DATA EVALUATION RECORD 11-24-92

STUDY IDENTIFICATION: Pierotti, M. V., and P. A. Moore. 1992. Confined Accumulation Study of SAN-582 H on Rotational Crops. Performed by Environmental Chemistry Section of Sandoz Agro, Inc., Des Plaines, Illinois. Field Study site located in Geneseo, Illinois. MRID No. 423805-01.

TYPE OF STUDY: Confined Accumulation in Rotational Crops

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CONCLUSIONS:

This study satisfied the data requirement for confined accumulation studies on rotational crops (165-1). The maximum concentration of any degradate reported was the sulfoxide of the thiolactic acid conjugate of SAN-582 H at 0.01 ppm in the winter wheat straw (planted 141 DAT/harvested 387 DAT). SAN-582 H and its identifiable degradates (oxalamide, the sulfoxide of the thiolactic acid conjugate of SAN-582 H, and the sulfonate of SAN-582 H) did not appear to accumulate in 3 rotational crops (wheat, lettuce, and carrots) planted in silty clay loam soil treated with SAN-582 H at the maximum field application rate of 1.5 lb ai/acre, and the exaggerated rates of 3.0 lb ai/acre for the soybean and 4.0 lb ai/acre for the corn subplots. Rotated crops were planted 141, 322, and 332 days following soil treatment. Immature winter wheat was harvested 207 days after planting and winter wheat grain and straw were harvested 246 days after planting. Immature spring wheat was harvested 42 days after planting and spring wheat grain and straw were harvested 74 days after planting. Lettuce and carrots were harvested 32 and 76 days after planting, respectively. The sulfoxide of the thiolactic acid conjugate of SAN-582 H was detected at 0.01 ppm in the winter wheat straw. In all other crops oxalamide, the sulfoxide of the thiolactic acid conjugate, and the sulfonate, when present in sufficient quantities to be identified in any of the 3 rotational crops, were all less than 0.01 ppm.

MATERIALS AND METHODS:

^{14}C-SAN-582 H (radiochemical purity of 99.6%, specific activity 43.18 mCi/mmole) was diluted with methanol, non radioactive SAN-582 H (99.6% pure) and 7.5 L SAN-582 H formulation inerts to produce a stock solution with a specific activity of 17,196 dpm/ug SAN-582 H. Dosing solutions for the 1.5 lb a.i./acre, 3.0 lb a.i./acre, and 4.0 lb a.i./acre treatment rates were prepared by corresponding dilution of aliquots of the stock solution with deionized water. Non-radioactive reference standards of SAN-582 H and related metabolites were synthesized with a chemical purity >96% for use in identifying SAN-582 H and its degradates in soil and plant parts.

The field portion of the study was conducted at Geneseo, Illinois. The confined accumulation study consisted of six plots (Fig 1): primary corn and soybean crop plots each for the maximum rate (1.5 lb a.i./acre), exaggerated rate of 3.0 lb a.i./acre for soybean and 4.0 lb a.i./acre for corn, and respective control plots for each corn and soybeans. Each plot consisted of four 55 gallon drums containing soil 76 cm deep (silty clay loam containing 19% sand, 53% silt, 28% clay, pH 6.3, 2.5% organic material, and CEC 15.8 meq/100 g). Each drum (subplot) was 0.25 m^2 in cross sectional area per plot.

Corn and soybean seeds were planted on 10 June 1990, and the next day (11 June 90, 0 DAT), the plots were treated accordingly with ^{14}C-SAN-582 H. Mature corn and soybean RACs were harvested on 19 Oct 90 (130 DAT) and on 17 Oct 90 (128 DAT), respectively.

Rotational crops were planted individually in the four subplots for each primary crop (soybean or corn) and for each treatment rate. Winter wheat was planted in subplot 1 on 30 Oct 90 (141 DAT); spring wheat was planted in subplot 2 on 29 April 91 (322 DAT); lettuce was planted in subplot 3 on 9 May 91 (332 DAT); and carrots were planted in subplot 4 on 9 May 91 (332 DAT). Immature and mature winter wheat RACs were harvested on 25 May 91 (348 DAT) and 3 July 91 (387 DAT), respectively. Immature and mature spring wheat RACs were harvested on 10 June 91 (364 DAT) and 12 July 91 (396 DAT), respectively. Lettuce was harvested on 10 June 91 (366 DAT), and carrots were harvested on 24 July 91 (408 DAT).

Soil cores (0-30 cm) were taken on 11 June 90 from each subplot during pretreatment and on the same day 4.5 hrs after treatment for all subplots. Soil cores were also taken during rotational plantings and harvest. The cores were subdivided into 10 cm regions to give 0-10 cm, 10-20 cm, and 20-30 cm sections. Rotational crop plants were sampled at the RAC stages. Following sampling, soil and plant specimens were frozen (-12 to -1 ^{0}F), shipped in dry ice, and stored frozen (-10 to 10 ^{0}F) until analysis. Previous storage stability data indicated that SAN 582 H and its soil metabolites were stable $\geq$3 years when stored at $\leq$10 ^{0}F. Storage stability data also indicated that SAN 582 H and its corn metabolites are stable for at least 24 months in corn

forage and fodder when stored $\leq 10^0$F. All soil samples were analyzed within 18 monmths of the sampling date and all rotational crops were analyzed within 4.5 months of the sampling date, except for carrot tops which were analyzed 10.5 months after harvest.

ANALYTICAL METHODS

Total radiocarbon in soil and plant samples was assayed by complete combustion of 0.3 to 1.0 g of sample in triplicate. Control soil and plant samples were spiked with ^{14}C-SAN-582 H to determine combustion recovery which ranged from 85-95%. Combustion values for treated samples were normalized using the combustion recovery. Samples were radioassayed by LSC.

Soil samples were extracted (Figure 1 shows complete extraction scheme) with methanol/water (1:1); the methanol removed by rotary evaporation and the resulting aqueous solution extracted with hexane, acidified and reextracted with methylene chloride. The aqueous solution was then freeze dried and the resulting residue dissolved sequentially in methanol and then deionized water. After the initial methanol/water (1:1) extraction, the soil was hydrolyzed in 1 N KOH to release bound residues. The resulting base hydrolysate was acidified to remove humic acids. The supernatant was freeze dried and the resulting residue dissolved sequentially in methanol and then deionized water. The remaining soil was combusted to determine the unextractable total radiocarbon residue (TRR).

Rotational crop samples were extracted with methanol/water (1:1) and the methanol removed by evaporation and the ensuing aqueous solution extracted with hexane, acidified and reextracted with methylene chloride. The aqueous solution was freeze dried and the resulting residue dissolved sequentially in methanol and then deionized water. After the initial methanol/water extraction, the plant tissue was hydrolyzed under acidic conditions to release bound residue. The resulting acidic hydrolysate was extracted with ethyl acetate under acidic and basic conditions. The remaining plant tissue, after acid hydrolysis, was combusted to determine the level of unextracted radioactivity. Tissues with levels $\geq$0.02 ppm were hydrolyzed under basic conditions. The base hydrolysate was acidified to precipitate lignin. The remaining solid tissue was crude cellulose. The lignin and crude cellulose were combusted to determine their TRR (See Figure 2 for complete extraction scheme).

REPORTED RESULTS:

1. The reported soil dissipation half-life for SAN-582 H applied at the maximum label application rate in the corn plot was 8.1 days. Contrary to the results reported on page 24, residues of SAN-582 H were reportedly detected in the 0-10, 10-20, and 20-30 cm soil segments at 130 DAT (Table VII), 141 DAT, and at 332 DAT (Table IX).

2. Immature winter wheat rotated on the corn subplot (planted 141 DAT/harvested 348 DAT) had a TRR of 0.0208 ppm and subsequent extractable fractions were <0.01 ppm (Table XVII). Winter wheat grain (planted 141 DAT/harvested 387 DAT) had a TRR of 0.0264 ppm and all extractable fractions were <0.01 ppm; the winter wheat straw had a TRR of 0.1744 ppm and TLC of the methanol soluble freeze-dried aqueous fraction identified the sulfoxide of the thiolactic acid conjugate of SAN-582 H at 0.0100 ppm and only one other band was ≥0.01 ppm (being very polar it remained at the origin in both solvent systems). Base hydrolysis of the solid yielded 0.0247 ppm (14.2% TRR) in lignin and 0.0207 ppm (11.9% TRR) in crude cellulose.

Winter wheat planted on the soybean subplot failed to grow reportedly from excessive precipitation (3/91) and poor drainage in that drum.

Immature spring wheat grown on the corn or soybean subplots (planted 322 DAT/harvested 364 DAT) had a maximum reported TRR of 0.0617 ppm. TLC of the methanol soluble fraction identified the sulfonate of SAN-582 H at a maximum of 0.0077 ppm. Spring wheat grain (planted 322 DAT/harvested 396 DAT) had a TRR of 0.0196 ppm. Spring wheat straw (planted 322 DAT/harvested 396 DAT) had a maximum TRR of 0.1417 ppm and TLC of the methylene chloride extract identified the sulfoxide of the thiolactic acid conjugate of SAN-582 H at a maximum of 0.0049 ppm and the remainder of the activity was diffuse with no one region >0.0049 ppm.

Lettuce grown on the corn and soybean subplots (planted 332 DAT/harvested 364 DAT) had a maximum reported TRR of 0.0382 ppm. All TLC fractions were <0.01 ppm.

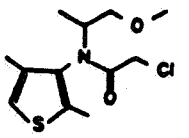
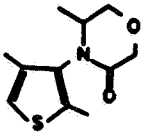
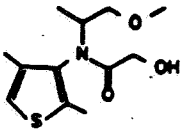
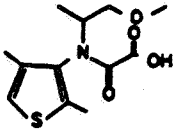
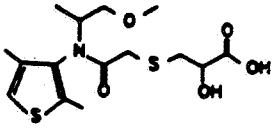
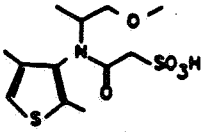
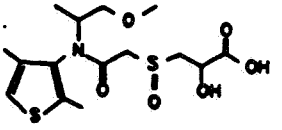
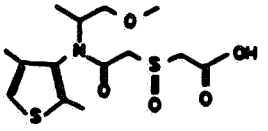
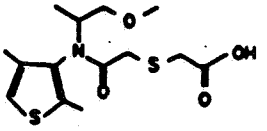
Carrot roots grown on the corn and soybean subplots (planted 332 DAT/harvested 408 DAT) had a TRR value of 0.0130 ppm. Carrot tops had a maximum reported TRR value of 0.0729 ppm (Table XIII). TLC analyses identified the oxalamide and the sulfoxide of the thiolactic acid conjugate, and the sulfonate, in which none exceeded 0.0051 ppm.

DISCUSSION:

1. It is noted on page 61 (Table V) that on subplot 4 at the 0-10 cm depth soil segment there was 9.1102 ppm of SAN-582 H found which is threefold more than in any other subplot (subplot 2) and twelvefold greater than that in subplot 3 treated at the same application rate. At 130 DAT the TRR in subplot 4 (4 lb ai/acre treatments) was less than that found in the other 3 subplots, even though at 0 DAT the TRR in subplot 4 was 3-12 times greater than that found in the other 3 subplots similarly treated. At a similar dissipation rate, it would be expected that with significantly higher confirmed application rates, the decline trend would be similar with time. This is not what is being shown in Tables V and VII, where it appears that the decline rate is more than 3-12 times greater than that being shown in the other subplots. This issue requires further discussion from the registrant.

2. This study as originally submitted was incomplete and written in an unorganized, meandering manner making it extremely difficult to locate essential information regarding the test parameters and results. Additional information was requested through the registration division from the registrant in order to supplement the original study because of errors and lack of placing necessary information in the correct places. Future similarly disorganized studies will be sent back unreviewed for the author to organize in a complete and concise manner for resubmission.

Table XXV. SAN-582H Model Metabolites

Designation	Chemical Name	Empirical formula	Structure	MW
SAN-582H	2-Chloro-N-((1-methyl-2-methoxy)ethyl)-N-(2,4-dimethyl-thien-3-yl)-acetamide	$C_{12}H_{18}ClNO_2S$		275
M9	4-(2,4-dimethyl-3-thienyl)-5-methyl-3-morpholinone	$C_{11}H_{15}NO_2S$		225
M11	N-(2,4-Dimethyl-3-thienyl)-2-hydroxy-N-(2-methoxy-1-methylethyl)-acetamide	$C_{12}H_{19}NO_3S$		257
Oxalamide (OX)	N-(2,4-Dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)-oxamic acid	$C_{12}H_{17}NO_4S$		271
Thiolactic acid conjugate (TA)	S-(2-(N'-(2,4-dimethyl-3-thienyl)-N'-(2-methoxy-1-methylethyl)amino-2-oxoethyl)-thiolactic acid	$C_{15}H_{23}NO_5S_2$		361
Sulfonate conjugate (S)	2-(N'-(2,4-Dimethyl-3-thienyl)-N'-(2-methoxy-1-methylethyl)amino-2-oxoethyl)-sulfonic acid	$C_{12}H_{19}NO_5S_2$		321
Sulfoxide of thiolactic acid conjugate (STA)	Sulfoxide of S-(2-(N'-(2,4-dimethyl--3-thienyl)-N'-(2-methoxy-1-methylethyl) amino-2-oxoethyl)-thiolactic acid	$C_{15}H_{23}NO_6S_2$		377
Sulfoxide of thioglycolic acid conjugate (STGA)	Sulfoxide of S-(2-(N'-(2,4-dimethyl--3-thienyl)-N'-(2-methoxy-1-methylethyl) amino-2-oxoethyl)-thioglycolic acid	$C_{14}H_{21}NO_6S_2$		347
Thioglycolic acid conjugate (TGA)	S-(2-(N'-(2,4-dimethyl-3-thienyl)-N'-(2-methoxy-1-methylethyl)amino-2-oxoethyl)-thioglycolic acid	$C_{14}H_{21}NO_5S_2$		331

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