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Jul. 8 1980

Date Out EFB: JUL 8 1980

To: Product Manager
TS-767

From: Dr. Willa Garner
Chief, Review Section N
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 524 - 308

Chemical Glyphosate

Type Product: H

Product Name: Roundup

Company Name: Monsanto

Submission Purpose:

EBB Code: other

Date in: 5/30/80

Date Completed: JUL 8 1980

ACTION CODE: 316 (321)

EFB # 480

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

Introduction. This is a review of several environmental fate-type studies of the surfactant [redacted] This the surfactant used in Roundup formulations, and is of concern to EEB since it appears to be highly toxic to fish (refer to minutes of May 19, 1980 meeting with Monsanto in this file). These studies were not sent to EFB for review previously even though the one study was submitted in 1974. The 1978 study was lost in RD until now. The technical information was forwarded by the company to EFB at our request. The structure of this surfactant was confirmed through a phone conversation with [redacted] Monsanto's supplier of the surfactant.

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[redacted] chemical.

physical properties. liquid at 25° C; miscible with water; MW range 1200-2000; non-volatile. See Monsanto specification sheet and September 10, 1979 cover letter in this file for further chemical information.

Directions for Use. See appropriate Roundup label. The concentration of surfactant on a W/W basis is about half that of the active in the formulation.

Discussion of Data.

[redacted] Surfactant: Biodegradation, Uptake, and ^{14}C Distribution," 2/12/74, J. T. Marvel, et. al. Acc. No. 093850

These laboratory studies used ^{14}C-[redacted] labeled surfactant (17 mc/mM). Three soils, a silty loam (1% OM, pH 6.5), a silty clay loam (6% OM, pH 7.0) and a sandy loam (1% OM, pH 5.7) were used. The degradation of [redacted] in aerobic shake flasks was studied over a seven week period by weekly monitoring of $^{14}CO_2$ evolution. The effect of surfactant on native soil microbes was studied by measuring the metabolism of ^{14}C-UL-labeled sucrose to $^{14}CO_2$. The uptake of soil residues by plants was also studied.

Carbon dioxide collectors were made with Ascarite, glass wool, and drierite, and CO_2 was released from these traps into phenethylamine trapping solution. LSC was performed using automatic external standardization with on-line computation. Soil was sterilized by autoclaving. [redacted]

Aerobic soil degradation. The aerobic shake flasks contained 5 g soil and 100 ml distilled water, and [redacted] was added to a total system concentration of 1 ppm. The pattern of degradation was similar in all three soils. After seven weeks 24-31% of the label was revovered as $^{14}CO_2$, 44-51% of the ^{14}C was associated with the soil, and 3-4% was in the supernatent. There was a burst of CO_2 evolution the first week followed by a slower, steady release over the remaining six weeks. The material balance was not particularly good-about 78% for all three soils.

Sterilization of the soil resulted in an essentially complete inhibition of CO_2 release, indicating that microbes are responsible for the breakdown of the [redacted] portion of the surfactant in the soil.

The nature of the degradates was investigated by observing the extraction characteristics of the residues. Soil was extracted with 2M NH_4OH, and the residues partitioned into chloroform. Direct extraction of the soil with chloroform was ineffective in removing label. About 75% of the parent [redacted] mixture partitions into chloroform from an NH_4OH or distilled water despersion under the conditions of this experiment.

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The 7 week data are not very useful for comparison purposes since the sterile controls were terminated after 1 week. Only one non-sterile sample, a silt loam flask, was terminated at 1 week. The results are summarized below as percent of applied label.

	% $^{14}CO_2$ release	% soil-associated	% supernatent
sterile 7 day	0.12	71	25
non-sterile 7 day	18	78	8

In both samples less than 10% of the soil-associated label can be extracted with NH_4OH. In the sterile sample 75% of the ^{14}C in the supernatent partitions into chloroform, (as expected for parent), while in the non-sterile silt loam only about 47% of the residues in the supernatent partition into chloroform, indicating a breakdown to more polar molecules.

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Effect of surfactant on ^{14}C-sucrose metabolism. The degradation of uniformly ^{14}C-labeled sucrose to CO_2 is a measure of native soil microflora activity since referenced work shows that soil sterilization completely prevents the process. In all three soils 1 ppm [redacted] had no deleterious effect on the metabolism of 10 ppm sucrose to CO_2 (37-63% evolution by 14 days). It should be noted that the pattern of sucrose metabolism to CO_2 is similar to that observed for the surfactant. The rate of CO_2 erolution slows dowon significantly after about 7 days, suggesting that this phenomenon may be a metabolic limitation of the experimental system.

Plant uptake studies. The uptake of label into corn and soybean plants from silt loam soil treated with 3.3 lb/A [redacted] was measured in this greenhouse study. The surfactant was applied to the soil surface when the plants were 16 days old, and uptake was observed for up to 6 weeks after treatment. Plants were grown in 4" x 4" pots, and cubicle controls were employed to correct for reuptake of released $^{14}CO_2$ into the plants. The nature of the ^{14}C-residues in the plants was investigated with an involved natural products screening scheme. The results of this study are briefly summarized.

The maximum uptake was observed in the 6 week soybean plants, where 0.33% of the label applied to the soil was found in the plants. The cubicle controls contained 0.17%, indicating that photosynthesis accounts for a significant fraction of the label in the experimental plants. The level of parent, determined by chloroform extractability, was <5% of uptake in both controls and treated plants. >95% of the ^{14}C was incorporated into natural plant constituents, and the natural product profiles were the same in treated plants and controls.

conclusions. There are several problems with experimental design. It is unclear why so much water was added to the soil (20 gm to 1 gm soil), sterile controls should have been carried for the full seven weeks for comparison purposes, and the material balances were not very good for the 7 weeks samples in the surfactant degradation study (about 78%). However, from the studies we can determine the basic degradation and persistence of the moiety of soil. Soil microbes metabolize the residues, and the parent chains have a half-life of a few weeks or less. The more-polor degradates, presumably short chain acids and glycolates (see aquatic dissipation study below), can be expected to enter the metabolic pathways at various points and be further degraded or incorporated into various biomolecules. The half-life for total residues is therefore rather meaningless.

at 1 ppm does not adversly effect those native soil microbes involved in sugar metabolism. The surfactant binds strongly to soil-a characteristic of molecules such as surfactants which are amphiphilic in nature. Residues from the surfactant can be taken up from the soil and incorporated into plant constituents, though it is unclear if the parent, moieties, or other degradates are taken up.

Surfactant: Biodegradation In Natural Waters," 8/21/78, M.C. Bandish and H.W. Frazier. Acc. No. 241017-3

In a 14 week study the degradation of (0.05 and 0.1 ppm) was investigated in three natural water/sediment systems. The studies were carried out in aerobic metabolism flasks at 30°C in the dark. The waters/sediments used were: lake water, pH 4.6; pond water, pH 7.4; river water, pH 7.8. The flasks were equipped with polyurethane organic volatiles traps and Ascarite CO_2 traps. Sterile water controls were obtained by millipore filtration. The effect of the surfactant on native aquatic microbes was investigated by studing the metabolism of ^{14}C-UL-sucrose to CO_2. LSC techniques were as in the soil study above.

As in the soil study, water sterilization completely inhibits CO_2 evolution in all three system, indicating that the portion of the surfactant can be degraded by microbial metabolism. at 0.1 ppm had no effect on the metabolism of 10 ppm surcose to CO_2 (50-80% of label liberated as $^{14}CO_2$ in 7 weeks), implying no deleterious effect on native microflora involved in carbohydrate metabolism.

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By 14 weeks respective samples containing 0.1 ppm [redacted] had released 47% (lake), 40% (river), and 38% (pond) of the label as $^{14}CO_2$. Similar results were observed for the 0.05 ppm samples. The higher degree of metabolism in lake water most likely results from that water containing a more active microbe population since the level of surcrose metabolism to CO_2 was also higher in lake water. In the 14 week 0.1 ppm samples, 8-23% (depending on the water) of the label was associated with the sediment, and 32-53% was in the supernatent (filtrate). The results were similar for the 0.05 ppm samples. Material balances were 89-99% for all samples.

At the conclusion of the study the filtrates were concentrated under reduced pressure (rotary evaporator at 40 °C) for further characterization. Depending on the sample, 2-32% of the label was lost due to volatilization during the concentration process. Since [redacted] is itself not volatile under these conditions, some metabolites which are volatile under reduced pressure were produced over the course of the study.

Metabolites were characterized by anion exchange chromatography (D-1[HCO_3^-] resin, Bio-Rad, eluants varied from 50% aqueous methanol to 1 M NH_4HCO_3) and high voltage electrophoresis (HVE). Both techniques showed that [redacted] is degraded to negatively-charged species. Based on elution pattern, carboxylic acids are among the metabolites. The parent mixture can be distinguished from the mixture of degradates by both separation techniques. From the amount of parent remaining after 14 weeks, the half-life of the parental [redacted] moiety is estimated to be 3-4 weeks in natural water.

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Conclusions. This study was well carried out. The results are substantially similar to those obtained in the soil degradation study, but the metabolites were characterized in greater detail. Aquatic microflora metabolize the [redacted] portion of [redacted], and the surfactant does not affect adversly native microbes involved in carbohydrate metabolism. The half-life of parent is about 3-4 weeks. The half-life for the total degradation of label to CO_2 is about 15-30 weeks. This value is not particularly meaningful however, since the lower molecular weight acidic compounds generated can enter the metabolic pools and be further degraded or incorporated into biomolecules which are degraded at various rates.

Recommendations. None required. These studies are sufficient to determine the basic mode of degradation and the persistence of the surfactant [redacted] in soil and water.

The information used for this review was the submitted studies and the technical information supplied to EFB by the registrant and [redacted]

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