrangement acid was a maximum 11.4 ppb at 4 months; and the rearrangement ester was a maximum 18.5 ppb at 21 days.

In the 6- to 12-inch depth at 21 days, and 2, 6, and 12 months posttreatment (only intervals where total extracted residues exceeded 3.0 ppb), MON 12000 was 2.8-4.1 ppb at at sampling intervals, and MON 12000 desmethyl was detected once at 1.8 ppb at 6 months. Residues were not characterized (<3.0 ppb) below 12 inches. Unextractable [^{14}C]residues were maximums of 50.4 ppb in the 0- to 6-inch depth at 12 months, and ≤3.1 ppb at all other depths (Table II).

In the 0- to 6-inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000 was 1.5-5.8 ppb, aminopyrimidine was 8.3-17.7 ppb, MON 12000 desmethyl was 3.3-4.1 ppb, and the rearrangement acid was ≤0.7 ppb; MON 12000 acid and the rearrangement ester were not detected (<0.3 ppb; Table XXII). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeters A and B were 0.079-0.122% of the applied at 18.5 months posttreatment (Figures 34 and 35).

In loam soil at the Iowa site treated at 0.17 lb ai/A with pyrazole ring-labeled [1-^{14}C]MON 12000, MON 12000 dissipated with a registrant-calculated half-life of 33.0 days from the upper 12 inches and an observed half-life of 1-2 months from the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was a maximum 152.8 ppb at 1 day posttreatment, 64.4-78.2 ppb at 3 through 21 days, 43.2 ppb at 1 month, 16.5-17.3 ppb at 2 through 6 months, and 5.1-6.8 ppb at 12 and 18.5 months (Table XIX). 3-Chlorosulfonamide acid was a maximum 8.2 ppb at 2 months; 3-chlorosulfonamide ester was a maximum 19.0 ppb at 21 days; MON 12000 acid was a maximum 6.0 ppb at 1 month; MON 12000 desmethyl was a maximum 4.0 ppb at 21 days; the rearrangement acid was a maximum 10.3 ppb at 4 months; the rearrangement ester was a maximum 5.9 ppb at 6 months; and MON 12000 guanidine was a maximum 3.6 ppb at 2 months.

In the 6- to 12-inch depth at 2 through 18.5 months posttreatment (only intervals where total extracted residues exceeded 3.0 ppb), MON 12000 was a maximum 3.6 ppb at 2 months; 3-chlorosulfonamide acid was a maximum 4.8 ppb at 12 months; and the rearrangement acid was not detected. In the 12- to 18-inch depth at 21 days, and 12 and 18.5 months, MON 12000 was detected once 2.8 ppb at 21 days; 3-chlorosulfonamide acid was a maximum 2.6 ppb at 18.5 months; and the rearrangement acid was detected once 1.5 ppb at 12 months. Residues were not characterized (<3.0 ppb) below 18 inches. Unextractable [^{14}C]residues were maximums of 49.2 ppb in the 0- to 6-inch depth at 18.5 months, and ≤3.2 ppb at all other depths (Table II).

In the 0- to 6-inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000 was 4.4-7.7 ppb, 3-chlorosulfonamide acid was 5.2-7.2 ppb, 3-chlorosulfonamide ester was ≤2.1 ppb, MON 12000 acid was ≤0.9 ppb, MON 12000 desmethyl was ≤1.5 ppb, and the rearrangement acid was ≤2.8 ppb; the rearrangement ester and MON 12000 guanidine were not detected (<0.3 ppb; Table XXII). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeter B were 1.627% of the applied at 18.5 months posttreatment (Figure 37). Cumulative [^{14}C]residues in the leachate samples collected from

Lysimeter A were 0.321% of the applied at 18.5 months posttreatment (Figure 36).

In loam soil at the Iowa site treated at 0.16 lb ai/A with pyrazole ring-labeled [1-^{14}C]MON 12000 formulated with the safener MON 13900, MON 12000 dissipated with a registrant-calculated half-life of 6.7 days from the upper 12 inches and an observed half-life of 1-2 months from the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was 59.3-76.6 ppb at 0 through 3 days posttreatment, 25.6-50.9 ppb at 7 days through 1 month, 9.9-32.5 ppb at 2 through 12 months, and 3.6 ppb at 18.5 months (Table XX). 3-Chlorosulfonamide acid was a maximum 6.0 ppb at 2 months posttreatment; 3-chlorosulfonamide ester was a maximum 7.0-11.8 ppb at 1 through 12 months; MON 12000 acid was ≤5.2 ppb throughout the study; MON 12000 desmethyl was ≤4.3 ppb throughout the study; the rearrangement acid was 3.7-4.9 ppb at 6 through 18.5 months; the rearrangement ester was ≤4.6 ppb throughout the study; MON 12000 guanidine was a maximum 5.5 ppb at 4 months. In the 6- to 12-inch depth at 14 days through 18.5 months posttreatment, MON 12000 was a maximum 5.0 ppb at 2 months; 3-chlorosulfonamide acid was ≤3.2 ppb; MON 12000 acid was ≤1.4 ppb; the rearrangement acid was ≤1.9 ppb; and MON 12000 guanidine was ≤4.1 ppb. In the 12- to 18-inch depth at 6 and 12 months posttreatment (only intervals where total extracted residues exceeded 3.0 ppb), 3-chlorosulfonamide acid was 2.6-2.8 ppb. Residues were not characterized (<3.0 ppb) below 18 inches. Unextractable [^{14}C]residues were maximums of 38.2 ppb in the 0- to 6-inch depth at 18.5 months, and ≤4.0 ppb at all other depths (Table II).

In the 0- to 6-inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000 was 3.2-4.8 ppb, 3-chlorosulfonamide acid was 3.6-3.8 ppb, and 3-chlorosulfonamide ester was 1.0-1.9 ppb; MON 12000 acid, MON 12000 desmethyl, the rearrangement acid, the rearrangement ester, and MON 12000 guanidine were not detected (<0.3 ppb; Table XXII). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeter A were 0.371% of the applied at 18.5 months posttreatment (Figure 38). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeter B were 0.755% of the applied at 18.5 months posttreatment (Figure 39).

During the Iowa studies, rainfall plus irrigation totaled 7.30 inches at 31 days posttreatment, 10.38 inches at 62 days, 18.58 inches at 123 days, 43.00 inches at 366 days, and 63.85 inches at 567 days. Throughout the study, the air temperatures ranged from -11 to 93 F; soil temperatures were not provided. The slope of the test plot was ≤2%, and the depth to the water table ranged from 18 to 87 inches throughout the study.

COMMENTS:

1. The soil columns collected during this study were stored frozen for up to approximately 15.5 months prior to analysis. In an on-going, scientifically-sound freezer storage stability study (MRID 42661415; Study 4 of this submission), MON 12000 was found to be stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for 12 months. Data provided in an additional field dissipation study (MRID 42976304; Study 3 of this submission) for soil samples collected during a confined rotational crop study provide supporting evidence which suggest that MON 12000 is stable in sandy loam soil stored frozen for up to 3 years.

   In MRID 42661415, 3-chlorosulfonamide acid was found to be stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for 12 months; additional storage stability data provided from the rotational crop study for 3-chlorosulfonamide acid suggest that this degradate is reasonably stable in sandy loam soil stored frozen for up to 3 years.

   Also in MRID 42661415, aminopyrimidine was found to be unstable in loam soil under similar storage conditions; aminopyrimidine averaged 101% of the applied immediately posttreatment, 69.1% after 2 months of frozen storage, and 29.6-32.6% after 8 and 12 months. Therefore, it is reasonable to assume that any aminopyrimidine that may have been in the soil samples at the time of collection would have dissipated during storage. In contrast, data for aminopyrimidine from the crop study suggested that this degradate remained stable during 3 years of frozen storage; the study author of MRID 42976304 (in which the data from the crop study was included) suggested that the dissipation of aminopyrimidine during frozen storage may be dependent upon the soil type, and that the apparent loss or binding of aminopyrimidine may be due to some interaction with the loam soil that was not observed in the sandy loam soil.

   Additional data from the confined rotational crop study (also included in this report in Table IX) were presented which suggest that 3-chlorosulfonamide ester was stable when stored frozen for 26-32 months, but MON 12000 acid, MON 12000 desmethyl, and the "rearrangement ester" were slightly unstable. However, the data provided from the crop study is limited and inconclusive.

2. The leachate samples were stored frozen for up to approximately 16 months prior to analysis. No storage stability data were presented for water samples for MON 12000 or its degradates. Therefore, the data reported for the actual leachate field samples should be considered only supplemental. Analysis of leachate samples are not specifically required by Subdivision N guidelines.

3. Due to the high silt and clay content of the Iowa soil, significant compaction occurred during insertion of the steel pipes, resulting in soil columns with typical lengths of ≤30 inches. Unsuccessful

attempts were made to locate a test plot at the Iowa location in which soil compaction would be less severe. During the study, standing water ("supernatant") collected from the top of the soil columns was present at all sampling intervals except those through 7 days posttreatment. Additionally, the late application date and the early freezing temperatures that occurred in 1991 represent environmental conditions which are atypical of the corn growing season. According to the study authors, the late seasonal application, soil compaction, and standing water provide a worst-case scenario for the dissipation of MON 12000 in soil, and provide information about the anaerobic aquatic metabolism of MON 12000 in the field.

4. According to the study authors, the "leachate" samples collected at the North Carolina site on July 31 through August 5, 1991 consisted primarily of floodwater resulting from heavy rainfall.

5. Residues reported as "% of the applied" were calculated from the total MON 12000 residues of the 0- or 1-day sample results.

6. Data obtained from two of the lysimeters at the North Carolina site ("Lysimeter A" treated with MON 12000-Pd with safener, and "Lysimeter B" treated with MON 12000-Pz only) were considered to be invalid. According to the study authors, "the rapid appearance of leachate, bromide, and radioactivity, prior to soil column saturation, was inconsistent with the other lysimeters [page 36]" and suggested that the column constructions were faulty; visual examination after collection verified that the soil columns contained "unnatural channels".

7. The Iowa soil column that was to be treated with MON 12000-Pd plus safener and collected at 18.5 months was apparently not treated. Therefore, no data is available beyond 12 months for soil treated in this manner at the Iowa.

8. For characterization of bound residues, select extracted soils were Soxhlet-extracted sequentially with acetonitrile:water (60:40, v:v) and ethyl acetate for 24 hours per extraction; the Soxhlet extractions allowed for significant reduction in radioactivity bound to the soil. The extracts were analyzed by HPLC as previously described, and were found to contain the same degradates as were found in the original extracts. However, Soxhlet extraction of soil samples fortified with MON 12000 resulted in the hydrolysis of the parent to chlorosulfonamide ester and aminopyrimidine [page 29]. Therefore, the data provided from the Soxhlet extractions of the actual field samples is of limited value.

9. The "rearrangement ester" was unexpectedly generated from MON 12000-Pz-fortified tap water samples during the rotary-evaporation step due to an increased concentration of salts in solution. In addition, the salt content in the tap water also interfered with the quantitation of 3-chlorosulfonamide acid. Recoveries from leachate samples and

bottled water samples after fortification with the various compounds were reasonable and suggest that reported results for parent and the various degradates in the field leachate samples are reasonable.

10. Although a few recoveries of aminopyrimidine from fortified soil and water samples were low, the majority were reasonable.

11. At the North Carolina test site, no vegetation was observed on the soil columns throughout the study. At the Iowa site, vegetation was clipped by hand and left on the soil surface; additionally, glyphosate was applied at 0.75 lb ai/A on July 10 and August 17, 1992.

12. In order to provide adequate sample for further analysis, a soil core (2-inch diameter) was apparently collected at 12 months posttreatment from an additional in-situ soil column (all treatments at both test sites). However, analysis of the soil cores was deemed unnecessary.

13. The North Carolina test plot was planted to peanuts in 1989 and was treated with aldicarb, metolachlor, acifluorfen-sodium, bentazone plus dichlorprop, acephate, fluazifop-butyl, diazinon, and chlorothalonil; in 1990, the plot was planted to soybeans and treated with acifluorfen-sodium, bentazone plus dichlorprop, and sethoxydim. The Iowa test plot was planted to alfalfa in 1989 and 1990, and to winter wheat in 1990-1991; no pesticides were applied.

DATA EVALUATION RECORD

DER 6

CHEM 128721 MON 12000 §164-1

FORMULATION--06--WETTABLE POWDER (WP)

STUDY ID 42661412
Beasley, R.K. 1993a. Dissipation of MON 12000 and MON 12000 metabolites in field soil. Monsanto Study No. MSL 12356; Harris Study No. 9200520; Stewart Study No. 90-42-R-2. Unpublished study performed by Harris Laboratories, Inc., Lincoln, NE; Monsanto Company, St. Louis, MO; and Stewart Agricultural Research Services, Inc., Macon, MO. Submitted by Monsanto Company, St. Louis, MO.

STUDY ID 42976302
Beasley, R.K. 1993b. Dissipation of MON 12000 and MON 12000 metabolites in field soil. Monsanto Study No. MSL 12892; Harris Study Nos. 9200520, 9200536, and 15628; Stewart Study No. 90-42-R-2. Unpublished study performed by Harris Laboratories, Inc., Lincoln, NE; Monsanto Company, St. Louis, MO; and Stewart Agricultural Research Services, Inc., Macon, MO. Submitted by Monsanto Company, St. Louis, MO.

DIRECT REVIEW TIME = 51

REVIEWED BY: M. Anderson TITLE: Staff Scientist

EDITED BY: K. Ferguson TITLE: Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager
ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: K. Poff
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: K L P 8/8

CONCLUSIONS:

Terrestrial Field Dissipation

1. Study MRID #42976302 is acceptable and contributes towards satisfying the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

2. MON 12000 [Halosulfuron, 25% WP] dissipated with half-lives of 18-60 days from the upper 6 inches of plots of sandy clay loam (56% sand, 22% silt, 22% clay, 1.2% organic matter, pH 6.0, CEC 13.2 meq/100 g) soil in California and loam (38% sand, 38% silt, 24% clay, 4.5% organic matter, pH 6.5, CEC 17.3 meq/100 g) soil in Iowa that were treated with MON 12000 twice, at approximately 0.125 lb ai/A (23 g/ha) and 0.094 lb ai/A (17 g/ha), in Spring 1990. Also, MON 12000 dissipated with half-lives of 6-34 days from plots of loam (24% sand, 50% silt, 26% clay, 4.8% organic matter, pH 7.7, CEC 22.7 meq/100 g) soil in Illinois and clay loam (30% sand, 34% silt, 36% clay, 2.1% organic matter, pH 8.3, CEC 21.3 meq/100 g) soil in Texas that were treated with MON 12000 once, at approximately 0.125 lb ai/A, in Spring 1990. MON 12000 was <0.004 ppm below the 6-inch soil depth at all test sites at all sampling intervals No MON 12000 residues were observed at or above 2 ppb detection limit 123 days after the last treatment. No MON 12000 soil metabolites were observed at or above the lower limit of method validation (G.C.), 5 ppb, in any of the samples at any interval or depth. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the four studies duration. During the California study, rainfall plus irrigation was 20.35 inches throughout the entire 18-month period. During the Iowa study, rainfall plus irrigation was 73.17 inches throughout the entire 18-month period. During the Illinois and Texas studies rainfall plus irrigation was 69.91 inches, and 58.23 inches respectively throughout the entire 18-month period.

METHODOLOGY:

MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester; 25% WP, Monsanto] was broadcast twice at 0.125 plus 0.094 lb ai/A or once at 0.125 lb ai/A to test plots in California, Iowa, Illinois, and Texas between April and July 1990. At each site, an untreated plot located 200-225 feet from the treated plot served as a control. All plots were planted to corn approximately at the time of the initial application of MON 12000. For sampling purposes, each treated plot was divided into three subplots. At intervals up to approximately 18 months posttreatment, five soil cores (0- to 48-inch depth) were randomly collected from each subplot of the treated plots and from the control plots using a tractor-mounted hydraulic zero-contamination soil corer. The soil was frozen and shipped to the analytical laboratory, where the cores from the treated plots were recored to a 1-inch diameter. The soil cores from the treated and control plots were divided into 6-inch segments, and the resulting segments were composited according to site, soil depth, and sampling interval. The composited samples were thoroughly homogenized, then stored frozen until extraction and analysis.

At the Vacaville, California, site, MON 12000, tank-mixed with the herbicide acetochlor (MON 8422) and the safener MON 13900 [3-dichloracetyl-5-(2-furanyl)-2,2-dimethyl-oxazolidine], was broadcast at 0.126 lb ai/A onto a bareground plot (110 x 110 feet) of sandy

No [^{14}C]degradate was detected at >5 ppb below the 6-inch soil depth at either site. At 18.5 months posttreatment, cumulative [^{14}C]residues in leachate samples collected from 36-inch deep lysimeters located at the North Carolina and Iowa sites were 0.047-0.434% and 0.078-1.627% of the applied, respectively.

In sandy loam soil at the North Carolina site treated at 0.11 lb ai/A with pyrimidine ring-labeled [2-^{14}C]MON 12000, MON 12000 dissipated with a registrant-calculated half-life of 11.8 days in the upper 12 inches and an observed half-life of approximately 2 weeks in the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was 29.4-53.4 ppb at 0 through 3 days posttreatment, 15.5 ppb at 14 days, 9.6 ppb at 30 days, 5.4 ppb at 64 days, and ≤1.0 ppb 122 through 559 days (Table X). Aminopyrimidine was a maximum 6.9 ppb at 7 days posttreatment; MON 12000 acid was a maximum 3.7 ppb at 21 days; MON 12000 desmethyl was a maximum 1.2 ppb at 3 days; the rearrangement acid was a maximum 1.7 ppb at 21 days; and the rearrangement ester was a maximum 3.1 ppb at 21 days. In the 6- to 12-inch depth at 14 and 122 days posttreatment (only intervals where total extracted residues exceeded 3.0 ppb), MON 12000 was 1.5 ppb at 14 days and 0.8 ppb at 122 days; aminopyrimidine was not detected at 14 days and was 1.4 ppb at 122 days; and MON 12000 acid was 0.9 ppb at 14 days, and was not detected at 122 days. Residues were not characterized (<3.0 ppb) below 12 inches. Unextractable [^{14}C]residues were maximums of 18.6 ppb in the 0- to 6-inch depth at 64 days, 17.1 ppb in the 6- to 12-inch depth at 191 days, and ≤2.4 ppb at all other depths (Table I).

In the 0- to 6- inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000, aminopyrimidine, MON 12000 acid, the rearrangement acid, and the rearrangement ester were each <0.3 ppb; MON 12000 desmethyl was ≤3.4 ppb (Table XV). At 18.5 months posttreatment, cumulative [^{14}C]residues in the leachate samples collected from Lysimeters A and B totaled 0.089 and 0.434% of the applied, respectively (Figures 16 and 17). [^{14}C]Residues isolated from the leachates included MON 12000, MON 12000 acid, the rearrangement acid, and the rearrangement ester.

In sandy loam soil at the North Carolina site treated at 0.20 lb ai/A with pyrimidine ring-labeled [2-^{14}C]MON 12000 formulated with the safener MON 13900, MON 12000 dissipated with a registrant-calculated half-life of 6.7 days from the upper 12 inches and an observed half-life of approximately 1-2 weeks from the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was 121.7 ppb immediately posttreatment, 75.6-87.5 ppb at 3 and 7 days, 30.4 ppb at 14 days, 19.5-24.6 ppb at 21 days and 30 days, 1.0 ppb at 12 months, and <0.3 ppb at 18.5 months (Table XI). Aminopyrimidine was a maximum 17.6 ppb at 7 days posttreatment; MON 12000 acid was a maximum 4.0 ppb at 7 days; MON 12000 desmethyl was ≤2.9 ppb throughout the study; the rearrangement acid was ≤0.8 ppb throughout the study; and the rearrangement ester was a maximum 4.9 ppb at 1 day. In the 6- to 12-inch depth at 14 through 122 days posttreatment (only intervals where

total extracted residues exceeded 3.0 ppb), MON 12000 was a maximum 2.8 ppb at 14 days; aminopyrimidine was ≤1.7 ppb at 14 days through 4 months; MON 12000 acid was a maximum 1.5 ppb at 14 days; MON 12000 desmethyl was a maximum 1.2 ppb at 14 days; and the rearrangement acid was ≤0.5 ppb at 14 days through 4 months. Residues were not characterized (<3.0 ppb) below 12 inches. Unextractable [^{14}C]residues were maximums of 32.7 ppb in the 0- to 6-inch depth at 1 month, 4.2 ppb in the 6- to 12-inch depth at 4 months, and ≤2.3 ppb at all other depths (Table I).

In the 0- to 6-inch depth of the lysimeter soil at 18.5 months posttreatment, MON 12000 was 2.5 ppb; MON 12000 desmethyl was 1.5 ppb; and aminopyrimidine, MON 12000 acid, the rearrangement acid, and the rearrangement ester were each <0.3 ppb (Lysimeter Replicate B, Table XV). Cumulative [^{14}C]residues in the leachate samples collected from Lysimeter B were 0.047% of the applied at 18.5 months posttreatment (Figure 19). Results from Lysimeter A were considered invalid due to faulty soil column construction.

In sandy loam soil at the North Carolina site treated at 0.19 lb ai/A with pyrazole ring-labeled [1-^{14}C]MON 12000, MON 12000 dissipated with a registrant-calculated half-life of 4.2 days from the upper 12 inches and an observed half-life of approximately 1-2 weeks from the upper 6 inches. In the 0- to 6-inch soil depth, MON 12000 was 139.1 ppb immediately posttreatment, 56.6-80.3 ppb at 3 and 7 days, 19.0-22.5 ppb at 14 days through 1 month, 3.2 ppb at 64 days, and was not detected (<0.3 ppb) at 18.5 months (Table XII). 3-Chlorosulfonamide acid was a maximum 4.8 ppb at 21 days; 3-chlorosulfonamide ester was a maximum 8.5-24.2 ppb at 0 through 21 days; MON 12000 acid was a maximum 8.4 ppb at 1 month; MON 12000 desmethyl was a maximum 5.7 ppb at 7 days; the rearrangement acid was not detected throughout the study; the rearrangement ester was a maximum 7.0 ppb at 1 month; and MON 12000 guanidine was a maximum 10.9 ppb at 21 days.

In the 6- to 12-inch depth at 14 days through 6 months posttreatment (only intervals where total extracted residues exceeded 3.0 ppb), MON 12000 was a maximum 3.0 ppb at 14 days; 3-chlorosulfonamide ester was ≤0.9 ppb; MON 12000 acid was ≤0.6 ppb; MON 12000 desmethyl was ≤0.5 ppb; the rearrangement acid was detected once at 0.5 ppb at 2 months; and MON 12000 guanidine was 0.7-1.6 ppb. In the 12- to 18-inch depth at 21 days through 6 months, MON 12000 acid was ≤1.5 ppb, MON 12000 desmethyl was not detected, and MON 12000 guanidine was 1.0-4.0 ppb. In the 18- to 24-inch depth at 21 days and 6 months, MON 12000 acid was ≤1.2 ppb, MON 12000 desmethyl was ≤0.9 ppb, and MON 12000 guanidine was ≤2.1 ppb. Residues were not characterized (<3.0 ppb) below 24 inches. One unidentified polar [^{14}C]metabolite was ≤5.6, ≤4.0, and ≤1.0 ppb in the 0- to 6-, 6- to 12-, and 12- to 18-inch soil depths, respectively, at 7 through 30 days posttreatment (page 39). Unextractable [^{14}C]residues were maximums of 26.2 ppb in the 0- to 6-inch depth at 21 days and ≤5.3 ppb at all other depths (Table I).

month period. Throughout the study, the air temperatures ranged from 18 to 104 F; the soil temperatures, measured at each sampling interval, ranged from 53 to 94 F at a 2-inch depth, and from 59 to 86 F at a 4-inch depth. The slope of the test plot was 2-3%, and the annual depth to the water table was 30-50 feet.

COMMENTS:

1. Soil samples were stored frozen for up to 26-34 months prior to analysis. In an on-going, scientifically-sound freezer storage stability study (MRID 42661415; Study 4 of this submission) MON 12000 was found to be stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for 12 months. Data provided in an additional field dissipation study (MRID 42976304; Study 3 of this submission) for soil samples collected during a confined rotational crop study provide supporting evidence which suggest that MON 12000 is stable in sandy loam soil stored frozen for up to 3 years.

   In MRID 42661415, 3-chlorosulfonamide acid was found to be stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for 12 months; additional storage stability data provided from the rotational crop study for 3-chlorosulfonamide acid suggested that this degradate is reasonably stable in sandy loam soil stored frozen for up to 3 years.

   Also in MRID 42661415, aminopyrimidine was found to be unstable in loam soil under similar storage conditions; aminopyrimidine averaged 101% of the applied immediately posttreatment, 69.1% after 2 months of frozen storage, and 29.6-32.6% after 8 and 12 months. Therefore, it is reasonable to assume that any aminopyrimidine that may have been in the soil samples at the time of collection would have dissipated during storage. In contrast, data for aminopyrimidine from the crop study suggested that this degradate remained stable during 3 years of frozen storage; the study author of MRID 42976304 (in which the data from the crop study was included) suggested that the dissipation of aminopyrimidine during frozen storage may be dependent upon the soil type, and that the apparent loss or binding of aminopyrimidine may be due to some interaction with the loam soil that was not observed in the sandy loam soil.

2. The MON 12000 degradates, 3-chlorosulfonamide ester and MON 12000 guanidine, were isolated as major degradates in an aerobic soil metabolism study (MRID 42139410) and an additional field (lysimeter) study (MRID 42976303; Study 2 of this submission). Although the study author stated that 3-chlorosulfonamide ester is readily hydrolyzed to 3-chlorosulfonamide acid, it is clear that the ester can be isolated at significant levels within the first 1-2 months after application. 3-Chlorosulfonamide ester and MON 12000 guanidine should have been investigated in this study. However, because the additional field study provides sufficient information on the dissipation of MON 12000 and its various degradates when applied to

bareground as a wettable powder, no additional information is required for this study.

3. Because MON 12000 was converted to the rearrangement ester prior to GC analysis, it was necessary to remove any of the ester present in the original sample prior to conversion of the parent. According to the study author, the rearrangement ester was removed by column chromatography (not further described). The study author did not indicate whether attempts were made to quantify any ester removed by the chromatography columns.

4. MON 12000, formulated as MON 12007 (code name SARS 15012), was applied as a tank mix with two other Monsanto agricultural chemicals: acetochlor (formulated as MON 8422; code name SARS 24822) and MON 13900 (a safener; code name SARS 53013). MON 8422 and MON 13900 were applied at approximately 3.0 and 0.375 lb ai/A, respectively. At the Iowa and California sites, MON 13900 and MON 8422 were not applied with MON 12000 in the second (postemergence) application.

5. According to the study author, the data from the California site were intended as supporting data for only parent MON 12000; consequently, these samples were not analyzed for degradates [page 21]. Additionally, field dissipation studies were also conducted in Hollandale, Minnesota (preemergent) and New Holland, Ohio (pre-plant incorporated + postemergent). The study author stated that the samples collected from these two sites were not analyzed because the data provided from the other four sites were sufficient to fulfill regulatory requirements [page 85].

6. At the California site, temperatures for freezer storage ranged from -22 to 46 F. According to the field report, the higher recorded freezer temperature resulted when the thermograph probe was temporarily knocked out of the freezer. The samples were reported to have remained frozen throughout the study.

7. Soil temperatures were provided for individual sampling intervals only; soil temperatures determined daily for the duration of the study are preferable.

8. The California test plot was treated with trifluralin, EPTC, and methomyl in 1985, pebulate in 1987, and 2,4-D in 1989; no pesticides were applied in 1986 or 1988. The Iowa plot was treated with metolachlor and atrazine in 1987, metolachlor and bentazone plus dichlorprop in 1988, and trifluralin and bentazone plus dichlorprop in 1989; the treatment history for 1985 and 1986 is unknown. The Illinois plot was treated with alachlor and atrazine in 1985; no pesticides were applied in 1986 through 1989. The Texas plot was treated with trifluralin, methomyl, and linuron in 1985; trifluralin in 1986; trifluralin, methomyl, and endosulfan in 1987; trifluralin, azinphosmethyl, acephate, cyfluthrin, and sulprofos in 1988; and trifluralin and azinphosmethyl in 1989.

9. During the study, at the California site, glyphosate was applied twice (three times to the control plot) on February 21, 1991 and June 17, 1991 (and May 14, 1991 to the control plot) at 1.5 lb ai/A/application; additionally, the plot was cultivated (depth not reported) for weed control on June 19 and July 1, 1990. At the Iowa site, cyanazine was applied at 2.0 lb ai/A on June 11, 1990, and 2,4-D amine was applied at 1.0 lb ai/A on July 10, 1990. At the Illinois site, cyanazine and pendimethalin were applied at 2.0 and 1.5 lb ai/A, respectively, on June 11, 1990, and glyphosate was applied at 24 ounces/A on June 7, 1991, and again on September 6, 1991. At the Texas site, chlorpyrifos was applied at 1.0 lb ai/A on April 18, 1990, and glyphosate was applied at 1.0 lb ai/A on September 15, 1990, and again on February 8, 1991; additionally, the plot was cultivated (depth not reported) for weed control on May 1 and May 11, 1990.

DATA EVALUATION RECORD

DER 7

CHEM 128721 MON 12000 §164-1

FORMULATION--06--WETTABLE POWDER (WP)

STUDY ID 42661413
Beasley, R.K. 1993c. Dissipation of MON 12000 and MON 12000 metabolites in turf soil. Monsanto Study No. MSL 12357; Hazleton Study No. 6103-156; Stewart Study No. 90-42-R-4. Unpublished study performed by Hazelton Wisconsin, Inc., Madison, WI; Monsanto Company, St. Louis, MO; and Stewart Agricultural Research Services, Inc., Macon, MO. Unpublished study submitted by Monsanto Company, St. Louis, MO.

STUDY ID 42976304
Beasley, R.K. 1993d. Dissipation of MON 12000 and MON 12000 metabolites in turf soil. Monsanto Study No. MSL 12893; Hazleton Study No. HWI-6103-156; Stewart Study No. 90-42-R-4. Unpublished study performed by Monsanto Company, St. Louis, MO; Stewart Agricultural Research Services, Inc., Macon, MO, Hazelton Wisconsin, Inc, Madison, WI; and Harris Laboratories, Inc., Lincoln, NE. Unpublished study submitted by Monsanto Company, St. Louis, MO.

DIRECT REVIEW TIME = 42

REVIEWED BY: M. Anderson TITLE: Staff Scientist

EDITED BY: K. Ferguson TITLE: Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: K. Poff
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: K. Poff

CONCLUSIONS:

Terrestrial Field Dissipation

1. Study MRID #42661413 and MRID #42976304 is acceptable and contributes in satisfying the Terrestrial Field Dissipation (164-1) data requirement for MON 12000.

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2. MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester; 25% WP] dissipated with observed half-lives of <1 month from the upper 6 inches of turf-covered plots of sandy loam (66% sand, 20% silt, 14% clay, 0.5% organic matter, pH 6.8, CEC 10.0 meq/100 g), loamy sand (80% sand, 12% silt, 8% clay, 1.5% organic matter, pH 6.0, CEC 2.7 meq/100 g), and silt loam (20% sand, 54% silt, 26% clay, 2.0% organic matter, pH 7.2, CEC 12.4 meq/100 g) soils in California, Georgia, and Missouri that were treated with MON 12000 three times, at approximately 0.063-0.125 lb ai/A/application, in Spring and Summer 1990. MON 12000 was ≤0.008 ppm below the 6-inch soil depth at all test sites at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged < 5 ppb (lower limit of method validation) at all soil depths throughout the study. In California, rainfall plus irrigation was 39.90 inches through the entire 7-month study. In Georgia and Missouri rainfall plus irrigation was 40.44 inches throughout the entire 4-month study and 30.30 inches throughout the entire 4-month study respectively.

METHODOLOGY:

MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester; 25% WP, Monsanto] was broadcast three times at approximately 0.063, 0.125, and 0.063 lb ai/A to plots of turf in California and Georgia, and at 0.063, 0.125, and 0.125 lb ai/A to a plot of turf in Missouri between May and September 1990. At each site, an untreated plot located 110-200 feet from the treated plot served as a control. All sites were irrigated to supplement rainfall during the study. For sampling purposes, the treated plots were divided into three subplots. At intervals up to approximately 7 months posttreatment, five soil cores (0- to 48-inch depth) were randomly collected from each subplot of the treated plots and from the control plots using a hydraulic zero-contamination soil corer. The soil was frozen and shipped to the analytical laboratory, where the cores from the treated plots were recored to a 1-inch diameter. The soil cores from the treated and control plots were divided into 6-inch segments, and the resulting segments were composited according to site, soil depth, and sampling interval. The composited samples were thoroughly homogenized, then stored frozen until extraction and analysis.

At the Temeluca, California, site, MON 12000 was broadcast three times, at 0.061, 0.122, and 0.062 lb ai/A, onto a plot (90 x 110 feet) of sandy loam soil (66% sand, 20% silt, 14% clay, 0.5% organic matter, pH 6.8, CEC 10.0 meq/100 g) containing mature Kentucky Bluegrass; the applications were made on June 15, August 1, and September 10, 1990, using a backpack sprayer. An untreated plot (30 x 70 feet), located 190 feet from the treated plot, was maintained as a control. The grass on the test plot was mowed and the clippings were removed at 1- to 2-week intervals from mid-June through mid-December 1990 (the first 6 months of the study), and at 2- to 5-week

intervals from mid-December 1990 through mid-March 1991. Soil samples were collected from each subplot of the treated plot and from the control plot prior to treatment; at 0, 1, 4, and 10 days after the first and second treatments; and at 0, 1, 4, 10, and 21 days, and 1, 2, 3, 4, 5, 6, and 7 months after the final treatment. The soil samples were stored frozen at -8 to 34 F for up to 28 months prior to extraction.

At the Camilla, Georgia, site, MON 12000 was broadcast three times, at 0.063, 0.124, and 0.063 lb ai/A, onto a plot (38 x 216 feet) of loamy sand soil (80% sand, 12% silt, 8% clay, 1.5% organic matter, pH 6.0, CEC 2.7 meq/100 g) containing mature Bermudagrass; the applications were made on June 1, July 24, and August 28, 1990, using a tractor-mounted boom sprayer. An untreated plot (28 x 72 feet), located 110 feet from the treated plot, was maintained as a control. The grass on the test plot was mowed and the clippings were removed on May 31, 1990 (1 day prior to the first application of MON 12000), at 1- to 25-day intervals from May 31 through August 27, and once more on September 21 (24 days after the final treatment of MON 12000). Soil samples were collected from each subplot of the treated plot and from the control plot prior to treatment; at 0, 1, 4, and 10 days after the first and second treatments; and at 0, 1, 4, 10, and 21 days, and 1, 2, and 4 months after the final treatment. The soil samples were stored frozen at -18 to 17 F for up to approximately 35 months prior to extraction.

At the Clarence, Missouri, site, MON 12000 was broadcast three times, at 0.063, 0.125, and 0.125 lb ai/A, onto a plot (60 x 150 feet) of silt loam soil (20% sand, 54% silt, 26% clay, 2.0% organic matter, pH 7.2, CEC 12.4 meq/100 g) containing mature Colonial Bentgrass; the applications were made on May 23, July 5, and August 17, 1990, using a backpack sprayer. An untreated plot (50 x 80 feet), located 200 feet from the treated plot, was maintained as a control. The grass on the test plot was mowed and the clippings were removed on May 23, 1990 (prior to the first application of MON 12000), and at 15- to 34-day intervals from May 23 through September 13 (27 days after the final treatment of MON 12000). Soil samples were collected from each subplot of the treated plot and from the control plot prior to treatment; at 0, 1, 4, and 10 days after the first and second treatments; and at 0, 1, 4, 10, and 21 days, and 1, 2, and 4 months after the final treatment. The soil samples were stored frozen at -34 to 25 F for up to approximately 31 months prior to extraction.

Analytical methods: To analyze for MON 12000, subsamples (75 g) of the soil were mixed with portions of celite and sea sand, then extracted twice with acetonitrile:water (75:25, v:v) by shaking on a mechanical shaker for 15 minutes; after each extraction, the samples were centrifuged, and the extracts were filtered through glass wool. The extracts were combined and mixed with saturated aqueous sodium chloride:deionized water (6:250, v:v), and the solutions were partitioned twice against methylene chloride. After each partitioning, the organic phases were filtered through sodium sulfate

and combined. The organic solutions were concentrated to dryness at room temperature on a rotary evaporator, and the resulting residues were redissolved in methylene chloride:methanol (85:15, v:v). The solutions were diluted with methylene chloride, then purified on Florisil SPE columns; the columns were rinsed sequentially with methylene chloride and methylene chloride:methanol (95:5, v:v), and eluted with methylene chloride:methanol (85:15, v:v). To convert MON 12000 to 3-chloro-5-[(4,6-dimethoxy-2-pyrimidinyl)amino]-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester (the "rearrangement ester"), aliquots of 0.5 M potassium carbonate solution were added to the column eluants, and the samples were stirred overnight. After stirring, the solutions were partitioned twice against methylene chloride; after each partitioning, the organic phases were filtered through sodium sulfate and combined. The organic solutions were concentrated to dryness at room temperature on a rotary evaporator. The residues were redissolved in isooctane:ethyl acetate (95:5, v:v), and the solutions were purified on silica SPE columns; the columns were rinsed twice with isooctane:ethyl acetate (95:5, v:v), and eluted with isooctane:ethyl acetate (70:30, v:v). The eluants were concentrated to dryness at room temperature, and the residues were redissolved in isooctane:ethyl acetate (95:5, v:v). Aliquots of the solution were analyzed by GC with nitrogen/phosphorous detection. The identification and quantitation of MON 12000 in the extracts were achieved by comparison to MON 12000 reference standards. The detection limit was 2 ppb. Average recoveries from soil samples collected at the test sites and fortified with MON 12000 at 0.001-0.10 ppm were 63.96-125.7% of the applied.

For analysis of the MON 12000 degradates aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine) and 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid], subsamples (75 g) of the soil were mixed with portions of celite and sea sand, and extracted twice with acetonitrile:water (75:25, v:v) by shaking on a mechanical shaker for 15 minutes. After each extraction, the samples were centrifuged, and the extracts were filtered through glass wool and combined. The combined extracts were concentrated at room temperature on a rotary evaporator to remove acetonitrile; the remaining aqueous solutions were diluted with deionized water, and the pH was adjusted to >10 with 2.5 N NaOH. The solutions were partitioned twice against methylene chloride; after each partitioning, the organic phases were filtered through sodium sulfate and combined.

The organic phases, containing aminopyrimidine, were diluted with isooctane and concentrated at "ice bath temperatures" using a "cold finger" rotary evaporator. The remaining solutions were purified on amino SPE columns, and the columns were eluted with ethyl acetate:isooctane (20:80, v:v). The eluant was concentrated at "ice bath temperatures". Aliquots of the concentrated solutions were analyzed by GC with nitrogen/phosphorous detection. The identification and quantitation of aminopyrimidine in the extracts were achieved by comparison to reference standards; aminopyrimidine

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was quantitated to a lower limit of 5 ppb. Average recoveries from soil samples fortified at 0.005-0.10 ppm were 38.69-120.3% of the applied.

The aqueous phases remaining from the methylene chloride partitionings, which contained any 3-chlorosulfonamide, were acidified to pH <2 with 2 N sulfuric acid, then partitioned twice against ethyl acetate; after each partitioning, the organic phases were filtered through sodium sulfate and combined. For derivatization of 3-chlorosulfonamide to its trimethyl derivative, the combined organic solutions were concentrated to dryness on a rotary evaporator, diluted with acetone, and treated sequentially with methanol, 0.1 N HCl, and TMS-diazomethane. The samples were mixed by swirling, stoppered loosely, and allowed to stand overnight at room temperature. When necessary, additional TMS-diazomethane was added, and the samples were allowed to stand for an additional hour. The derivatized samples were concentrated to dryness, and the resulting residues were redissolved in ethyl acetate. The solutions were diluted with isooctane, and purified on silica SPE columns. The columns were eluted with ethyl acetate:isooctane (30:70, v:v), and the eluants were concentrated to dryness. The resulting residues were redissolved in ethyl acetate:isooctane (20:80, v:v), and aliquots of the solutions were analyzed by GC with electron-capture detection. The identification and quantitation of 3-chlorosulfonamide in the extracts were achieved by comparison to reference standards; 3-chlorosulfonamide was quantitated to a lower limit of 5 ppb. Average recoveries from soil samples fortified at 0.005-0.10 ppm were 59.08-122.3% of the applied.

DATA SUMMARY:

MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxylic acid methyl ester; 25% WP] dissipated with observed half-lives of <1 month from the upper 6 inches of plots of turf-covered sandy loam, loamy sand, and silt loam soils in California, Georgia, and Missouri that were treated with MON 12000 three times, at 0.063-0.125 lb ai/A/application, in Spring and Summer 1990. MON 12000 was ≤0.008 ppm below the 6-inch soil depth at all three test sites at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the study.

At the California site, MON 12000, applied at 0.061, 0.122, and 0.062 lb ai/A in June, August, and September 1990, respectively, dissipated completely (<0.002 ppm) within 1 month of application to a plot of sandy loam soil containing mature Kentucky Bluegrass. In the 0- to 6-inch soil depth, MON 12000 averaged 0.005, 0.003, and 0.002 ppm immediately after the first, second, and final treatments, respectively. MON 12000 was an average maximum of 0.007 ppm at 4 days after the second treatment, and averaged ≤0.003 ppm at all

sampling intervals following the final treatment (Table 6). MON 12000 averaged <0.002 ppm below the 6-inch soil depth at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all soil depths throughout the study.

During the study, rainfall plus irrigation totaled 8.31 inches between the first and second treatments, 14.69 inches between the first and third treatments, 17.50 inches at 21 days after the final treatment, and 39.90 inches through the entire 7-month study. Throughout the study, the air temperatures ranged from 29 to 109 F; the soil temperatures, measured at each sampling interval, ranged from 49 to 85 F at a 2-inch depth, and from 47 to 84 F at a 4- or 6-inch depth. The slope of the test plot was 2-8%, and the annual depth to the water table was ≤1 foot.

At the Georgia site, MON 12000, applied at 0.063, 0.124, and 0.063 lb ai/A in June, July, and August 1990, respectively, dissipated with a registrant-calculated half-life of 4.2 days in a plot of loamy sand soil containing mature Bermudagrass. In the 0- to 6-inch soil depth, MON 12000 averaged 0.007, 0.012, and 0.011 ppm immediately after the first, second, and final treatments, respectively. MON 12000 was an average maximum of 0.017 ppm at 1 day after the second treatment, and averaged 0.010 ppm 1 day after the final treatment, 0.007 ppm at 7 days, 0.004 ppm at 10 days, and <0.002 ppm by 21 days (Table 5). MON 12000 averaged <0.002 ppm below the 6-inch soil depth at all sampling intervals. The degradates aminopyrimidine and 3-chlorosulfonamide were <0.005 ppm at all depths throughout the study.

During the study, rainfall plus irrigation totaled 11.54 inches between the first and second treatments, 19.70 inches between the first and third treatments, 21.14 inches at 7 days after the final treatment, 22.34 inches at 14 days, and 40.44 inches throughout the entire 4-month study. Throughout the study, the air temperatures ranged from 26 to 105 F; the soil temperatures, measured at each sampling interval, ranged from 49 to 97 F at a 2-inch depth, and from 56 to 90 F at a-4-inch depth. The slope of the test plot was ≤0.25%, and the annual depth to the water table was 35-50 feet.

At the Missouri site, MON 12000, applied at 0.063, 0.125, and 0.125 lb ai/A in May, July, and August 1990, respectively, dissipated with a registrant-calculated half-life of 24.6 days and an observed half-life of approximately 1-2 weeks from the upper 6 inches of a plot of silt loam soil containing Colonial Bentgrass. In the 0- to 6-inch soil depth, MON 12000 averaged 0.008, 0.037, and 0.039 ppm immediately after the first, second, and final treatments, respectively. MON 12000 was an average maximum of 0.046 ppm 1 day after the second treatment; and averaged 0.029 ppm 1 day after the final treatment, 0.022 ppm at 10 days, and ≤0.004 ppm by 21 days (Table 4). In the 6- to 12-inch soil depth, MON 12000 was an average maximum of 0.008 ppm at 2 months after the final treatment, and averaged <0.002 ppm at 4 months. MON 12000 averaged <0.002 ppm below the 12-inch soil depth at all sampling intervals. The degradates

aminopyrimidine and 3-chlorosulfonamide averaged <0.005 ppm at all depths throughout the study.

During the study, rainfall plus irrigation totaled 8.41 inches between the first and second treatments, 14.99 inches between the first and third treatments, 17.69 inches 14 days after the final treatment, and 30.30 inches throughout the entire 4-month study. Throughout the study, the air temperatures ranged from 18 to 99 F; the soil temperatures, measured at each sampling interval, ranged from 36 to 82 F at a 2-inch depth, and from 36 to 78 F at a 4-inch depth. The slope of the test plot was <1%, and the annual depth to the water table was 70 feet.

COMMENTS:

1. Soil samples were stored frozen for up to 24-35 months prior to analysis for MON 12000. In an on-going, scientifically-sound freezer storage stability study (MRID 42661415; Study 4 of this submission) MON 12000 was found to be stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for 12 months. Data submitted in this field study for soil samples collected during a confined rotational crop study provide supporting evidence which suggest that MON 12000 is stable in sandy loam soil stored frozen for up to 3 years.

   Additionally, soil samples were stored frozen for up to 28-35 months prior to analysis for the degradates 3-chlorosulfonamide acid and aminopyrimidine. In MRID 42661415, 3-chlorosulfonamide acid was found to be stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for 12 months; additional storage stability data provided from the rotational crop study for 3-chlorosulfonamide acid suggested that this degradate is reasonably stable in sandy loam soil stored frozen for up to 3 years.

   Also in MRID 42661415, aminopyrimidine was found to be unstable in loam soil under similar storage conditions; aminopyrimidine averaged 101% of the applied immediately posttreatment, 69.1% after 2 months of frozen storage, and 29.6-32.6% after 8 and 12 months. Therefore, it is reasonable to assume that any aminopyrimidine that may have been in the soil samples at the time of collection would have dissipated during storage. In contrast, data for aminopyrimidine from the crop study suggested that this degradate remained stable during 3 years of frozen storage; the study author of this field study suggested that the dissipation of aminopyrimidine during frozen storage may be dependent upon the soil type, and that the apparent loss or binding of aminopyrimidine may be due to some interaction with the loam soil that was not observed in the sandy loam soil. Further, the study author suggested that the low recoveries (primarily 40-60%) of aminopyrimidine from fortified clay soil from this study (12- to 18-inch depth at the Missouri site) resulted from this interaction between soil type and apparent loss or binding of the degradate.

2. In addition to aminopyrimidine and 3-chlorosulfonamide acid, the MON 12000 degradates, 3-chlorosulfonamide ester and MON 12000 guanidine, were isolated as major degradates in an aerobic soil metabolism study (MRID 42139410) and an additional field (lysimeter) study (MRID 42976303; Study 2 of this submission). Although the study author stated that 3-chlorosulfonamide ester is readily hydrolyzed to 3-chlorosulfonamide acid, it is clear that the ester can be isolated at significant levels within the first 1-2 months after application. 3-Chlorosulfonamide ester and MON 12000 guanidine should have been investigated in this study. However, because the concentrations of parent MON 12000 were exceptionally low even in the soil samples collected immediately posttreatment, it is highly unlikely that any of the degradates would have been present at quantifiable levels.

3. Because MON 12000 was converted to the "rearrangement ester" prior to GC analysis, it was necessary to remove any of the ester present in the original sample prior to conversion of the parent. According to the study author, the "rearrangement ester" was removed by column chromatography (not further described). The study author did not indicate whether attempts were made to quantify any ester removed by the chromatography columns.

4. In this study, MON 12000 was formulated as MON 12007, and has the code name SARS 15012.

5. Soil temperatures were provided for individual sampling intervals only; soil temperatures determined daily for the duration of the study are preferable.

6. During the study, the plots at the California site were treated once with siduron, as Tupersan, at 13.5 lb/A on March 17, 1990, and once with triclopyr, as Turflon, at 0.8 qt/A. The plots at the Missouri site were treated with anilazine at 1.24 lb ai/A on June 19, 1990. No pesticides were applied at the Georgia site during the study.

7. The California test plot was treated with endothal, siduron, and "2,4-D Activate" in 1985 and 1986; siduron, endothal, chlorothalonil, chlorthal-dimethyl and "Growsafe" in 1987; and triadimefon in 1989; the treatment history for 1988 is unavailable. The Georgia plot was treated with pendimethalin in 1985; benefin, metolachlor, aldicarb, chlorpyrifos, methomyl, chlorothalonil, chlorothalonil plus sulfur, and acifluorfen-sodium in 1986; and sethoxydim, esfenvalerate, thiodicarb, and propargite in 1989; in 1987 and 1988, the plots were fallow, and no pesticides were applied. The Missouri plot was treated with thiram in 1986; no pesticides were applied in 1985 and 1988. The Missouri plot was also treated with an experimental fungicide in 1987, and an experimental plant growth regulator in 1989; the experimental products reportedly had chemistries that do not conflict with MON 12000.

DATA. EVALUATION RECORD

DER 8

CHEM 128721 MON 12000 §171-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42661415
Beasley, R.K. 1993e. Storage stability of MON 12000 and its metabolites in or on soil. Laboratory Project No. MSL 12358. Unpublished study performed and submitted by Monsanto Company, St. Louis, MO.

DIRECT REVIEW TIME = 10

REVIEWED BY: M. Anderson TITLE: Staff Scientist

EDITED BY: C. Cooke TITLE: Staff Scientist
K. Ferguson Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: K. Poff
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: K. Poff

CONCLUSIONS:

Ancillary Study - Freezer Storage Stability

1. Freezer storage stability studies are not specifically required by Subdivision N guidelines.

2. MON 12000 [Halosulfuron] and its degradate, 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid] were stable in loam soil that was fortified at 0.02 ppm and stored frozen at <0 F for up to 12 months. In contrast, the degradate aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine) was unstable during 12 months of storage in loam soil fortified at 0.02 ppm and stored at <0 F; aminopyrimidine averaged 101% of the applied immediately posttreatment, 69.1% after 2 months of frozen storage, and 29.6-32.6% after 8 and 12 months.

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METHODOLOGY:

Subsamples (75 g) of loam soil (28% sand, 48% silt, 24% clay, 2.2% organic matter, pH 6.7, CEC 9.5 meq/100 g) were fortified at 0.02 ppm with MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxyic acid methyl ester; purity 96.95%, Monsanto] dissolved in acetonitrile. Additional subsamples of the soil were fortified with both MON 12000 degradates, aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine; purity 98%, Monsanto) and 3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid; purity 98%, Monsanto], each at 0.02 ppm; the degradates were dissolved in acetonitrile. The fortified soil samples were stored frozen at <0 F; duplicate samples were removed for analysis at intervals up to approximately 12 months posttreatment for MON 12000 and its degradates. Samples were extracted on the day of collection and analyzed within "several days".

To analyze for MON 12000, subsamples (75 g) of soil were mixed with portions of celite and sea sand, and extracted twice with acetonitrile:water (75:25, v:v) by shaking on a mechanical shaker for 15 minutes; after each extraction, the samples were centrifuged, and the extracts were filtered through glass wool and combined. Saturated aqueous sodium chloride:deionized water (6:250, v:v) was added to the combined extracts, and the solutions were partitioned twice against methylene chloride; after each partitioning, the organic phases were filtered through sodium sulfate and combined. The organic solutions were concentrated to dryness at room temperature on a rotary evaporator, and the residues were redissolved in methylene chloride:methanol (85:15, v:v). The solutions were diluted with methylene chloride, then purified on Florisil SPE columns; the columns were rinsed sequentially with methylene chloride and methylene chloride:methanol (95:5, v:v), and eluted with methylene chloride:methanol (85:15, v:v). To convert MON 12000 to 3-chloro-5-[(4,6-dimethoxy-2-pyrimidinyl)amino]-1-methyl-1H-pyrazole-4-carboxylic acid-methyl ester (the "rearrangement ester"), aliquots of 0.5 M potassium carbonate solution were added to the column eluants, and the samples were stirred overnight. After stirring, the solutions were partitioned twice against methylene chloride; after each partitioning, the organic phases were filtered through sodium sulfate and combined. The organic solutions were concentrated to dryness at room temperature on a rotary evaporator, the residues were redissolved in isooctane:ethyl acetate (95:5, v:v), and the solutions were purified on silica SPE columns; the columns were rinsed twice with isooctane:ethyl acetate (95:5, v:v), and eluted with isooctane:ethyl acetate (70:30, v:v). The eluants were concentrated to dryness at room temperature, and the residues were dissolved in isooctane:ethyl acetate (95:5, v:v). Aliquots of the solution were analyzed within 8 days by GC with nitrogen-specific detection. The identification and quantitation of MON 12000 in the extracts were achieved by comparison to MON 12000 reference standards. The

detection limit was 2 ppb. The average analytical recovery from soil samples fortified with MON 12000 was 98.3% of the applied.

For analysis of the MON 12000 degradates aminopyrimidine and 3-chlorosulfonamide acid, subsamples (75 g) of soil were mixed with portions of celite and sea sand and extracted twice with acetonitrile:water (75:25, v:v) by shaking on a mechanical shaker for 15 minutes; after each extraction, the samples were centrifuged, and the extracts were filtered through glass wool and combined. The combined extracts were concentrated at room temperature on a rotary evaporator to remove acetonitrile; the remaining aqueous solutions were diluted with deionized water, and the pH was adjusted to >10 with 2.5 N NaOH. The solutions were partitioned twice against methylene chloride; after each partitioning, the organic phases were filtered through sodium sulfate and combined. The organic phases, containing any aminopyrimidine, were diluted with isooctane and concentrated at "ice bath temperatures" using a rotary evaporator. The remaining solutions were purified on amino SPE columns, and the columns were eluted with ethyl acetate:isooctane (20:80, v:v). The eluant was concentrated "with ice" using a rotary evaporator. Aliquots of the concentrated solutions were analyzed within 4 days by GC with nitrogen-specific detection. The identification and quantitation of aminopyrimidine in the extracts were achieved by comparison to reference standards; aminopyrimidine was quantitated to a lower limit of 5 ppb. The average analytical recovery from soil samples fortified with aminopyrimidine was 101% of the applied.

The aqueous phases remaining from the methylene chloride partitionings, which contained any 3-chlorosulfonamide, were adjusted to pH <2 with 2 N sulfuric acid, then partitioned twice against ethyl acetate; after each partitioning, the organic phases were filtered through sodium sulfate and combined. For derivatization of 3-chlorosulfonamide to its trimethyl derivative, the combined organic solutions were concentrated to dryness on a rotary evaporator, diluted with acetone, and treated sequentially with methanol, 0.1 N hydrochloric acid, and TMS-diazomethane. The samples were mixed by swirling, stoppered loosely, and allowed to stand overnight at room temperature. When necessary, additional TMS-diazomethane was added, and the samples were allowed to stand for an additional hour. The derivatized samples were concentrated to dryness, and the residues were redisssolved in ethyl acetate. The solutions were diluted with isooctane, and purified on silica SPE columns. The columns were eluted with ethyl acetate:isooctane (30:70, v:v), and the eluants were concentrated to dryness. The residues were redissolved in ethyl acetate:isooctane (20:80, v:v), and aliquots of the solutions were analyzed within 1 day by GC with electron-capture detection. The identification and quantitation of 3-chlorosulfonamide in the extracts were achieved by comparison to reference standards; 3-chlorosulfonamide was quantitated to a lower limit of 5 ppb. The average analytical recovery from soil samples fortified with 3-chlorosulfonamide was 97.3% of the applied.

DATA SUMMARY:

MON 12000 [3-chloro-5-([([(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl)amino]sulfonyl)-1-methyl-1H-pyrazole-4-carboxyic acid methyl ester; purity 96.95%] was stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for up to 12 months. Throughout the study, recoveries of MON 12000 averaged 91.8-118% of the applied with discernable pattern of decline (Table 1). Similarly, the MON 12000 degradate,

3-chlorosulfonamide acid [5-(aminosulfonyl)-3-chloro-1-methyl-1H-pyrazole-4-carboxylic acid; purity 98%]

was stable in loam soil fortified at 0.02 ppm and stored frozen at <0 F for up to 12 months. Throughout the study, recoveries of 3-chlorosulfonamide acid averaged 81.5-97.3% of the applied, with no discernable pattern of decline. In contrast, the degradate,

aminopyrimidine (4,6-dimethoxy-2-pyrimidinamine; purity 98%)

was unstable in loam soil fortified at 0.02 ppm and stored at <0 F for up to 12 months. Aminopyrimidine averaged 101% of the applied immediately posttreatment, 69.1% after 2 months of frozen storage, and 29.6-32.6% after 8 and 12 months.

COMMENTS:

1. The study author stated that this is an interim report, and that additional data for longer storage intervals will provided when they become available.

2. Because MON 12000 was converted to the rearrangement ester prior to GC analysis, it was neccessary to remove any of the ester present in the original sample prior to conversion of the parent. According to the study author, the rearrangement ester was removed by column chromatography (not further described).

3. The soil samples fortified in this study were collected from the 0- to 6-inch soil depths at a test site near New Holland, Ohio, that was used for a terrestrial field dissipation study (MRID 42976302, Study 1 of this submission). The soil CEC results reported in this review were taken from Study 1.

4. The reported results for the storage stability samples were not corrected for analytical recoveries.