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



OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES October 30, 2001

MEMORANDUM

- SUBJECT: EFED RED Chapter for Ziram PC Code: 34805 (Ziram); Case No. 2180; DP Barcodes: D276759; D260984 and D260985.
- TO: S. Lewis, Branch Chief L. Parsons, CRM Special Review and Reregistration Division (7508C)
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The EFED Integrated Environmental Risk Assessment for Ziram is attached. The following is a short overview of our findings. Several studies are lacking, but based on the available data, EFED concludes the following concerning the potential environmental risk from the use of Ziram:

Ziram is a dimethyldithiocarbamate fungicide that is acutely very highly toxic and poses acute and chronic risk to most endangered and non-endangered aquatic organisms, should the compound enter aquatic habitats. The major sites considered in this risk assessment include terrestrial food and non-food uses. Acute terrestrial risk (and chronic risk for mammals) in endangered and non-endangered avian and mammalian species may occur from the application of ziram to foliage or other wildlife food items mainly due to the compound's higher application rates and multiple applications, rather than the compound's toxicity. Avian chronic reproductive effects could not be assessed due to a lack of toxicity data. A proper assessment for risks to terrestrial and aquatic plants could not be conducted due to a lack of toxicity data. Ziram's susceptibility to degradation, especially in neutral and acidic environments, reduces the probability of prolonged exposure to the chemical. The chemical is expected to dissipate relatively quickly under many conditions, hydrolyzing rapidly under neutral to acidic conditions in a matter of hours. In acidic soils, ziram degraded with half-lives that were typically in hours; in water, the compound also photolyzed rapidly. In addition, ziram degraded much faster under aerobic than anaerobic conditions during soil metabolism studies. While ziram can reach surface water by spray drift or runoff (it is relatively highly soluble and does not bind to most soils), it is not likely to persist. The main degradates are volatiles such as CS_2 , CO_2 and COS, and are not expected to persist in soil and water. However, ziram may pose ecological risk to aquatic organisms through pulse dosing, due to the compound's high application rates, multiple applications and short intervals between those applications. The compound can be available following rain events during the growing season and especially on days following application. In addition, since ziram is relatively highly soluble and is very highly toxic to aquatic organisms, there is a possibility of acute risk to amphibians and their larval stages through dermal exposure from terrestrial broadcast spray applications and through aquatic exposures, respectively.

Major Conclusions

Terrestrial Risks

- C Low acute risk to avian species. However, endangered birds may be adversely affected.
- C Chronic risk to avian species could not be assessed due to a lack of toxicity data.
- C High acute risk to endangered and non-endangered mammals (other than granivores) from both single and multiple applications.
- C Chronic risk to endangered and non-endangered mammals (other than granivores) with either single and multiple applications.
- C As Ziram is practically non-toxic ($LD_{50} > 100 \text{ ug/bee}$) to honeybees, low risk is assumed. C There were no ecological incidents involving terrestrial organisms found in the EFED
- C There were no ecological incidents involving terrestrial organisms found in the EFED incidents database for Ziram.

Aquatic Risks

- C Using a Tier II model for refinement (PRZM/EXAMS), the present assessment suggests potential acute risk to endangered and non-endangered freshwater fish, freshwater invertebrates and estuarine invertebrates.
- C Chronic risk could not be assessed due to a lack of toxicity data.
- C Low risks to aquatic plants, however more data is needed. C There were no ecological incidents involving aquatic organ
- C There were no ecological incidents involving aquatic organisms found in the EFED incidents database for Ziram.

Water Resources

C The compound can be available following rain events during the growing season and especially on days following application. It does not appear to be likely to substantially leach into soils, because it is highly labile.

Data Gaps

Environmental Fate (required studies)

- C <u>Terrestrial Field Dissipation (164-1)</u>: One study, conducted at two sites was found to have several deficiencies. To upgrade the study, the registrant is required to address the problems found in it. Alternatively, a new study, conducted at only one site must be submitted.
- C <u>Aerobic Soil Metabolism (one soil with near neutral pH)</u> EFED is concerned about the results obtained from the submitted study because it was conducted on a soil that had a very low pH of 5.4, which may rise the rate of degradation of ziram by promoting hydrolysis. It is acknowledged, however, that the major degradate observed in this study, 1,1-dimethylurea was not observed in the hydrolysis study and the degradates observed in the hydrolysis study were not present in big quantities in this study. However, to resolve the uncertainty about the role of hydrolysis in the study, EFED requires a new a new Aerobic Soil Metabolism Study (162-1) conducted in a soil with a near neutral pH.

Ecotoxicity (required studies)

- C <u>Avian reproduction studies (72-2) for Ziram</u>: Birds may be subject to repeated or continuous exposure to the pesticide, especially preceeding or during the breeding season. The preferred test species are mallard duck and bobwhite quail. Both are required.
- C <u>Fish Full Life Cycle Test (72-5) for ziram</u>: The preferred test species is the fathead minnow (*Pimephales promelas*). FIFRA requires a fish life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The LC50 of the freshwater species, the bluegill sunfish (*Leopmis macrochirus*), is 0.0097 ppm (MRID# 423863-03).
- C <u>Freshwater aquatic invertebrate life-cycle test (72-4) for ziram</u>: The preferred test species is the water flea (*Daphnia magna*). FIFRA requires the freshwater aquatic invertebrate life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The waterflea (*Daphnia magna*) LC50 is 0.048 ppm (MRID# 423863-05).
- C <u>Estuarine/marine fish life-cycle test (72-5) for ziram</u>: The preferred test species is the sheepshead minnow (*Cyprinodon variegatus*). FIFRA requires a fish life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The LC50 of the estuarine marine species, the sheepshead minnow (*Cyprinodon variegtus*), is 0.84 ppm (MRID# 437816-01).
- C <u>Estuarine/marine aquatic invertebrate life-cycle test (72-4) for ziram</u>: The preferred test species is the Mysid *(Americamysis bahia)*. FIFRA requires the estuarine/marine aquatic invertebrate life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The acute LC50's for the eastern oyster (*Crassostrea virginia*) and the mysid shrimp (*Mysidopis bahia*) are 0.077 ppm and 0.014 ppm respectively (MRID's 437816-02 and 437816-03).
- C <u>Terrestrial (Tier I: Guideline 122-1) and Aquatic plant testing (Tier II: Guideline 123-2)</u> is required for ziram for the following reasons: 1) It has outdoor non-residential terrestrial uses and 2) It may move off-site by runoff (solubility >10 ppm in water) or may move by drift (aerial). The *Selenastrum capricornutum* study has been submitted to EPA and has fulfilled guideline requirements, but the *Lemna gibba* study has not been submitted. In addition, the four other algae species must be tested due to ziram's

apparent toxicity to green algae. These studies must be submitted in order for the Agency to complete a terrestrial and aquatic plant risk assessment.

Recommended Label Language

EFED recommends that the following language be included on the appropriate labels:

Environmental Hazards

Manufacturing Use:

This pesticide is toxic to fish and aquatic invertebrates. Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA. Do not contaminate water when disposing of equipment washwaters.

End Use Products:

This product is toxic to fish, aquatic invertebrates oysters and shrimp. Do not apply directly to water, to areas where surface water is present or to intertidal areas below the mean high water mark. Drift and runoff may be hazardous to aquatic organisms in water adjacent to treated areas. Do not contaminate water when disposing of equipment washwaters or rinsate.

Statement to minimize the potential for surface water contamination for all end-use products:

This chemical can contaminate surface water through ground spray applications. Under some conditions, it may also have a high potential for runoff into surface water after application. These include poorly draining or wet soils with readily visible slopes toward adjacent surface waters, frequently flooded areas, areas overlaying 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.

Spray Drift Management

The Agency has been working with the Spray Drift Task Force, EPA Regional Offices and State Lead Agencies for pesticide regulation and other parties to develop the best spray drift management practices. The Agency is proposing interim mitigation measures for aerial applications that should be placed on product labels/labeling as specified in section V of this document. The Agency has completed its evaluation of the new data base submitted by the Spray Drift Task Force, a membership of U.S. pesticide registrants, and is developing a policy on how to appropriately apply the data and the AgDRIFT computer model to its risk assessments for pesticides applied by air, orchard airblast and ground hydraulic methods. After the policy is in place, the Agency may impose further refinements in spray drift management practices to reduce off-target drift and risks associated with aerial as well as other application types where appropriate. In the interim, labels should be amended to include the following spray drift related language:

For products that are applied outdoors in liquid sprays (except mosquito adulticides), regardless of application method, the following must be added to the labels: **"Do not allow this product to drift"**

Endangered Species Statement

The Agency has developed the Endangered Species Protection Program to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that address these impacts. The Endangered Species Act requires federal agencies to ensure that their actions are not likely to jeopardize listed species or adversely modify designated critical habitat. To analyze the potential of registered pesticide uses to affect any particular species, EPA puts basic toxicity and exposure data developed for REDs into context for individual listed species and their locations by evaluating important ecological parameters, pesticide use information, the geographic relationship between specific pesticides uses and species locations, and biological requirements and behavioral aspects of the particular species. This analysis will take into consideration any regulatory changes recommended in this RED that are being implemented at this time. A determination that there is a likelihood of potential impact to a listed species may result in limitations on use of the pesticide, other measures to mitigate any potential impact, or consultations with the Fish and Wildlife Service and/or the National Marine Fisheries Service as necessary.

The Endangered Species Protection Program as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989) is currently being implemented on an interim basis. As part of the interim program, the Agency has developed County Specific Pamphlets that articulate many of the specific measures outlined in the Biological Opinions issued to date. The Pamphlets are available for voluntary use by pesticide applicators on EPA's website at <u>www.epa.gov/espp</u>. A final Endangered Species Protection Program, which may be altered from the interim program, is scheduled to be proposed for public comment in the Federal Register before the end of 2001.

Endocrine Disruption

EPA is required under the Federal Food, Drug, and Cosmetic Act (FFDCA), as amended by the Food Quality Protection Act (FQPA), to develop a screening program to determine whether certain substances (including all pesticide active and other ingredients) "may have an effect in humans that is similar to an effect produced by a naturally-occurring estrogen, or other such endocrine effects as the Administrator may designate." Following the recommendations of its Endocrine Disrupting Screening and Testing Advisory Committee (EDSTAC), EPA determined that there was scientific basis for including, as part of the program, the androgen- and thyroid-hormone systems, in addition to the estrogen-hormone system. EPA also adopted EDSTAC's recommendation that the Program include evaluations of potential effects in wildlife. For pesticidal chemicals, EPA will use FIFRA and, to the extent that effects in wildlife may help determine whether a substance may have an effect in humans, FFDCA has authority to require the wildlife evaluations. As the science develops and resources allow, screening of additional hormone systems may be added to the Endocrine Disruptor Screening Program (EDSP).

Based on available scientific literature, ziram may have characteristics of an endocrine disrupting compound. The compound may possibly exhibit effects on birds and mammals. These effects include possible thyroid and adrenal involvement in birds and mammals. Based on all these data, EFED recommends that when appropriate screening and or testing protocols being considered under the Agency's EDSP have been developed, ziram be subjected to more definitive testing to better characterize effects related to its possible endocrine disrupting activity under the current use pattern.



Office of Prevention, Pesticides, and Toxic Substances

Environmental Fate and Ecological Risk Assessment for the Reregistration of Ziram

Shaughnessy Number: 34805

Zinc bis(dimethyldithiocarbamate) "Ziram"

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I. ENVIRONMENTAL RISK CONCLUSIONS

Executive Summary

Several studies are lacking, but based on the available data, EFED concludes the following concerning the potential environmental risk from the use of Ziram:

Ziram is a dimethyldithiocarbamate fungicide that is acutely very highly toxic and poses high acute and chronic risk to most endangered and non-endangered aquatic organisms, should the compound enter aquatic habitats. The major sites considered in this risk assessment include terrestrial food and non-food uses. Acute terrestrial toxicity (and chronic risk for mammals) in avian and mammalian species may occur from the application of ziram to foliage or other wildlife food items mainly due to the compound's higher application rates and multiple applications, rather than the compound's toxicity. Avian chronic reproductive effects could not be assessed due to a lack of toxicity data. A proper assessment for risks to terrestrial and aquatic plants could not be conducted due to a lack of toxicity data. Ziram's susceptibility to degradation, especially in neutral and acidic environments, reduces the probability of prolonged exposure to the chemical. The chemical is expected to dissipate relatively quickly under many conditions, hydrolyzing rapidly under neutral to acidic conditions in a matter of hours. In acidic soils, ziram degraded with half-lives that were typically in hours; in water, the compound also photolyzed rapidly. In addition, ziram degraded much faster under aerobic than anaerobic conditions during soil metabolism studies. While ziram can reach surface water by spray drift or runoff (it is relatively highly soluble and does not bind to most soils), it is not likely to persist. The main degradates are volatiles such as CS₂, CO₂ and COS, and are not expected to persist in soil and water. However, ziram may pose ecological risk to aquatic organisms through pulse dosing, due to the compound's high application rates, multiple applications and short intervals. The compound can be available following rain events during the growing season and especially on days following application. In addition, since ziram is relatively highly soluble and is very highly toxic to aquatic organisms, there is a possibility of acute risk to amphibians and their larval stages through dermal exposure from terrestrial broadcast spray applications and through aquatic exposures, respectively.

- C Low acute risk to avian species. However some endangered birds may be adversely affected.
- C Chronic risk to avian species could not be assessed due to a lack of toxicity data.
- C High acute risk to endangered and non-endangered mammals (other than granivores) from both single and multiple applications.
- C Chronic risk to endangered and non-endangered mammals using either single or multiple applications (other than granivores).
- C As Ziram is practically non-toxic ($LD_{50} > 100 \text{ ug/bee}$) to honeybees, low risk is assumed.
- C Using a Tier II model for refinement (PRZM/EXAMS), the present assessment suggests potential acute risk to endangered and non-endangered freshwater fish, freshwater invertebrates and estuarine invertebrates. Chronic risk to aquatic organisms could not be assessed due to a lack of toxicity data. A proper assessment for risks to terrestrial and aquatic plants could not be conducted due to a lack of toxicity data.

- C There were no ecological incidents found in the EFED incidents database for Ziram.
- C The compound can be available after rain events during the growing season and especially on days following application. It does not appear to be likely to substantially leach into soils, because it is highly labile.

II. INTRODUCTION

Zinc-dimethyldithiocarbamate (Ziram) is a fungicide that is registered for use on variety of fruits and vegetables. The mode of action of the dimethyldithiocarbamate fungicides is not clearly understood. It has been suggested that they may act by interfering with metal enzyme catalysts.

Use Characterization

Yearly use is about 1,950,000 to 2,689,000 pounds of active ingredient (a.i.) on about 454,000 to 555,000 acres. Approximately 39% is used on almonds, 29% on apples, and 8% each for pears, peaches and pecans, 3% on grapes and all other food/feed uses were <2% each. For the rest of the sites usage is less than 20%. Formulation is a dry flowable (Granuflo and 76DF).

Use Sites (taken from use closure memo of 5/22/01)

<u>Terrestrial food + feed crop</u>: apples, apricots, blackberries, blueberries, cherries, nectarines, peaches, pears, pecans, strawberries (this use is not being supported and is ineligible for reregistration due to lack of data), almonds, grapes, and tomatoes.

<u>Terrestrial non-food+outdoor residential</u>: Flowering plants, nursery plants, pine seedlings, Douglas and Shasta firs (grown as Christmas trees).

Application Equipment: Air carrier sprayer; Aircraft; Ground; Hand held duster; High volume ground sprayer; Low volume ground sprayer; Low volume sprayer; Sprayer.

Application Methods: Drench; Dust; High volume spray (dilute); Industrial preservative treatment; Low volume spray (concentrate); Preservative treatment; Spray.

Application Rates: Rates vary with crop and disease; multiple applications are allowed on most use sites. Maximum (seems to be) approximately 55 lbs a.i./A per crop cycle. (72 lb formulated product). **Annual Pounds Used**: The largest markets in terms of total pounds a.i. allocated primarily to almonds (39%), apples (29%), pears, peaches and pecans (approx 8% each), grapes (3%), all other food/feed uses were <2% each.

% Crop Treated: Crops with a high percentage of the total U.S. planted acres treated (weighted average) include almonds (49% of crop treated), pears (29% of crop treated), nectarines (23% of crop treated), apricots (19%), apples (18%), peaches (13%) all other crops (<10%).

Ziram Use Profile					
сгор	max lb ai/A per applications	max # applications	minimum application interval (days)	comments	
almonds	6.1	4	3*	apply no later than 5 weeks after petal fall	
apples/pears/ eastern US	6.1	7	7	14 day PHI	
apples/pears/ western US	6.1	4	10	apples 14 day PHI pears 5 day PHI	
peaches/ nectarines eastern US	6.1	9	7	14 day PHI. Do not apply more than 54.7 lbs ai per crop cycle	
peaches/ nectarines western US peach leaf curl only	7.6	6	3*	make application after leaf drop and/or at bud swell	
apricots	6.1	5	7		
cherries eastern US	6.1	5	7	14 day PHI	
cherries western US	6.1	4	5	30 day PHI	
pecans	6.1	8	14	55 day PHI	
ornamentals and trees	6.1	NS	7	apply as needed throughout growing season	
grapes	3.0	7	7		
tomatoes	3.0	6	7	7 day PHI	
blueberries	2.3	2	7	do not apply later than 3 weeks after full bloom	
**strawberries	1.5	4	5-10		

Ziram Use Profile

**strawberries1.545-10*only under certain circumstances such as very warm, humid conditions

** this use is not being supported and is ineligible for reregistration due to lack of data

Toxicity Data and Approach to Risk Assessment

Toxicity testing reported in this document does not represent all species of bird, mammal, or aquatic organisms. Only two **surrogate species** for both freshwater fish and birds are used to represent all freshwater fish (2000+) and bird (680+) species in the United States. For mammals, acute toxicity studies are usually limited to the Norway rat or the house mouse. Estuarine/marine testing is usually limited to a crustacean, a mollusk, and a fish. Neither reptiles nor amphibians are tested. The assessment of risk or hazard makes the assumption that avian and reptilian toxicity are similar. The same assumption is used for fish and amphibians. Generally, the most

toxic endpoints for the technical grade active ingredient (TGAI) are used in the assessment to represent each group of organism.

The current terrestrial assessment was based on EEC's derived from halflives of 35 days (default value) and 1 day (based on an aqueous photolysis half-life of 8.7 hrs plus a 3x safety factor = approximately 24 hrs or 1 day). The assessment used crop groupings representing similar use patterns and application scenarios (lbs ai/A and # of applications). The aquatic assessment used a refined approach through calculation of EEC's by the PRZM/EXAMS model using similar logic as the terrestrial assessment in grouping uses.

III. INTEGRATED ENVIRONMENTAL RISK CHARACTERIZATION

Ziram is a dimethyldithiocarbamate fungicide that is acutely very highly toxic and poses high acute and chronic risk to most endangered and non-endangered aquatic organisms, should the compound enter aquatic habitats. The major sites considered in this risk assessment include terrestrial food and non-food uses. The assessment suggests potential acute terrestrial toxicity (and chronic risk for mammals) in endangered and non-endangered avian and mammalian species may occur from the application of ziram to foliage or other wildlife food items mainly due to the compound's higher application rates and multiple applications, rather than the compound's toxicity. Avian chronic reproductive effects and risk could not be assessed due to a lack of toxicity data. A proper assessment for risks to terrestrial and aquatic plants could not be conducted due to a lack of toxicity data. In addition, since ziram is relatively highly soluble and is very highly toxic to aquatic organisms, there is a possibility of acute risk to amphibians and their larval stages through dermal exposure from terrestrial broadcast spray applications and through aquatic exposures, respectively.

Under neutral and acidic environments, it appears that ziram is quickly reduced to volatiles such as CS_2 , CO_2 , and COS under most conditions, except anaerobic aquatic metabolism. Therefore, the probability of prolonged exposure to the chemical under such conditions is reduced. However, in alkaline medium, based on the information extracted from the hydrolysis at pH 9 study, it appears that ziram remains, mostly as DDC (dimethyldithiocarbamic acid), which is not a true degradation product of ziram, but an analogous salt.

Ziram's susceptibility to degradation, especially in neutral and acidic environments, reduces the probability of prolonged exposure to the chemical. The chemical is expected to dissipate very quickly under many conditions, hydrolyzing rapidly under neutral to acidic conditions in a matter of hours. Ziram degrades rapidly through hydrolysis (halflives of 0.17 to 151 hours with quicker degredation occuring at lower pH levels), aqueous photolysis (8.7 hours), soil photolysis (8-9 hours) and anaerobic metabolism (14.1 days under anaerobic conditions). In acidic soils, ziram degraded with half-lives that were typically in hours; in water, the compound also photolyzed rapidly. In addition, ziram degraded much faster under aerobic than anaerobic conditions during soil metabolism studies. The main degradates are volatiles such as CS₂, CO₂ and COS, and are not expected to persist in soil and water. However, in alkaline medium, ziram and its nonvolatile metabolites dimethyldithiocarbamic acid (DDC), N.N-dimethylformamide (DMF), and N.N-dimethylthioforamide (DMTF) are likely to be more persistent in soils or waters. The uncertainties related to the persistence of DDC, DMF, and DMTF could be a major

concern for terrestrial and aquatic organisms of arid and semiarid regions. However, the toxicity of the degradates to organisms (terrestrial and aquatic) is unknown. It is unlikely that many aquatic organisms live under extremely high pH conditions, therefore exposure will likely be very limited. While ziram can reach surface water by spray drift or runoff, it is not likely to persist. The compound is relatively highly soluble (65 mg/L) and binds to clay particles in soil (K_{ads} = 2.9 to 7.6 in three soils, and 68.1 in clay). Ziram may pose ecological risk to aquatic organisms through pulse dosing, due to the compound's high application rates, multiple applications and short intervals. The compound can be available after rain events during the growing season and especially on days following application.

Ziram ionizes to form dimethyldithiocarbamate ions that can be biodegraded in soil, releasing carbon disulfide and forming dimethylamine (DMA). Dimethylamine may be potentially transformed into a suspected carcinogen *N*-nitrosodimethylamine (NDMA) in of nitrite under anoxic environments. However, the presence of an anoxic environment would be an atypical scenario in terrestrial landscape. Ziram also possesses antibacterial properties, particularly for gram-positive organisms, and this would hinder biodegradation under many situations. If NDMA happens to form in situ, the compound is sensitive to light, especially ultraviolet light and will degrade rapidly through photolytic degradation. Thus, the risk to terrestrial wildlife may be limited.

<u>Terrestrial Risk</u>

The results of the assessment suggest potential acute and chronic risk to mammals (other than granivores) from both single and multiple applications. Acute risk is low to avian species and chronic risk could not be assessed due to a lack of toxicity data. Mammals may be exposed but die in burrows unseen. Use of Ziram during breeding season may have adverse effects on local mammalian populations. EECs were calculated using the default half-life of 35 days due to a lack of foliar data and also refined using a 1 day half-life. Risks were of a greater magnitude using 35 days. However, taking the short intervals (3-14 days) between applications into account, it is more likely that ziram is degrading enough during those intervals that efficacy would not be achieved without another application. Thus a shorter half-life than 35 days may be a more likely and realistic scenario. Nevertheless, even using a 1 day half-life, LOCs were still exceeded. The results of a mammalian metabolism study (MRID 423910-01) using groups of rats found that overall recoveries of administered radioactivity ranged from 78.9 to 92.4%, appears to be rapidly absorbed, exreted via urine and expired air with significant amounts excreted in feces with small amounts widely distributed throughout the body.

Aquatic Risk

Aquatic organisms were differentially sensitive to ziram. Freshwater fish (LC50=0.008 mg/l) were more sensitive than their estuarine counterparts (LC50=0.84 mg/l) by 2 orders of magnitude and estuarine invertebrates (LC50=0.014 mg/l) were more sensitive than their freshwater counterparts (LC50= 0.048 mg/l). Using a Tier II model for refinement (PRZM/EXAMS), the present assessment found acute risk to endangered and non-endangered freshwater fish, freshwater invertebrates and estuarine invertebrates. Although the parent is short lived, multiple applications on weekly intervals may affect aquatic organisms through chronic pulse doses, should the compound enter aquatic habitats. However, chronic risk to aquatic organisms could not be sufficiently analyzed due to a lack of toxicity data. In addition, since

ziram is relatively highly soluble and is very highly toxic to aquatic organisms, there is a possibility of acute risk to amphibians through dermal exposure from broadcast spray applications.

Endangered Species

Endangered species LOCs for ziram are exceeded for acute risks to herbivorous and insectivorous birds and mammals from single and multiple applications to pome fruits, stone fruits and nut crops; herbivorous birds and mammals plus insectivorous mammals from single and multiple applications to vegetable crops and grape. In addition the chronic LOC is exceeded for endangered mammals from single and multiple applications to all uses of ziram.

Acute LOCs for endangered freshwater fish and invertebrates, including mollusks and crustaceans, are exceeded for all uses of ziram. Although the endangered species LOC for estuarine invertebrates has been exceeded, there are no federally listed species in this group.

The EFED assessment found a potential for adverse effects to terrestrial and aquatic species. However, chronic risk to avian and aquatic species could not be sufficiently analyzed due to a lack of toxicity data. The chemical does appear to degrade quickly, thus reducing time of exposure. However, multiple applications on weekly intervals may affect organisms through chronic pulse doses. It is not known if endangered plants my be affected due to a lack of toxicity data. In addition, since ziram is relatively soluble and is very highly toxic to aquatic organisms, there is a possibility of acute risk to endangered amphibians through dermal exposure from broadcast spray applications. Amphibians may also be affected on a chronic basis from the pulse dosing due to multiple applications at high rates and short intervals between applications. Based on the avian data, endangered reptiles are also assumed to be at risk from the uses of ziram.

The Agency is currently engaged in a Proactive Conservation Review with the US Fish and Wildlife Service (FWS) and the National Marine Fisheries Service (NMFS) under section 7(a)(1) of the Endangered Species Act. The objective of this review is to clarify and develop consistent processes for endangered species risk assessments and consultations. Subsequent to the completion of this process, the Agency will reassess the potential effects of ziram use to federally listed threatened and endangered species. At that time, the Agency will also consider any regulatory changes recommended in the RED that are being implemented. Until such time as this analysis is completed, the overall environmental effects mitigation strategy articulated in this document and any County Specific Pamphlets as described in Section IV of the RED which address ziram, will serve as interim protection measures to reduce the likelihood that endangered and threatened species may be exposed to ziram at levels of concern.

Endocrine Disruption

EPA is required under the Federal Food, Drug, and Cosmetic Act (FFDCA), as amended by the Food Quality Protection Act (FQPA), to develop a screening program to determine whether certain substances (including all pesticide active and other ingredients) "may have an effect in humans that is similar to an effect produced by a naturally-occurring estrogen, or other such endocrine effects as the Administrator may designate." Following the recommendations of its Endocrine Disrupting Screening and Testing Advisory Committee (EDSTAC), EPA determined that there was scientific basis for including, as part of the program, the androgen- and thyroid-

hormone systems, in addition to the estrogen-hormone system. EPA also adopted EDSTAC's recommendation that the Program include evaluations of potential effects in wildlife. For pesticidal chemicals, EPA will use FIFRA and, to the extent that effects in wildlife may help determine whether a substance may have an effect in humans, FFDCA has authority to require the wildlife evaluations. As the science develops and resources allow, screening of additional hormone systems may be added to the Endocrine Disruptor Screening Program (EDSP).

Based on available scientific literature, ziram may have characteristics of an endocrine disrupting compound. The compound may possibly exhibit effects on birds and mammals. These effects include possible thyroid and adrenal involvement in birds and mammals. Mammalian studies submitted to the agency indicate increased incidence of thyroid C-cell tumors (adenoma and/or carcinoma) and increased thyroid gland C-cell hyperplasia in male rats (MRID 42156-01). Another study cited increased cortical hypertrophy with vacuolation in the adrenals in male dogs and increased incidence of prominent ultimobranchial cysts in the thyroid in female dogs.

Ziram may be readily absorbed into the body in the presence of oils, including the skin. The zinc component of the parent can be selectively stored in the body with the highest concentrations found in the male reproductive system, specifically in the prostate. High concentrations may be found in bone, liver, kidney, pancreas and endocrine glands (EXTOXNET: National Library of Science 1993). A primary target organ is the thyroid. Wasting away of the testes has been noted as a toxic effect of ziram in birds and mammals (EXTOXNET: National Toxicity Program 1983).

Based on these data, EFED recommends that when appropriate screening and or testing protocols being considered under the Agency's EDSP have been developed, ziram be subjected to more definitive testing to better characterize effects related to its possible endocrine disrupting activity under the current use pattern.

IV. ENVIRONMENTAL FATE AND TRANSPORT ASSESSMENT

Summary

The table below summarizes the physico-chemical properties of ziram and its major metabolites. Generally ziram degrades very rapidly via hydrolysis, photodegradation, and aerobic soil metabolisms. It has a very short half-life, and ranges from 0.17 to 42 hours under natural degradative processes except hydrolysis at alkaline medium and an anaerobic soil metabolism. Rapid degradative processes of ziram suggest that ziram would not persist in environment. However, in alkaline medium, ziram and its nonvolatile metabolites dimethyldithiocarbamic acid (DDC), N.N-dimethylformamide (DMF), and N.N-dimethylthioforamide (DMTF) are likely to be more persistent in soils or waters. The uncertainties related to the persistence of DDC, DMF, and DMTF could be a major concern for the soils of arid and semiarid regions. Laboratory and field data suggest that ziram is not very mobile, and neither leaching nor volatility are expected to play an important role in the dissipipation of ziram. A detailed fate assessment can be found on the following paragraphs.

Parent Compound (Ziram)

Hydrolysis, photodegradation, and aerobic soil metabolisms are the main degradative processes for ziram. Observed half-lives (0.17-42 hours) are generally fast under the expected use condition, generating major volatiles such as carbon disulfide (CS₂), carbon dioxide (CO₂), and carbon oxide sulfide or carbonyl sulfide (COS). Laboratory studies suggest that ziram hydrolyzed very rapidly and yielding CS₂ (\$80% of applied ziram) at pH 5 and pH 7 but degraded ($t_{1/2}$ =151 hours) moderately at pH 9. Nonvolatile metabolite thiram (13.8% of applied ziram) at pH 7 and DDC (. 67.0 % of applied ziram) at pH 9 were also formed during the hydrolysis experiments. Other major persistent degradation products (\$18%) of ziram were identified as DMF and DMTF in the aqueous photolysis experiment.

The degree of adsorption of ziram in the studied soils was found not to be a function of the amount of organic matter ($r^2 = 0.31$) rather than the amount of clay contents ($r^2 = 0.96$) of the soils. Volatilization is not expected to be a major route of dissipation due to ziram's low vapor pressure. The major degradates of ziram are volatiles, and are not expected to persist in soil or water. Therefore, subsurface mobility of ziram will be minimal.

In terrestrial dissipation studies, ziram (Ziram 76DF[®]) dissipation appeared to be biphasic, with faster degradate initially following application, followed by a slower degradation until the end of the study. However, storage stability data were inadequate for the parent compound in both locations as well as its degradates for the California site. A concurrent study must be conducted and submitted to the Agency. Required data for aquatic dissipation and bioaccumulation are not available for ziram during the preparation of this report, however, a rapid hydrolysis of ziram under a neutral pH suggests that ziram would not persist long enough in water to cause substantial bioaccumulation in aquatic species.

Ziram ionizes to form dimethyldithiocarbamate ions that can be biodegraded in soil, releasing carbon disulfide and forming dimethylamine (DMA). Dimethylamine may be potentially transformed into a suspected carcinogen *N*-nitrosodimethylamine (NDMA) in of nitrite under anoxic environments. However, the presence of an anoxic environment would be an atypical scenario in terrestrial landscape. Ziram also possesses antibacterial properties, particularly for gram-positive organisms, and this would hinder biodegradation under many situations. If NDMA happens to form in situ, the compound is sensitive to light, especially ultraviolet light and will degrade rapidly through photolytic degradation. Thus, the risk to terrestrial wildlife may be limited.

Parameter		Value	Reference/Comments
Molecular Weight	307.5 g Mole ⁻¹		MRID 442284-01
Water Solubility	65 mg L ⁻¹		Product chemistry data
Vapor pressure	Negligible		Agrochemical Handbook [†]
	Ziram	Persistence: Major Degradates [‡]	
Hydrolysis t _{1/2} pH 5 pH 7 pH 9	0.173 Hours 17.70 Hours 151.0 Hours	CS_2 CS_2 and DDC COS and DDC	MRID 43866701
Photolysis t _{1/2} in water Xenon lamp Dark	8.7 Hours . stable	DMF and DMTF	MRID 44097701
Photolysis $t_{1/2}$ on soil Xenon lamp (15 mg L ⁻¹) Xenon lamp (3 mg L ⁻¹) Dark (15mg L ⁻¹) Dark (3 mg L ⁻¹)	8.02 Hours 8.94Hours 16.0 Hours 24.0 Hours	Thiram Thiram	MRID 43642501
Soil metabolism Aerobic t _{1/2}	42 Hours	CO ₂ and 1,1-dimethylurea.	MRID 43985801
Soil metabolism Anaerobic $t_{1/2}$	339 Hours	CO ₂	MRID 44228402
	Mobility	Adsorption-Desorption	
Batch Equilibrium		.9-68.1 314-3732 40-4093	MRID 43873501
	1	Field Dissipation	·
Terrestrial Dissipation $t_{1/2}$ in soil surface layer (0-3") California 0-10 days 15-540 days North Carolina 0-10 days 15-539 days	5.2 Days 206 Days 6.7 Days 144 Days		MRID 44548301
Aquatic Dissipation	NA§		NA
Bioaccumulation	NA		NA

Selected Physical, Chemical, and Environmental Fate Properties of Ziram

CS₂ (carbon disulfide) COS Carbon Oxide Sulfide CO₂(Carbon dooxide) DDC Dimethyldithiocarbamic acid Thiram DMF (N.N-dimethylformamide) DMTF (N.N-dimethylthioforamide) 1,1-dimethylurea

Degradates of Ziram

In the laboratory studies, thiram was detected in various degradative processes but it maximized (13.8 %) during the hydrolysis (pH 9) at the 4-hours period than declined to 11.0% within 72 hours. Also, 67 percent DDC, a nonvolatile compound of similar parent structure of ziram, is persisting at higher pH level at the end of hydrolysis experiment (30 days). This chemical is likely to form complex with sodium under alkaline medium.

Other notable non volatiles degradates such as DMF and DMTF were also formed at pH 9 and gradually increased to more than 18 % of the applied ziram at the end of the aqueous photolysis experiment (24 hours). Another major metabolite (1,1-dimethylurea) was identified at the 7th day of aerobic soil metabolism study, reached the peak at 10.48%, then decreased to 5.25% at end of the experiment (60 days). The uncertainties related to the persistence of DDC, DMF and DMTF could be a major concern for the soils of arid and semiarid regions. While the laboratory studies successfully characterized the degradates of ziram, formation and decline of the concerned metabolites have not been adequately described in hydrolysis and photodegradation studies. The true extent of ziram's ultimate fate can only be assessed through a review of additional environmental fate studies capable of identifying the fate characteristic of ziram's degradates.

Ziram has the formula $[(CH_3)_2NSS]_2^{2-}Zn^{++}$.

Dimethyldithiocarbamic acid and salt, depending on pH:

$$S^{-}Na^{+}$$
 SH
/ (CH₃)₂ - N-C=S and (CH₃)₂ - N - C = S

Thiram is a dimer of dimethyldithiocarbamic acid:

Hydrolysis

The hydrolysis of ziram was pH dependent, with hydrolytic decomposition being faster at the lower pH's. The calculated half-lives were 0.173, 17.7, and 151 hours (- 6 days) at pH's 5, 7, and 9, respectively. The study periods were #72 hours for the pH 5 and 7 buffered solutions, for the pH 9 buffered solution, the study period was 30 days. It is noted that the major product in the pH 9 solution is not a true degradation or decomposition product. The main decomposition

products observed were volatile: CS_2 (maximum of 96.8% of the applied after 1 hour in the pH 5 solution, 81.6% at 72 hours in the pH 7 solution, and 16.43% at 21 hours in the pH 9 solution) and COS (maximum of 18.6% of the applied 30 days after treatment in the pH 9 solution. One non-volatile product was DDC (appeared to be a transient component, it was 11.6% at 0.117 hour in the pH 5, but decreased substantially by 1 hour post-treatment, at 0.15%; it was also present in the pH 9 solution at a maximum of 66.7% at 30 days post-treatment). DDC is not a true degradation product of ziram, but an analogous salt. Another non-volatile product was thiram, at up to 13.78% of the applied at 4 hours post-treatment in the pH 7 solution. It had decreased to 11.0% by 72 hours, which was the last test interval.

Aqueous Photolysis

In aqueous photolytic conditions, ziram degraded with a half-life of 8.7 hours, as opposed to the dark control that did not degrade substantially during the same study period (24 hours). About 15 degradates were observed throughout the study, the major degradates (>10%) after 24 hours of irradiation were N,N-dimethylformamide (23.7% of the applied), and N,N-methylthioformamide (18.1% of the applied). The patterns of formation/decline of these degradates did not reveal whether they would persist or degrade after 24 hours under the described experimental conditions.

Soil Photolysis

In a soil photolysis study, ziram was applied at two treatment rates of approximately 15 and 3 ppm to sandy loam soil samples that were incubated aerobically for up to 72 hours. Both irradiated treatment rates show similar degradation half-life of ziram at about 8-9 hours. In contrast, the dark controls had half-lives of about 16-24 hours. The soil was acidic, which may have promoted hydrolysis and confounded the results. It is acknowledged, however, that in water, photolysis was important (a clue that indicates that on soils it could be important too), and, in addition, the dark control showed much slower degradation rates than the exposed sample. In both kinds of samples, the degradates profiles is similar (up to 10 degradates). The only degradate at >10% was thiram, at about 25% in the 24 hour study. However, the pattern of formation/decline of thiram suggests that the level was declining toward the 10% level. Also, the persistence of thiram oxide was considered to be an artifact of the test solvent acetonitrile (CH₃CN).

Aerobic Soil Metabolism

In an aerobic sandy loam soil, ziram dissipated with a half-life of 1.75 days. Samples were incubated for up to 60 days. EFED has some concerns regarding the results obtained from this study because it was also conducted on a soil at a lower pH (5.4). This pH may raise the rate of degradation of ziram by promoting hydrolysis. However, the major degradate observed in this study, 1,1-dimethylurea (10.5% at day 30) was not observed in the hydrolysis study, and the degradates observed in the hydrolysis study were not present in large quantities in this study. Therefore, hydrolysis is likely not affecting the rate in this study. In the study, seven minor degradates were detected (<10%) and CO_2 accounted for 48.3% of the applied at 60 days.

Anaerobic Soil Metabolism

In an anaerobic soil metabolism study, ziram was applied to an aerobic sandy loam soil and incubated for one day, after which approximately $\frac{1}{3}$ of the radioactivity was undegraded parent. The samples were then flooded and submitted under a nitrogen atmosphere. It was found that under anaerobic conditions ziram degraded at a decreased speed, compared to the aerobic conditions. The half-life was 14.1 days under anaerobic conditions. Up to10 minor degradates (at <10%) were detected. At the end of the 30 day anaerobic incubation, 35.2% of the applied was CO₂.

Mobility

Based on Batch Equilibrium studies, ziram, at five concentrations ranging from 0.2 to 4.0 ppm and in four soil types with %OC ranging from 0.2 to 1.8, appeared to be moderately mobile in sand, silt loam and sandy loam soils, but shows low mobility in a clay soil. The samples were equilibrated for up to 24 hours. The Freundlich, K_{ads} and K_{OC} constants ranged from 2.9 to 7.6 and 314 to 1232, respectively, for three of the soils tested. For the clay soil, K_{ads} =68.1, and K_{OC} =3732. The Freundlich, K_{des} constants ranged from 40 to 4093 for the four soils tested.

Terrestrial Dissipation

The registrant conducted two terrestrial field dissipation studies for ziram. Although both studies were on bareground, they were representative of typical use sites, as well as the East and West coasts of the US. One was conducted on a sand soil in Wake County, NC (peaches), and the other was conducted on a sandy loam soil in Tulare County, CA (almonds). The product used was Ziram 76 DF[®], which was broadcast applied nine times (at 7- to 10-day intervals) as a spray to bareground plots at 8 lb/A/application. Ziram, dissipated from the 0- to 3-inch soil depth with initial half-lives of 6.7 days and 5.2 days (0- to 10-day data in both cases) following the ninth application, at the North Carolina and California sites, respectively. The dissipation appeared to become slow after the first two weeks. The subsequent half-lives were 144 days (15to 539-day data) and 206 days (14- to 540-day data), respectively. These studies, however, can only be considered supplemental at this time because storage stability data were inadequate for the parent compound (both sites) and the degradate 1,1-dimethylurea (California site). In addition, at the North Carolina site, Hurricane Fran delivered approximately 8 inches of rain eight days following the ninth application. Furthermore, the California study presents difficulties in the interpretation of data because there was high variability in the data from day 0 to 10 days post-treatment To resolve the questions presented by these studies, the registrant must, at least, provide suitable storage stability data demonstrating that ziram and the degradate 1,1dimethylurea are stable for the maximum period of storage stability. The source of the variability in the studies must be explained satisfactorily. If the registrant cannot explain the uncertainties, it must conduct and submit one new study at a carefully selected site that represents the majority of the use sites.

Bioconcentration

Although a bioaccumulation in fish study is not available, due to the relatively rapid hydrolysis of ziram (half life is about 17 hours at pH 7), it appears that ziram would not persist long enough in water to cause substantial bioaccumulation in fish tissue.

V. AQUATIC EXPOSURE AND RISK ASSESSMENT

Based on ecological effects data, the aquatic toxicity endpoints used in the current assessment can be characterized as follows:

ZIRAM:

- С Fish (freshwater) acute: Very highly toxic ($LC_{50} = 0.008 \text{ mg/l}$)
- Fish (freshwater) chronic: No data
- Fish (estuarine) acute: Highly toxic ($LC_{50} = 0.84 \text{ mg/l}$)
- Fish (estuarine) chronic: No data
- Invertebrate (freshwater) acute: Very highly toxic ($LC_{50} = 0.048 \text{ mg/l}$)
- Invertebrate (freshwater) chronic: No data
- CCCCCCCC Invertebrate (estuarine) acute: Very highly toxic ($LC_{50}/EC_{50}=0.014$ mg/l)
- Invertebrate (estuarine) chronic: No data
- С Aquatic plants: EC50 = 0.067 mg/l

* For the full compliment of toxicity data, please see Appendix II

Risk to Nontarget Aquatic Animals

Exposure to aquatic non-target organisms is possible through surface water runoff, soil erosion, and off-target spray drift. Directions and precautions must be followed in order to reduce the possibility of incidents occurring from the proposed use of ziram. EFED normally uses the GENEEC model to predict Tier I EEC's in an aquatic environment. Where aquatic LOCs are exceeded with this Tier I screening estimate, as was the case with ziram, PRZM/EXAMS is used as a Tier II model refinement. The input parameters used in the GENEEC model are similar to those used in PRZM/EXAMS. Details on the model inputs can be found in Appendix IV.

Freshwater Fish and Invertebrates

Acute risk quotients are tabulated below. There were no chronic data available to assess risk.

Crop/Regional Scenarios	Application Rate x No. Applications at "x" day Intervals	Peak EEC (mg/l)	Acute RQ (Peak EEC / LC ₅₀) for Fish	Acute RQ (Peak EEC / LC ₅₀) for Invertebrates
	I	PRZM/EXAMS		
Cherries (WI)	6.1 lb ai/A x 5 apps at 7 da intervals	0.027	3.40	0.50
Peaches (OR)	7.6 lb ai/A x 6 apps at 3 da intervals	0.03	3.75	0.63
Tomato (NJ)	3.0 lb ai/A x 6 apps at 7 da intervals	0.03	3.75	0.60
Grapes (NY)	3.0 lb ai/A x 7 apps at 7 da intervals	0.02	2.50	0.42
Blueberries (FL)	2.3 lb ai/A x 4 apps at 7 da intervals	0.05	6.25	1.04

Tier II (PRZM/EXAMS) risk quotients for freshwater fish based on a fathead minnow LC_{50} of 0.008 mg/l and freshwater invertebrates based on a Daphnid EC50 of 0.048 mg/l.

Crop/Regional Scenarios	Application Rate x No. Applications at "x" day Intervals	Peak EEC (mg/l)	Acute RQ (Peak EEC / LC ₅₀) for Fish	Acute RQ (Peak EEC / LC ₅₀) for Invertebrates		
	Levels of Concern					
Endangered species may be affected (acute risk)			≥ 0.05			
Acute risk may be mitigated through restricted use, in addition to endangered species risk			<u>≥</u> 0.1			
High acute risk, including endangered species			<u>≥</u> 0.5			

Tier II (PRZM/EXAMS) risk quotients for freshwater fish based on a fathead minnow LC_{50} of 0.008 mg/l and freshwater invertebrates based on a Daphnid EC50 of 0.048 mg/l.

*LOC exceedences are in bold

The results suggest that high acute, restricted use and endangered species LOCs are exceeded for freshwater fish and invertebrates for most use patterns (high acute risk represents 88.9% of the RQs above).

Estuarine and Marine Fish and Invertebrates

The acute risk quotients are tabulated below. There were no data available to assess chronic risk.

Crop/Regional Scenarios	Application Rate x No. Applications at "x" day Intervals	Peak EEC (mg/l)	Acute RQ (Peak EEC / LC ₅₀) for Fish	Acute RQ (Peak EEC / LC ₅₀) for Invertebrates	
	PRZM	EXAMS			
Cherries (WI)	6.1 lb ai/A x 5 apps at 7 da intervals	0.027	0.03	2.00	
Peaches (OR)	7.6 lb ai/A x 6 apps at 3 da intervals	0.03	0.04	2.14	
Tomato (NJ)	3.0 lb ai/A x 6 apps at 7 da intervals	0.03	0.04	2.14	
Grapes (NY)	3.0 lb ai/A x 7 apps at 7 da intervals	0.02	0.02	1.43	
Blueberries (FL)	2.3 lb ai/A x 4 apps at 7 da intervals	0.05	0.06	3.60	
Levels of Concern					
Endangered species may be affected (acute risk)			<u>></u> 0.05		
Acute risk may be mitigated through restricted use, in addition to endangered species risk			<u>></u> 0.1		
High acute risk, inclu	ding endangered species		<u>≥</u> 0.5		

Tier II (PRZM/EXAMS) risk quotients for estuarine/marine fish based on a sheepshead minnow LC ₅₀ of 0.84 mg/l and
estuarine/marine invertebrates based on a Mysid EC50 of 0.014 mg/l.

*LOC exceedences are in bold

The results suggest that high acute, restricted use and endangered species LOCs are exceeded for estuarine invertebrates.

Aquatic Plant Risk: Peak EEC= 0.05 ppm / EC50 of 0.067 ppm= RQ of 0.75 < LOC of 1.0 There are no data to fully assess terrestrial or aquatic risks to plants.

Aquatic Ecological Incident Data

There were no ecological incidents found in the EFED incidents database for Ziram.

VI. DRINKING WATER ASSESSMENT

Estimation of Drinking Water Concentrations

The Tier I and II Drinking Water assessments are based on the worst case scenario, which oftentimes is the maximum number of applications, with the maximum application rate, and the minimum application interval. Appendix IV shows printouts from the electronic copies of the drinking waters memoranda, in which EFED submitted their Tier I and II Drinking Water Concentrations of Ziram to SRRD and HED. The memoranda provide background information about the three models used for the estimation of drinking waters, as well as some information about their limitations. They also list the parameters selected for use in the models, as well as printouts of the output files of the GENEEC and SCIGROW runs. The PRZM/EXAMS model [PRZM 3.12 (Pesticide Root Zone Model)/EXAMS 2.97.5 (Exposure Analysis Modeling System)] was applied to estimate the ziram concentrations in an index reservoir. In absence of a western stone fruit scenario, the Wisconsin Cherry/Stone Fruits Scenario was used as surrogate; however, the worst case application rate and interval were utilized in the model (application rate 7.6 lb a.i./A, 6 applications at 3 days intervals). Results obtained are summarized in the following tables:

Estimated Tier I Concentrations of Ziram in Drinking Water			
Chemical	Surface Water		Groundwater
	Acute Chronic		Acute and Chronic
Ziram	860 ppb	19 ррb	0.03 ppb

Estimated Tier II Concentrations of Ziram in Surface Drinking Water				
Chemical	Acute (Peak)	Chronic (Annual)	Mean 36-Year Annual	
Ziram	575 ppb	4.2 ppb	2.5 ppb	

Based on the Tier I and Tier II models, and the best environmental fate data available, EFED recommends that the following estimated environmental drinking water concentrations of ziram be used in the Human Health Risk Assessment:

Surface Water:	Acute:	575 ppb
	Chronic:	4.2 ppb
	Mean 36-Year	2.5 ppb
Ground Waters:	Acute and Chronic:	0.03 ppb

Surface Water

The surface water estimates for drinking water were based on an index reservoir scenario which is often a more conservative estimate. The surface water estimates are further refined by the use of PCAs. In this case, we do not have a PCA developed for cherry and stone fruit. Therefore a default PCA of 0.87 was used. This makes it an even more conservative estimate for surface water sourced drinking water.

Ziram can be applied up to 6 times, at a high rate (up to 7.6 lb a.i./A) and at short intervals between applications (depending on the crop as short as 3 days). The compound is relatively highly soluble (65 mg/L) and binds to clay particles in soil (K_{ads} = 2.9 to 7.6 in three soils, and 68.1 in clay). Ziram appears to be highly labile under most conditions (half-lives: hydrolysis pH 7 <1 day, aqueous photolysis <1 day, photolysis on soil <1 day, aerobic soil metabolism=1.75 days), which would reduce the availability of the compound. Therefore, relatively small amounts of the chemical can be available after rain events during the growing season and especially on days following application.

Ground Water

Although ziram appears to show mobility in most soils, it does not appear to be likely to leach in soils substantially, because it is highly labile. Should the chemical reach anaerobic regions in the subsoils, the level of persistence is increased (half-life anaerobic soil metabolism = 14.1 days). Additionally, soils of high pH would promote persistence and formation of analogous transformation products (DDC). Ziram and DDC would have more potential to leach in such vulnerable sites.

VII. TERRESTRIAL EXPOSURE AND RISK ASSESSMENT

Based on ecological effects data, the toxicity endpoints used in the current terrestrial assessment can be characterized as follows:

- Avian acute oral: Moderately toxic ($LD_{50} = 97 \text{ mg/kg of body weight}$)
- Avian acute dietary: Practically non-toxic ($LC_{50} = 5156$ ppm)
- Avian reproduction: No data
- Mammalian acute oral: Moderately toxic ($LD_{50} = 320 \text{ mg/kg}$ of body weight; M and F combined)
- Mammalian chronic (reproduction): Decreased body weights and food consumption (NOAEL = 207 ppm)
- Honey bee acute: Practically non-toxic ($LD_{50} > 100 \text{ ug/bee}$)

st For the full compliment of toxicity data, please see Appendix f If I

Avian Acute and Chronic Risk: The following tables provide avian acute risk quotients from exposure to both single and multiple (calculated with a 1 day half-life and a 35 day default half-life) applications of non-granular products containing ziram. Avian chronic levels of concern for single and multiple broadcast applications of non-granular products could not be calculated due to a lack of available toxicity data.

Use/App. Method	No. Apps. X Rate (Ibs ai/A)	Food Items	Max EEC (ppm) ¹	Acute RQ (EEC/LC ₅₀)	
		Single Application			
Blueberries	1 x 2.3 lbs ai/A	Short grass	552		0.12
		Tall grass	253		0.01
		Broadleaf plants/Insects	311		0.06
		Seeds	35		0.00
Grapes and Tomato	1 x 3.0 lbs ai/A	Short grass	720		0.14
		Tall grass	330		0.06
		Broadleaf plants/Insects	405		0.08
		Seeds	45		0.00
Apricots/Apples/Pears /Peaches/Cherries	$1 \ge 6.1$ lbs ai/A	Short grass	1464		0.30
Eastern and Western		Tall grass	671		0.13
USA/pecans/almonds		Broadleaf plants/Insects	824		0.16
		Seeds	92		0.02
Peaches/Nectarines	1 x 7.6 lbs ai/A	Short grass	1824		0.35
Western USA		Tall grass	836		0.16
		Broadleaf plants/Insects	1026		0.20
		Seeds	114		0.02
		Levels of Concern			
Endangered species may	y be affected (acute	risk)			<u>></u> 0.1
Acute risk may be mitig	gated through restric	ted use, in addition to endanger	ed species risk		<u>></u> 0.2
High acute risk, includi	ng endangered speci	es			<u>></u> 0.5

Avian Acute Risk Quotients for single broadcast spray applications of Ziram, based on a Bobwhite Quail LC ₅₀ of	
5156 ppm. No chronic (reproduction) data are available.	

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

*LOC exceedences are in bold

The residues expected on avian food items after a single application of non-granular ziram products are based on the highest residue concentrations immediately after application (Fletcher, 1994). The results suggest that avian endangered species levels of concern are exceeded for food items other than seeds at rates of 6.1 and 7.6 lbs ai/A and at the lower rates only for shortgrass. In addition, the restricted use LOC was exceeded for shortgrass at the higher rates.

Use/App. Method	Rate (Ibs ai/A) x No. Apps.	Food Items	Max EEC (ppm) ¹	Acute Max RQs (EEC/LC ₅₀)	
		Multiple Application ²			
Blueberries	2.3 lbs ai/A	Short grass	556		0.12
	(2 applications at 7 da interval)	Tall grass	255		0.05
	at / da intervar)	Broadleaf plants/Insects	313		0.06
		Seeds	35		0.00
	3.0 lbs ai/A	Short grass	726		0.14
	(6-7 applications at 7 da interval)	Tall grass	333		0.06
	at / da intervar)	Broadleaf plants/Insects	408		0.08
		Seeds	45		0.01
Apricots/Apples/Pears /Peaches/Cherries Eastern USA	6.1 lbs ai/A (5-7 applications at 7 da interval)	Short grass	1476		0.30
		Tall grass	676		0.13
		Broadleaf plants/Insects	830		0.16
		Seeds	92		0.02
	6.1 lbs ai/A	Short grass	1511		0.30
Cherries Western USA	(4 applications at 5 da interval)	Tall grass	693		0.13
OBA	at 5 da mervar)	Broadleaf plants/Insects	850		0.16
		Seeds	94		0.02
Peaches/Nectarines	7.6 lbs ai/A	Short grass	2085		0.40
Western USA	(6 applications at 3 da intervals)	Tall grass	955		0.20
	at 5 du intervais)	Broadleaf plants/Insects	1173		0.23
		Seeds	130		0.03
		Levels of Concern			
Endangered species may	y be affected (acute r	isk)			<u>></u> 0.1
Acute risk may be mitig	ated through restrict	ed use, in addition to endangered	l species risk		<u>></u> 0.2
High acute risk, includin	ng endangered specie	es e	-		> 0.5

Avian Acute Risk Quotients for multiple broadcast spray applications of Ziram, based on a Bobwhite Quail LC₅₀ of 5156 ppm and a half-life of 1 day. No chronic (reproduction) data are available.

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

² For multiple applications, EFED uses EECs based on Hoerger and Kenega (1972) and Fletcher et al (1994), with first-order dissipation from foliage between applications. If foliar dissipation data are not available, a 35 day default value is used. However, in this case, halflives were very short under many degredation parameters (aqueous photolysis, soil metabolism, etc...). Thus a 1 day half-life was used with a 3x safety factor (8 hrs x 3=24 hrs). *LOC exceedences are in bold

The residues expected on avian food items after multiple applications of non-granular ziram products are based on the highest residue concentrations after the last application (Fletcher, 1994). The results suggest that using maximum application rates and minimum intervals, endangered and restricted use LOCs are exceeded for use patterns with higher application rates for all food items other than seeds. LOC's were not exceeded for any use pattern using average EECs to calculate RQs.

Use/App. Method	Rate (Ibs ai/A) x No. Apps.	Food Items	Max EEC (ppm) ¹	Acute RQ (EEC/LC ₅₀)	
		Multiple Application ²			
Blueberries	2.3 lbs ai/A	Short grass	1,033		0.20
	(2 applications at 7 da interval)	Tall grass	473		0.10
	at / da intervar)	Broadleaf plants/Insects	581		0.10
		Seeds	65		0.01
Grapes and Tomato	3.0 lbs ai/A	Short grass	3,454		0.70
	(6-7 applications at 7 da interval)	Tall grass	1,583		0.30
	at / da intervar)	Broadleaf plants/Insects	1,943		0.40
		Seeds	216		0.04
Apricots/Apples/Pears /Peaches/Cherries Eastern USA	6.1 lbs ai/A (5-7 applications at 7 da interval)	Short grass	7,024		1.40
		Tall grass	3,219		0.60
		Broadleaf plants/Insects	3,951		0.80
		Seeds	439		0.09
Cherries Western	6.1 lbs ai/A (4 applications at 5 da interval)	Short grass	5,079		1.00
USA		Tall grass	2,328		0.50
	at 5 da intervar)	Broadleaf plants/Insects	2,857		0.60
		Seeds	317		0.06
Peaches/Nectarines	7.6 lbs ai/A	Short grass	9,482		1.80
Western USA	(6 applications at 3 da intervals)	Tall grass	4,346		0.80
	at 5 du miter vais)	Broadleaf plants/Insects	5,334		1.03
		Seeds	593		0.11
		Levels of Concern			
Endangered species may	y be affected (acute r	isk)			<u>></u> 0.1
Acute risk may be mitig	ated through restrict	ed use, in addition to endanger	ed species risk		<u>></u> 0.2
High acute risk, includin	e e		-		≥ 0.5

Avian Acute Risk Quotients for multiple broadcast spray applications of Ziram, based on a Bobwhite Quail LC_{50} of 5156 ppm and a 35 day default half-life. No chronic (reproduction) data are available.

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

² For multiple applications, EFED uses EECs based on Hoerger and Kenega (1972) and Fletcher et al (1994), with first-order dissipation from foliage between applications. If foliar dissipation data are not available, a 35 day default value is used. *LOC exceedences are in bold

The residues expected on avian food items after multiple applications of non-granular ziram products are based on the highest residue concentrations after the last application (Fletcher, 1994). The results suggest that using maximum application rates and minimum intervals, acute high risk, endangered and restricted use LOCs are exceeded for use patterns with higher application rates for all food items other than seeds. These results were based on a 35 day half-life default value.

Mammalian Acute and Chronic Risk: To assess acute risk to mammals from the use of foliar spray products, an estimated dietary endpoint value calculated from the LD_{50} value is used. The EEC is then divided by this calculated dietary value to determine mammalian RQ's. Estimating the potential for adverse effects to wild mammals is based upon EFED's draft 1995 SOP of mammalian risk assessments and methods used by Hoerger and Kenaga (1972) as modified by Fletcher et al. (1994). The concentration of ziram in the diet that is expected to be acutely lethal to 50% of the test population (LC_{50}) is determined by dividing the LD_{50} value (usually a rat LD_{50})

by the percentage, expressed as a decimal, of body weight consumed. A risk quotient is then determined by dividing the EEC by the derived dietary value. Risk quotients are calculated for three separate weight classes of mammals (15, 35, and 1000 g), each presumed to consume four different kinds of food (grass, forage, insects, and seeds).

The acute toxicity endpoint being used in the following table is not a typical LC_{50} , but a specified quantity of food which can be expected to be consumed in a day for which residues equal a single acute dose. McCann et al. (1981) compared rat LC_{50} values with published rat LD_{50} values. The data showed that the LD_{50} and LC_{50} values for rats can't be used interchangeably and that the LC_{50} values calculated from the LD_{50} values are generally not toxicologically equivalent to actual LC_{50} values from the study. Kenega (1977) made similar observations about avian toxicity tests. McCann (1981) also stated that the calculated values were different 35% of the time when compared to actual LC_{50} values, could result in incorrect decisions in relation to acute hazard as much as 35% of the time. The hazard could be overestimated 29% of the time and underestimated 6% of the time. These are only predictive screening indices of potential hazard. In all cases where actual results from a dietary test (LC_{50}) are available or needed, these results should be factored into the assessment to provide a more realistic picture of dietary hazard potential. In instances where a clear conclusion can't be made from calculated values, the need for a wild mammal dietary test (40 CFR 158.490; guideline 71-3) should be considered.

Rate Body in lbs ai/A Weight (g)	EEC (ppm) ¹			Herbivore/Insectivore Acute RQ ²			Granivore		
	Short Grass	Forage/ Small Insects	Large Insects	Seeds	Short Grass	Forage/ Small Insects	Large Insects	Acute RQ ² Seeds	
2.3	15	552	253	311	35	1.6	0.8	0.9	0.02
	35	552	253	311	35	1.1	0.5	0.6	0.02
	1000	552	253	311	35	0.3	0.1	0.1	0.00
6.1	15	1464	671	824	92	4.3	2.0	2.4	0.06
	35	1464	671	824	92	3.0	1.4	1.7	0.04
	1000	1464	671	824	92	0.7	0.3	0.4	0.00
7.6	15	1824	836	1026	114	5.4	2.5	3.0	0.07
	35	1824	836	1026	114	3.8	1.7	2.1	0.05
	1000	1824	836	1026	114	0.9	0.4	0.5	0.01

Mammalian Acute (Single and multiple applications)

Mammalian (Herbivore/Insectivore and Granivore) Acute risk quotients (RQs) for single broadcast spray applications of Ziram to foliage, based on a rat LD₅₀ of 320 mg/kg of body weight.

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

² RQ = EEC (mg/kg)

LD50 (mg/kg)/ % Body Weight Consumed

where the % body weight consumed varies with body size and diet:.

Herbivores/insectivores: 95% for 15 g wt; 66% for 35 g wt; 15% for 1000 g wt.

Granivores: 21% for 15 g wt; 15% for 35 g wt; 3% for 1000 g wt.

*LOC exceedences are in bold

The residues expected on mammalian food items after a single application of non-granular ziram products are based on the highest residue concentrations immediately after application (Fletcher,

1994). The results suggest that mammalian acute, restricted use and endangered species levels of concern are exceeded for food items other than seeds.

			EEC (ppm) ¹ Maximum			Herbivor Acute R(
Site/ Rate in lbs ai/A	Body Weight (g)	Short Grass	Forage/ Small Insects	Large Insects	Seeds	Short Grass	Forage/ Small Insects	Large Insects	Granivore Acute RQ ² Seeds
2.3	15	556	255	313	35	1.6	0.8	0.9	0.00
	35	556	255	313	35	1.1	0.5	0.6	0.00
	1000	556	255	313	35	0.3	0.1	0.1	0.00
6.1	15	1511	693	850	94	4.5	2.1	2.5	0.00
	35	1511	693	850	94	3.1	1.4	1.8	0.00
	1000	1511	693	850	94	0.7	0.3	0.4	0.00
7.6	15	2085	955	1173	130	6.2	2.8	3.5	0.00
	35	2085	955	1173	130	4.3	2.0	2.4	0.00
	1000	2085	955	1173	130	2.0	0.4	0.5	0.00

Mammalian (Herbivore/Insectivore and Granivore) Acute risk quotients (RQs) for multiple broadcast spray
applications of Ziram to foliage, based on a rat LD ₅₀ of 320 mg/kg of body weight and a 1 day half-life.

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

² RQ = EEC (mg/kg)

LD50 (mg/kg)/ % Body Weight Consumed

where the % body weight consumed varies with body size and diet:.

Herbivores/insectivores: 95% for 15 g wt; 66% for 35 g wt; 15% for 1000 g wt.

Granivores: 21% for 15 g wt; 15% for 35 g wt; 3% for 1000 g wt.

For multiple applications, EFED uses EECs based on Hoerger and Kenega (1972) and Fletcher et al (1994), with first-order dissipation from foliage between applications. If foliar dissipation data are not available, a 35 day default value is used. However, in this case, halflives were very short under many degredation parameters (aqueous photolysis, soil metabolism, etc...). Thus a 1 day half-life was used with a 3x safety factor (8 hrs x 3= 24 hrs).

*LOC exceedences are in bold

The residues expected on mammalian food items after a multiple application of non-granular ziram products (based on a 1 day half-life) are based on the highest residue concentrations immediately after application (Fletcher, 1994). The results suggest that mammalian acute, restricted use and endangered species levels of concern are exceeded for all food items other than seeds.

Mammalian (Herbivore/Insectivore and Granivore) Acute risk quotients (RQs) for multiple broadcast spray	
applications of Ziram to foliage, based on a rat LD ₅₀ of 320 mg/kg of body weight using a 35 day default half-life.	

			EEC (ppm) ¹ Maximum			Herbivor RQ ²	Herbivore/Insectivore Acute RO ²			
Site/ Rate in lbs ai/A	Body Weight (g)	Short Grass	Forage/ Small Insects	Large Insects	Seeds	Short Grass	Forage/ Small Insects	Large Insects	Granivore Acute RQ ² Seeds	
2.3	15	1,033	473	581	65	3.1	1.4	1.7	0.00	
	35	1,033	473	581	65	2.1	1.0	1.2	0.00	
	1000	1,033	473	581	65	0.5	0.2	0.3	0.00	

			EEC (ppm) ¹ Maximum			Herbivore/Insectivore Acute RQ ²				
Site/ Rate in lbs ai/A	Body Weight (g)	Short Grass	Forage/ Small Insects	Large Insects	Seeds	Short Grass	Forage/ Small Insects	Large Insects	Granivore Acute RQ ² Seeds	
6.1	15	7,024	3,219	3,951	439	20.8	9.6	11.7	0.30	
	35	7,024	3,219	3,951	439	14.5	6.6	8.1	0.20	
	1000	7,024	3,219	3,951	439	3.3	1.5	1.9	0.00	
7.6	15	9,482	4,346	5,334	593	28.1	12.9	15.8	0.30	
	35	9,482	4,346	5,334	593	19.6	9.0	11.0	0.30	
	1000	9,482	4,346	5,334	593	4.5	2.0	2.5	0.00	

Mammalian (Herbivore/Insectivore and Granivore) Acute risk quotients (RQs) for multiple broadcast spray applications of Ziram to foliage, based on a rat LD₅₀ of 320 mg/kg of body weight using a 35 day default half-life.

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

² RQ = EEC (mg/kg)

LD50 (mg/kg)/ % Body Weight Consumed

where the % body weight consumed varies with body size and diet:.

Herbivores/insectivores: 95% for 15 g wt; 66% for 35 g wt; 15% for 1000 g wt.

Granivores: 21% for 15 g wt; 15% for 35 g wt; 3% for 1000 g wt.

For multiple applications, EFED uses EECs based on Hoerger and Kenega (1972) and Fletcher et al (1994), with first-order dissipation from foliage between applications. If foliar dissipation data are not available, a 35 day default value is used. *LOC exceedences are in bold

The residues expected on mammalian food items after a multiple application of non-granular ziram products (based on a 35 day default half-life) are based on the highest residue concentrations immediately after application (Fletcher, 1994). The results suggest that mammalian acute, restricted use and endangered species levels of concern are exceeded for most food items other than seeds.

Mammalian Chronic (Single and multiple applications)

The following tables summarize the mammalian chronic risk quotients for single and multiple broadcast applications of non-granular products based on rat reproductive toxicity data.

Use/App. Method	Rate (Ibs ai/A)	Food Items	Max EEC (ppm) ¹	Chronic RQ (EEC/NOAEC) Max	
		Single Application		WIAX	
Blueberries	2.3 lbs ai/A	Short grass	552		2.67
		Tall grass	253		1.22
		Broadleaf plants/Insects	311		1.50
		Seeds	35		0.17
Grapes and Tomato	3.0 lbs ai/A	Short grass	720		3.50
		Tall grass	330		1.60
		Broadleaf plants/Insects	405		2.00
		Seeds	45		0.22

Mammalian (Rat) chronic risk quotients for single broadcast spray applications of Ziram, based on a rat NOAEC of 207 ppm in the diet.

Use/App. Method	Rate (Ibs ai/A)	Food Items	Max EEC (ppm) ¹	Chronic RQ (EEC/NOAEC) Max	
Apricots/Apples/Pears /Peaches/Cherries Eastern and Western USA	6.1 lbs ai/A	Short grass	1464		7.10
		Tall grass	671		3.24
		Broadleaf plants/Insects	824		4.00
		Seeds	92		0.44
Peaches/nectarines Western USA	7.6 lbs ai/A	Short grass	1824		8.80
		Tall grass	836		4.04
		Broadleaf plants/Insects	1026		5.00
		Seeds	114		0.55
	Leve	ls of Concern			
Chronic risk					<u>≥</u> 1.0

Mammalian (Rat) chronic risk quotients for single broadcast spray applications of Ziram, based on a rat NOAEC of	
207 ppm in the diet.	

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

*LOC exceedences are in bold

The residues expected on mammalian food items after a single application of non-granular ziram products are based on the highest residue concentrations immediately after application (Fletcher, 1994). The results suggest that mammalian chronic levels of concern are exceeded for all food items other than seeds.

Use/App. Method	Rate (Ibs ai/A) x No. Apps.	Food Items	Max/Ave EEC (ppm) ¹	Chronic RQ (EEC/NOAEC) Max/Ave
		Multiple Application ²		
Blueberries	2.3 lbs ai/A (2 applications at 7 da interval)	Short grass	556/197	2.70 /0.95
		Tall grass	255/83	1.23 /0.40
		Broadleaf plants/Insects	313/104	1.50 /0.50
		Seeds	35/16	0.17/0.08
Grapes and Tomato	3.0 lbs ai/A (6-7 applications at 7 da interval)	Short grass	726/257	3.50 /1.24
		Tall grass	333/109	1.61 /0.52
		Broadleaf plants/Insects	408/136	2.00 /0.70
		Seeds	45/21	0.22/0.10
Apricots/Apples/Pears /Peaches/Cherries Eastern USA	6.1 lbs ai/A (5 applications at 7 da interval)	Short grass	1476/523	7.13/2.52
		Tall grass	676/221	3.26/1.07
		Broadleaf plants/Insects	830/277	4.01/1.34
		Seeds	92/43	0.44/0.21
Cherries Western	6.1 lbs ai/A (4 applications at 5 da interval)	Short grass	1511/535	7.30/2.60
USA		Tall grass	693/227	3.35/1.10
		Broadleaf plants/Insects	850/283	4.12/1.37
		Seeds	94/44	0.45/0.21
Peaches/nectarines	7.6 lbs ai/A (6 applications at 3 da interval)	Short grass	2085/738	10.1/3.6
		Tall grass	955/313	4.6/1.5
		Broadleaf plants/Insects	1173/391	5.7/1.9
		Seeds	130/61	0.63/0.3

Mammalian (Rat) chronic risk quotients for multiple broadcast spray applications of Ziram, based on a rat NOAEC of 207 ppm in the diet using a 1 day half-life.

Mammalian (Rat) chronic risk quotients for multiple broadcast spray applications of Ziram, based on a rat NOAEC of 207 ppm in the diet using a 1 day half-life.

Use/App. Method	Rate (Ibs ai/A) : No. Apps.	x Food Items	Max/Ave EEC (ppm) ¹	Chronic RQ (EEC/NOAEC) Max/Ave	
	Lev	vels of Concern			
Chronic risk					<u>> 1.0</u>

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

² For multiple applications, EFED uses EECs based on Hoerger and Kenega (1972) and Fletcher et al (1994), with first-order

dissipation from foliage between applications. If foliar dissipation data are not available, a 35 day default value is used. However, in this case, halflives were very short under many degredation parameters (aqueous photolysis, soil metabolism, etc...). Thus a 1 day half-life was used with a 3x safety factor (8 hrs x 3=24 hrs). *LOC exceedences are in bold

The residues expected (based on a 1 day half-life) on mammalian food items after multiple applications of non-granular ziram products are based on the highest residue concentrations after the last application (Fletcher, 1994). Chronic LOC's are exceeded for all food items other than seed under maximum application scenarios and also using average EECs for the higher application rates of 6.1 and 7.6 lbs ai/A.

Mammalian (Rat) chronic risk quotients for multiple broadcast spray applications of Ziram, based on a rat NOAEC
of 207 ppm in the diet using a 35 day default half-life.

Use/App. Method	Rate (Ibs ai/A) x No. Apps.	Food Items	Max EEC (ppm) ¹	Chronic RQ (EEC/NOAEC) Max/Ave	
		Multiple Application ²			
Blueberries	2.3 lbs ai/A (2 applications at 7 da interval)	Short grass	1,033		5.00
		Tall grass	473		2.30
		Broadleaf plants/Insects	581		2.80
		Seeds	65		0.30
Grapes and Tomato	3.0 lbs ai/A (6-7 applications at 7 da interval)	Short grass	3,454		16.70
		Tall grass	1,583		7.60
		Broadleaf plants/Insects	1,943		9.30
		Seeds	216		1.00
Apricots/Apples/Pears /Peaches/Cherries Eastern USA	6.1 lbs ai/A (5 applications at 7 da interval)	Short grass	7,024		34.00
		Tall grass	3,219		15.60
		Broadleaf plants/Insects	3,951		19.10
		Seeds	439		2.12
Cherries Western USA	6.1 lbs ai/A (4 applications at 5 da interval)	Short grass	5,079		24.50
		Tall grass	2,328		11.20
		Broadleaf plants/Insects	2,857		13.80
		Seeds	317		1.50
Peaches/nectarines	7.6 lbs ai/A (6 applications at 3 da interval)	Short grass	9,482		45.80
		Tall grass	4,346		21.00
		Broadleaf plants/Insects	5,334		25.80
		Seeds	593		2.90
	Level	s of Concern			
Chronic risk					<u>> 1.0</u>

¹ EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

² For multiple applications, EFED uses EECs based on Hoerger and Kenega (1972) and Fletcher et al (1994), with first-order dissipation from foliage between applications. If foliar dissipation data are not available, a 35 day default value is used. *LOC exceedences are in bold

The residues expected (based on a 35 day default half-life) on mammalian food items after multiple applications of non-granular ziram products are based on the highest residue concentrations after the last application (Fletcher, 1994). Chronic LOC's are exceeded for most (95% of the RQs) food items under maximum application scenarios.

Terrestrial Insects

Currently, EFED does not assess risk to nontarget terrestrial insects. Results of acceptable studies are used for recommending appropriate label precautions. As Ziram is practically non-toxic ($LD_{50} > 100$ ug/bee) to honeybees low risk is assumed.

Terrestrial Ecological Incident Data

There were no ecological incidents found in the EFED incidents database for Ziram. However, the number of documented kills in the Ecological Incident Information System is believed to be but a very small fraction of total mortality caused by pesticides. Mortality incidents must be seen, reported, investigated, and have investigation reports submitted to EPA to have the potential for entry into the database. Incidents often are not seen, due to scavenger removal of carcasses, decay in the field, or simply because carcasses may be hard to see on many sites and/or few people are systematically looking. Poisoned birds may also move off-site to less conspicuous areas before dying. Incidents seen may not get reported to appropriate authorities capable of investigating the incident because the finder may not know of the importance of reporting incidents, may not know who to call, may not feel they have the time or desire to call, may hesitate to call because of their own involvement in the kill, or the call may be long-distance and discourage callers, for example. Incidents reported may not get investigated if resources are limited or may not get investigated thoroughly, with residue analyses, for example. Also, if kills are not reported and investigated promptly, there will be little chance of documenting the cause, since tissues and residues may deteriorate quickly. Reports of investigated incidents often do not get submitted to EPA, since reporting by states is voluntary and some investigators may believe that they don't have the resources to submit incident reports to EPA.

Incident reports submitted to EPA since approximately 1994 have been tracked by assignment of I-#s in an Incident Data System (IDS), microfiched, and then entered to a second database, the Ecological Incident Information System (EIIS). This second database has some 85 fields for potential data entry. An effort has also been made to enter information to EIIS on incident reports received prior to establishment of current databases. Although many of these have been added, the system is not yet a complete listing of all incident reports received by EPA. Incident reports are not received in a consistent format (e.g., states and various labs usually have their own formats), may involve multiple incidents involving multiple chemicals in one report, and may report on only part of a given incident investigation (e.g., residues). While some progress has been made in recent years, both in getting incident reports submitted and entered, there has never been the level of resources assigned to incidents that there has been to the tracking and review of laboratory toxicity studies, for example. This adds to the reasons cited above for why

EPA believes the documented kills are but a fraction of total mortality caused by lindane and other highly toxic pesticides.

Incidents entered into EIIS are categorized into one of several certainty levels: highly probable, probable, unlikely, or unrelated. In brief, "highly probable" incidents usually require carcass residues in avian and/or mammalian species, and/or clear circumstances regarding the exposure. "Probable" incidents include those where residues were not available and/or circumstances were less clear than for "highly probable." "Possible" incidents include those where multiple chemicals may have been involved and it is not clear what the contribution was of a given chemical. The "unlikely" category is used, for example, where a given chemical is practically nontoxic to the category of organism killed and/or the chemical was tested for but not detected in samples. "Unrelated" incidents are those that have been confirmed to be not pesticide-related.

Incidents entered into the EIIS are also categorized as to use/misuse. Unless specifically confirmed by a state or federal agency to be misuse, or there was very clear misuse such as intentional baiting to kill wildlife, incidents would not typically be considered misuse. Data entry personnel often do not have a copy of the specific label used in a given application, and would not usually be able to detect a variety of label-specific violations, for example.

<u>APPENDIX I</u> : Literature Cited

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APPENDIX II

Toxicity Data

Toxicity testing reported in this section does not represent all species of bird, mammal, or aquatic organism. Only two **surrogate species** for both freshwater fish and birds are used to represent all freshwater fish (2000+) and bird (680+) species in the United States. For mammals, acute studies are usually limited to Norway rat or the house mouse. Estuarine/marine testing is usually limited to a crustacean, a mollusk, and a fish. Also, neither reptiles nor amphibians are tested. The assessment of risk or hazard makes the assumption that avian and reptilian toxicity are similar. The same assumption is used for fish and amphibians.

Ecological Effects Characterization

Risk assessment of a pesticide's ecological effects integrates the results of exposure and toxicity data to evaluate the likelihood of adverse ecological effects on a non-target species. The means of integrating these exposure factors is the risk quotient (RQ) method. Risk quotients are calculated by dividing estimated environmental concentrations (EECs) of the pesticide by acute and chronic toxicity values. EECs are based on the maximum application rates for that pesticide.

Risk quotients are then compared to the Agency's levels of concern (LOCs). These LOCs are used to analyze potential risk to non-target organisms and the need to consider regulatory action. The criteria are used to indicate when a pesticide used as directed has the potential to cause adverse effects on non-target organisms. LOCs currently address the following risk presumption categories: (1) acute high: high potential for acute risk for all nontarget organisms which may warrant regulatory action in addition to restricted use classification; (2) acute restricted use: potential for acute risk for all nontarget organisms, but may be mitigated through restricted use classification; (3) acute endangered species: endangered species may be adversely affected by use; and (4) chronic risk: potential for chronic risk may warrant regulatory action. Currently, the Agency does not perform assessments for chronic risk to plants, acute chronic risks to non-target insects, or chronic risk from granular/bait formulations to birds or mammals. In addition, the Agency considers any incident data that is submitted concerning adverse effects on non-target species.

Spray Applications to Foliage

The estimated environmental concentration (EEC) values used for foliar terrestrial exposure are derived from the Kenega nomograph, as modified by Fletcher et al. (1994), based on a large set of actual field residue data. The upper limit values from the nomograph represent the 95th percentile of residue values from actual field measurements (Hoerger and Kenega, 1972). The Fletcher et al. (1994) modifications to the Kenaga nomograph are based on measured field residues from 249 published research papers, including information on 118 species of plants, 121 pesticides, and 17 chemical classes. These modifications represent the 95th percentile of the expanded data set. Risk quotients are based on the most sensitive LC_{50} and NOAEC for birds and the derived dietary value for mammals (based on acute LD50 lab rat studies). EFED uses the FATE model for multiple applications, incorporating the appropriate dissipation half-life to generate EECs. For single application EECs, day zero maximum Fletcher residue values are used (lbs ai/A x 240, 110, 135, and 15 ppm).

Risk Presumption	<u>RQ</u>	<u>LOC</u>
	Birds	
Acute High Risk	$\underline{\text{EEC}^1/\text{LC}_{50}}$, $\underline{\text{LD}_{50}/\text{sq}}$ ft ² or $\underline{\text{LD}_{50}/\text{day}^3}$	<u>0.5</u>
Acute Restricted Use	<u>EEC/LC₅₀</u> , LD ₅₀ /sq ft or LD ₅₀ /day (or LD ₅₀ \leq 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC ₅₀ , LD ₅₀ /sq ft or LD50/day	0.1
Chronic Risk	EEC/NOAEC	<u>1</u>
	Wild Mammals	
Acute High Risk	EEC/LC ₅₀ , LD ₅₀ /sq ft or LD ₅₀ /day	<u>0.5</u>
Acute Restricted Use	<u>EEC/LC₅₀</u> , LD ₅₀ /sq ft or LD ₅₀ /day (or LD ₅₀ \leq 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC ₅₀ , LD ₅₀ /sq ft or LD ₅₀ /day	0.1
Chronic Risk	EEC/NOAEC	<u>1</u>
	mental Concentration (ppm) on avian/mammalian food items	
mg/ft ²	³ mg of toxicant consumed/day	
LD50 * wt. of bird	LD50 * wt. of bird	

RQ Calculations, LOCs, and Risk Presumptions for Terrestrial Animals

RQ Calculations, LOCs, and Risk Presumptions for Aquatic Animals

Risk Presumption	<u>RO</u>	LOC
Acute High Risk	$\underline{\text{EEC}}/(\underline{\text{LC}}_{50} \text{ or } \underline{\text{EC}}_{50})$	<u>0.5</u>
Acute Restricted Use	$\underline{\text{EEC}/(\text{LC}_{50} \text{ or EC}_{50})}$	<u>0.1</u>
Acute Endangered Species	$\underline{\text{EEC}/(\text{LC}_{50} \text{ or EC}_{50})}$	0.05
Chronic Risk	EEC/(NOAEC)	<u>1</u>

RQ Calculations, LOCs, and Risk Presumptions for Plants

Risk Presumption	<u>RO</u>	LOC
	Terrestrial and Semi-Aquatic Plants	
Acute High Risk Acute Endangered Species	EEC ¹ /EC ₂₅ EEC/EC ₀₅ or NOAEC	$\frac{1}{1}$
	Aquatic Plants	
Acute High Risk Acute Endangered Species EEC = lbs ai/A	EEC ² /EC ₅₀ EEC/EC ₀₅ or NOAEC	$\frac{1}{\underline{1}}$

 $\frac{1}{EEC} = lbs ai/A$

 $\frac{2}{\text{EEC}} = (ppb/ppm)$ in water

Toxicity to Terrestrial Animals

Avian Acute Oral Toxicity

One avian acute oral study using the TGAI is required to establish the toxicity of Ziram to birds. The preferred test species are mallard duck or bobwhite quail. Results of these tests are tabulated below.

Species	% ai	LD50 (mg/kg)	Toxicity Category	MRID No./ year	Study Classification ¹
Northern bobwhite quail (Colinus virginianus)	98.5	97	moderately toxic	417257-01 1989	Core
Mallard duck (Anas platyrhynchos)	NS	196	moderately toxic	437235-01 1994	Core

¹ Core (study satisfies guideline). Supplemental (study is scientifically sound, but does not satisfy guideline)

Since the LD50s are 97 and 196 mg/kg, Ziram is moderately toxic to waterfowl and upland gamebird species on an acute oral basis. The guideline (71-1) is fulfilled (MRID's 417257-01 and 437235-01).

Avian Subacute Dietary Toxicity

Two subacute dietary studies using the TGAI are required to establish the toxicity of Ziram to birds. The preferred test species are mallard duck and bobwhite quail. Results of these tests are tabulated below.

Species	% ai	5-Day LC50 (ppm) ¹	Toxicity Category	MRID No./ Year	Study Classification
Northern bobwhite quail (Colinus virginianus)	99	>5200	Prac. Non-toxic	423863-01 1992	Core
Mallard duck (Anas platyrhynchos)	99	5156	Prac. Non-toxic	423863-02 1992	Core

¹ Test organisms observed an additional three days while on untreated feed.

Since the LC50's fall in the range of 5156 and >5200 ppm, Ziram is practically non-toxic to avian species on a subacute dietary basis. The guideline (71-2) is fulfilled (MRID's 423863-01 and 423863-01).

Avian Chronic

Avian reproduction studies using the TGAI are required for Ziram because the following condition is met: (1) birds may be subject to repeated or continuous exposure to the pesticide, especially preceeding or during the breeding season. The preferred test species are mallard duck and bobwhite quail. No data was available or submitted for Ziram. The guideline (71-4) is not fulfilled.

Mammals, Acute and Chronic

Wild mammal testing is required on a case-by-case basis, depending on the results of lower tier laboratory mammalian studies, intended use pattern and pertinent environmental fate characteristics. In most cases, rat or mouse toxicity values obtained from the Agency's Health Effects Division (HED) substitute for wild mammal testing. These toxicity values are reported below.

Mammalian Toxicity

Species/ Study Duration	% ai	Test Type/Classification	Toxicity Value	Affected Endpoints	MRID No.
laboratory rat (Rattus norvegicus)	98.5	Acute Oral LD50	320 mg/Kg M+F	Death	413404-01
laboratory rat	97.8	Reproduction Study-	NOAEL=207 ppm	Body wt loss and	439358-01
(Rattus norvegicus)	77.0	2 Generation/core	LOAEL=540 ppm	decreased food consumption	457550 01

An analysis of the results indicate that ziram is categorized as moderately toxic to small mammals on an acute oral basis. The guideline (81-1 and 83-4) is fulfilled.

Insects

A honey bee acute contact study using the TGAI is required for Ziram because its use will result in honey bee exposure. Results of this test are tabulated below.

Nontarget Insect A	cute Cont	act Toxicity			
Species	% ai	LD50 (µg/bee)	Toxicity Category	MRID No./Year	Study Classification
Honey bee	98.5	>100	Prac. Non-toxic	416679-01 1990	Core

The reported results indicate that Ziram is practically non-toxic to bees on an acute contact basis. The guideline (141-1) is fulfilled. (MRID 416679-01).

Toxicity to Aquatic Animals

Freshwater Fish, Acute

Two freshwater fish toxicity studies using the TGAI are required to establish the toxicity of Ziram to fish. The preferred test species are rainbow trout (a coldwater fish) and bluegill sunfish (a warmwater fish). Results of these tests are tabulated below.

Species/ Flow-through or Static	% ai	96-hour LC50 (ppm)	Toxicity Category	Study Identification	Study Classification
Bluegill Sunfish (Leopmis macrochirus)	98.9	0.0097	Very highly Toxic	423863-03	Core

Freshwater Fish Acute Toxicity

Species/ Flow-through or Static	% ai	96-hour LC50 (ppm)	Toxicity Category	Study Identification	Study Classification
Carp (Cyprinus carpio)	Tec	0.27	Highly Toxic	00072559	Supplemental
Rainbow trout (Oncorhynchus mykiss)	98.9	1.7	Moderately Toxic	423863-04	Core
Rainbow trout (Oncorhynchus mykiss)	Tec	0.27	Highly Toxic	00072559	Supplemental
Fathead Minnow (Pimephales promelas)	99.0	0.008	Very Highly Toxic	Maloney and Palmer (1956) Water and Sewage Works 103:509- 513 (ID#05003523)	Supplemental

Since the LC50 falls in the range of 0.008 to 1.7 ppm, Ziram is categorized as moderately to very highly toxic to freshwater fish on an acute basis. The guideline (72-1) is fulfilled.

Freshwater Fish, Chronic

EFED has requested that a Fish Full Life Cycle Test (Guideline 72-5) using the TGAI for ziram. The preferred test species is the fathead minnow (*Pimephales promelas*). The guideline (72-5) has not yet been fulfilled. The study must be conducted to fully satisfy the requirement. The study was requested for the following reasons:

- C The pesticide is intended for use such that its presence in water is likely to be continuous or recurrent.
- C FIFRA requires a fish life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The LC50 of the freshwater species, the bluegill sunfish (*Leopmis macrochirus*), is 0.0097 ppm (MRID# 423863-03).

Freshwater Invertebrates, Acute

A freshwater aquatic invertebrate toxicity test (guideline 72-2) using the TGAI is required to establish the toxicity of Ziram to aquatic invertebrates. The preferred test species is *Daphnia magna*. Results of this test are tabulated below.

Species/Static or Flow- through	% ai	48-hour LC50 (ppm)	Toxicity Category	MRID No. Author/Year	Study Classification
Waterflea (Daphnia magna)	98.9	0.048	Very Highly Toxic	423863-05	Core

Freshwater Invertebrate Acute Toxicity

Ziram is categorized as very highly toxic to aquatic invertebrates on an acute basis. The guideline (72-2) is fulfilled.

Freshwater Invertebrate, Chronic (Guideline 72-4)

EFED has requested the freshwater aquatic invertebrate life-cycle test (guideline 72-4) using the TGAI of Ziram. The preferred test species is the water flea (*Daphnia magna*). The guideline (72-4) has not yet been fulfilled. The study was requested for the following reasons:

- C The pesticide is intended for use such that its presence in water is likely to be continuous or recurrent.
- C FIFRA guidelines require both the freshwater aquatic invertebrate life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The waterflea (*Daphnia magna*) is 0.048 ppm (MRID# 423863-05).

Toxicity to Estuarine and Marine Animals

Estuarine and Marine Fish, Acute

Acute toxicity testing with estuarine/marine fish using the TGAI is required for Ziram because the end-use product is expected to reach marine/estuarine habitats. The preferred test species is sheepshead minnow. Results of these tests are tabulated below.

Estuarine/Marine Fish Acute Toxicity						
Species/Static or Flow-through	% ai	96-hour LC50 (ppm) (measured/nominal)	Toxicity Category	MRID No. Author/Year	Study Classification	
Sheepshead minnow (Cyprinodon variegatus)	98.9	0.84	Highly Toxic	437816-01	Core	

Since the LC50 is 0.84 ppm, Ziram is categorized as highly toxic to estuarine/marine fish on an acute basis. The guideline (72-3a) is fulfilled.

Estuarine and Marine Fish, Chronic

EFED has requested the estuarine/marine fish life-cycle test (guideline 72-5) using the TGAI of Ziram. The preferred test species is the sheepshead minnow (*Cyprinodon variegatus*). The guideline (72-5) has not yet been fulfilled. The study must be conducted to fully satisfy the requirement. The study was requested for the following reasons:

- C The pesticide is intended for use such that its presence in water is likely to be continuous or recurrent.
- C FIFRA requires a fish life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The LC50 of the estuarine marine species, the sheepshead minnow (*Cyprinodon variegtus*), is 0.84 ppm (MRID# 437816-01).

Estuarine and Marine Invertebrates, Acute

Acute toxicity testing with estuarine/marine invertebrates using the TGAI is required for Ziram because the end-use product is intended for direct application to the marine/estuarine environment or the active ingredient is expected to reach this environment because of its use in

coastal counties. The preferred test species are mysid shrimp and eastern oyster. Results of these tests are tabulated below.

Species/Static or Flow-through	% ai.	LC50/EC50 (ppm) (measured)	Toxicity Category	MRID No.	Study Classification
Eastern oyster (shell deposition or embryo- larvae) (Crassostrea gigas)	98.0	0.077	Very highly toxic	437816-02	Core
Mysid (Americamysis bahia)	98.0	0.014	Very highly toxic	437816-03	Core

Estuarine/Marine Invertebrate Acute Toxicity

Since the LC50/EC50 falls in the range of 0.014 to 0.077 ppm, Ziram is categorized as very highly toxic to estuarine/marine invertebrates on an acute basis. The guidelines (72-3b and 72-3c) are fulfilled.

Estuarine and Marine Invertebrate, Chronic

EFED has requested the estuarine/marine aquatic invertebrate life-cycle test (guideline 72-4) using the TGAI of Ziram. The preferred test species is the Mysid *(Americamysis bahia)*. The guideline (72-4) has not yet been fulfilled. The study must be conducted to fully satisfy the requirement. The study was requested for the following reasons:

- C The pesticide is intended for use such that its presence in water is likely to be continuous or recurrent.
- C FIFRA guidelines require the estuarine/marine aquatic invertebrate life-cycle test for any pesticide if the aquatic acute LC50 or EC50 is less than 1 ppm. The acute LC50's for the eastern oyster (*Crassostrea virginia*) and the mysid shrimp (*Mysidopis bahia*) are 0.077 ppm and 0.014 ppm respectively (MRID's 437816-02 and 437816-03).

Toxicity to Plants

Terrestrial

Currently, terrestrial plant testing is not required for pesticides other than herbicides except on a case-by-case basis (*e.g.*, labeling bears phytotoxicity warnings incident data or literature that demonstrate phytotoxicity). EFED requires terrestrial plant testing for Ziram due to a label statement recommending no applications to target plants in leaf.

Aquatic

In the *Selenastrum capricornutum* study (123-2) an EC50 of 0.067 ppm was observed (MRID# 438339-01). Since the aquatic plant toxicity guideline has not yet been fulfilled, EFED cannot completely determine risk to aquatic plants for ziram.

Aquatic plant testing (Tier II: Guideline 123-2) is required for ziram for the following reasons: 1) It has outdoor non-residential terrestrial uses and 2) It may move off-site by runoff (solubility >10 ppm in water) or may move by drift (aerial). The *Selenastrum capricornutum* study has been submitted to EPA and has fulfilled guideline requirements, but the *Lemna gibba* study has not been submitted. In addition, the four other algae species must be tested due to ziram's apparent toxicity to green algae. These studies must be submitted in order for the Agency to complete a terrestrial and aquatic plant risk assessment.

APPENDIX III: Environmental Fate Study Summaries

161-1 Hydrolysis (MRID# 43866701)

Dimethyldithiocarbamic acid, zinc salt [¹⁴C]Ziram, at 2.8-2.9 ppm, hydrolyzed with a pH dependent rate in sterile aqueous buffered solutions maintained at 25.2±0.2°C through the study

periods. The rate of hydrolytic decomposition decreases with increasing pH. The study periods were relatively short, except for the pH 9 buffered solution, for which the study period was 30 days. (For the pH 5 solutions, the study period was only about 1 hour, and for the pH 7 buffered solution, the study period was only 72 hours.)

pН	(t _{1/3})/hours	Degradates
5	0.173	CS_2 (up to 96.8% of the applied at 1 hour), DDC (up to 11.6% at 0.117 hours, then only 0.15% at 1 hour)
7	17.7	CS_2 (up to 81.6% of the applied at 72 hours), thiram (up to 13.8% at 4 hours, and decreased to 11.0% through 72 hours)
9	151	COS (up to 18.6% of the applied at 30 days)

Note:

 $\overline{\text{CS}_2}$:carbon disulfide

COS: carbonyl sulfide or carbon oxide sulfide

DDC: metallic complex of DDC such as dimethyldithiocarbamic acid, Na^+ or NH_4^+ salts Thiram: tetramethylthiuramdisulfide

The material balances ranged from 96.1-105% of the initially applied radioactivity at pH 5, 88.1-97.4% at pH 7, and 90.9-100.6% at pH 9. All hydrolysis products greater than or equal to 10% of the initially applied radioactivity were identified.

161-2 Photolysis in Water (MRID# 44097701)

¹⁴C-Ziram, at 3.1 ppm, in pH 9 aqueous buffer that was continuously exposed to xenon light for 24 hours, degraded with a first order half-life of 8.7 hours. In the light exposed aqueous solution, ¹⁴C-ziram comprised a mean of 100% of the applied radioactivity at hour 0, 100% at hour 1, 98.3% at hour 4, 87.8% at hour 6, 49.9% at hour 12, 31.5% at hour 18, and 15.1% at hour 24. In contrast, the dark control did not degrade substantially during the same study period (97.2% of the applied still undegraded after 24 hours).

About 15 degradates were observed throughout the study, the major degradates of ziram after 24 hours of irradiation were N,N-dimethylformamide (23.7% of the applied at 24 hour), and N,N-methylthioformamide (18.1% of the applied radioactivity at 18-24 hours).

The recoveries for the irradiated samples ranged from 92.7 to 102.1% while for the dark control, the recoveries ranged from 103.1 to 103.2%.

161-3 Photodegradation on Soil (MRID# 44228401)

¹⁴C-Ziram, photodegraded with half-lives of 8.94 and 8.02 hours on irradiated sandy loam soil samples that were incubated at 25±1°C and 75% of the field moisture capacity for up to 72 hours, and treated at about 15 and 3 ppm, respectively. In the irradiated sandy loam soil, ziram comprised a mean of 68.4 to 72.5% of the applied radioactivity immediately after application, 43.9 ti 36.9% at hour 2 posttreatment, 44 to 30.7% at hour 4 posttreatment, 28.7 to 16.2% at hour 8 posttreatment, 17 to 10.1% at hour 16 posttreatment, and 9.4 to 7.6% at hour 24 posttreatment.

The soil was irradiated with a UV-filtered xenon light source for alternating 12 hour light and dark cycles for 24 hours at 25°C. After 24 hours of irradiation, 90.6% (15 ppm samples) and 92.4% (3 ppm) of the applied ziram had dissipated from the soil by a combination of degradation and volatilization. Ten degradates were detected in the 15 ppm treated samples, of which only thiram and thiram-oxide exceeded 5.49% of the applied radioactivity. The degradate thiram was about 25% of the applied radioactivity through the 24 hour study.

In contrast, ziram dissipated with half-lives of 16.2 and 24 hours in soil samples treated at the same respective treatment rates, but kept in the dark. In the dark control samples, the degradate profile observed in the samples was similar to that of the irradiated samples.

The soil was acidic, which may have promoted rapid hydrolysis and confounded the results. It is noted that in water, photolysis was important and photolysis may be anticipated on soil too.

162-1 Aerobic Soil Metabolism (MRID# 43985801)

EFED is concerned about the results obtained from this study because it was conducted ona soil that had a very low pH. A low pH of 5.4 may rise the rate of degradation of ziram by promoting hydrolysis. It is acknowledged, however, that the major degradate observed in this study, 1,1-dimethylurea was not observed in the hydrolysis study, and the degradates observed in the hydrolysis study were not present in significant quantities in this study. In order to clear the uncertainty created by the use of a low pH soil, EFED requires a new study to confirm the behavior of ziram in aerobic soils when the pH is near neutral.

¹⁴C-Ziram, at 3.05 ppm, dissipated from a sandy loam soil incubated in the dark at $25\pm1^{\circ}$ C and 75% of the field moisture capacity, with a first order half-life of 1.75 days. Samples were incubated for up to 60 days.

In the sandy loam soil, ziram comprised (mean of 2 replicates) of 85.1% of the applied radioactivity immediately after treatment, 74.3% after 1 hour, 66.5% at hour 6 posttreatment, 54.7% after 18 hours posttreatment, 46.3% 1 day posttreatment, 44.0% 3 days posttreatment, and 1.55% after one week (7 days) posttreatment.

The major metabolites observed through the study were 1,1-dimethylurea, which was not detected until day 7, at 8.65% of the applied radioactivity, then it was 8.67 at day 14, 10.5% at day 30, and 5.25% at day 60. Seven minor degradates were detected (<10%). The major volatile metabolite was ¹⁴CO₂, which accounted for 48.3% of the initially applied radioactivity at 60 days posttreatment. CS₂ was a minor metabolite, at <2%.

162-2 Anaerobic Soil Metabolism (MRID# 44228402)

¹⁴C-Ziramm at 2.99 ppmm degraded at a half-life of 14.1 da;ys in sandy loam soil that was incubated in the dark at 25±1°C and 75% of the field moisture capacity for up to 30 days. The samples were maintained for one day under aerobic conditions and later under anaerobic conditions (flooding and nitrogen atmosphere).

In the sandy loam soil, ¹⁴C-Ziram comprised 79.8% of the applied immediately after treatment (mean of 2 replicates), 38.7% at day 1 during the aerobic phase of study, 33.6% of the applied

radioactivity at the start of the anaerobic conditions, 24.7% at day 2, 16.8% at day 7, and 6.62% at day 30 during the anaerobic phase.

A total of 10 degradates were detected at any given time. All the degradates were <8% of the applied radioactivity. A high portion of the radioactivity was found was volatiles at the end of the 30 day anaerobic incubation. At that test interval, 35.2% of the applied was CO_2 , and 2.44% was found as CS_2 .

163-1 Mobility Batch Equilibrium and Adsorption/Desorption (MRID# 43873501)

¹⁴C-Ziram (radiochemical purity >96%), at 0.2, 0.6, 1.0, 2.0, and 4.0 ppm in non-sterilized sandy loam, silt loam, sand, and clay soil treated with 0.01 N CaCl₂ solution in the dark at $25\pm1^{\circ}$ C for up to 4 hours (except clay soil, which was equilibrated for 24 hours) showed that ziram residues are mobile in sand, silt loam, and sandy loam soils and was less mobile in clay soil.

¹⁴C-Ziram adsorbed with Freundlich K_{ads} values of 2.9 (r²=0.983) in sand, 7.6 (r²=986) in silt loam, 5.7 (r²=991) in sandy loam, and 68.1 (r²=0.922) in clay. 1/n values range from 0.334 to 0.948 indicating that the adsorption is not linear for all the soils used. The K_{ads} values show that ziram is moderately adsorbed in all soils used in this study with the exception of clay soil. Therefore, ziram is moderately mobile in sand, silt loam, and sandy loam soils, but less mobile in clay soil.

Soil Type	%OC	K _{ads}	1/n	K _{oc}	K _{des}	1/n
MS clay	1.8	68.1	0.334	3732	451	0.721
MD sand	0.2	2.9	0.948	1232	81	1.470
MD silt loam	1.0	7.6	0.651	759	4093	2.082
CA sandy loam	1.8	5.7	0.872	314	40	1.010

A summary of the results obtained in the study can be tabulated as follows:

164-1 Terrestrial Field Dissipation on Bareground Plots at North Carolina, and California (representative of Peach and Almond use Patterns, Respectively), (MRID#'s 44548301, and 44548302)

These studies were generally sound and provided supplemental information on the terrestrial field dissipation of ziram on bareground plots of sand soil, in Wake County, NC, and sandy loam soil, in Tulare County, CA. The studies, however, do not meet Subdivision N Guidelines because storage stability data were inadequate for the parent compound (both sites) and the degradate 1,1-dimethylurea (California site). In addition, at the North Carolina site, Hurricane Fran delivered approximately 8 inches of rain eight days following the ninth application. Furthermore, the California study presents difficulties in the interpretation of data because there was high variability in the data from day 0 to 10 days posttreatment. To upgrade these studies, the registrant at least <u>must</u> provide suitable storage stability data demonstrating that parent and degradate 1,1-dimethylurea are stable for the maximum period of storage stability. If the source of variability in the studies is the analytical methodology, the registrant must develop new

reliable analytical methods and conduct and submit one new study. The location of the study should be selected as in the previous case, representative of typical crops.

Ziram 76 DF[®] was broadcast applied nine times (at 7- to 10-day intervals) as a spray, to bareground plots of sand and sandy loam soils in North Carolina and California. The nominal application rate was 8 lb/A/application. In all cases, the 0- to 3-inch depth data were used to calculate half-lives. The active ingredient, ziram, dissipated with initial first-order half-lives of 6.7 days and 5.2 days (0- to 10-day data in both cases), following the ninth application in NC and CA, respectively. It appears that the dissipation did not follow a first order pattern all throughout the study. At the North Carolina and California sites, the second half-lives were 144 days (15- to 539-day data) and 206 days (14- to 540-day data), respectively.

At the North Carolina site, the parent compound was present in the 0- to 3-inch soil depth at 4.2-10.1 ppm immediately following each of the first eight applications. Following the ninth application, the parent compound was 7.3-8.3 ppm from 0 to 2 days posttreatment, was 10.3 ppm at 3 days, decreased to 4.4 ppm by 7 days, was 0.69-1.2 ppm from 90 to 270 days and was 0.24 ppm at 539 days. The parent compound was present in the 3- to 6-inch depth at 0.06-0.19 ppm immediately following each of the nine applications except application six. It increased to a maximum of 0.22 ppm by 8 hours posttreatment, and was last detected at 0.18 ppm at 3 days. The parent was not detected below the 3- to 6-inch soil depth. The degradate 1,1-dimethylurea was not detected.

At the California site, the parent compound was present in the 0- to 3-inch soil depth at 0.93-6.9 ppm immediately following each the nine applications. Following the ninth application, the parent was 2.1-5.2 ppm from 0 to 3 days posttreatment, was 0.79-1.5 ppm from 7 to 62 days and was 0.23 ppm at 540 days. The parent compound was present in the 3- to 6-inch depth at 0.08-0.15 ppm immediately following each of the first eight applications, was detected sporadically at #0.11 ppm from day 0 to 21 days posttreatment ans was not detected by 30 days. The parent compound was detected sporadically at #0.11 ppm in the 6- to 12-inch depth up to 1 day posttreatment and was not detected at that depth beyond day 1 with the exception of 210 days. The parent was not detected below the 6- to 12-inch soil depth. The degradate 1,1-dimethylurea was not detected.

APPENDIX IV: Tier I and Tier II Drinking Water Memorandum

U. S. ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, DC 20460

MEMORANDUM

SUBJECT: Tier I Estimated Environmental Concentrations of Ziram, for use in Human Health Risk Assessment (PC Code Ziram 034805; DP Barcode D276759)

FROM:	Jose Melendez, Chemist Environmental Risk Branch V Environmental Fate and Effects Division (7507C)
THROUGH:	Mah T. Shamim, Ph.D., Chief Environmental Risk Branch V Environmental Fate and Effects Division (7507C)
TO:	S. Lewis, Branch Chief, and Laura Parsons, Team Reviewer Reregistration Branch I Special Review and Reregistration Division (7508C)

This memo presents the Revised Tier I Estimated Environmental Concentrations (EECs) for Ziram, calculated using FIRST (surface water) and SCIGROW (ground water) for use in the human health risk assessment. EEC's were revised for Ziram because the registrant proposed new application rates for certain crops. In addition, the EEC's for surface drinking waters were estimated using the most recent model, FIRST, instead of GENEEC.

For Ziram, the surface water acute (peak) value is **860 ppb**, and the chronic value is **19 ppb**. The groundwater screening concentration is **0.03 ppb** of Ziram. In the previous assessment of drinking waters, the surface water acute (peak) value was 260 ppb, and the chronic value was 8 ppb. The groundwater screening concentration was 0.04 ppb of Ziram. These values represent upper-bound estimates of the concentrations of the ziram that might be found in surface and ground water due to the use of Ziram on peaches and nectarines (Western US) at an application rate of 45.2 lb a.i./A/season [7.6 lb a.i./A applied 6 times at 3 day intervals].

Should the results of this assessment indicate a need for further refinement, please, contact us as soon as possible so that we may schedule a Tier II assessment.

Background Information on FIRST:

FIRST is a new screening model designed to estimate the pesticide concentrations found in water for use in drinking water assessments. It provides high-end values on the concentrations that might be found in a small drinking water reservoir due to the use of pesticide. Like GENEEC, the model previously used for Tier I screening level, FIRST is a single-event model (one run-off event), but can account for spray drift from multiple applications. FIRST takes into consideration the so called Index Drinking Water Reservoir by representing a larger field and pond than the standard GENEEC scenario. The FIRST scenario includes a 427 acres field immediately adjacent to a 13 acres reservoir, 9 feet deep, with continuous flow (two turnovers per year). The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 8% of the applied pesticide into the pond. This amount can be reduced due to degradation on field and the effect of binding to soil. Spray drift is equal to 6.4% of the applied concentration from the ground spray application and 16% for aerial applications. FIRST also makes adjustments for the percent crop area. While FIRST assumes that the entire watershed would not be treated, the use of a PCA is still a screen because it represents the highest percentage of crop cover of any large watershed in the US, and it assumes that the entire crop is being treated. Various other conservative assumptions of FIRST include the use of a small drinking water reservoir surrounded by a runoff-prone watershed, the use of the maximum use rate, no buffer zone, and a single large rainfall.

Background Information on SCI-GROW:

SCIGROW provides a groundwater screening exposure value to be used in determining the potential risk to human health from drinking water contaminated with the pesticide. Since the SCI-GROW concentrations are likely to be approached in only a very small percentage of drinking water sources, i.e., highly vulnerable aquifers, it is not appropriate to use SCI-GROW for national or regional exposure estimates.

SCI-GROW estimates likely groundwater concentrations if the pesticide is used at the maximum allowable rate in areas where groundwater is exceptionally vulnerable to contamination. In most cases, a large majority of the use area will have groundwater that is less vulnerable to contamination than the areas used to derive the SCIGROW estimate.

Modeling Inputs and Results:

The tables below summarize the input values used in the model runs for FIRST 1.0 and SCIGROW, respectively. The lowest non-sand K_D was used in FIRST 1.0. The median K_{OC} value was used in SCIGROW. Three times the available aerobic soil metabolism half-life for ziram was used for FIRST and one time for SCIGROW. Twice the aerobic soil metabolism value used in the model, was used in lieu of the aerobic aquatic metabolism, as per current EFED guidelines. The modeling results associated with the use of ziram on peaches and nectarines (Western US), which represent the worst case scenario, are presented in a table below. Attached to this memo are copies of the original printouts generated from FIRST and SCIGROW runs.

cc: HED

Environmental Fate Input Parameters for FIRST.

Parameter	ZIRAM Value	Source
PC Code	034805	N/A
Water Solubility	65 ppm	EFGWB One-Liner ¹
Hydrolysis Half-Life (pH 7)	0.74 days	MRID 43866701
Aerobic Soil Metabolism t_{y_2} , (3X the available value)	5.25 days	MRID 43985801
Aerobic Aquatic Metab. t_{χ_2} (2X the Aerob. Soil Metab.)	10.5 days	MRID 43985801
Aqueous Photolysis Half-Life (at pH 7)	0.363 days	MRID 44097701
Soil Water Partition Coefficient (Lowest non sand K _d)	5.7	MRID 43873501
Pesticide is Wetted-In	No	Product Label
Crop (W = Western)	Peaches/Nectarines (W)	Registrant Provided
PCA	0.87	Default Value
Depth of Incorporation (Broadcast)	0.0	Product Label

Table 2. Environmental Fate Input Parameters for SCIGROW.

Parameter	ZIRAM Value	Source
Organic Carbon Partition Coefficient (Median K _{OC})	537	MRID 43873501
Aerobic Soil Metabolism Half-Life	1.75 days	MRID 43985801

Table 3. Modeling Results for Use ZIRAM on Peaches and Nectarines (Western US)

Parameter	ZIRAM Value	Source
Сгор	Peaches/Nectarines (W)	Registrant Provided
Application Method	Aerial	Product Label
Application Rate	7.6 lb a.i./A	Registrant Provided
Application Frequency	6	Registrant Provided
Application Interval	3 days	Registrant Provided
FIRST 1.0 Peak Untreated Water Concentration	860 ppb	FIRST Output
FIRST 1.0 Annual Average Untreated Water Concentration	19 ppb	FIRST Output
SCIGROW Ground Water Concentration	0.03 ppb	SCIGROW Output

¹Wauchope et.al., 1993

FIRST Printout (two FIO runs and a run for Peaches and Nectarines-Western US):

RUN No. 1 FOR Ziram	ON App/Pear-E * INPUT VALUES *
ONE(MULT) INTERVAL	& SOIL SOLUBIL APPL TYPE %CROPPED INCORP Kd (PPM) (%DRIFT) AREA (IN)
6.100(10.098) 7 7	5.7 65.0 AERIAL(16.0) 87.0 .0
FIELD AND RESERVOIR Ha	
METABOLIC DAYS UNTIL	HYDROLYSIS PHOTOLYSIS METABOLIC COMBINED (RESERVOIR) (RESEFF) (RESER.) (RESER.)
	N/A .36- 45.01 10.50 8.51
UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.0 AUG 1, 2001
PEAK DAY (ACUTE) CONCENTRATION	ANNUAL AVERAGE (CHRONIC) CONCENTRATION
415.357	9.267
RUN No. 2 FOR Ziram	ON Peac/Nec-E * INPUT VALUES *
	& SOIL SOLUBIL APPL TYPE %CROPPED INCORP Kd (PPM) (%DRIFT) AREA (IN)
	5.7 65.0 AERIAL(16.0) 87.0 .0
FIELD AND RESERVOIR Ha	lf-life VALUES (DAYS)
	HYDROLYSIS PHOTOLYSIS METABOLIC COMBINED (RESERVOIR) (RESEFF) (RESER.) (RESER.)
	N/A .36- 45.01 10.50 8.51
UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.0 AUG 1, 2001
PEAK DAY (ACUTE) CONCENTRATION	ANNUAL AVERAGE (CHRONIC) CONCENTRATION
416.557	
RUN No. 3 FOR Ziram	ON Peac/Nec-W * INPUT VALUES *
RATE (#/AC) No.APPS ONE(MULT) INTERVAL	& SOIL SOLUBIL APPL TYPE %CROPPED INCORP Kd (PPM) (%DRIFT) AREA (IN)
	5.7 65.0 AERIAL(16.0) 87.0 .0
FIELD AND RESERVOIR Ha	lf-life VALUES (DAYS)
	HYDROLYSIS PHOTOLYSIS METABOLIC COMBINED (RESERVOIR) (RESEFF) (RESER.) (RESER.)

5.25	2	N/A	.36-	45.01	10.50	8.51
UNTREATED	WATER CONC	(MICROGRAMS/L	ITER (PP	PB))	Ver 1.0 AUG	1, 2001
	DAY (ACUTE ICENTRATION	,	AVERAGE ONCENTRA	•	1IC)	
8	59.631		19.15	;9		

SCIGROW Printout:

RUN	No. 1	FOR Zir	am		INPUT VA	ALUES	
APP RAT	L (#/AC) E			SOIL 2) KOC		AEROBIC ISM (DAYS)	
7	.600	б	45.600	5	37.0	1.8	
GROU	ND-WATER	SCREEN	NING CONC	ENTRATI	ONS IN PPI	3	
			.033538				
A= F=	.292 -3.133			-	535 D= 45.600	2.734 GWSC=	

APPENDIX V : Data Requirements

Guideline #	Data Requirement	Is Data Requirement Satisfied?	MRID #'s	Study Classification
71-1	Avian Oral LD ₅₀	Yes Yes	417257-01 423863-02	Core Core
71-2	2 Avian Dietary LC_{50} 's	Yes yes	423863-01 423863-02	Core Core
71-4	Avian Reproduction (2 species)	No		
72-1	2 Freshwater Fish LC_{50}	Yes Yes	423863-03 423863-04	Core Core
72-2	Freshwater Invertebrate Acute LC_{50}	Yes	423863-05	Core
72-3(a)	Estuarine/Marine Fish LC ₅₀	Yes	437816-01	Core
72-3(b)	Estuarine/Marine Mollusk EC50	Yes	437816-02	Core
72-3(c)	Estuarine/Marine Shrimp EC ₅₀	Yes	437816-03	Core
72-4(a)	Freshwater Fish Early Life-Stage	Reserved		
72-4(b)	Estuarine Fish Early Life-Stage	Reserved		
72-4(c)	Estuarine Invertebrate Life-Cycle	No		
72-4(d)	Freshwater Invertebrate Life-Cycle	No		
72-5	Freshwater Fish Full Life-Cycle Estuarine Fish Full Life-Cycle	No No		
81-1	Acute Mammalian LD ₅₀	Yes	413404-01	Core
83-5	2-generation mammalian reproduction	Yes	439358-01	Core
122-1(a)	Seedling Emergence	No		
122-1(b)	Vegetative Vigor	No		
123-2	Aquatic Plant Growth	Partial	438339-01	Core
123-1(a)	Seedling Emergence	Reserved		
123-1(b)	Vegetative Vigor	Reserved		
123-2	Aquatic Plant Growth	No		
144-1	Honey Bee Acute Contact LD ₅₀	Yes	416679-01	Core
Non- guideline				

Ecological Effects Data Requirements for:Ziram

Environmental Fate Data Requirements for: Ziram

Guideline #	Data Requirement	Is Data Requirement Satisfied?	MRID #'s	Study Classification
161-1	Hydrolysis	Y	43866701	С
161-2	Photodegradation in Water	Y	44097701	С
161-3	Photodegradation on Soil	Y	43642501	С
161-4	Photodegradation in Air	N/A	N/A	W
162-1	Aerobic Soil Metabolism	Ν	43985801	S
162-2	Anaerobic Soil Metabolism	Y	44228402	С

162-3	Anaerobic Aquatic Metabolism	N/A	N/A	N/A
162-4	Aerobic Aquatic Metabolism	N/A	N/A	N/A
163-1	Leaching- Adsorption/Desorption	Y	43873501	С
163-2	Laboratory Volatility	N/A	N/A	W
163-3	Field Volatility	N/A	N/A	W
164-1	Terrestrial Field Dissipation	Ν	44548301 44548302	S(1)
165-4	Accumulation in Fish/ Bioconcentration	N/A	N/A	W

C=Core; S=Supplemental; W=Waived; N/A=Not Applicable

(1). One study, conducted at two sites was found to have several deficiencies. To upgrade the study, the registrant is required to address the problems found in it. Alternatively, a new study, conducted at only one site must be submitted.