REPORT TITLE

Response by Makhteshim Agan of North America, Inc. to the Environmental Fate and Ecological Effects Division (EFED) Addendum to the Ecological Risk Assessment of Endosulfan and Appendix 1 to 2007 Addendum: Environmental Fate and Ecological Risk Assessment of Endosulfan (DATE: October 31, 2007)

AUTHORS

Christopher Mackay, Ph.D. John K. Schupner, M.S.

PREPARED BY

AMEC Earth & Environmental 285 Davidson Avenue, Suite 405 Somerset, NJ 08873

REPORT DATE

12 February 2008

REPORT IDENTIFICATION

AMEC Earth & Environmental Project Report: 76861-02/12/08

SPONSOR/SUBMITTER

Makhteshim Agan of North America, Inc. (MANA) 4515 Falls of Neuse Road, Suite 300 Raleigh, NC 27609

TABLE OF CONTENTS

EXECUTIVE SUMMARY	3
INTRODUCTION	5
Memorandum	6
Exposure Characterization	6
Persistence	6
Exposure Modeling	6
Monitoring and Long-Range Transport	7
Surface Water	8
Bioaccumulation	8
Effects Characterization	9
Risk Conclusions	9
Appendix	11
2. NEW DATA ON BIOACCUMULATION	11
2.1 Findings from Empirical Bioaccumulation Studies	12
2.1.1. Bioconcentration/Bioaccumulation by Fish	12
2.1.2 Bioconcentration/Bioaccumulation by Invertebrates	13
2.2 Findings From Bioaccumulation Modeling	13
2.2.1 Bioaccumulation in Aquatic Organisms.	13
Model Inputs and Assumptions	14
Food Web Structure	14
Exposure Concentrations	14
Chemical Properties	15
Model Output: Biomagnification	17
2.2.2 Bioaccumulation in Terrestrial Organisms	18
2.3 Conclusions from Endosulfan Bioaccumulation Assessment	19
3. NEW DATA ON ECOLOGICAL EFFECTS	20
3.2 Aquatic Organisms: Sediment Exposure	20
4. NEW INFORMATION ON AQUATIC EXPOSURE	21
5. NEW INFORMATION ON MONITORING AND LONG-RANGE TRANSPORT	24
Endosulfan In Surface Water	24
Endosulfan In Atmosphere	29
Endosulfan In Precipitation	29
Endosulfan In Airborne Particles	29
Endosulfan In Sediment	30
Endosulfan in Mountainous Regions	31
Endosulfan in Arctic Areas	31
6. ECOLOGICAL RISK CHARACTERIZATION	32
6.1 Risk Estimation	32
6.1.1 Post 2002 ERA Incident Data	32
6.1.2 Aquatic Organisms: Water Column Exposure	32
6.1.3 Aquatic Organisms: Sediment Exposure	33
6.1.4 Terrestrial Organisms: Piscivorous Wildlife	34
6.2 Risk Conclusions	34
REFERENCES	35

EXECUTIVE SUMMARY

Makhteshim-Agan of North America Inc. (MANA), has prepared this response to the USEPA Environmental Fate and Ecological Effects Division's (EFED) Addendum to the Ecological Risk Assessment of Endosulfan and Appendix 1 to 2007 Addendum: Environmental Fate and Ecological Risk Assessment of Endosulfan (DATE: October 31, 2007, DP Barcode: D346213, PC Code: 079401, Docket ID: EPA-HQ-OPP-2002-0262).

The Addendum and Appendix to the Environmental Fate and Ecological Risk Assessment were reviewed by MANA and found to contain some omissions, statements and interpretations that require further consideration prior to the finalization of the subject Assessment. The areas of most concern include:

- Reliance upon new bioaccumulation data that has not been subjected to the standard quality review usually demanded by the Agency.
- Preliminary bioaccumulation modeling efforts that are new to this assessment and have applied methods and assumptions whose underlying uncertainty has not been sufficiently represented or quantified.
- Overly conservative PRZM/EXAMS modeling assumptions (i.e. compounding upper 90% CI or greater parameters, no inclusion of buffers, reduced application rates, not reflecting mitigation measures on present labeling, unrealistic half-lives) that have made the projections practically impossible.
- Misleading interpretation of Florida Water Monitoring Program and site S178.
- Selective presentation of off-site residue data.
- Over emphasis of literature publications of trace residue measurements in remote locations that do not meet the Agency's usual data quality standards.
- Lack of Agency review of Endosulfan Task Force (ETF) submitted report Evaluation And Interpretation Of Environmental Data On Endosulfan In Arctic Regions (MRID 467343-01).
- Misinterpretation of 2002 ERA Incident Data (EIIS), where actually only four of the reported incidents occurred in or after 2002 (one terrestrial and three aquatic), and only one incident is known to be associated with the use of endosulfan.
- Failing to incorporate current mitigation measures/usage information.

MANA acknowledges the preliminary nature of these efforts, but is concerned that risk management decisions may be inadvertently based on this "preliminary" assessment. Bioaccumulation modeling is new to the assessment for endosulfan and the methods and parameter assumptions may require further review and characterization. It appears that the mitigation actions specified on the current label and approved by the Agency have not been considered in this assessment. Exposure assessments continue to be based on

overly conservative and unrealistic assumptions. MANA believes that the Agency should revise the input parameters used for calculating the estimated environmental concentrations (EECs) for endosulfan based on current environmental fate data, labeled uses, rates, and specified buffers (300 foot spray buffer, 30 foot vegetative buffer), as well as relevant sensitive parameters in PRZM/EXAMS. Furthermore, it is currently unclear to MANA the precise relevance of much of the transport and bioaccumulation modeling to the current re-registration of endosulfan. The off-site movement and long range transport requires a proper risk based analysis that is currently not presented.

MANA respectively requests consideration of these comments in order to achieve an objective and science-based evaluation for all endosulfan stakeholders.

INTRODUCTION

Endosulfan is a non-systemic insecticide defined as the sulfite diester of a chlorinated cyclodiene. It is a mixture of two stereoisomers; α -endosulfan and β -endosulfan. α -endosulfan, also referred to as Endosulfan (I) comprises 64-67% of the technical grade endosulfan with the remainder as β -endosulfan, or Endosulfan (II).

Based on its selectivity towards target pests, relatively benign impact on beneficial insects, its unique mode of action, and low insect resistance, endosulfan is considered by many growers as an excellent tool to be incorporated as part of Integrated Pest Management (IPM) and Resistance Management programs.

MANA appreciates the Agency's efforts in the re-registration of endosulfan and welcomes the opportunity to comment on the *Environmental Fate and Ecological Effects Division (EFED) Addendum to the Ecological Risk Assessment of Endosulfan and Appendix 1 to 2007 Addendum: Environmental Fate and Ecological Risk Assessment of Endosulfan in order to clarify various misperceptions that are present concerning endosulfan.*

The Addendum and Appendix to the EFED Risk Assessment contains information that has not been thoroughly reviewed prior to incorporation into the assessment. Exposure estimates continue to be based on overly conservative, unrealistic assumptions. It appears that the mitigation actions specified on the current label and approved by the Agency have not been considered in this assessment. Bioaccumulation modeling is new to the assessment of endosulfan and the methods and assumptions are debatable. Offsite movement and long range transport requires a risk based analysis that is mostly lacking in the document. MANA is taking the opportunity to comment on these and other issues in this response.

Memorandum

Page 2

Exposure Characterization

Persistence

<u>Agency comment</u>: "Endosulfan is expected to be more persistent than how it was characterized in the 2002 ERA. This conclusion is based on the newly submitted toxicity data on endosulfan sulfate, the major degradate of endosulfan, which shows that endosulfan sulfate is similar in toxicity to the parent compound."

<u>MANA Response</u>: It appears that the expectation of increased persistence is based on a projected longer half life for the active endosulfan sulfate metabolite of endosulfan. While it is agreed that endosulfan sulfate possesses a toxicity that is comparable to endosulfan, a *de facto* equation of endosulfan sulfate properties to endosulfan is highly unrealistic. Endosulfan is not endosulfan sulfate. Furthermore, endosulfan sulfate is not the exclusive, and in most cases not even the major metabolite of endosulfan degradation. If the Agency wants to consider endosulfan sulfate in the evaluation of endosulfan persistence, then it is only reasonable to treat it as a separate chemical entity with its own rates of production (which is a function of, but not equal to the endosulfan application rate), fate and transport characteristics, and rate of degradation to non-toxic metabolites.

Exposure Modeling

<u>Agency comment</u>: "Revised exposure modeling was conducted based on total endosulfan residues (α + β +sulfate)..."

<u>MANA response</u>: The Agency's modeling has attempted to use data for all forms of endosulfan selectively and combined this into one model. This is inappropriate for the reasons detailed above. Endosulfan is not endosulfan sulfate nor *vice versa*. Simple summation is an attempt to make the conceptualization fit the simulation model. Each substance has its own manifestation rate and environmental fate characteristics and thus should be modeled separately with the summation only occurring at the point of presentation to the receptor.

<u>Agency comment</u>: "Predicted surface water EECs increased by 20-40% compared to EECs used in the 2002 ERA, which reflects the addition of endosulfan sulfate in the exposure modeling."

<u>MANA response</u>: The addition of endosulfan sulfate in the model has increased EECs through the use of DT_{50} data for total endosulfan from an aerobic soil metabolism study. Data for all of the other parameters were for either alpha or beta isomers and not specific

to endosulfan sulfate. This results in the assessment of a hybrid compound that does not exist in nature which thereby introduces uncertainty that is highly unpredictable. The consideration of endosulfan sulfate does not require its summation to endosulfan nor the interchange of selected chemical and environmental parameters. The state of environmental modeling is capable of considering endosulfan sulfate for what it is: a partial metabolite of endosulfan degradation. MANA would like the Agency to restructure these assumptions and approach to simulate what is known to be the true nature of the material in the environment.

<u>Agency comment</u>: "Predicted peak, 21-d mean, and 60-d mean surface water EECs are: 23, 9.3, and 6.8 ppb (Florida tomato scenario)... Sediment pore water EECs of about 4 ppb were predicted..."

<u>MANA response</u>: The PRZM/EXAMS modeling performed for this new assessment has not incorporated the 300 foot spray buffer and the 30 foot vegetative buffer, besides the lower application rates and numbers. An assumption of no buffer effect on reduction of loading to water bodies is unrealistic and represents a use scenario that is in contravention of the label, and is therefore an illegal situation. The mitigation actions currently part of the Endosulfan label should be reflected in the model.

The 21 day and 60 day pore water concentrations are essentially unchanged from the initial peak value, which is unrealistic and likely an artifact of the modeling approach whereby sensitive parameters (e.g. CN, PRBEN, etc) are set to unrealistic values (MRID 44953102).

<u>Agency comment</u>: "California strawberry and Florida tomato EECs may be underestimated because the use of plastic mulch practices, which are expected to increase endosulfan runoff, could not be modeled accurately."

<u>MANA response</u>: Runoff from plastic mulch practices varies considerably and is dependent on area mulched, slope and contour of the field, orientation of rows, soil properties and agricultural practices. The Rice *et al.* (2001) study is based on 5 to 7% slope, but slopes in Florida are typically 1% or less. In all cases mandated spray buffers and vegetative buffer strips would be expected to reduce runoff losses to water bodies, whether plastic mulch is used or not.

Monitoring and Long-Range Transport

<u>MANA comment</u>: The transport of small quantities of endosulfan off-site is not disputed. However, there is no trend towards an increase in concentrations at distant sites. The risk or toxicological significance of exposure to these small quantities would be insignificant within the risk paradigm used by the Agency (i.e. chronic risk quotients less than 1.0). This leads to open supposition as to effects and does not improve the risk characterization. Clearly the levels measured in the vast majority of cases where mid to long range transport has been observed are well below the Agency's levels of concern.

Page 2

Surface Water

<u>Agency comment</u>: "These data suggest that in the vicinity of row crops where endosulfan is reportedly applied, endosulfan residues have been routinely detected in both the water column and benthic sediments. Additionally, the data indicate that residues exceed OPP acute and chronic risk levels of concern (e.g., south Florida and California)..."

<u>MANA response</u>: It is not clear what "routinely detected" indicates or what the frequency of occurrence is. Most of the Agency's concerns appear to revolve around data collected in South Florida, where EFED refers to one particular and unique sampling site (S 178), where endosulfan has been detected only before 2000 at levels above the Water Quality Standard (0.056 ppb); since May of 2000 this site, S178, had only one minor exceedance in March of 2007 (0.19 ppb endosulfan). EFED did not mention all the other monitoring sites that have shown no endosulfan detections or exceedances of the WQS. According to the Southern Florida Water Management District (SFWMD), there were 63 surface water sampling events (S 178) resulting in 8 exceedances of the WQS, 6 of them occurred during 1993 and 1996. The implemented product stewardship program (1998) and recent label mitigations (RED 2002) seem to be effective. See additional comments to the Appendix.

Bioaccumulation

Page 5

<u>Agency comment</u>: "Depuration of endosulfan (α and β isomers) and its primary degradate (endosulfan sulfate) appears rapid in fish (half life 2-6 days) based on limited data. However, the ability of fish and other aquatic organisms to depurate endosulfan in the environment may be ameliorated in areas of broad-scale endosulfan contamination..."

<u>MANA response</u>: MANA agrees that, based on the available data, depuration in fish is rapid. However, we cannot see any mechanism by which endosulfan concentration in the environment would "ameliorate" this depuration. If this refers to the establishment of equilibrium between excretion and uptake, then it should be represented as the ratio of the two rate coefficients. Qualitative caution based on a suspicion of amelioration does not aid in the risk characterization.

<u>Agency comment</u>: "Based on one study with daphnids and preliminary aquatic bioaccumulation modeling results, biomagnification of endosulfan appears unlikely in typical aquatic food webs."

<u>MANA response</u>: MANA concurs that biomagnification is unlikely in aquatic food webs, which has also been posited for Arctic systems (MRID 46734301).

<u>Agency comment</u>: "Based largely on indirect evidence from terrestrial bioaccumulation modeling, the biomagnification of endosulfan by terrestrial organisms appears to be a concern with predicted biomagnification factors ranging from 2.5 to 28 for herbivorous and carnivorous wildlife at the top of arctic food webs."

<u>MANA response</u>: MANA disagrees with the methods and conclusions drawn from the terrestrial bioaccumulation modeling for arctic food webs. Existing metabolism studies should have been considered in the analysis. The agency has already acknowledged that the depuration half life of endosulfan in fish is 2-6 days; long-term feeding studies (cows, rats, mice) also did not indicate any potential for bioaccumulation. This should be taken into account in the evaluation of potential for bioaccumulation.

See additional comments to the Appendix.

Effects Characterization

<u>Agency comment:</u> "Based on comparisons made within the same species, the toxicity of endosulfan sulfate and the parent isomers (α , β) generally appears similar based on acute studies with bluebill sunfish and mallard duck, but somewhat less toxic with bobwhite quail. This information was used to support the assumption that endosulfan sulfate is similar in toxicity to the parent compounds."

<u>MANA response</u>: The ETF has previously stated that the toxicity of endosulfan sulfate is similar to the alpha and beta isomers of endosulfan. MANA is in agreement with the Agency's statement (see also recent submission – MRID 47276001).

Page 6

<u>Agency comment:</u> "Sediment toxicity of endosulfan sulfate was evident at pore water concentrations as low as 1.5 ppb based on 28-d exposures with an estuarine/marine amphipod."

<u>MANA response</u>: This statement is inaccurate. As indicated in the text and Table 3.3 of the Appendix, the Lowest Observed Adverse Effect Concentration (LOAEC) was 4.0 μ g/L pore water.

See additional comments to Appendix.

Risk Conclusions

<u>Agency comment:</u> "Risk quotient (RQ) predicted for aquatic organisms resulting from water column exposure to endosulfan are about 20% to 40% higher compared to the 2002 ERA. This increase reflects the addition of endosulfan sulfate to the exposure modeling and data indicating it is of similar toxicity to the parent isomers (α and β)."

<u>MANA response:</u> First, a change in the RQ does not equate to an increase in probability or magnitude of impact. Evaluation of risk characterization based on the amount that the hypothesized exposure exceeds the toxicity threshold is irrelevant within the risk paradigm applied. Second, MANA disagrees with the manner in which endosulfan sulfate has been added to the exposure modeling. The parameters that appear to have been changed are the aerobic soil metabolism half-life and aerobic aquatic metabolism half-life (represented by twice the soil value from laboratory studies that do not reflect real life). Other data used are a mix of values for the alpha and beta isomers. In addition, selection of CN and PRBEN are not specified. See comments above at Exposure Modeling, and additional comments to the Appendix below.

<u>Agency comment:</u> "Risks to freshwater and estuarine/marine invertebrates resulting from sediment exposure to endosulfan are evident from the integration of exposure and effect characterization. The RQ values for sediment-dwelling invertebrates range form 0.9 to 2.8 depending on species. These RQ values are based on predicted total endosulfan residues compared to endosulfan sulfate toxicity values, which assumes similar toxicity of endosulfan sulfate and total endosulfan residues."

<u>MANA response</u>: The EEC's for pore water from PRZM/EXAMS do not reflect the behavior of endosulfan in estuarine sediment water systems as seen in the pore water analyses in the sediment toxicity study (MRID 46929001). In PRZM/EXAMS, the 21 day and 60 day pore water concentrations are essentially unchanged from the initial peak value, whereas in the laboratory study the pore water concentrations decreased approximately 75% in 28 days. PRZM/EXAMS does not appear to adequately model estuarine sediment pore water concentrations in this situation, probably as the result of errors in the application of environmental degradation rates. Hence, exposure is probably less as projected and thus the RQ values are lower as predicted.

See additional comments to Appendix.

<u>Agency comment:</u> "Based on preliminary results from an aquatic food web bioaccumulation model, risks to piscivorous wildlife appear relatively modest with mean predicted acute RQ values exceeding the Agency acute LOC of 0.1 for one of eight species modeled (0.15 for river otter) and 90th percentile estimates exceeding the LOC for three of eight species modeled (0.18, 0.39, 0.20 for mink, river otter and belted kingfisher, respectively). Predicted chronic RQ values did not exceed the Agency LOC for any of the eight species modeled."

<u>MANA response:</u> Although the bioaccumulation model appears to require further considerations to improve its accuracy (see comments on Appendix below), we are in agreement that the acute and chronic risks to piscivorous wildlife are minimal.

<u>Agency comment:</u> "Risks to nontarget terrestrial wildlife did not change from the 2002 ERA as a result of this addendum, because currently available terrestrial exposure models could not address total residue exposure."

<u>MANA response</u>: Although predicted risks to non-target terrestrial wildlife did not change from the 2002 ERA because of limitations in the terrestrial exposure model, it is our opinion that exposure of wildlife to the parent isomers and degradates through food would be less since they volatilize, wash off of plant surfaces, and bind or further degrade in soil.

<u>Agency comment:</u> "...there is direct evidence (measured residues) that endosulfan bioaccumulates in terrestrial systems and indirect evidence (modeling) that endosulfan has a significant potential to biomagnify in certain terrestrial food webs. Monitoring data and incident reports confirm that endosulfan is moving through aquatic and terrestrial food chains and that its use has resulted in adverse effects on the environment adjacent to and distant from it registered use sites."

<u>MANA response</u>: MANA disagrees that adverse effects are seen distant from sites where it is used. There is no evidence to support that statement. If the tentative results of limited biotic sampling (pg g^{-1} to ng g^{-1} concentrations in lipids) and bioaccumulation modeling (BMF 2.5 to 28) are evaluated, residue concentrations are below those of concern (MRID 46734301). Concentrations in water at the pg L⁻¹ to the low ng L⁻¹ level and in air or precipitation at pg m⁻³ to ng m⁻³ or pg L⁻¹ to low ng L⁻¹ levels are also much lower than any effects levels and should be assessed from a risk perspective.

Appendix

Page 1

2. NEW DATA ON BIOACCUMULATION

<u>Agency comment</u>: "The purpose of this review is to indicate how the Agency's understanding of the bioaccumulation potential of endosulfan (and sulfate metabolite) might change as a result of additional information being considered since the publication of EPA's 2002 ERA for endosulfan. This review is considered preliminary for two reasons. First, it is not intended to be comprehensive. Specifically, the literature review of empirical bioaccumulation studies focused on controlled experiments of endosulfan bioconcentration or bioaccumulation rather than uncontrolled field studies on the distribution of endosulfan in various environmental compartments. The scope was constrained ... primarily because of practical limitations (time constraints) and also the expectation that biomagnification of endosulfan (and degradates) in aquatic food webs would not likely be a major factor given its moderate hydrophobicity (log K_{ow} 3-4.5)... Second, the available data were not subjected to formal data evaluation procedures (e.g., Data Evaluation Records), again, due to time and resource constraints."

<u>MANA response</u>: The literature reviewed is stated to be of empirical bioaccumulation studies, but laboratory studies on bioconcentration and studies on bioaccumulation are presented. A clearer distinction should be made between bioconcentration and

bioaccumulation. Table 2-2 is labeled as containing information on bioaccumulation, but also contains data from bioconcentration studies as well, such as DeLorenzo *et al.* (2002). Available data were not subjected to formal data evaluation procedures (e.g., Data Evaluation Records), again, assumed due to time and resource constraints. Studies do not appear to satisfy the Agency's acceptability criteria. This can be misleading and confusing to a registrant when the Agency does not evaluate the acceptability of studies, whether registrant generated or from the open literature. Hence, one does not know: 1) which studies the Agency accepts, or 2) if the assessment will change once the studies are formally reviewed. Some previously cited studies could be dismissed resulting in a change of the assessment. MANA requests that any studies cited should be evaluated for its quality and integrity prior to using them in an assessment, preliminary or otherwise as it was done for the *Environmental Fate and Ecological Risk Assessment for the Reregistration Eligibility Decision on Endosulfan*.

The BCF of "endosulfan" in fish, as reported in the studies cited, spanned a 600 fold range from approximately 20 to 11,600 (L kg⁻¹ wet wt.). However, the measured analytical target varies between studies (endosulfan, alpha + beta, alpha + beta + sulfate) making comparisons impossible. MANA recommends that BCFs should be developed, at the very least, based on α -endosulfan and β -endosulfan.

Page 2

2.1 Findings from Empirical Bioaccumulation Studies

2.1.1. Bioconcentration/Bioaccumulation by Fish

<u>Agency comment</u>: "Bioconcentration data were identified and reviewed for seven species of fish... The reported BCF values for fish ranged from approximately 20 to 11,600 (L/kg wet wt.)... An evaluation of the fish BCF data quality indicates most of the BCF values have significant limitations because none of the BCF studies satisfied all three screening criteria (documentation of steady state conditions, measurement and stability of exposure concentrations, and quantification of parent and metabolite compounds). Based on these screening criteria, BCF values for fish from the highest quality studies appear to be in the 1000 to 3000 range..."

<u>MANA response</u>: MANA agrees that most of the BCF values have significant limitations because none of the studies satisfy the requirements for a bioconcentration study. Using all of this data may lead to supposition and biased conclusions based on inaccuracies (i.e., the absence of necessary information as well as the presence of incorrect information). Formal data evaluation is paramount and should be done first in order to prevent the perpetuation and citation of invalid studies in EPA's ecological risk assessments.

BCF values for fish from the highest quality studies, which appear to be in the 1,000 to 3,000 range, are probably the most reliable estimates. With the reportedly rapid

depuration as shown in studies conducted with many different species, the probability of bioaccumulation in higher trophic levels or food chain biomagnification appears to be very low.

2.1.2 Bioconcentration/Bioaccumulation by Invertebrates

<u>Agency comment</u>: "Bioconcentration studies with aquatic invertebrates were available for five species of invertebrates... Based on the studies presented in Table 2-1, the bioconcentration of endosulfan in aquatic invertebrates appears to be lower than those reported for fish, ranging from about 20 to 600 (L/kg w.w.)...

Bioaccumulation studies (i.e., those that included exposure to multiple uptake routes) were available for three invertebrates...

Bioaccumulation factors (Table 2-2) for the eastern oyster and D. magna for total endosulfan are approximately 600. In a short-term study by DeLorenzo et al (2002), uptake of endosulfan from food (contaminated algae) by D. magna was documented as negligible compared to uptake from the water column."

<u>MANA response</u>: Studies of bioconcentration and bioaccumulation with aquatic invertebrates do not appear to have been scrutinized with the same rigor as the fish studies. However, MANA agrees that bioconcentration and bioaccumulation in invertebrates is much less than in fish (BAF \leq 600) based on the available data.

Page 6

<u>MANA response</u>: In Table 2.2, it is not clear why DeLorenzo *et al.* (2002) was labeled as a microcosm study. It was in fact a bench-scale bioaccumulation study.

2.2 Findings From Bioaccumulation Modeling

2.2.1 Bioaccumulation in Aquatic Organisms

<u>Agency comment</u>: "A preliminary application of an aquatic food web bioaccumulation model (Arnot and Gobas, 2004) was used to explore several assessment questions related to the bioaccumulation of endosulfan by aquatic organisms."

<u>MANA comment</u>: Food web bioaccumulation models are relatively new to pesticide registration and certainly new to this assessment. However, it is unclear if the model attempting to represent endosulfan I and II ($\alpha \& \beta$ isomers) or a fictitious chemical consisting of a mix of properties reminiscent of endosulfan I and II. MANA is deeply concerned by the manner that the Agency is inconsistently intermixes parameters for endosulfan and endosulfan sulfate. Even though endosulfan sulfate is one of the metabolic and degradation products of endosulfan, both are separate chemicals with

different physical and biological properties. Applying the properties of one upon the other introduces a bias to the predictions. Biases with regard to properties such as toxicity are small since the values are reasonably similar. However, the free interchange or pooling for other parameters can be quite large. Other values such as degradation metabolism rates can result in high levels of bias resulting in poor precision. Hence, in the interest of developing accurate projections, it is recommended that these two separate chemicals be treated as two separate chemicals.

Page 7

Model Inputs and Assumptions

Food Web Structure

<u>Agency comment</u>: "A simple aquatic food web was assumed consisting of phytoplankton, zooplankton, filter feeding invertebrates, benthic feeding invertebrates, small and mediumsize forage fish and piscivorous fish. Feeding preferences are defined in Table 9 of Attachment B and basically consist of higher trophic level organisms consuming various fractions of organisms at lower trophic levels based on typical feeding ecology for organism groups."

<u>MANA response</u>: Comments here are related to the Appendix and Attachment B. Two assumptions in the model are in contradiction with known observations. First, the model assumes zooplankton uptake through residues in phytoplankton. DeLorenzo *et al.* (2002) contradicts this assumption. Uptake of endosulfan from contaminated algae by *D. magna* is negligible compared to uptake from the water column. This is consistent considering the volumes of exposure and relative partition properties of an algal biomass verses water. Second, the assumed diet for mallard duck (34% phytoplankton, 33% zooplankton and 33% benthic invertebrates) is not consistent with the life history for this species. Mallards are dabblers and not filter feeders. Hence, they cannot feed on materials they cannot see. According to USEPA (1993), they eat plants, seeds, and invertebrates.

Exposure Concentrations

<u>Agency comment</u>: "Endosulfan concentrations in water were assumed to range from 0.1-5 ppb (total chemical) based on 60-d average concentrations predicted from PRZM/EXAMS for different crop exposure scenarios (USEPA, 2002). Freely dissolved concentrations in pore water were assumed equivalent to overlying water which is supported by subsequent PRZM/EXAMS modeling of pore water concentrations shown in Table 4-2."

<u>MANA response</u>: Bioconcentration and bioaccumulation factors are, by definition, the ratio of body burden in a target receptor to exposure concentration (in water or ingestate). It is by application independent of the exposure concentration. Therefore, setting the exposure concentration as a uniform independent variable within the foodweb model negates this property while adding irrelevant uncertainty. If the BCF or BAF does change

with concentration, then it must be clearly indicated that the application of these ratios are concentration-specific and therefore cannot be used *per se* in predicting target receptor body burdens. Future applications should set the exposure concentrations as a determinant value or, better still, should be examined over a range of concentrations to determine whether the assumption of water concentration independence is satisfied.

Another concern with the bioaccumulation model is the dichotomy in the parameterization of PRZM/EXAMS and the bioconcentration model. PRZM/EXAMS developed concentrations for a specific pond referred to as "EPA Pond". This is a small local waterbody. The bioconcentration model was parameterized predominantly based on the parameters purported by Arnot and Gobas (2004). These parameters were not intended to simulate a water body akin to EPA Pond, but rather were specifically developed to simulate the Great Lakes: a water body whose scale dictates very different physical and chemical properties. Likewise, the parameters derived from USGS' NAWQA was nonspecific to this type of waterbody used for the assumptions and the defaults for the National Ambient Water Quality Assessment.

The data in Table 4-2 contradicts the statement above that endosulfan concentrations in pore water and overlying water are equivalent. The 60d concentrations in pore water are approximately 60% of surface water. It appears that the Agency is improperly using surface water as being synonymous with overlying water.

In the sensitivity analysis presented in Attachment B, it is reported that bioaccumulation predictions are sensitive to log K_{ow} and water concentration. Since the bioaccumulation model is dependent to a large extent on PRZM/EXAMS output, the issues associated with the assumptions made in PRZM/EXAMS and the resulting EECs are relevant. This is addressed in the comments on Section 4.

Chemical Properties

<u>Agency comments</u>: "The log K_{ow} of endosulfan was assumed to range between 3.55 and 4.78 based on reported data for α and β -endosulfan (Table 11 of Attachment B). A mean K_{oc} of 13600 was used (range: 10000-16000) based on measured data (Table 10 of Attachment B). Chemical metabolic rate by biota was set to zero. Although endosulfan can be metabolized to endosulfan sulfate by biota, available data indicates this degradate is approximately equal in toxicity to the parent compounds (α and β endosulfan). Thus, the assumption of chemical metabolic rate of zero is considered reasonable."

<u>MANA response</u>: K_{ow} values obtained via Sangster Research Laboratory's online model present a wide range of values for α (3.55-4.74) and β (3.62-4.78). Measured K_{ow} values are available for both endosulfan isomers as well as endosulfan sulfate. The use of QSAR data in this situation is inappropriate and needlessly increased uncertainty since observed values are readily available. We suggest the model be modified to use available empirical results. This will have significant effects on the prediction of the BCF as well as

the water concentrations that were erroneously used as independent distribution for the derivation of the BCF distribution.

Although the sulfate is of approximately equal toxicity, it is not the only degradate. The chemical metabolic rate by biota should not be set to zero. This resulted in an over prediction of the expected body burdens. It has been demonstrated that metabolism occurs by oxidation and hydrolysis to the sulfate, diol, hydroxyether, lactone, ether, hydroxy endosulfan carboxylic acid, in many species from bacteria to mammals. In higher animals, the principal metabolite is the non-toxic endosulfan diol and not equitable endosulfan sulfate.

MANA is very concerned that the bioaccumulation model assumes no metabolism. This highly significant assumption was predicated on the basis that endosulfan is metabolized to endosulfan sulfate and that this is irrelevant because the toxicity of endosulfan sulfate is the same as endosulfan. This assumption fails to take into account two important facts. First, endosulfan sulfate is not the only metabolite of endosulfan. The other major metabolite, the desulfonated endosulfan diol, has shown by far lower toxicity than endosulfan or endosulfan sulfate. Furthermore, while endosulfan sulfate is a metabolite of endosulfan sulfate is a so subject to desulfonation that, while reportedly slower than the desulfonation of endosulfan I, it is significant and will effect the equilibrium concentration of endosulfan I and II within the target organisms. Therefore, a realistic consideration for *in vivo* metabolism in future iterations for this model should be applied.

The cited BCF value for yellow tetra is very high compared to values cited for other species of fish (11.583 for yellow tetra vs. maximum value of ~3.000 in other species Previous studies show a relatively rapid depuration for fish, but EPA combined). dismisses data due to two studies that show steady state accumulation, which took longer to achieve than expected based upon a 2-6 day half life. This fact was dismissed with an unsupported assumption that elimination does not follow first order kinetics. The slow assumption of equilibrium may just as likely be the result of absorption not following first order kinetics. This latter condition is more likely to be true since endosulfan is absorbed through passive absorption, and will be subject to competitive lipophilic partition between organic compartments outside of the receptor organism (dissolved carbon, suspended carbon, associated organisms, etc.), as well as inside the organism. These various lipophilic compartments with their various affinities and capacities would be the most likely factors that would result in a lack of consistency in the concentration verses rate relationship. Instead of eliminating aberrant data, a ratio-based BCF was included (5,670). Although lower than the original value, it still skews BCF values. However, low "suspect" data were eliminated from EFED's evaluation.

Both fresh- and salt-water species were analyzed without due attention to possible differing degradation in various settings. The model should have been made specific for one or the other situations.

One would think that K_{oc} should have a more prominent role in the model since K_{oc} is directly related to K_{ow} . The K_{oc} for endosulfan is relatively high and partitioning to

soil/sediment is significant. Bioavailability of the adsorbed fraction would appear to be low if one considers the results of the invertebrate bioaccumulation studies in Table 2.2 (BSAF = 0.059, BAF ranged 16.8 to 656).

<u>Agency comment</u>: "The Arnot and Gobas model was run using a Microsoft® Excel spreadsheet and Monte Carlo simulations (10,000 trials of randomly selected parameters) using Crystal Ball 2000. Assumptions regarding distribution types and variance parameters are provided in Attachment B."

<u>MANA response</u>: The sensitivity analysis indicates the greatest sensitivity to estimates for K_{ow} and aqueous concentration. These values however are not independent. Variability in the K_{ow} in PRZM-EXAMS must be correlated with K_{ow} in the bioconcentration model. Predictions are artificially skewed and the variability inflated since the models are making predictions based on two very different simulation assumptions. This also holds for TOC and any other parameter that the two models share in common. The sensitivity analysis indicates the second greatest sensitivity to estimates for aqueous concentration. It should be pointed out again that both the BCF and BAF are supposed to be concentration-independent coefficients. Taking the ratio of an independently variable body burden over an independently variable water concentration will result in a meaningless distribution. A specific body burden is projected for a specific aqueous concentration. Therefore must be correlated 1:1 otherwise the BCF/BAFs cannot be assumed to be concentration-independent and must be qualified or quantified as a non-linear relation.

Elsewhere, the bioaccumulation/bioconcentration model does not account for other correlations between variables, but rather treats them all as independent. The failure to account for correlation between variable parameters in the Monte Carlo will result in an artificial skew of the distribution and a significant inflation in the variability (i.e. erroneously high 95 percentile predictions). The majority of the parameters used in the bioaccumulation/bioconcentration assessment was entered as structured distributions; specifically log transformed normal. This was not justified in either the Agency's analysis or the reported data sources. It is improper to assume a distribution for the values without a justification for that assumption. There was no test as to whether the data actually fit a normal distribution, fit some other form of distribution, or would be best represented as a bound (uniform) or empirical (data set) distribution. This introduces a great deal of unpredictable and unaccounted-for variability in the assessment.

Page 8

Model Output: Biomagnification

<u>Agency comment</u>: "...it appears that biomagnification of endosulfan is not significant, as the calculated biomagnification factors (BMF) are near or below unity. Predicted BMF values near or below unity also occur when comparing lipid-normalized concentrations in tissue determined at higher percentiles of the distribution (e.g., 75th and 90th percentiles, lipid normalized data not shown)." and "...the contribution of the diet to chemical

accumulation is minimal, which is consistent with the moderate hydrophobicity of endosulfan."

<u>MANA response</u>: Although we believe that the estimated exposure concentrations are unrealistic, it is of little consequence in terms of the outcome of the biomagnification modeling exercise. Empirical observations substantiate the fact that biomagnification of endosulfan is relatively low, food chain biomagnification appears insignificant, and therefore endosulfan is of no concern to the environment.

Page 9

2.2.2 Bioaccumulation in Terrestrial Organisms

<u>Agency comment</u>: "...Kelly et al. (2007) indicate that slowly-metabolized organic chemicals with relatively low to moderate K_{ow} values (i.e., log K_{ow} between 2-5) and high K_{OA} values (i.e., log $K_{OA} > 6$) have the potential to biomagnify in terrestrial and marine mammal food webs but not purely aquatic food webs. In their model, the conceptual basis for biomagnification of this group of compounds by terrestrial organisms relates largely to the greater ability of terrestrial organisms to assimilate food from their diet and their slower ability to eliminate these chemicals through respiratory processes relative to aquatic organisms."

<u>MANA response</u>: The somewhat arbitrary terms of "poorly metabolized" and "slowly metabolized" need to be defined. A distinction should be made between those chemicals that are "poorly or slowly metabolized" and are retained by the organism, and those chemicals which are not retained. The other routes of elimination that are relevant to endosulfan (e.g. urine, feces) appear to be ignored. In the case of endosulfan, it has been demonstrated in several mammalian species that metabolism occurs by oxidation and hydrolysis to the sulfate, diol, hydroxyether, lactone, ether, hydroxy endosulfan carboxylic acid. Parent material and metabolites are excreted relatively rapidly in the feces and urine. For male and female rats this is biphasic, with an earlier half life of 6 to 14 hour and a later half life of 33 to 67.5 hour (WHO 1999). Thus, endosulfan should not be included in this "*group of compounds*".

The Kelly et al. (2007) paper states "... less hydrophobic compounds ($K_{OW} < 10^5$) such as ... and endosulfans ($K_{ow} = 10^{3.7}$) did not biomagnify in the piscivorous food web, they showed a high degree of biomagnification in the lichen -caribou - wolf food chain and in air-breathing organisms of the marine mammalian food web (Fig. 1 and fig. S4, D to F)". The supplement to the Kelly paper states "...endosulfans ($K_{ow} = 10^{3.7}$) did not biomagnify in the piscivorous food web, they showed a high degree of biomagnification in the lichen-caribou-wolf food chain and in air-breathing organisms of the marine mammalian food web (Fig. 1 and fig. S4, D to F)". However, an examination of the figures, either in the original paper, or in the supplement, reveals that there is no mention of endosulfan in figures 1 or S4 D to F. Endosulfan is not represented. It appears that insufficient data for endosulfan are represented in the conclusions of the Kelly *et al.* (2007) paper.

Page 10

<u>Agency comment</u>: "....BMFs would be about 7 for male beluga and about 3 for female beluga. For ringed seal, in the 1 to 2 range for female and males, respectively" and "Given the limited amount of endosulfan data available from this study and uncertainties associated with the actual diets of these species, these BMF values are considered exploratory and should be viewed with caution."

<u>MANA response</u>: MANA agrees that the BMFs are "exploratory". The extremely limited data set for endosulfan precludes any definitive statement concerning the biomagnification of endosulfan in arctic food webs.

Table 2.8

<u>MANA response:</u> It is not clear what "N" signifies in Table 2.8. The supplement to the Kelly et al. (2007) paper indicates that tissues and organs of harvested common eider ducks, beluga whales, and ringed seals were collected, but there is no indication as to how many individual animals were sampled. The N given in their Tables (and Table 2.8) could very well be samples from one animal or samples from multiple animals. Without contacting the authors, we simply do not know the nature of the samples. Also there are results given as mean values, but no confidence intervals. The standard deviation (SD) for lichen, sediment, and salmon is not given. The 95% CI's that are given are wide, based on few samples and/or highly variable results. It is apparent that the sampling plan that was used for this study is not sufficient to characterize endosulfan residues in the Arctic ecosystem.

Page 11

2.3 Conclusions from Endosulfan Bioaccumulation Assessment

<u>Agency comment</u>: "Bioaccumulation modeling studies published in the literature indicate that biomagnification of endosulfan by terrestrial (air-respiring) organisms is a concern, with predicted BMF values ranging from 2.5 to 28 for herbivorous and carnivorous wildlife, respectively. "

<u>MANA response</u>: MANA respectfully disagrees with this interpretation which is based on sparse and highly variable data. EFED comes to this conclusion despite the statement made in section 2.2.2 that BMF values are considered exploratory and should be viewed with caution (page 12). There is little that can be deducted from the information with any reasonable level of certainty. The Agency appears to agree by stating in the last bullet point of Section 2.3 –

<u>Agency comment (Sect.2.3)</u>: "Measured data on endosulfan in marine mammalian food webs considered in this assessment appear limited for evaluating biomagnification, and more data specific to endosulfan should be evaluated for confirming model projections of biomagnification in terrestrial organisms."

<u>MANA response</u>: MANA agrees that data specific to biomagnification in marine mammalian food webs is limited. However, much can be predicted by utilizing existing metabolism and pharmacokinetic studies. They should have been considered in the analysis. Studies have demonstrated that endosulfan is rapidly eliminated from animal tissues. Based on metabolism (MRID 00004257) and residue studies (cow - MRID 44082703; and chicken - MRID 44099102), endosulfan is excreted fairly rapidly in urine and feces, and would not be expected to be retained in animals. The half-life has been determined to be approximately 7 days in female rats (Dorough et al. 1978). Half-lives between 1.1 and 3.1 days were observed for organs and tissues of goats (Indraningsih et al. 1993). The half-life in rabbits has been determined to be approximately 6 hours for beta-endosulfan and 235 hours for alpha-endosulfan (Gupta and Ehrnebo, 1978). The evidence indicates that the elimination of endosulfan and its metabolites after oral exposure is fairly rapid and mainly through the feces.

3. NEW DATA ON ECOLOGICAL EFFECTS

3.2 Aquatic Organisms: Sediment Exposure

Page 15

<u>Agency comment</u>: "Based on the pore water concentrations from the 10-d sediment exposures presented in Table 3-3, it appears that the freshwater midge, Chironomus tentans, is about a factor of 10 more sensitive to endosulfan sulfate compared to the estuarine amphipod, Leptocheirus plumulosus. Because the effects of endosulfan sulfate on amphipod growth were not measured in the 10-d study, L. plumulosus may be more sensitive to endosulfan sulfate compared to C. tentans."

<u>MANA response</u>: The hypothesis that *L. plumulosus* (MRID 46929001) may be more sensitive to endosulfan sulfate compared to *C. tentans* (MRID 46382605) is not supported by the available data. The Agency's comparison of the two studies is invalid as it is comparing different endpoints, growth (*C. tentans*) versus survival (*L. plumulosus*). Growth was not measured in the 10 day study with *L. plumulosus*, but it was measured in a 28 day study. The Agency's estimate of the 28 day NOAEC for growth in the estuarine amphipod, *L. plumulosus* (based on MRID 46929001) is 1.58 µg/L in pore water, whereas the 10 day NOAEC for growth in the midge, *C. tentans* (MRID 46382605) is 2.7 µg/L (within a factor of <2). The results based on bulk sediment concentrations are nearly the same, 0.48 mg kg⁻¹ versus 0.56 mg kg⁻¹ for the 28 day amphipod and 10 day midge NOAEC's, respectively. Growth of the amphipod would likely be affected to a larger extent in a 28 day study as compared to a 10 day exposure. Therefore, it is unlikely that the amphipod is more sensitive to endosulfan than the midge.

4. NEW INFORMATION ON AQUATIC EXPOSURE

Page 16

<u>Agency comment</u>: "...EFED has subsequently revised exposure modeling to include the racemic mixture of parent compounds and their primary degradate, endosulfan sulfate, all of which have similar toxicities."

<u>MANA response</u>: PRZM-EXAMS projections were determined for total endosulfan. There is no such chemical. The α - and β -isomers, while share the same formula, differ significantly in a number of environment aspects, particularly that related to multimedia persistence. Endosulfan sulfate is a different chemical in view of its properties and environmental behavior. As such they should be treated that way.

<u>Agency comment</u>: "A summary of the chemical-specific model inputs used in this assessment are provided in Table 4-1."

<u>MANA response</u>: Inclusion of the endosulfan sulfate appears to have been accomplished by selective use of input parameters for each isomer or total endosulfan as shown in Table 4.1 of the document. The only parameter that includes the sulfate is the aerobic soil metabolism half life, which is for total endosulfan (MRID 43812801). In that case an upper 90% CI of the mean half-life for total endosulfan ($\alpha \& \beta$ isomers and the sulfate) was used ($t_{1/2}$ =1335.6 days). This is a very conservative assumption as the mean half-life is 797.8 days.

Water solubility data used is for the α isomer (530 µg/L) as reported in Montgomery (1993), rather than 330 µg/L from the product chemistry submission (MRID 41421502), which is approximately the same as the β isomer. Endosulfan sulfate solubility is reported to be 117 µg/L.

The data used for the aerobic soil metabolism half-life calculation should be modified to reflect new data for endosulfan sulfate (MRID 46119101, amended by MRID 46119105). In the new study, the DT_{50} of endosulfan sulfate ranged from 117 to 412 days, with a mean of 200.2 and upper 90% CI of 316.6 days.

The data used for the aerobic aquatic metabolism half-life is defaulted to 2671.2 days or twice the aerobic soil metabolism half life upper 90% CI. The application of a 2-fold multiple upon the above-mentioned soil half life to predict the aerobic half life does not represent a doubling of the predictive value. This is because the variance in the distribution does not scale directly with the magnitude of the values. Hence the predicted value, regardless of other factors related to its validity, is not a 90 percent upper confidence limit, but rather something very much in excess of 90 percent confidence. This is an excessively conservative value.

Previously submitted studies (MRID 44917801 and MRID 44917802), which were classified as supplemental, resulted in a half life for total endosulfan ranging from 18 to 21 days. An additional aerobic aquatic metabolism study is available (MRID 46119102) that resulted in DT_{50} values of 3.4 and 35.1 days in two sediment systems (Krempe & Ohlau). A conservative estimate to use would therefore be 35.1 days.

The data used for the anaerobic aquatic metabolism half life is defaulted to 382 days or twice the upper 90% CI of the half-life from the anaerobic soil study (MRID 41412904). For the same reasons given above for the aerobic soil metabolism half life, this is >90% CI and overly conservative. Guerin (1999) demonstrated that more than 85% of α -endosulfan degraded over 30 days in anaerobic systems that were buffered between pH 6.8 and 7.2. A DT₅₀ or t_{1/2} was not calculated and raw data is not provided in the report. However, it seems reasonable to conclude that the anaerobic aquatic metabolism half life is \leq 30 days and that 30 days is a more reasonable, yet still a very conservative assumption instead the one used by EFED (382 days).

The K_{oc} chosen is for α -endosulfan (10600 L kg⁻¹), rather than a weighted average of the α , β , and sulfate based on typical field residues ratios (10660 L kg⁻¹). However, the difference is minimal and is probably inconsequential to the outcome.

This assessment does not reflect the new label requirements of a 30 foot vegetative buffer, 100 foot spray buffer for ground applications, or a 300 foot buffer for aerial applications. The use of the default value of 5% for spray drift in the PRZM/EXAMS simulation is extremely conservative and unrealistic given that the Spray Drift Task Force (SDTF 1997) estimate of typical spray drift is 2% (without a buffer). SDTF has determined that *"The amount of material that deposits on the ground decreases rapidly with distance and is already approaching zero at 250 feet downwind"*. A conservative maximum estimate of spray drift for an aerial application to tomatoes (with buffer) using AgDrift was previously determined to be 0.83% (MRID 44953103).

In the USDA NRCS publication *Conservation Buffers to Reduce Pesticide Losses* (USDA 2000), it is stated –

"All buffers can provide some protection of waterbodies if they are sited between pesticide-treated fields and water. Physical separation of spraying operations and water reduces the chances for direct application to water ... It can also reduce spray drift into water."

The data from several studies cited in the USDA document demonstrate the effectiveness of vegetative buffer strips in removing pesticides from runoff. For chemicals with a high affinity to adsorb to soil particles (i.e., high K_{oc}), removal ranged from 57 to 100% for chemicals with K_{oc} ranging from 1100 to 8000 (Boyd, *et al.*, 1999; Cole, *et al.*, 1997; Patty, *et al.*, 1997; Rhode, *et al.*, 1980). Boyd *et. al.* (1999) found that sediment deposition in vegetative filter strips was equally, if not more, important than infiltration for mass removal. The primary route of removal through buffer strips is through removal of the sediment from the runoff. The weighted average K_{oc} of endosulfan is 10660. Endosulfan is rapidly

removed from the water column by adsorption to soil/sediment particles. The current label requirements for a 300 foot spray buffer and a 30 foot vegetative buffer will reduce off target movement of endosulfan substantially through reduced spray drift and reduced sediment load. Not considering these mitigation steps in the PRZM/EXAMS modeling is adding a bias towards extreme conservatism that leads to misleading conclusions as to the risk to aquatic systems.

The document does not provide a comprehensive list of the PRZM/EXAMS input parameters. The document states that the appropriate chemical-specific PRZM input parameters were selected in accordance with EFED guidance, some being similar to those used in 2002, but no new environmental fate data was incorporated.

There is a lack of transparency in regard to the parameter values that were used in the PRZM/EXAMS model runs, particularly the runoff curve numbers (CN) or <u>PR</u>oportion of sorbed chemical delivered to <u>BEN</u>thic zone (PRBEN) values. The models have been shown to be sensitive to these parameters (MRID 44953102). A full and transparent accounting of the values that were used is necessary in order for MANA to verify the inputs and evaluate the model results.

PRZM/EXAMS modeling should be reevaluated based on the current label requirements. Endosulfan applications for strawberries and tomatoes as reflected on the current label for Thionex 3EC are:

	Label-Specified Application			
Scenario	Rate per	Number of	Maximum	
	Application	Applications	per season	
	(lb a.i./acre)	per Year	(lb a.i./acre)	
Strawberries	1	2	2	
Tomatoes	0.5 to 1	2 to 4	2	

Typical endosulfan applications for strawberries and tomatoes are:

	Realistic Application		
Scenario	Rate per	Number of	
	Application	Applications	
	(lb a.i./acre)	per Year	
Strawberries ^a	1	1	
Tomatoes ^b	0.75	1	

^a According to Quantitative Use Assessment (QUA) report by Steve Nako, Biological Evaluation and Analysis Division (BEAD), EPA QUA, Dated April 22, 1999, revised by David Donaldson September 10, 2000. These estimates generally agree with marketing research data from Doane and Mike Buckley and Associates.

^b Mike Buckley and Associates (based on 1997 Marketing Research Data) as presented in MRID 44953103.

Page 18

Table 4.2

<u>MANA response</u>: In Table 4.2, the EEC's for pore water from PRZM/EXAMS are inconsistent with empirical data, particularly for estuarine systems. For the tomato scenario, the 21 day and 60 day pore water concentrations (4.4 and 4.3 μ g/L, respectively) are essentially unchanged from the initial peak value (4.5 μ g/L). In the 28 day estuarine sediment chronic toxicity study with the estuarine amphipod, *L. plumulosus* (MRID 46929001), the pore water concentrations decreased approximately 75% in 28 days. PRZM/EXAMS does not appear to adequately model estuarine sediment pore water concentrations and the RQ values are misleading. When the EEC values are adjusted for the apparent decrease in pore water concentration, the RQ value decreases to 0.9 for Florida tomatoes and 0.5 for California strawberries, both below the LOC.

5. NEW INFORMATION ON MONITORING AND LONG-RANGE TRANSPORT

Page 19

Endosulfan In Surface Water

<u>MANA response</u>: MANA disagrees with the tone that is set in this section. There appears to be a bias that, prior to an appropriate risk based evaluation of the data, the appearance of endosulfan in any media is harmful.

<u>Agency comment</u>: "Since 1991, the South Florida Water Management District's (SFWMD) non-target quarterly water quality monitoring program has been analyzing a number of pesticides including endosulfan at 34 sites (Figure 5-1). Endosulfan and endosulfan sulfate were detected in surface waters and benthic sediments at several locations in the south Miami-Dade County farming area. Endosulfan has been measured at concentrations exceeding the chronic surface water quality standard of 0.056 μ g/L (Figure 5-2) for a number of years (assuming endosulfan sulfate has similar toxicity to parent endosulfan).

<u>MANA response</u>: MANA has accessed 34 *Pesticide Surface Water Quality Reports* at the SFWMD website:

http://my.sfwmd.gov/portal/page? pageid=2754,19862620& dad=portal& schema=PORTAL

The Agency has presented data from 21 of these reports as a bar chart in Figure 5.2. It appears that data for sampling periods where endosulfan was either (1) not detected, (2) detected, but less than the limit of quantitation (<LOQ), or (3) did not exceed Ambient Water Quality Criteria (AWQC), were omitted from the chart. Non-detects, samples

<LOQ, or below AWQC were reported by SFWMD at several sampling periods (e.g., August 1999, April 1999, August 2001, September 2002, March 2003, October 2003, July 2004, August 2005, May 2006). These omissions give the impression that the frequency of endosulfan detects, and the frequency of AWQC exceedance, is higher than the actual frequency. From the 34 reports spanning the timeframe of December 1998 to March 2007 it can be seen that there were 11 instances where the freshwater chronic criterion (0.056 μ g/L) is reported to have been exceeded and one where the acute criterion (0.22 μ g/L) is reported to have been exceeded. Most of these exceedances are related to one site, which is S178 with a very unique setting and history. As stated before, at S178 there were 63 surface water sampling events that resulted in 8 exceedances of Florida Water Quality Standard (0.056 ppb), 6 of them occurred during 1993 and 1996. Since then the frequency of endosulfan detects and its concentration have been significantly reduced. Therefore, it seems that the implemented product stewardship program (1998) and recent label mitigations (RED 2002) are effective.

The sampling within the SFWMD program is not frequent enough to be able to characterize long term chronic exposure of aquatic organisms to endosulfan. Therefore, comparison of the concentrations of endosulfan to chronic water quality criteria is inappropriate. It is more appropriate to compare to the maximum criteria concentration (0.22 μ g/L), in which case the criterion has been exceeded only once in the nearly ten years of SFWMD monitoring reports.

The reported endosulfan concentrations within the SFWMD program should be viewed with caution since the samples were unfiltered. This is important since endosulfan partitions to soil and sediment rapidly and analysis of unfiltered samples is not indicative of endosulfan in solution. In some cases the reported values exceed the laboratory derived solubility limit for endosulfan. Therefore the actual concentration of endosulfan in solution is most likely less than the values reported by SFWMD.

<u>Agency comment</u>: The University of South Carolina (USC) and the National Oceanic and Atmospheric Administration (NOAA) also conducted a monitoring study targeting areas where endosulfan was used (Delorenzo et al., 2001). The USC/NOAA monitoring data have been compared with data collected by the SFWMD; total toxic residues of endosulfan (alpha and beta endosulfan plus endosulfan sulfate) in both studies collected at similar locations and times are roughly equivalent (Table 5-1). These data suggest that in the vicinity of row crops where endosulfan is reportedly applied, endosulfan residues have been routinely detected in both the water column and benthic sediments. Additionally, the data indicate that total endosulfan residues have moved to areas distant from where it was initially applied and that the residues are sufficiently high, when compared to toxicity values of aquatic organisms to exceed the Office of Pesticide Programs' (OPP) acute and chronic risk levels of concern."

<u>MANA response</u>: Another study referenced in this section, DeLorenzo *et al.* (2001), is used to compare results with the SFWMD studies (Table 5.1), since the time of sampling and areas sampled were reported as similar. However, there were significant differences in the timing of sampling events that is not apparent in the table because the exact dates

for the SFWMD samples are not given. Another significant difference is that water samples taken in the DeLorenzo study were apparently filtered through a 90 mm glass fiber filter (Gelman GF/F) prior to analysis and are thus not comparable with the unfiltered results in the SFWMD monitoring studies. The effectiveness of this filtration step is unknown since pore size was not indicated.

The statement made on page 19 -

"...total toxic residues of endosulfan (alpha and beta endosulfan plus endosulfan sulfate) in both studies collected at similar locations and times are roughly equivalent (Table 5.1)"

is thus inaccurate. In addition, the use of the term "toxic residues" is an incorrect assumption in that toxicity has not been verified or tested with these samples. Table 5.1 suffers from the same bias as has been pointed out for Figure 5.2 in that it is selective in its presentation of data or presents inaccurate data. Comparison of these results with fish or invertebrate NOEC values to obtain risk quotients is not appropriate as exposure to particle bound endosulfan is likely very different from that in laboratory aquatic toxicity studies with endosulfan in solution.

It should be made clear that the agricultural area investigated in these accounts, which is near the Everglades in Florida, is very unique due to manmade channels and water diversions. It is not representative of the majority of agricultural settings. The sample location (SFWMD Site 178 and NOAA/USC Site C) highlighted in the Appendix is "located directly adjacent to a large agricultural field" on a Canal (C111), usually closed by a weir, which means that the water is being hold up and the sampling station reflect almost a "retention pond". This scenario reflects an unrealistic absolute worst case scenario that is not relevant to the majority of agricultural sites where endosulfan is used. Of all the 305 water samples analyzed in DeLorenzo *et al.* (2001), 11 (3.6%) exceeded the chronic AWQC of 0.056 ug/L and 9 (3%) exceeded OPP's LOC (RQ>1) based on an NOEC of 0.070 μ g/L. All of these exceedances occurred at one site, Site C (adjacent to the S178 structure). There were 28 samples taken at Site C.

Page 21

<u>Agency comment</u>: "Results of the field studies conducted during 2002 -2004 by Herman-Fetcho et al. (2005) and 1993 -1997 by Scott et al. (2002) also indicate the presence of endosulfan in surface water samples from southern Florida and Florida Bay. In a two year study, endosulfan was frequently detected in the South Florida canals and Biscayne Bay, with an average concentration of 11 ng/L (Herman-Fetcho et al., 2005). Endosulfan concentrations were higher near vegetable production areas where endosulfan is applied. The study also indicates that endosulfan has the highest hazard potential to aquatic organisms among the pesticides evaluated.

<u>MANA response</u>: In regard to the other referenced studies in the unique setting of South Florida, Harman-Fetcho *et al.* (2005) analyzed filtered samples and also made comparisons with the SFWMD monitoring studies, which as previously stated, were

unfiltered samples. Such comparisons, apparently cited as confirmation of, or concurrence with their results, are inappropriate given the different methodology used.

The results of this study indicate the presence of endosulfan at an average concentration <0.020 μ g/L which is below the OPP Level of Concern (RQ = 0.020/0.070 = 0.29) and less than the chronic AWQC (CCC) of 0.056 μ g/L in freshwater. The authors report a maximum concentration for total endosulfan of 0.098 μ g/L. This appears to be the sum of the highest reported values in the range of reported values for the two isomers and endosulfan sulfate from all 14 samples, not from one sample. The derivation of this value is suspect. The raw data are not presented in the report.

Reference is made to a study by Scott *et al.* (2002) that indicates endosulfan was found in water samples from South Florida and Florida Bay and the occasional exceedance of the chronic water quality criterion. It should be noted again that this investigation revolves around the unique agricultural practices and water management canal systems in southern Florida and is not relevant to other areas. The highest frequency of detects and the samples with the highest concentration of endosulfan were associated with canal site A3 (C-111; site S178) adjacent to a large agricultural field. The method of sample preparation (e.g., filtration) is not indicated in the paper, so it is not possible to know if the values given are water concentrations, or if a portion of the reported values was associated with suspended soils or sediments.

<u>Agency comment</u>: Scott et al. (2002) reported that endosulfan was detected at 100% of the sites sampled. Endosulfan residues in surface waters from irrigation canals and Florida Bay occasionally exceeded the chronic water quality criterion. While endosulfan concentrations at these sites did not result in any reported fish kills, residues exceeded concentrations that are known to cause chronic effects in copepods, clams, and oysters.

<u>MANA response</u>: The Agency fails to mention that, according to the authors, "*Chronic effects...could not be attributed to endosulfan exposure*". This selective and biased citing of the literature distorts the facts and should have no place in the risk assessment.

Page 24

<u>Agency comment</u>: "Endosulfan sulfate had the highest detection frequency at 17.2% and the 95th percentile concentration was 0.14 μ g/L compared to the detection frequencies of 5.2% to 5.4% and the 95th concentrations of 0.11 and 0.07 μ g/L for parent endosulfan and β -endosulfan, respectively."

<u>MANA response</u>: Citing this information seems to be intended to show that endosulfan is widespread and problematic in surface water in California, when in fact endosulfan sulfate was behind eight other pesticides with detection frequencies ranging from 18.8 to 57.2%. Citing only the upper 95th percentile concentration indicates a bias in reporting. It is a worst case, low probability occurrence. The CDPR document (CDPR 2000) also gives the 75th and 50th percentiles for endosulfan sulfate, parent endosulfan and beta endosulfan as 0.0658 & 0.025, 0.049 & 0.024, and 0.0377 & 0.023 µg/L, respectively. The 95th

percentile concentrations are equal to or twice the OPP LOC, but below the OPP LOC (RQ<1) at the other percentiles. It is worth noting that CDPR has not included endosulfan in any of the action groups that represent those compounds of most concern for surface water contamination.

<u>Agency comment</u>: "Furthermore, in 1998, Calleguas Creek in California and the Yakima River in Washington State were classified as impaired water bodies under the Section 303d of the Clean Water Act due to presence of endosulfan as well as other chemicals."

<u>MANA response</u>: The actual contribution of endosulfan to water quality impairment for Calleguas Creek is difficult to verify since this water body is impacted by a large number of other factors, including: algae, ammonia, boron, chlordane, chloride, chlorpyrifos, copper, dacthal, DDT, dieldrin, endosulfan, fecal coliform, hexachlorocyclohexane / HCH, mercury, nickel, nitrate, nitrite, nitrogen, organophosphorus pesticides, PCBs, sediment toxicity, sedimentation / siltation, selenium, sulfates, total dissolved solids, toxaphene, toxicity, trash, and zinc.

Likewise, the Agency notes that endosulfan was cited as a contributing factor in the Washington State 303d listing for the Yakima River, along with other chemicals and factors that contribute to water quality. The actual contribution of endosulfan to water quality impairment is difficult to verify since this water body appears to be impacted by a large number of factors, including: 4,4'-DDE, arsenic, DDT, dieldrin, dissolved oxygen, endosulfan, fecal coliform, instream flow, mercury, PCBs, pH, silver, temperature, and turbidity.

<u>Agency comment</u>: "Water samples from four temperate lakes in south-central Canada show the presence of α -and β -endosulfan (Muir et al., 2004). Mean concentration levels of α -endosulfan ranged from 28.5 – 1.3 pg L⁻¹, and those of β -endosulfan from 10.3 – 0.0 pg L⁻¹ in lakes Opeongo, Nipigon, Britt Brook, and Virgin pond. No agricultural area was within 31 miles (50 Km) of any of these lakes, suggesting that the presence of endosulfan resulted from atmospheric transportation and deposition. Monitoring and modeling results suggest that under the conditions prevailing in south-central Canada, endosulfan can potentially undergo regional-scale atmospheric transport and reach lakes outside endosulfan use areas."

"Recent monitoring data for endosulfan shows the presence of endosulfan in waters of isolated lakes in Ontario and New Brunswick (UNEP, 2002). Endosulfan, was detected in all lake trout collected from these isolated lakes; endosulfan tissue residues ranged from <0.1-0.8 ng g⁻¹ww. Endosulfan was higher in Labrador lakes. The results suggest the wide dispersal of endosulfan from areas of use to isolated lakes."

<u>MANA response</u>: As for the recent monitoring and determination of endosulfan residues in water at remote locations, distant transport raises some concern, but each case should be evaluated based on an evaluation of health risks and risk to the environment. The concentrations being reported are generally trace quantities and appear to be insignificant from a toxicological perspective. Water concentrations at the pg L⁻¹ level and tissue residues <0.1-0.8 ng g⁻¹ ww are clearly not of toxicological concern. Based on the

available bioaccumulation data and toxicological data that are available there are orders of magnitude differences between these levels and the no effect levels of the most sensitive receptors. Using the highest water concentration as reported by Muir *et al.* (2004) and the aquatic invertebrate NOEC of 70 ng L⁻¹, the RQ = 0.029/70 = 0.0004. The lake trout residue data from UNEP (2002) of 0.8 ng g⁻¹ (ww) is of no toxicological or ecological concern. No Observed Adverse Effects Levels in all aquatic, avian and mammalian tests performed to date are orders of magnitude above the low residue levels reported.

Page 24 - 25

Endosulfan In Atmosphere

Endosulfan In Precipitation

<u>MANA comment</u>: Agency accounts of concentrations from endosulfan in the atmosphere and precipitation are based on many studies. Detailed summary accounts of the analytical methods or circumstances by which the data were obtained are lacking. The citation, Harman-Fetcho *et al.* (2000), does not appear in the reference list, but is assumed to be:

Harman-Fetcho, J.A., L.L. McConnell, C.P. Rice, and J.E. Baker. 2000. Wet deposition and air-water gas exchange of currently used pesticides to a sub-estuary of the Chesapeake Bay. Environ. Sci. Technol., 34, 1462-1468.

We attempted to obtain the articles cited, but given the timeframe allotted for this response, have been unable to obtain all of the articles. A check on the available literature indicates that many of the analyses (not Harman-Fetcho *et al.*, 2000) are apparently by GC-ECD and thus analytical interference (e.g., co-elution of other analytes with endosulfan components) is a possible confounding factor (see MRID 46734301).

Endosulfan concentrations in the pg m⁻³ to low ng m⁻³ range in air and pg L⁻¹ to low ng L⁻¹ range in precipitation, when further diluted in receiving media, would be orders of magnitude from toxicity thresholds. Coupled with the relatively low bioaccumulation of endosulfan in aquatic and terrestrial systems the risk to ecological receptors appears low.

Page 27

Endosulfan In Airborne Particles

<u>Agency comment</u>: "Within the IADN project, endosulfan concentrations were also measured in airborne particulate (filter-retained) matter. Average concentration levels were approximately 7.5 pg·m-3 for α -endosulfan and 2.9 pg·m-3 for β -endosulfan from 1995 to 2000. Seasonal differences for particles were much less pronounced as compared with the gas-phase data."

<u>MANA response</u>: As indicated above for air and precipitation, analyses are apparently by GC-ECD and thus analytical interference (e.g., co-elution of other analytes with endosulfan components) is a possible confounding factor. Once again we note that concentrations of endosulfan on airborne particles are in the low pg m⁻³ level and must be considered a relatively low risk to ecological receptors.

<u>Agency comment</u>: "Endosulfan associated with airborne dust was also measured on a cotton farm in Australia during the growing season. Total endosulfan residues (α - + β - + - sulfate) in airborne dust ranged from 0.07 to 1.04 μ g·g⁻¹ [Leys et al. (1998)]."

<u>MANA response</u>: Citing measured concentrations of endosulfan on airborne dust on a cotton farm in Australia is irrelevant to use in the U.S. or to the aforementioned IADN data. The application methods utilized, rate of application, meteorological data and measures of off farm movement (if any), are necessary for this information to be useful. Relating the data in some way to exposure and effects is necessary to put this information into a risk assessment context.

Endosulfan In Sediment

<u>Agency comment</u>: "The presence of endosulfan in the sediments is well documented in the National Sediment Contaminant Point Source Inventory (NSI) databases... In the NSI data base, 199 detections for α -endosulfan, ranged from 0 to 11000 μ g·Kg⁻¹; 667 detections for β -endosulfan, ranged 0 to 67500 μ g·Kg⁻¹, and 195 detections for endosulfan sulfate ranged from 0.2 to 900 μ g·Kg⁻¹ (after culling data to eliminate dubious data, e.g. ND and < codes) in the sediments were reported between 1980 and 1999 (Figure 5-4)."

<u>MANA response</u>: MANA does not contest that endosulfan is found in some sediments. This is not unexpected based on the high K_{oc} and rapid partitioning to soil and sediment and the observed soil loss from agricultural practices. The Agency presents an incomplete account of this information by citing the number of detections, culling non-detects and < values, and not including the total number of analyses performed. This information is essential in order to put these results in context. There appears to be 41,613 samples in the database that have been analyzed for endosulfan. Of these, 1061 (0.025 of the total) had detectable levels of endosulfan.

<u>Agency comment</u>: "Seventy sediment samples were collected over a 10-county area in the agriculture dominated Central Valley of California, with most sampling sites located in irrigation canals and small creeks, to investigate the distribution of 26 pesticides including endosulfan (Weston et al., 2004). Total endosulfan concentrations in sediments ranged from 571 µg·Kg⁻¹ to <1.0 µg·Kg⁻¹ ... Endosulfan concentrations were below the acute toxicity of aquatic invertebrates in the majority of samples; however, the study suggests that endosulfan may have contributed to toxicity in the tailwater ponds or a few irrigation canals where concentrations exceeded several hundred µg·Kg⁻¹ . Endosulfan residues have been detected in several sites (Figure 5-4) in south Florida. The concentrations of endosulfan in sediment samples ranged from 100 µg·Kg⁻¹ to non-detect."

MANA response: The Agency omits considerable detail from the account of the Weston et al. (2004) study. First and foremost is that endosulfan was a relatively minor factor in the samples analyzed and in the sediment toxicity as compared to pyrethroids, which the authors found likely responsible for much of the toxicity in 17 of the 23 samples with toxicity. The range of values given for the endosulfan concentrations in sediments can give a false impression of the magnitude of sediment contamination. The high value (571 µg·Kg⁻¹) is actually the result for one sample taken at a tailwater pond. The mean endosulfan concentration of all sediment samples with results above the detection limit (1 ng g⁻¹) was 34 μ g Kg⁻¹. The mean endosulfan concentration with the tailwater site (LL) removed is 6.1 µg Kg⁻¹. Based on a mean organic carbon content of 1.16%, the average normalized sediment endosulfan concentration is 529 μ g Kg⁻¹ OC. Measured 10-day LC₅₀ values for Chironomus tentans, the most sensitive organism, were 0.96, 3.24, and 5.22 mg Kg⁻¹ of organic carbon (OC) for α -, β -, and endosulfan sulfate respectively. The acute restricted use LOC is minimally exceeded for α – endosulfan (RQ = 0.55) and β – endosulfan (RQ = 0.16), and not exceeded for endosulfan sulfate (RQ = 0.10). The chronic LOC has not been exceeded.

Data cited for South Florida appears to be misplaced here.

Page 28

Endosulfan in Mountainous Regions

Endosulfan in Arctic Areas

<u>MANA comment</u>: MANA recognizes that the appearance of a chemical in various media and at locations away from areas of use raises questions and concerns related to chemicals that are characterized as POPs under the Stockholm Convention. Endosulfan is not currently characterized as a POP as it does not meet all of the criteria for inclusion.

The ETF submitted a report to the Agency titled *Evaluation And Interpretation Of Environmental Data On Endosulfan In Arctic Regions* (MRID 46734301). That report summarized and interpreted environmental data on endosulfan in arctic regions. The primary objective was to assemble a broader basis for evaluation of behavior and exposure to endosulfan and consideration of the abiotic and biotic residues profile within an ecotoxicological and human health risk context. MANA encourages the Agency to review the report and consider it for the ongoing risk evaluation.

The conclusions of the report were – "Based on stable endosulfan levels in the environment, the virtual absence of trophic magnification and biomagnification in the food chain, a negligible ecological risk to marine mammals and a negligible human dietary risk, concerns of adverse effect to human health and the environment cannot be demonstrated that may suggest classification as a POP."

Page 37

6. ECOLOGICAL RISK CHARACTERIZATION

6.1 Risk Estimation

6.1.1 Post 2002 ERA Incident Data

<u>Agency comment</u>: "Since the 2002 RED chapter was issued where 91 incidents were reported, a total of 18 additional incidents have been reported (15 involving aquatic organisms and 3 involving terrestrial organisms) associated with the use of endosulfan. Specific details of the incidents are described in Table 6-1 and 6-2; 89% of the incidents were assigned a certainty index of "highly probable" to "probable" for endosulfan. Six of the incidents were the result of registered use, three were the result of misuse (intentional or accidental); it is unknown if the nine remaining incidents resulted from misuse or a registered use."

<u>MANA response</u>: This account of the EIIS data is misleading. The data in Table 6.1 indicate that only four of the purported eighteen additional incidents occurred since the 2002 RED was issued, one terrestrial (1012626-001) and three aquatic (1014189-001, 1014884-022, 1018075-001). Only one incident is known to be associated with the use of endosulfan (September 2002 in Riverside-CA, fish kill due to runoff from cotton field). Since 1996 out of the 18 reported incidents that were allegedly associated with the use of endosulfan (15 involving aquatic organisms and 3 involving terrestrial organisms), only 6 of the incidents were the result of registered use, 3 were the result of misuse (intentional or accidental); the cause of the nine remaining incidents is unknown. The implemented mitigation measures (2002 RED), which will be effective this year, will help to further reduce any potential incidents related to the use of endosulfan.

Page 42

6.1.2 Aquatic Organisms: Water Column Exposure

<u>Agency comment</u>: "Results from the aquatic exposure modeling of total endosulfan $(\alpha+\beta+sulfate)$ in surface water combined with the toxicity information for endosulfan indicate that freshwater and saltwater fish and invertebrates are potentially at risk from endosulfan application at the allowable maximum label rates."

<u>MANA response</u>: As stated previously, the modeling has used data for all forms of endosulfan selectively and combined into one model. This is inappropriate, as it assumes erroneously that the two isomers and the sulfate have the same behavior in the environment. Each entity has its own environmental fate characteristics and should be modeled separately and then assessed as a whole.

In addition, MANA believes that the PRZM/EXAMS modeling should incorporate the 300 foot spray buffer and the 30 foot vegetative buffer as on current product labels. Spray buffers reduce or eliminate spray drift to water bodies. Vegetative buffers affect a reduction of sediment loading to water bodies, particularly important for high K_{oc} chemicals, as indicated by USDA (2000). To not consider the impact of these mitigation measures is unwarranted.

<u>Agency comment</u>: "...PRZM/EXAMS modeling of the total endosulfan concentrations did result in modest increases in EEC values compared to the 2002 ERA. Specifically, the peak, 21-d and 56-d average EECs for endosulfan (α + β) increased by 21%, 41% and 39%, respectively, compared to the EECs for α + β endosulfan from the 2002 ecological risk assessment."

<u>MANA response</u>: These modest increases appear to be the result of modified data inputs to PRZM/EXAMS. Specifically the use of an aerobic soil metabolism DT_{50} for total endosulfan in order to incorporate endosulfan sulfate into the model. This is propagated further by doubling this value for input as an aerobic aquatic metabolism half-life. All other data input to PRZM/EXAMS are for the alpha and/or beta isomers. An aerobic aquatic metabolism study is available (MRID 46119102) that resulted in DT_{50} values of 3.4 and 35.1 days in two sediment systems (Krempe & Ohlau). A conservative estimate to use would therefore be 35.1 days.

MANA is re-evaluating the PRZM/EXAMS modeling scenario for endosulfan using new data and the current label recommendations for application rate and buffers. The appropriateness of various default assumptions is also being assessed. This effort could not be completed within the comment period allotted for this response.

Page 43

6.1.3 Aquatic Organisms: Sediment Exposure

<u>Agency comment</u>: "Results from the aquatic exposure modeling of total endosulfan $(\alpha+\beta+sulfate)$ in sediment pore water combined with the toxicity information for endosulfan indicate that freshwater and estuarine invertebrates are potentially at risk from endosulfan application at the allowable maximum label rates. Risk quotients (ratios of estimated exposure concentrations to the most sensitive toxicity endpoint) derived for predicted sediment pore water concentrations are provided in Table 6-5 for the Florida tomato and California strawberry crop scenarios. The calculated RQ values ranged from 1.6 to 2.8 for the California strawberry and Florida tomato crop scenarios, respectively for estuarine."

<u>MANA response</u>: As stated previously, the pore water concentrations predicted in PRZM/EXAMS are essentially unchanged from the initial peak value through to 60 days. This is unrealistic, particularly for estuarine sediments. In a 28 day laboratory sediment toxicity study of endosulfan sulfate to an estuarine amphipod (MRID 46382606), the pore water concentration declined by 75%. PRZM/EXAMS does not appear to be an adequate model to predict estuarine sediment pore water concentrations of endosulfan.

Exposure is expected to be less in estuarine sediments, so the RQ value is overly conservative. However, the magnitude of RQ values are such that exceedance of the LOC is relatively small. The lower application rates and buffers on the current label would be expected to reduce the exposure and RQs.

Page 44

6.1.4 Terrestrial Organisms: Piscivorous Wildlife

<u>Agency comment</u>: "Exposure concentrations in the diet of piscivorous wildlife were predicted using an aquatic food web bioaccumulation model... the acute LOC of 0.1 is exceeded ... all RQ values are less than 0.4 or less, indicating the magnitude of risk is relatively small..."

<u>MANA response</u>: Although MANA has several issues with the bioaccumulation modeling, it appears that piscivorous wildlife are at relatively low risk and therefore additional comment is unnecessary.

6.2 Risk Conclusions

<u>Agency comment</u>: "Risk quotient (RQ) predicted for aquatic organisms resulting from water column exposure to endosulfan are about 20% to 40% higher compared to the 2002 ERA. This increase reflects the addition of endosulfan sulfate to the exposure modeling and data indicating it is of similar toxicity to the parent isomers (α and β)."

<u>MANA response</u>: The modest increase in EEC and RQ values is expected based on the modeling scenario and parameter data selected by the Agency. However, the evidence that water and sediment concentrations do not remain elevated, due to volatilization, degradation, and adsorption to soil/sediment, does not appear to be adequately assessed.

Results from a farm pond study (MRID 41164101) have shown that the water concentration of total endosulfan in two ponds peaked in 6 to 7 days following the last of three applications (1 lb ai/a applied at approximately two week intervals) and declined thereafter. Sediment concentrations peaked in 6 to 12 days following the last application and declined thereafter, being below detection limits (5 μ g kg⁻¹) in an average of 18 weeks.

It is important to note that spray drift or vegetative buffers were not utilized in this farm pond study and thus this was a worst case scenario. All measures of ecosystem structure and function were indistinguishable from the baseline or reference ponds at the end of the study. The current label limits application to twice per year and requires buffers. Therefore, concentrations would be expected to be less, exposure less, and risk significantly mitigated.

REFERENCES

By Author

Arnot, J.A. and F.A.P.C. Gobas. 2004. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. Environ. Toxicol. Chem. 23(10): 2343-2355.

Boyd, P.M., L.W. Wulf, J.L. Baker, and S.K. Mickelson,1999. Pesticide transport over and through the soil profile of a vegetative filter strip. American Society of Agricultural Engineers. ASAE Paper no.992077

California Department of Pesticide Regulation (CDPR). 2000. Memorandum to Bob Rollins, Agricultural Program Supervisor III. Environmental Monitoring and Pest Management Branch. Subject: Recommendation for priority surface water monitoring studies on selected pesticides.

http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/m080200.pdf

Cole, J.T., J.H. Baird, N.T. Basta, R.L. Huhnke, D.E. Storm, G.V. Johnson, M.E. Payton, M.D. Smolen, D.L. Martin, and J.C. Cole. 1997. Influence of buffers on pesticide and nutrient runoff from bermudagrass turf. J. Environ. Qual. 26:1589-1598.

Deema P, Thompson E, Ware GW. 1966. Metabolism, storage and excretion of C-14endosulfan in the mouse. J Econ Entomol 59:546-550.

DeLorenzo, M.E., Taylor, L.A., Lund, S.A., Pennington, P.L., Strozier, E.D., and M.H. Fulton. 2002. Toxicity and bioaccumulation potential of the agricultural pesticide endosulfan in phytoplankton and zooplankton. Arch. Environ. Chem. Toxicol. 42:173-181.

DeLorenzo, M., T. Chandler, M. H. Fulton, G. I. Scott, D. Bearden, P. B. Key, K. Chung, H. F. Downing, A.K. Leight, J. Daugomah, S. A. Lund, R. Sumner, D. Wilson, E. Strozier, S. Sivertsen, A. Dias, P. Jenkins, and B. Shaddrix. 2001. An evaluation of pesticide loading from the Dade County agricultural area to the Everglades Panhandle and Florida Bay via the C-111 canal. Final Report to the South Florida Water Management District, Everglades Systems Research Division, 3301 Gun Club Road, West Palm Beach, FL 33411

Dorough HW, Huhtanen K, Marshall TC, et al. 1978. Fate of endosulfan in rats and toxicological considerations of apolar metabolites. Pesticide Biochemistry Physiology 8:241-252.

Gupta, P. K. and M. Ehrnebo, 1978. Pharmacokinetics of α - and β -Isomers of Racemic Endosulfan Following Intravenous Administration in Rabbits. Drug Metabolism And Disposition 7(1): 7-10.

Harman_Fetcho, J. A., C. J. Hapeman, L. L. McConnell, T. L. Potter, C. P. Rice, Sadeghi A.A., Ramona Smith R.D., Bialek, Sefton K.A. and B. A. Schaffer. 2005. Pesticide occurance in selected South Florida canals and Biscayne Bay during high agriculture activity. J. Agric. Food Chem. 53: 6040-6048.

Harman-Fetcho, J.A., L.L. McConnell, C.P. Rice, and J.E. Baker. 2000. Wet deposition and air-water gas exchange of currently used pesticides to a sub-estuary of the Chesapeake Bay. Environ. Sci. Technol., 34, 1462-1468.

Indraningsih, McSweeney CS, Ladds PW. 1993. Residues of endosulfan in the tissues of lactating goats. Aust Vet J 70(2):59-62.

Leys, J.F., F.J. Larney, J.F. Müller, M.R. Raupach, M.R. McTainsh, G.H. Lynch. 1998 Anthropogenic dust and endosulfan emissions on cotton farm in northern New South Wales, Australia. Sci. Tot. Environ. 220, 55-70.

Patty, L., B. Real, and J.J. Gril. 1997. The use of grassed buffer strips to remove pesticides, nitrate and soluble phosphorous compounds from runoff water. Pesticide Sci. 49:243-251.

Kelly, B.C., Ikonomou, M.G., Blair, J.D., Morin, A.E., and F.A.P.C. Gobas. 2007. Food Web-Specific Biomagnification of Persistent Organic Pollutants. Science. 317:236-239.

Kellner, H.M. & Eckert (1983) Hoe 02671-14C. Pharmacokinetics and residue determinations after oral and intravenous administration to rats. Unpublished study No. tep 74/1; bereich c/analytisches project oe 87/45; Hoechst report 01-l42-0382-83, 15 February 1983; document No. A49475, translation of document A27971. Submitted to WHO by Hoechst Schering AgrEvo GmbH, Frankfurt-am-Main, Germany.

Muir D.C.G., C. Teixeira, and F. Wania. 2004. Emperical and modeling evidence of regional atmospheric transport of current-use pesticides. Environ. Toxic and Chem. 23: 2421-2432.

Rice, J. P., L.L. McConnell, L.P. Heighton, A.M. Sadeghi, A.R. Isensee, J.R. Teasdale, A.A. Abdul-Baki, J.A. Harman-Fetcho, and C.J. Hapeman. 2001. Runoff Loss of Pesticides and Soil: A Comparison between Vegetative Mulch and Plastic Mulch in Vegetable Production Systems. J. Environ. Qual. 30:1808–1821.

Rohde, W.A., L.E. Asmussen, E.W. Hauser, R.D. Wauchope, and H.D. Allison. 1980. Trifluralin movement in runoff from a small agricultural watershed. J. Environ. Qual. 9(1):37-42.

Scott, G.I., H. Fulton, E. F. Wirth, G. T. Chandler, P.B. Key, J.W. Daugomah, D. Bearden, K. W. Chung, E. D. Strozier, Delorenzo, S. Sivertsen, A. Dias, M. Sanders, J. M. Macauley, L.R. Godman, M. W. Lacroix, G. W. Thayer, and J. Kucklick. 2002. Toxicological Studies in Tropical Ecosystems: an ectoxicological Risk Assessment of Pesticide Runoff in South Florida Estuarine Ecosystems. J. Agric. Food Chem. 50:4400-4408.

South Florida Water Management District (SFWMD). *Pesticide Surface Water Quality Reports.* Available on-line at: http://my.sfwmd.gov/portal/page? pageid=2754,19862620& dad=portal& schema=PORTAL Accessed 21 January 2008.

Spray Drift Task Force (SDTF). 1997. A Summary of Aerial Application Studies. Available on-line at: <u>http://www.agdrift.com/PDF_FILES/Aerial.pdf</u> Accessed 17 January 2008.

United Nations Environment Programme (UNEP). 2002. UNEP Chemicals. Regionally Based Assessment of Persistent Toxic Substances – North America Regional report, December 2002.

http://www.chem.unep.ch/pts/regreports/North%20America%20full%20report.pdf

United States Department of Agriculture (USDA). 2000. *Conservation Buffers to Reduce Pesticide Losses*. United States Department of Agriculture Natural Resources Conservation Service (USDA-NRCS), National Water and Climate Center, and the United States Environmental Protection Agency (USEPA) Office of Pesticide Programs. Washington, DC. March 2000.

United States Environmental Protection Agency (USEPA). 2002. Environmental Fate and Ecological Risk Assessment for the Reregistration Eligibility Decision on Endosulfan. DP Barcode D238673. U.S. Environmental Protection Agency, Office of Pesticide Programs, Environmental Fate and Effects Division, Washington, DC.

USEPA. 2001. National sediment Quality Survey. Database 1980 to 1999. MS Access 97 database files. Prepared by EPA's Office of Science and Technology, Standards and Health Protection Division (EPA-823-C-01-001).

USEPA. 2000. Quantitative Use Assessment (QUA). Biological Evaluation and Analysis Division (BEAD), EPA QUA, Dated April 22, 1999, revised by David Donaldson September 10, 2000.

USEPA, 1993, *Wildlife Exposure Factors Handbook*, Volumes I and II, Office of Research and Development, Washington, D.C. EPA/600/R-93/187.

Weston D.P. J. You., and M.J. Lydy. 2004. Distribution and toxicity of sedimentassociated pesticides in agriculture-dominated water bodies of California's Central Valley. Environ. Sci. and Tech. 38: 2752-2759

World Health Organization. 1999. Pesticide residues in food - 1998 evaluations. Part II - Toxicological. World Health Organization, WHO/PCS/99.18, 1999.

References with MRID number

MRID 00004257 Deema, P.; Thompson, E.; Ware, G.W. (1966) Metabolism, storage, and excretion of C14-Endosulfan in the mouse. Journal of Economic Entomology 59(3):546-550. (Also in unpublished submission received Jul 14, 1967 under 8F0632; submitted by FMC Corp., Philadelphia, Pa.; CDL:091099-A)

MRID 41164101 Cornaby, B.; Maciorowski, A.; Griffith, M.; et al. (1989) Assessment of the Fate and Effects of Endosulfan on Aquatic Ecosystems Adjacent to Agricultural Fields Planted with Tomatoes: Laboratory Project ID N0954-5700. Unpublished study prepared by Battelle in cooperation with Hickey's Agri-Services Laboratory, Inc. 2260 p.

MRID 41412904 Gildemeister, H. (1988) HOE 002671-14C Anaerobic Metabolism of Endosulfan in a Sandy Loam and a Silt Loam Soil: Project Nos. OI-134/04/03 B; A 37589. Unpublished study prepared by Hoechst Aktiengesellschaft Analytisches Laboratorium & Radiochemisches Laboratorium. 44 p.

MRID 41421502 Asshauer, J. (1979) HOE 052618 and HOE 052619 (Alpha--and Beta Endosulfan): Solubility in Water: Lab Project Number: B 154/87: A 36704. Unpublished study prepared by Hoechst Aktiengesellschaft. 13 p.

MRID 43812801 Stumpf, K.; Dambach, P.; Lenz, O. (1995) Metabolism of (Carbon 14)-Labeled Endosulfan in Five Soils Under Aerobic Conditions: Code: Hoe 002671, Hoe 052618, Hoe 052619: Lab Project Number: CB88/037: A53618: RR06/A914A. Unpublished study prepared by Hoechst Schering AgrEvo GmbH. 85 p.

MRID 44082703 Leah, J.; Reynolds, C. (1996) Endosulfan: Distribution, Elimination and the Nature of the Metabolite Residues in the Milk and Edible Tissues of a Lactating Cow: Lab Project Number: A 57041: TOX/94306: TOX/94308A. Unpublished study prepared by AgrEvo UK Ltd. 134 p.

MRID 44099102 Reynolds, C. (1996) Endosulfan: Distribution, Elimination, and the Nature of the Metabolite Residues in the Eggs and Edible Tissues of the Laying Hen: Lab Project Number: TOX/94306: A 56354: TOX/95/142-2. Unpublished study prepared by AgrEvo UK Ltd. 104 p.

MRID 44917801 Gildemister, H. (1985) Hoe 002671--(carbon 14) (Endosulfan): Aerobic Aquatic Metabolism Study with the Insecticide Endosulfan: Lab Project Number: (B)106/85: A31182. Unpublished study prepared by Hoechst Analytisches Laboratorium. 35 p.

MRID 44917802 Stumpf, K. (1990) Endosulfan: Summary Comments Regarding the Bioavailability in Water/Sediment Systems and Potential Degradability in Water: Lab Project Number: A44231: A45100: A31128. Unpublished study prepared by Hoechst Schering AgrEvo GmbH. 20 p.

MRID 44953102 Ramanarayanan, T.; Allen, R. (1999) Endosulfan (AE F002671): Tier II Exposure Assessment; Sensitivity Analysis for PRZM (Ver 3.12), EXAMS (Ver 2.97.5) and AgDrift (Ver 1.02): Lab Project Number: 513BJ: B002224: BJ99E513. Unpublished study prepared by AgrEvo USA Company. 54 p.

MRID 44953103 Ramanarayanan, T.; Fischer, R.; Allen, R. (1999) Endosulfan (AE F002671): Tier II Surface Water Exposure Assessment and Comparison to Aquatic Toxicity End-Points: Lab Project Number: BJ99E514: B002255: WEI622.06-B. Unpublished study prepared by AgrEvo USA Company. 282 p.

MRID 46119101 Schnoeder, F. 2002. Endosulfan [14C]-AE F051327 Soil Metabolism and Degradation. Prepared by Covance Laboratories GmbH, Muenster, Germany. Covance Study # 1490-019. Bayer CS # C019647. Submitted by Endosulfan Task Force.

MRID 46119102 Jonas, W. 2002. Degradation of [14C]- Endosulfan in Two Aerobic Water/Sediment Systems. Prepared by NATEC Institut, Hamburg, Germany. Study # NA 019404. Bayer CS # C022921. Submitted by Endosulfan Task Force (ETF).

MRID 46119105 Schnoeder, F. 2002. Endosulfan [14C]-AE F051327 Soil Metabolism and Degradation. Amendment to Final Report (C019647). Prepared by Covance Laboratories GmbH, Muenster, Germany. Covance Study # 1490-019. Bayer CS # C020629. Submitted by Endosulfan Task Force.

MRID 463826-05 Putt, A.E. 2004. Endosulfan Sulfate-Toxicity to Midge (Chironomus tentans) During a 10-Day Sediment Exposure. Study conducted by Springborn Smithers Laboratories, Wareham, Massachusetts. Study sponsored by Bayer CropScience, Research Triangle Park, NC

MRID 463826-06 Putt, A.E. 2004. Endosulfan Sulfate-Toxicity to Marine Amphipods (Leptocheirus plumulosus) During a 10-Day Sediment Exposure. Study conducted by Springborn Smithers Laboratories, Wareham, Massachusetts. Study sponsored by Bayer CropScience, Research Triangle Park, NC

MRID 46734301. Mackay, N. and D. Arnold. 2005. Evaluation and Interpretation of environmental data on endosulfan in Arctic regions. Report Number CEA.107. Non-guide line study submitted by Endosulfan Task Force. Prepared by Cambridge Environmnetal Assessments. Cambridge CB3 8NN., UK.

MRID 469290-01. Putt, A.E. Endosulfan Sulfate – Toxicity to Estuarine Amphipods (Leptocheirus plumulosus) During a 28-Day Sediment Exposure. Study conducted by Springborn Smithers Laboratories, Wareham, MA Study sponsored by Bayer CropScience LP on behalf of Endosulfan Task Force.