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DP Barcodes: D260885, D261571, D267012, D267629

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

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

2/28/2001

MEMORANDUM

SUBJECT: Transmittal of EFED's RED chapter for molinate (Chemical # 041402), EFED's data requirements and recommendations. (Reregistration Case # 818845)

FROM: F. Nicholas Mastrota and James Breithaupt
Environmental Risk Branch II
Environmental Fate and Effects Division 7507C

James Breithaupt 3/6/01
F. Nicholas Mastrota 3/6/01

THROUGH: Tom Bailey, Chief Tom A. Bailey 3/6/01
Environmental Risk Branch II
Environmental Fate and Effects Division 7507C

TO: Robert McNally/Wilhelmina Livingston, PM 60
Special Review and Reregistration Division (7508W)

Attached to this memo is the EFED chapter for the Molinate RED (Reregistration Case # 818845). This attached documents contain drop-in chapters for the environmental fate assessment, the ecological risk assessment, integrated risk characterization, and drinking water. It also contains the registrant responses to previous molinate reviews and the information provided by the USA Rice Federation.

The following actions are addressed in this document:

Barcode	MRID	Comments
D261751	44970001 44970002 44970003	90-day response, Combination Field Dissipation Studies, Imai and Kowatsuka literature article (1982)
D265738	None	30-day response to HED assessment dealing with drinking water
D259945	44926501 44926502	30-day response to molinate ecotoxicity and water monitoring assessments
D260885	44956601 44956602	Aerobic Soil Metabolism (including 10/13/99 fax of raw data from registrant)

Summary of Ecological Risk and Drinking Water Assessments

Drinking Water

- Molinate has been detected frequently in surface water adjacent to rice growing areas and downstream from rice growing areas in California, Arkansas, Mississippi, Louisiana, and Texas. No detections have been observed in Missouri, and monitoring data are not available in Tennessee. There is very limited rice production in Tennessee. Intakes for a number of drinking water utilities, some of which serve large populations, are located downstream of areas where molinate is used.

- EFED has received molinate-specific laboratory studies that simulate water treatment at Sacramento, CA. In these studies, disinfection using chlorination (2.5 ppm) converted parent molinate to molinate sulfoxide, a toxic metabolite (Ross, 1983, DP Barcode D267629). An analysis of the water treatment plants in the molinate use area and impacted downstream areas indicate that chlorination was used as a disinfectant except for a plant using potassium permanganate as an additional oxidant (MRID 44926503). However, the efficiency of water treatment practices to remove toxic residues of molinate may vary significantly between intakes. Variables such as spiking rates of oxidants, size of the distribution system, use of aeration, and storage/treatment times may provide different pesticide removal efficiencies. Therefore, using the results of one intake's treatment may not be accurate for another intake.

- Holding periods for rice tailwater are possible in California because the climate is drier than the Southern Region. Consequently, the concentrations of molinate in surface water in California are generally lower than in the Southern Region.

- In ground water, molinate has been detected at levels ranging from 0.005-1.5 ug/L. Most of the detections did not exceed 0.056 ug/L (Arkansas, Mississippi, and California), but there were two higher detections of 0.11 ug/L in Texas and 1.5 ug/L in Missouri. Based on the persistence in aquatic metabolism studies, EFED expects persistence of molinate in ground water if it reaches ground water.

Terrestrial Organisms

- Risk to mammalian reproduction (highly certain).

- Risk of reproductive impairment is assumed but uncertain in birds. EFED needs additional data for confirmation.

- Molinate is a likely endocrine disruptor in rodents. Additional data are needed to confirm endocrine disruption in non-mammalian animals.

- Minimal risk to terrestrial plants (uncertain, additional data needed for confirmation).

Aquatic Organisms--California

- Acute risk to fish, amphibians, and aquatic invertebrates is minimal (high certainty).

- Chronic risk to freshwater invertebrates that live in agricultural drains and small rivers is predicted but with low certainty, since chronic toxicity was based on the acute:chronic ratio and not direct measurements.

- Risk of reproductive impairment is assumed but uncertain in freshwater fish. EFED needs additional data for confirmation.

- Minimal risk to estuarine areas because estuaries are distant from use sites (moderate certainty).

- Minimal risk to aquatic plants (highly certainty).

Aquatic Organisms--Southern Region

- Acute risk to fish, amphibians, and aquatic invertebrates, especially in smaller water bodies subject to high exposure from rice drainage (low certainty due to highly variable toxicity data).

- Chronic risk to freshwater fish from possible reproductive effects (uncertain, additional data needed for confirmation).

- Chronic risk to freshwater invertebrates (moderate certainty, based partly on estimated chronic toxicity derived using the acute:chronic ratio).

- Acute risk to estuarine fish and invertebrates is minimal (moderate certainty).

- Chronic risk to reproductive success in estuarine fish and invertebrates is possible, but not known due to lack of life-cycle toxicity data (uncertain, additional data needed for confirmation).

- Risk to nontarget aquatic plants (low certainty).

Non-Target Terrestrial Plants

- Risk to non-target terrestrial plants is assumed because of lack of valid data.

Requirements for Additional Data

Required Study	Guideline Number
Environmental Fate	
Surface water monitoring data[a]	--
Ecological Effects	
Avian reproduction study, quail	72-1(a)
Avian reproduction study, duck	72-1(b)
Fish life-cycle study	72-5
Seedling emergence study, Tier II	123-1(a)
Vegetative vigor study, Tier II	123-1(b)

[a] For intakes with drinking water estimates that may be close to the drinking water level of comparison. HED is incorporating the estimates of drinking water exposure into the dietary risk assessment.

A complete listing of submitted data and data requirements for ecological risk may be found in Appendix C of the EFED RED Chapter. Also, a complete listing of submitted data and data requirements for environmental fate and transport may be found in Appendix D of the EFED RED Chapter. No additional environmental fate guideline studies are required for molinate.

Details:

Monitoring Data for Surface Water Intakes

The registrant should collect monitoring data for parent and all residues in the tolerance expression for locations with estimated concentrations that are similar to the Drinking Water Level of Comparison. Based on a 10/31/2000 meeting between EFED and HED, the metabolites that were determined to be of concern include molinate sulfoxide, molinate sulfone, 3-keto and 4-keto molinate, hydroxy molinate (2-, 3-, and 4-), molinate acid (carboxymethyl molinate), and ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate). Because water treatment data indicate that chlorination affects molinate transformation (Ross, 1983), EFED recommends that the monitoring program be conducted at actual water treatment plants which are representative of water treatment systems used in the molinate use area and downstream. The water sampling strategy should be designed to allow analysis of water treatment effects on molinate residue removal and transformation. Protocols should be submitted prior to monitoring. The value of these data is high because the contribution of molinate metabolites of concern to the dietary exposure assessment is unknown. Also, it is unclear if water treatment removes the metabolites.

Avian Reproduction

Avian reproduction studies with the mallard and the bobwhite using the TGAI are required for all pesticides with outdoor uses. These studies were previously listed as "reserved", but now are required. These studies are especially important for molinate since mammalian studies indicate that molinate can cause reproductive toxicity. The information provided by these studies will be of high value.

Freshwater invertebrate life-cycle

A freshwater invertebrate life-cycle study that was previously requested is no longer required. EFED has upgraded a previously submitted life-cycle study with the daphnid (MRID 406578-02) from supplemental to core. This study now fulfills guideline requirement 72-4(b).

Freshwater fish life-cycle

A freshwater fish life-cycle test using the TGAI (72-5) is required for molinate because the end-use product is intended to be applied directly to water and both of the following triggers are met: (1) the EEC is greater than one-tenth of the NOAEL in the fish early life-stage (8.6 times greater) and the invertebrate life-cycle test (30.3 times greater), and (2) studies of other organisms indicate the reproductive physiology of fish may be affected. The reproductive toxicity of molinate has been clearly demonstrated in mammalian studies, and this toxicity also may be expressed in other vertebrates, including fish. The preferred test species is fathead minnow. The information provided by these studies will be of high value.

A fish early life-stage study that was conducted with the rainbow trout (MRID 406578-01) was classified as supplemental and does not fulfill the 72-4(a) guideline requirement. This study does not need to be repeated if an acceptable fish life -cycle study (72-5) is submitted. Note, however, that the 72-4(b) guideline requirement still needs to be fulfilled with a freshwater invertebrate life-cycle study.

Seedling emergence study, Tier II

Terrestrial plant testing is required for molinate because it is an herbicide with non-residential terrestrial use patterns, may be applied aerially, is volatile (vapor pressure > 1.0×10^{-5} torr at 25°C), and may pose hazards to endangered or threatened plant species. A study must be submitted to replace a previous study (MRID 416136-11) because the seedling emergence section of this study was classified as invalid. Therefore, no data on the effects of molinate on seedling emergence are now available. The information provided by these studies will be of moderate value.

Vegetative vigor study, Tier II

Terrestrial plant testing is required for molinate because it is an herbicide with non-residential terrestrial use patterns, and it may be applied aerially, is highly volatile (vapor pressure > 1.0×10^{-5} torr at 25°C), and may pose hazards to endangered or threatened plant species. A study must be submitted to replace a previous study (MRID 41613611) because the vegetative vigor section of this study was classified as supplemental. This study did not fulfill the 123-1(b) guideline requirement because plant dry weights were not measured, EC_{25} values were not calculated for percent seedling emergence, visual assessments were not conducted in control plants, and the progression of application rates was 4-fold rather than 2-fold. The information provided by these studies will be of moderate value.

Aquatic plant growth and reproduction, Tier II

The test guideline 123-3 is fulfilled for all five required test species. Studies with *Pseudokirchneria subcapitata*, *Skeletonema costatum*, and a freshwater diatom (MRID 41613612, 41613613, and 41702703) were originally classified as supplemental because the tests were conducted for 4 days instead of the required 5 days. However, EFED now considers the 4-day test to be sufficient for fulfilling guideline requirements, and these studies have been upgraded to core. A submitted Tier II aquatic plant growth study with blue-green algae, *Anabaena flos-aquae*, was classified as supplemental (MRID 4172701). Although this study was not classified as core, it did provide sufficient information to conclude that blue-green algae is considerably less sensitive to molinate than is the green algae, *Pseudokirchneria subcapitata*. Repeating this study would not likely improve our risk assessment for molinate. Therefore, EFED is waiving the requirement to repeat this study.

Recommendations for Labeling

Labels for **manufacturing** use should contain the following Environmental Hazard statement:

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

Labels for **end**-use **granular products** should contain the following Environmental Hazard statement:

> "This pesticide is toxic to fish and aquatic invertebrates. Release of tail water after treatment should be delayed as long as possible to reduce hazard to aquatic organisms. Do not contaminate water when disposing of equipment washwaters or rinsate."

The Environmental Hazard statement for **non-granular end**-use **products** should be as follows:

> "This pesticide is toxic to fish and aquatic invertebrates. Release of tail water after treatment should be delayed as long as possible to reduce hazard to aquatic organisms. Drift may be hazardous to aquatic organisms in neighboring areas. Do not contaminate water when disposing of equipment washwaters or rinsate."

The label for Arrosolo® (Registration Number 10182-260) also contains additional statements under the "Environmental Hazards." These statements should be retained if they were imposed to mitigate risk of propanil, which is a dual active ingredient of Arrosolo®.

EFED RED Chapter for Molinate

I. Environmental Risk Conclusions

Note: Conclusions of ecological risk are based on a screening level assessment. In the past, these risks would have been characterized as "high" acute or chronic risk. However, recognizing the uncertainty in the ability of a screening level assessment to quantify the level or significant of risk, the EFED is changing the wording of the conclusions when exceeding the LOC is based solely on screening level risk assessment. This change does not reflect a change in the risk assessment process, or alter the criteria of exceeding the LOC's. Also, it does not change the other presumptions of risk, including those related to restricted use and endangered species.

Use Information

- Molinate is registered to be applied on rice by air and ground equipment.
- About 500,000 acres of rice are grown in California and 2,500,000 acres in the Mid-South and the Southeastern U.S.

Terrestrial Organisms

- Risk to mammalian reproduction (highly certain).
- Risk of reproductive impairment is assumed but uncertain in birds. EFED needs additional data for confirmation.
- Molinate is a likely endocrine disruptor in rodents. Additional data are needed to confirm endocrine disruption in non-mammalian animals.
- Minimal risk to terrestrial plants (uncertain, additional data needed for confirmation).

Aquatic Organisms--California

- Acute risk to fish, amphibians, and aquatic invertebrates is minimal (high certainty).
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- Minimal risk to estuarine areas because estuaries are distant from use sites (moderate certainty).

- Minimal risk to aquatic plants (highly certainty).

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- Acute risk to fish, amphibians, and aquatic invertebrates, especially in smaller water bodies subject to high exposure from rice drainage (low certainty due to highly variable toxicity data).

- Chronic risk to freshwater fish from possible reproductive effects (uncertain, additional data needed for confirmation).

- Chronic risk to freshwater invertebrates (moderate certainty, based partly on estimated chronic toxicity derived using the acute:chronic ratio).

- Acute risk to estuarine fish and invertebrates is minimal (moderate certainty).

- Chronic risk to reproductive success in estuarine fish and invertebrates is possible, but not known due to lack of life-cycle toxicity data (uncertain, additional data needed for confirmation).

- Risk to nontarget aquatic plants (low certainty).

Non-Target Terrestrial Plants

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Drinking Water

- Molinate has been detected frequently in surface water adjacent to rice growing areas and downstream from rice growing areas in California, Arkansas, Mississippi, Louisiana, and Texas. No detections have been observed in Missouri, and monitoring data are not available in Tennessee. There is very limited rice production in Tennessee. Intakes for a number of drinking water utilities, some of which serve large populations, are located downstream of areas where molinate is used.

- EFED has received molinate-specific laboratory studies that simulate water treatment at Sacramento, CA. In these studies, disinfection using chlorination (2.5 ppm) converted parent molinate to molinate sulfoxide, a toxic metabolite (Ross, 1983, DP Barcode D267629). An analysis of the water treatment plants in the molinate use area and impacted downstream areas indicate that chlorination was used as a disinfectant except for a plant using potassium permanganate as an additional oxidant (MRID 44926503). However, the efficiency of water treatment practices to remove toxic residues of molinate may vary significantly between intakes. Variables such as spiking rates of oxidants, size of the distribution system, use of aeration, and storage/treatment times may provide different pesticide removal efficiencies. Therefore, using the results of one intake's treatment may not be accurate for another intake.

- Holding periods for rice tailwater are possible in California because the climate is drier than the Southern Region. Consequently, the concentrations of molinate in surface water in California are generally lower than in the Southern Region.

- In ground water, molinate has been detected at levels ranging from 0.005-1.5 ug/L. Most of the detections did not exceed 0.056 ug/L (Arkansas, Mississippi, and California), but there were two higher detections of 0.11 ug/L in Texas and 1.5 ug/L in Missouri. Based on the persistence in aquatic metabolism studies, EFED expects persistence of molinate in ground water if it reaches ground water.

Additional Data Requirements

- No additional fate and transport data are required for molinate at this time. However, some monitoring data for parent and all residues in the tolerance expression may be necessary for those locations with estimated concentrations similar to the drinking water level of comparison. Protocols should be submitted prior to any monitoring (if required).

- Data on avian reproduction, freshwater fish life-cycle, seedling emergence (Tier II), and vegetative vigor (Tier II) are required for ecological effects. The value of these data are high.

II. Introduction

Molinate is a thiocarbamate herbicide used only on rice to control barnyardgrass, sprangletop, broadleaf signalgrass, and various other non-aquatic weeds. Molinate is an inhibitor of shoot growth. The maximum per application rates of products containing molinate range from 3 to 5 lb ai/A, and the maximum per season application rates range from 6 to 9 lb ai/A. Products may be applied two or three times per growing season by either aircraft or ground equipment. Molinate is currently marketed under the brand names Ordram and Arrosolo, the latter of which contains both molinate and propanil as dual active ingredients. The formulations include emulsifiable

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concentrates (EC's, 3 and 8 lbs ai/gallon) and granular (15 % G). For the years 1988 through 1997, molinate was applied on average to approximately 40% (1,200,000 acres) of all rice acreage planted in the United States (2,992,000 acres).

Rice in the United States is grown primarily in two regions. One region, hereafter called the "Southern region", consists of the Gulf Coast of Texas and Louisiana and the Mississippi River Valley in Louisiana, Mississippi, Arkansas, Tennessee, and Missouri. Approximately 2,500,000 acres of rice are grown in this region annually. The second region is the Sacramento Valley and San Joaquin Valley in California, where approximately 500,000 acres of rice are grown annually. Use of molinate is widespread in both regions. Labels with products containing molinate restrict its use to the following states: Arkansas, California, Louisiana, Mississippi, Missouri, Tennessee, and Texas.

Approximately 80-85% of rice grown in the Southern region is "dry-seeded", meaning seeds are sowed and grown in dry seed beds for several weeks before flooding. If there is no rainfall, fields are irrigated with a small volume of water (i.e. flushed) to promote seed germination. The remaining 15-20% of rice production in this area, mainly in southern Louisiana, is "water-seeded", meaning that germinated seeds are aerially applied to water in flooded fields. Molinate may be applied to fields before or after they are flooded. EC products are typically applied before flooding. Arrosolo is commonly applied to control emerged weeds before flooding, and ORDRAM 8E is typically applied as a pre-plant incorporated application to water-seeded rice prior to flooding. Granular products are typically used for applications applied after flooding. Arrosolo may also be applied to flooded fields to control weeds that emerge out of the water. With water seeded rice in the Southern region, fields are drained a few days after seeding, and then reflooded several days later after the rice has sprouted. Granular molinate products may be applied at either flood, but most often would be applied after the permanent flood is established since draining the field would cause the efficacy of the application to be lost.

In California, the majority of rice production (98%) is water-seeded with a continuous flood. Unlike the Southern region, in California molinate is almost always applied as a granule to water in flooded fields. A small percentage of rice farmers in California uses "pin-point flood" culture, in which case molinate may be applied as a liquid to dry-ground before fields are flooded. California state regulations prevent rice farmers from discharging tailwater from rice fields for 28 days after application.

Sources of Monitoring Data

EFED has conducted a state-by-state regional assessment since molinate is applied only in California and in the south central/south eastern states of Arkansas, Louisiana, Missouri, Texas, and Tennessee. To obtain both ground and surface water concentrations for the purpose of aquatic risk assessment and drinking water exposure assessment, EFED has received monitoring data from the USGS, the State of Arkansas Department of Pollution Control and Ecology, the City of Sacramento, CA, the State of California Department of Environmental Regulation, and the

State of Texas. Some of these data were provided in the EPA STORET database. EFED used monitoring data for the drinking water assessment since the data were available for the areas where molinate is applied except for Tennessee, where only 3,000-5,000 acres of rice are grown in Lake County. Also, EFED has no official models to generate estimated environmental concentrations (EECs) from pesticide use on aquatic crops.

III. Integrated Environmental Risk Conclusions

Characterization of Terrestrial Risk

Molinate may present an acute risk to mammals, but the primary concern for terrestrial animals is chronic effects on reproduction. Numerous EPA guideline studies and non-guideline studies from the open literature provide strong evidence that molinate is very toxic to the male and female reproductive systems in rodents. Molinate sulfoxide, a metabolite and degradation product of molinate, exhibits even greater reproductive toxicity than the parent compound. Both molinate and molinate sulfoxide are believed to be endocrine disruptors in rodents. While the conclusion of chronic risk is very certain for rodents, it is less certain for other terrestrial wildlife. There are indications that differences in the way molinate is metabolized make it less toxic to the reproduction system of certain other mammals, including man. The reproductive toxicity of molinate to birds and other non-mammalian wildlife is unknown. Therefore, the Agency is requesting that avian reproductive studies be conducted.

Molinate is used exclusively on rice, in which flooded fields attract many types of wildlife, especially waterfowl and wading birds. The application timing (April-June) coincides with the breeding season for many terrestrial and semiaquatic vertebrates, including birds, mammals, reptiles, and amphibians. Therefore, the potential exists for molinate to cause reproductive impairment in a wide variety of wildlife.

The amount of exposure to terrestrial wildlife is directly related to the application methods and cultivation practices that are used. In California, molinate is mostly applied as a granular to permanently flooded fields. This method of application reduces the risk to wildlife since most of the granules would fall into the water and disintegrate. Even though birds and mammals would be exposed to granules which fall on the levees that surround and separate rice paddies, any risk would be short-lived because molinate is highly volatile, would dissipate rapidly from unincorporated granules, and has relatively low acute toxicity.

Appendix K provides a refined risk assessment for wildlife based on applications of molinate to flooded fields. This assessment shows that exposure to animals drinking from and feeding in treated rice paddies would not be high enough to pose an acute risk to wildlife, but would be high enough to pose a chronic risk of reproductive impairment.

In the Southern region, a small amount of molinate is applied as a pre-plant incorporated (PPI) spray to rice cultivated using the water-seeded method. This use poses little acute risk to terrestrial wildlife since soil incorporation greatly reduces the availability of residues and granules to wildlife. Application of molinate to exposed weeds without incorporation appears to pose greater risk to birds and mammals. Applications to emerged weeds occurs predominantly before flooding using Arrosolo, a product containing molinate and propanil, although a small amount of Ordram 8E is applied to emerged weeds postflood. These unincorporated uses of molinate pose acute and chronic risk to mammals. For birds, the acute risk is predicted to be of less concern than those based on reproductive effects.

There are no incidents reported in the EIIS database involving effects on terrestrial organisms. However, the primary risk from molinate is from reproductive impairment, a type of adverse effect which cannot be assessed by evaluating incident reports.

Characterization of Aquatic Risk

Scenarios for aquatic risks from molinate differ considerably between California and the Southern region. In California, molinate is usually applied onto flooded fields as granules. Rice growers are required to retain floodwater onsite for 28 days after the application of pesticides, which allows much of the pesticide residues to dissipate before the water is released into surface water. These mandatary holding periods appear to have been effective in mitigating risk of molinate to aquatic organisms in California because peak, annual mean, and seasonal mean concentrations of molinate have declined by factors of 12, 3, and 7, respectively. In the Southern region, application methods of molinate are variable; it may be applied as a liquid or granule prior to flooding or after flooding. There are no mandatory retaining periods in this region. In addition, heavy rainfall is much more common in the Southern region than in California. These heavy rainstorms are sometimes cause unscheduled releases of water. In general, the climate and growing practices make the use of molinate a greater risk in the Southern region than in California.

Aquatic residue levels in the Southern region are characterized by generally low basal levels during the spring with occasional peaks. These peaks probably are associated with the release of flood water from rice fields. Releases that occur soon after an application of molinate, before residues have had time to dissipate, are most problematic. In general, it appears that the most significant contamination of molinate in aquatic habitats would occur from unscheduled releases of water from either flooded or unflooded fields resulting from heavy rain occurring soon after application of molinate. Spikes caused by release of contaminated water from rice fields may occasionally result in molinate concentrations that exceed levels that are acutely toxic to fish and aquatic invertebrates. Effects would generally be localized and limited to small shallow bodies of water.

The potential for reproductive impairment in fish and other aquatic animals is a concern. In mammals, molinate has been shown to damage the reproduction system by inhibiting synthesis of estrogen and testosterone. Since the reproduction of fish, amphibians, crustaceans, and mollusks is also dependent on synthesis of estrogen and testosterone, molinate could cause reproductive impairment in these organisms as well. Molinate is applied mostly in the spring, which corresponds to active breeding of many fish and amphibians. As well as affecting freshwater habitats, use of molinate in the Gulf Coast region will also expose many coastal estuaries, which are important habitats for the reproduction of many marine organisms. Further aquatic life-cycle testing and endocrine disruption testing is very important to further assess this potential hazard.

Certainties and Uncertainties

Uncertainties in the ecological risk and drinking water assessments

Terrestrial Risk Assessment

There are some uncertainties in the terrestrial risk assessment. Uncertainty exists in the degree that soil incorporation and flooding of fields will mitigate risk by making molinate less available to wildlife. In addition, there is incomplete knowledge of the toxic effects of molinate on certain types of organisms. While there is strong evidence that molinate poses risk to mammal reproduction, data are lacking to confirm that similar reproductive toxicity is expressed in birds and other non-mammalian aquatic animals. Also, acute toxicity data for freshwater organisms was highly variable, with toxicity values from one source (Mayer and Ellersieck, 1986) being consistently lower (indicating greater toxicity) than those from other sources. Finally, the estimate of the chronic toxicity level for freshwater invertebrates is uncertain because it was extrapolated from the test species to a more sensitive species (the stone fly) using the acute-to-chronic ratio technique.

Aquatic Risk and Drinking Water Assessments

Use of Monitoring Data

There are several generic uncertainties associated with the use of water monitoring data for estimating drinking water exposure and for assessing risk to aquatic organisms. Monitoring data are not available everywhere for all uses of a given compound. In a given year, it is highly likely that peak concentrations are missed since sampling is not always conducted on a daily schedule or over the time necessary to detect peaks. Also, peak concentrations are not likely to be detected unless sampling is conducted in a stratified sampling pattern in highly vulnerable sites. Sampling is also not necessarily representative of the entire year unless sampling is conducted over a year. Since monitoring data depend on the weather in a particular year, data may not always be available for enough years to cover the range of weather in a given area of application. The associated information to interpret monitoring information, such as amount of use and the area treated in a watershed, the timing and amount of rainfall events that drive runoff events, and specific cultural practices are not always available. Inclusion of data from an area where no pesticide is applied tends to bias estimates of exposure downward when considered with data from use areas. In analyzing these data, efforts were made to only include data from areas where molinate was known to have been used.

Years of Monitoring Data

EFED is very certain about the drinking water conclusions for California, Missouri, Tennessee, and Arkansas for parent molinate. EFED is less certain about the Mississippi and Atchafalaya River intakes in Louisiana because of fewer years of monitoring data (4 years or less) compared to California (19 years). EFED is uncertain about the extent of exposure at Anahuac, Texas because the amount of water from other sources and the number of days that Lake Anahuac receives rice drainage is unknown.

Time-weighting of monitoring data

Time-weighting of monitoring data introduces uncertainties. In the case of molinate, the time-weighting of data over a year from seasonal data was conducted based on a request by the Health Effects Division (HED). While this approach leads to a consistent time basis for means of data, calculating an annual mean from seasonal data creates uncertainties in the final estimates due to extrapolation. The detections or lack of detections at the first sampling interval are extended to the time between January 1st and the first sampling interval. Also, the detections or lack of detections at the last sampling interval are extended to the time between December 31st and the last sampling interval. Non-detections at the beginning and end sampling intervals tend to bias the final estimates downward, while high detections at the end sampling intervals tend to bias the final estimates upward. Lower detection limits that are extrapolated for non-detections create less uncertainty than higher detection limits. Also, relatively few years of data are available for most molinate use areas, with the exception of the Sacramento River where extensive data (19 years) were available. This adds some uncertainty to our assessment.

Estimation of degradate concentrations in water based on laboratory, field, and monitoring studies

Estimation of degradate concentrations in surface water based on laboratory and field studies introduces uncertainties because levels of degradates relative to parent compound vary with time and because some degradates were not observed in environmental fate studies. Degradate concentrations are lowest relative to parent compounds immediately following the application and increase with time. The potable water studies provided highly variable estimates of the dietary contribution of the molinate sulfoxide and molinate acid degradates. As a result, no single adjustment factor for monitoring data will perfectly represent the contribution of degradates to ecological and drinking water exposure. The environmental fate studies used in the degradate calculations did not include any information on molinate sulfone, 3-keto molinate, or ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate). However, volatility is the primary route of dissipation and the other metabolites are formed in relatively low amounts with the exception of 4-keto molinate. As a result, EFED does not expect significant formation of these metabolites in water. While the degradate adjustment factor of 1.56 is an average number that will reasonably represent the contribution of degradates for both ecological and drinking water exposure, monitoring for all residues of concern is the only certain method to assess exposure. Therefore, some monitoring may be required for those intakes with EEC's close to the Drinking Water Level of Comparison.

The amount of the degradate 4-keto molinate exposure in the use season is uncertain. The Domagalski article states that between 10-30 % of detected molinate was present in the Sacramento River in California. However, this study was conducted in January, and molinate is applied in May-June primarily. The study author speculates that the higher levels of 4-keto molinate were a result of the longer time available for photolysis to occur. The degradate 4-keto molinate never reached significant levels (10 % of applied) in the laboratory or field studies. Also, none of the studies showed DIRECT photolysis, where a pesticide absorbs the light and degrades. Any formation of 4-keto molinate at levels higher than those observed for metabolism levels is apparently resulting from INDIRECT photolysis, where other organic substances pass the energy from sunlight to molinate.

Most of the monitoring data were for parent molinate only and not the degradates. Only some of the USGS monitoring data contained any information on the 4-keto molinate degradate. No monitoring data on the other degradates of concern was available. As a result, EFED has attempted to account for the presence of degradates in surface and ground water by incorporating data from aquatic field dissipation and an aerobic aquatic metabolism study from the laboratory.

Water Treatment

Most drinking water facilities with surface water intakes located downstream of rice production have some uncertainty about their water treatment processes. The registrant has submitted a document (MRID 44926503) that includes drinking water treatment for several intakes that are either near rice production or downstream of rice production. With the exception of an intake that uses potassium permanganate as an oxidant, the listed drinking water facilities use only chlorination as an oxidative process. However, the intake that uses potassium permanganate as an oxidant does not appear to receive rice drainage, and therefore the information on the non-exposed intake has no bearing on the risk assessment. Because chlorination purportedly transforms molinate to a toxic sulfoxide degradate, the majority of parent molinate present in raw water would still be present as the toxic metabolite molinate sulfoxide after treatment. The registrant claims that conventional water disinfection practices degrade molinate. They are correct in saying that PARENT molinate is degraded with chlorination, but predominantly to the toxic metabolite molinate SULFOXIDE. If the registrant has additional information about the effect of water treatments other than oxidants such as potassium permanganate, then it should be submitted.

The efficiency of water treatment practices varies from intake to intake. The studies dealing with water treatment were laboratory simulations of the water treatment practices at Sacramento, California. Other intakes may have different practices that may provide very different removal efficiencies. Variables such as spiking rates of oxidants, size of the distribution system, and storage/treatment times may provide different pesticide removal efficiencies. Therefore, using the results of one intake's treatment may not be accurate for another intake.

The water treatment practices at the Mississippi and Atchafalaya River intakes were not provided by the registrant. EFED is assuming that chlorination is the only oxidative treatment at these intakes.

Use of dilution calculations

Since Lake Anahuac was the only intake for which dilution calculations were used, additional uncertainties exist for this location. Dilution calculations assume instantaneous distribution throughout the receiving water body, which can be relevant with shallow, well-mixed water bodies that do not stratify, such as Lake Anahuac. Also, increasing time tends to lead to uniform concentrations in the receiving water body. However, many factors can increase error when this assumption is used, including gradients in water temperature, salt concentrations, and the presence of channelization that tend to localize concentrations of a pesticide. The location of the intake relative to the source water body can also influence how much pesticide actually reaches the intake. If an intake is located near the source water body or in an area with high localized concentrations, the concentrations in drinking water may be higher than estimated. If an intake is located further away from the source water body or in an area where the pesticide does not localize, the concentration in drinking water may be less than estimated. In addition, extrapolation of concentrations and flow rates from the source water body to longer time intervals is a possible source of error. For molinate in White's Bayou (source water body), the flow rates were expressed as cubic feet/second. These flow rates were extrapolated to cubic feet/day for the calculations, which assumes that the same flow rate occurs over an entire day. The concentrations in White's Bayou were also extrapolated to an entire day, when they actually represent a point in time.

IV. Environmental Fate Assessment

Zeneca has submitted many documents pertaining to the environmental fate and transport of molinate. While the data contained in these documents are generally deficient in terms of compliance with Subdivision N guidelines, the weight of evidence from the submitted studies and the monitoring data together satisfy all environmental fate and transport guidelines and provide a relatively consistent picture of the environmental fate and transport of molinate. Molinate is generally more persistent in the laboratory than in the field because of volatility that is not as predominant in the laboratory. Detailed summaries for each environmental fate guideline are presented in Appendix D.

Based on the submitted environmental fate and transport studies and the monitoring data, the route(s) of dissipation of molinate are, in descending order of importance, (1) volatility, (2) reversible partitioning to soil, (3) indirect photolysis of molinate to 4-keto molinate formed when molinate desorbs into the paddy water, (4) degradation leading to formation of many degradates at low percentages, (5) plant uptake, and (6) release of rice water from treated fields into surface water.

Molinate is stable to hydrolysis and direct photolysis, and does not appear to degrade rapidly under aquatic conditions in the laboratory. However, indirect photolysis may be occurring in the field. The metabolite 4-keto molinate was detected in all surface water samples in CA where parent molinate was detected at approximately 10-30 % (one sample contained 50 %) of total molinate load. In the Southern region, 4-keto molinate levels in water of 10-50 % of detected parent molinate have also been observed. The degradate 4-keto molinate may be occurring from both indirect photolysis and aquatic metabolism studies, since it did not reach 30 % of applied molinate in any of the metabolism studies. In the aquatic metabolism studies, molinate appeared to volatilize and reversibly partition to clay and organic matter. Up to about 20 % of applied molinate was present as degradates that did not individually reach significant levels (10 % of applied).

Based on batch equilibrium studies, molinate and the degradates hexamethyleneimine and molinate sulfoxide are moderately mobile to very mobile in the environment. The USGS (Majewski and Capel, Open-File Report 94-0506) cites Seiber et al. (1983) and Soderquist et al. (1977) as saying that the percentages of molinate lost from rice paddy water by volatilization were 35 % in 4 days and 78 % in 7 days. This finding is consistent with the Henry's Law constant of 1.3×10^{-6} m^3-atm/g-mol. In the field, applied molinate that did not volatilize tended to partition reversibly to sediment within a 3-day period, but the application rates could not be confirmed in some studies.

EFED has reviewed surface and ground water monitoring data for molinate and has found high detections and high frequencies of detections where rice is grown. In surface water in California, maximum levels of 43.7 ug/L have been observed following the holding periods. Maximum levels of 100-332 ug/L have been observed in the Southern region where there are no required holding periods. This appears to be inconsistent with the apparently rapid rate of volatility from the field. However, this may be associated with releases of tailwater from fields soon after application.

In ground water, molinate has been detected at levels ranging from 0.005-1.5 ug/L. Most of the detections did not exceed 0.056 ug/L (Arkansas, Mississippi, and California), but there were two higher detections of 0.11 ug/L in Texas and 1.5 ug/L in Missouri. Based on the persistence in aquatic metabolism studies, EFED expects persistence of molinate in ground water if it reaches ground water.

V. Aquatic Exposure and Risk Assessment

For ecological exposure in California, Mississippi, Louisiana, and Texas, EFED identified the body of water in each rice-producing state with the maximum observed concentration of parent molinate residues. EFED then used the maximum concentration for that year as estimates acute exposure, and the time-weighted annual (January-December) and seasonal (May-July) means as estimates of chronic exposure. For Arkansas, EFED used a different approach because the 1995 monitoring data were survey data for bayous, creeks, and rivers instead of targeted data to a small number of water bodies. For acute exposure in Arkansas, EFED took the maximum concentration from bayous, creeks, and rivers from the 1995 monitoring data. For chronic exposure in Arkansas, EFED calculated the upper 95th percentile value for each type of water body. Since there was no apparent monitoring data in Missouri and Tennessee, EFED did not specifically address ecological risk in these states because it is unlikely that higher concentrations of parent molinate will be observed than in Mississippi or Arkansas (100-332 ug/L). Table 1 below provides the EEC's for parent molinate that were used for ecological risk.

In Table 1, the maximum concentrations ranged from 43.7-332 ug/L (68.2-519 ug/L for parent and metabolites). The justification for the degradate adjustment factor of 1.56 for the parent monitoring data is provided in Table 3 located in Section VI (Drinking Water Assessment) below. The annual and seasonal means and the upper 95th percentiles ranged from 1.5-32.4 ug/L (2.3-45.9 ug/L for parent and metabolites). Concentrations were generally higher in the Southern Region because California has a drier climate and required holding periods to prevent release into surface water.

Table 1. Surface Water Levels from Monitoring Data used for Ecological Risk Assessment.

State	Location	Year	Frequency of Detection (Range of detection limits)	Parent Molinate			Parent + degradates of concern including adjustment factor (See Table 3 for justification of adjustment factor)		
				Maximum Concentration (ug/L)	Time-Weighted Annual Mean Concentration (ug/L)	Time-Weighted Seasonal (May-July) Mean Concentration (ug/L)	Maximum Concentration (ug/L)	Time-Weighted Annual Mean Concentration (ug/L)	Time-Weighted Seasonal (May-July) Mean Concentration (ug/L)
California	Colusa Drain	1996	27/35 (0.5, 1 ug/L)	43.7	4.8	12.1	68.2	7.5	18.9
Mississippi	Bogue Phalia River	1996	23/25 (0.004 ug/L)	100	7.5	29.0	156	11.7	45.2
Louisiana	Tensas River	1997	15/27 (0.004 ug/L)	32	1.5	6.0	49.9	2.3	9.4
Texas	White's Bayou	1994	18/21 (0.004 ug/L)	200	7.9	32.4	312	12.3	50.5
State	**Location**	**Year**	**Frequency of Detection (Range of detection limits)**	**Maximum Concentration (ug/L)**	**Upper 95th percentile of concentrations (ug/L)**	**Upper 95th percentile of concentrations (ug/L)**	**Maximum Concentration (ug/L)**	**Upper 95th percentile of concentrations (ug/L)**	**Upper 95th percentile of concentrations (ug/L)**
Arkansas	Bayous	1995	35/47 (0.005-0.02 ug/L)	47.2	29.4	29.4	73.6	45.9	45.9
	Creeks	1995	23/67 (0.005-0.02 ug/L)	332.7	17.4	17.4	519	27.1	27.1
	Rivers	1995	27/67 (0.005-0.02 ug/L)	45.7	10.7	10.7	71.3	16.7	16.7

21

IV. Aquatic Exposure and Risk Assessment

Table 2 below summarizes the toxicity of molinate to aquatic organisms. Measurements of the toxicity of molinate are highly variable, but least some studies classify molinate as highly toxic on an acute basis to freshwater fish, freshwater invertebrates, and saltwater invertebrates. Supplemental data categorizes molinate as slightly toxic to saltwater fish. Survival of early life stages of rainbow trout was affected at concentrations of 830 ppb or greater (NOAEL=390 ppb). However, this test does not measure the reproductive toxicity of molinate, which is expected to be the most sensitive chronic endpoint. Life-cycle testing of freshwater fish is therefore required. The mysid, a saltwater invertebrate, was the most sensitive species on a chronic basis, with larval survival being affected at concentrations as low as 45.2 ppb (NOAEL=25.6 ppb0. Reproduction of the waterflea was affected at 900 ppb. Based on acute toxicity data, the stonefly is considerably more sensitive to molinate than is the waterflea. An estimated NOAEL for the stonefly based on the acute-to-chronic ratio is 15.6 ppb.

Table 2. Summary of toxicity of molinate to aquatic organisms.

Type of Organism	Type of Study	Type of Toxicity Value	Range of Toxicity Values	Toxicity Category
Freshwater Fish	Acute	LC_{50}	0.21-42.8 ppm	Slightly to highly toxic
	Subchronic	LC_{50} (21-28 days)	0.18->8.6 ppm	--
	Early life-stage	NOAEL	0.390 ppm	--
Freshwater Invertebrates	Acute	LC_{50}	0.30-19.4 ppm	Slightly to highly toxic
	Life-cycle	NOAEL	0.11-0.38 ppm[1]	--
Saltwater Fish	Acute	LC_{50}	13-24 ppm[2]	Slightly toxic
Saltwater Invertebrates	Acute	LC_{50}	0.76-27 ppm	Slightly to highly toxic
	Life-cycle	NOAEL	0.0256 ppm	--
Aquatic Algae		EC_{50}	0.22-10 ppm	--
	Acute	NOAEL	0.17-4.5 ppm	--
Aquatic Vascular Plants		EC_{50}	3.3 ppm	--
	Acute	NOAEL	0.84 ppm	--

[1] Based on acute toxicity data, the stonefly is significantly more sensitive to molinate than are cladocerans like the water flea. Therefore, the chronic toxicity level was estimated for the stonefly based on the assumption that the acute-to-chronic ratio is similar for the stonefly and the water flea. The estimated NOAEL for the stonefly was 15.6 ppb.

[2] The two studies submitted on the acute toxicity to saltwater fish were both supplemental.

Risk to aquatic organisms was assessed by comparing observed monitoring levels to acute and chronic toxicity levels. This assessment was not based on risk quotients.

Monitoring in California have shown that imposition of mandatory water holding periods for rice growers has significantly reduced the concentration of molinate in streams and rivers. With these holding periods in place, molinate concentrations never reach concentrations that would cause an acute or subacute toxicity to fish. In the Southern region, concentrations measured in water monitoring also have generally been below toxic levels. However, in some small stream and tributaries, concentration have on occasion briefly approached or exceeded toxic levels. Therefore, some acute risk exists for sensitive fish living in small streams and tributaries that receive a substantial amount of drainage from rice fields, but overall, the acute risk of molinate to fish is small.

In California, molinate concentrations from monitoring are below levels that are acutely toxic to freshwater invertebrates. They are also below the chronic toxicity level that was measured for two species of cladocerans, but exceed the chronic toxicity level that was estimated for the stonefly. Thus, the Agency concludes that molinate poses low acute risk to aquatic invertebrates in California, but may pose a chronic risk to certain sensitive species such as the stonefly.

In the Southern Region, where concentrations of molinate are higher, monitoring concentrations occasionally exceed the acute toxicity level for the stonefly. In addition, concentrations routinely exceed the estimated chronic toxicity level for the stonefly and occasionally even the chronic level for the less sensitive cladoceran species, *Moina australiensis*. Thus, use of molinate on rice in the Southern region poses a risk to freshwater invertebrates, especially chronically.

Use of molinate in California is far removed from coastal estuaries and is therefore predicted to pose minimal risk to saltwater fish and invertebrates in that state. In the Southern region, rice is grown in Louisiana and Texas is often near estuaries or the Gulf of Mexico. The Agency does not have water monitoring data for molinate from estuaries. Therefore, the acute risk assessment for marine and estuarine fish and invertebrates will be based on concentrations measured in freshwater habitats of Louisiana and Texas. Molinate concentration in these habitats are well below the acutely toxic level measured for saltwater fish. Concentration remain slightly below the acute toxicity level for saltwater invertebrates,

The maximum detection of molinate in these states was 200 ppb from White's Bayou at Anahuac, Texas (Fig. 1). Mean concentrations for the season of molinate use, May through July, were also calculated based on monitoring data for the Tensas River in Louisiana. The highest seasonal mean was 5.89 ppb in 1997. The peak molinate detection in this river was 32 ppb. Molinate concentrations are likely to be lower in estuaries than in rivers because of dilution caused by tidal flux and mixing with seawater.

The lowest acute LC_{50} for effects of molinate on an estuarine fish was 12 ppm (12,000 ppb). The lowest acute LC_{50} obtained for a marine or estuarine invertebrate is 760 ppb for the mysid. Based on this value, the acute LOC would be exceeded if concentrations reach 380 ppb. As stated above, the maximum measured concentration in Texas and Louisiana was 200 ppb. Monitoring data indicate that molinate concentrations in the estuarine and marine habitats of Texas and Louisiana will remain well below concentrations that would be toxic to estuarine or marine fish. For saltwater invertebrates, molinate concentrations remain slightly below levels that are acutely toxic but exceeds levels that are chronically toxic. Thus, the Agency concludes that use of molinate on rice in the Southern region poses minimal acute risk to marine and estuarine fish, but poses risk to marine and estuarine invertebrates due to chronic effects.

A chronic risk assessment for freshwater and saltwater fish cannot be conducted at this time because data are available on the effects of molinate on fish reproduction. Considering the reproductive toxicity and endocrine disruption effects observed in mammals, the Agency believes that molinate has the potential to pose a chronic risk to fish due to reproductive effects.

VI. Drinking Water Assessment

Adjustment of Parent Molinate Concentrations for Degradates

Adjustment of parent molinate concentrations in ground water and surface water for degradates was necessary since there was no monitoring for any degradates with the exception of the photoproduct 4-keto molinate. Appendix E contains the justification for the factors for each metabolite for which there was adequate information in the environmental fate studies and water monitoring. To determine which molinate metabolites are of toxic concern, EFED and HED held a meeting of the HED MARC (Metabolism and Review Committee) on 10/31/2000. At the MARC meeting, EFED provided a list of metabolites that have been detected or have the potential to be detected in the aquatic laboratory and field dissipation studies. The metabolites that were determined to be of concern include molinate sulfoxide, molinate sulfone, 3-keto and 4-keto molinate, hydroxy molinate (2, 3, and 4), molinate acid (carboxymethyl molinate), and ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate). EFED used an adjustment factor of 1.56 for the monitoring data based on the submitted studies. No meaningful estimates of exposure for molinate sulfone, 3-keto molinate, or ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate) could be determined based on the submitted environmental fate studies or water monitoring. Even though adequate information on some of these metabolites was not available, EFED does not expect significant formation of these metabolites in water. Table 3 contains a summary of the degradates and the justification for the different factors associated with each.

Table 3. Metabolite Adjustment Factors for Surface and Ground Water Monitoring Data for both Ecological and Drinking Water Exposures.[1]

Metabolite	Study ID	Percent of parent at time interval[1]	Value used	Comments
Hydroxy molinate (2-,3-,4-), treated as sum	MRID 44956603 Aerobic Aquatic	mean--14.7 SD--20.4 CV--170 %	14.7 % for CA and Southern Region	0-21 day sampling intervals used in calculations.
Molinate sulfoxide and acid, treated as sum	MRID 41421803 and 41421804 Aquatic Field Dissipation	8 EC formulation mean--9.4 SD--16.1 CV--170 % 15G formulation mean--11 SD--15.3 CV--140 %	11 % for CA and Southern Region	Calculated for each interval if parent was detected in the studies.
Molinate sulfone, 3-keto molinate, and (S-ethyl-5-carboxypentyl thiocarbamate)	no data from laboratory or field studies		0[3]	
4-keto molinate	USGS article[4]		30 % (CA and Southern Region)	4-keto molinate was detected at 10-50 % of detected molinate in both CA and Southern Region. EFED used 30 % because most values were ≤30 %.
Adjustment Factor for both California and Southern Region			**1.56 (1+ 56 % as decimal)**	

[1] EFED adjusted the monitoring data because it only contained information on parent molinate and the degradate 4-keto molinate. Based on the 10-31-00 HED MARC meeting, the degradates in this table were considered to be of concern.
[2] EFED divided the amount of degradate at each time interval by the amount of parent present and multiplied by 100 to obtain the percent of parent as the degradate.
[3] These compounds were either not looked for or not found in aerobic aquatic metabolism or aquatic field dissipation studies. However, volatility is the primary route of dissipation (Sieber, et al., 1989, Soderquist, et al., 1977). Therefore, EFED believes that the estimate of 56 % of parent molinate as toxic degradates is a reasonable estimate for all toxic residues.
[4] Domagalski, J. 1996. Pesticides and Pesticide Degradation Products in Stormwater Runoff: Sacramento River Basin, California. American Water Resources Association, Water Resources Bulletin, Vol. 32, No.5.

Drinking Water from Ground Water

EFED did not run the SCI-GROW2 ground water model because it is inappropriate for rice. SCI-GROW2 assumes vulnerable soils with a shallow water table, but rice fields require impermeable layers to hold the floodwater. Also, SCI-GROW2 does not directly take into account the volatility of a given compound. Therefore, EFED based its assessment on monitoring data.

To provide estimates of dietary exposure from ground water used as drinking water, EFED is recommending the use of 0.056 ug/L for acute, chronic, and cancer assessment for parent molinate and 0.087 ug/L for total toxic residues of molinate. The 0.056 ug/L concentration was the maximum observed in recent USGS monitoring data from California and the Southern Region (Mississippi and Arkansas). Some of the wells in which detections were observed were drinking water wells. There were higher detections that were either due to runoff to open wells (0.56-29 ug/L) or from data of unknown quality or relevance (Missouri and Texas, 1.5 and 0.11 ug/L, respectively). In monitoring conducted by the State of Louisiana, there are also non-detections (LOD 0.11 ug/L) reported in 12 wells located near rice production,. However, other details such as total depth and depth of well casings were not available to interpret these non-detections. In Texas, there were no detections in the Trinity River Basin in recent USGS monitoring. However, EFED notes that if rice production increases, levels in ground water could approach the 0.11 ug/L detection in older monitoring.

The registrant also cited the same data that EFED cited with the exception of the 1.5 ug/L detection. There are no recent detections of parent molinate in ground water in the Trinity River Basin in Texas, and no monitoring for any degradates. In MRID 44970001, the registrant argues that EFED should recommend a maximum ground water value of 0.01 ug/L for dietary exposure assessment. This conclusion is based on a lower limit of detection in the non-detections (0.01 ug/L) and predominance of non-detections. However, even the more recent monitoring data show detections at up to five times this amount, and therefore do not support this conclusion.

In response to information obtained from the USA Rice Federation, additional ground water monitoring was also submitted. According to the submission dated June 2nd, 2000, 50 wells in Louisiana have been sampled for parent molinate residues in 1995, 1997, 1998, and 1999 with no detections (LOD <0.011 ug/L). In a 7/5/2000 fax from Larry LeJeune of the Louisiana Department of Agriculture and Forestry, 12 of the 50 wells are near rice production. However, details such as analytical procedures and depth of wells and well screens were not provided. Therefore, it is impossible to use this information in a drinking water assessment at this time.

Drinking Water from Surface Water

Calculation of Dietary Estimates

At the request of the Health Effect Division (HED), EFED provided maximum values for acute dietary assessment and time-weighed annual means (January-December) for chronic and cancer dietary assessment. In addition, EFED provided time weighted seasonal (May-July) means for any chronic concerns that may be caused by shorter exposure times. The May-July period of time contains the maximum concentrations in surface water because this is the application period of molinate, and paddy water can be released into surface water following application under some conditions. Appendix E contains the detailed descriptions of the monitoring data available for surface water, including graphs and tables of individual monitoring results for each year, along with additional information on the assessment.

Annual and Seasonal Means

EFED used monitoring data to estimate drinking water concentrations in California and the Southeastern U.S. The monitoring data available for this assessment were censored by different detection limits depending on the source of the data. When data are below the limit of detection (LOD), they are reported as non-detects. As a result, EFED calculated upper bounds of parent molinate exposure by using the limit of detection for non-detects and lower bounds by using zero for non-detects. The upper and lower bounds of parent molinate exposure are presented for each location below and the true exposure is between the two bounds. EFED provided the upper 95th percentile of the annual and seasonal means to assess drinking water exposure in Table 4 below.

When calculating annual and seasonal means, the percent error associated with the use of censored data was calculated for each annual and seasonal mean to estimate the amount of uncertainty in the monitoring data. The greater the error, the greater the uncertainty associated with each estimate. The percent error is affected by the amount of non-detections versus total samples, the total number of samples, the time distribution of the data, and the specific limit(s) of detection. When more samples are present over a wider period of time, there is more confidence in the analysis of the data, especially for calculating annual means. This is because wider time intervals around a given sampling interval tend to add more weight to a given sample. Potential skewing of the calculated means can result from this. To calculate the percent error associated with the use of censored data, the formula [(LOD mean-zero mean)*100/LOD mean] was used.

The surface water intakes with the highest exposure are Sacramento and West Sacramento. Maximum concentrations of parent molinate ranged from 1.52-2.13 ug/L, and annual and seasonal mean concentrations ranged from 0.29-0.54 ug/L. The intakes on the Mississippi and Atchafalaya Rivers in Louisiana had similar maximum parent molinate concentrations of 0.109-0.117 ug/L and annual and seasonal mean concentrations of 0.014-0.057 ug/L. Arkansas, Mississippi, Missouri, and Tennessee have no surface water intakes in rice-production areas, and therefore no exposure in drinking water from surface water.

Table 4. Monitoring EECs for parent molinate and residues of concern that may be used for acute, chronic, and cancer risk assessment for molinate.

Location (Source of Data) [Population]	Frequency of Detection (Range of detection limits)	Parent Molinate			Adjustment Factor for degradates of concern[3]	Parent + degradates of concern (See Table 3 above)		
		Maximum Concentration (ug/L)	Annual Means (ug/L)[1]	May-July Seasonal Means (ug/L)[2]		Maximum Concentration (ug/L)	Annual Means (ug/L)	May-July Seasonal Means (ug/L)
Sacramento, California (Upper 95th percentile of parent molinate levels in raw water from the Sacramento River after holding periods (1991-2000 data), [pop. 374,600][4]	65/117 (0.1 ug/L)	1.52	0.29	0.39	1.56	2.37	0.45	0.61
West Sacramento, California (Upper 95th percentile of parent molinate levels in raw water from the Sacramento River after holding periods (1991-2000 data) adjusted for the percent flow data at City of Sacramento, [pop. 30,000][4]	65/117 (0.1 ug/L)	2.13	0.41	0.54	1.56	3.32	0.64	0.84
Arkansas, Mississippi, Missouri, and Tennessee (no surface water intakes in rice-production areas)	Not Applicable	0	0	0	1.56	0	0	0

28

New Orleans Area (Upper 95th percentile of parent molinate levels in raw water from 1996-1999 USGS data in the Mississippi River at St. Francisville, LA), [pop 1.21 million][3]	13/58 (0.004 ug/L)	0.117	0.014	0.050	1.56	0.18	0.022	0.078
St. Mary Parish, Louisiana Intakes at Atchafalaya River (Upper 95th percentile of parent molinate levels in raw water from 1996-1999 USGS data at Melville, LA), [pop. 61,374][5]	15/57 (0.004 ug/L)	0.109	0.018	0.057	1.56	0.17	0.028	0.089
Lake Anahuac, Texas, (from dilution calculations) [pop. 1,960][6]	20/20 (0.004 ug/L)	0.073	0.0029[7]	0.0023[7]	1.56	0.114	0.005[7]	0.004[7]

[1] Time-weighted annual mean concentrations were requested by the Health Effects Division.
[1] Time-weighted seasonal (May-July) mean concentrations. May-July is the highest exposure period for molinate. EFED provided these to the Health Effects Division for any chronic effects that may be caused by shorter-term exposure to molinate.
[3] Based on a meeting between EFED and the HED MARC committee, EFED calculated an adjustment factor of 1.56 for the parent molinate monitoring data to account for degradates of concern (See Table 3 above).
[4] The City of West Sacramento gets all of their water from the Sacramento River, while the City of Sacramento gets 71.4 % of their water from the Sacramento River and 28.6 % from the American River. EFED divided the Sacramento concentrations by 71.4 % to estimate concentrations for West Sacramento. Even though West Sacramento gets more molinate in their water, they do not get taste and odor complaints as does Sacramento. The two cities are investigating this discrepancy.
[5] The intakes below the USGS sampling points at St. Francisville in the Mississippi River and at Melville in the Atchafalaya River are located at diluted portions of both rivers, and both rivers are channelized. There are no significant downstream sources of water to dilute the residues further. As a result, EFED expects concentrations similar to the estimates at these intakes. The annual means using zero for non-detections for 1996, 1998, and 1999 were at or below the limit of detection, while the means calculated using the limit of detection were above the limit of detection, indicating additional uncertainty in these estimates for this location.
[6] White's Bayou drains rice fields directly into Lake Anahuac, a drinking water supply for 1,960 people. However, there are other sources of water for this intake and EFED does not know the exact proportions. Also, rice production along White's Bayou has declined by approximately two-thirds since the year the data were generated (1994).
[7] These estimates have additional uncertainty because they are below the lowest detection limit of 0.004 ug/L.

VII. Terrestrial Exposure and Risk

Table 5 below summarizes the toxicity of molinate to terrestrial organisms. On an acute and subacute basis, molinate is slightly toxic to mammals and practically nontoxic to birds. Molinate is much more toxic on an chronic level. Numerous studies have shown that molinate impairs reproduction function in male and female rats. These effects appear to be at least in part due to endocrine disruption, specifically disruption of testosterone and estrogen production. These reproductive effects appear to be less pronounced in some groups of non-rodent mammals.

Table 5. Summary of toxicity of molinate to aquatic organisms.

Type of Organism	Type of Study	Type of Toxicity Value	Range of Toxicity Values	Toxicity Category
Mammals	Acute Oral	LD_{50}	534-651mg ai/kg	Slightly toxic
	2-Generation Reproduction	NOAEL	5-6 ppm	--
	Acute Oral	LD_{50}	>2250 mg ai/kg	Practically nontoxic
Birds	Subacute Dietary	LC_{50}	>5620 - 21,100 ppm	Practically nontoxic
Terrestrial Plants	Vegetative Vigor	E_{25}	0.22->4.0 lb/A[1]	--

[1] These values are from a supplemental study.

Risk assessment for mammals indicate that unincorporated applications of molinate, whether by granular or EC product, pose a risk to small herbivorous and insectivorous mammals. Soil incorporation of applications are expected to limit this risk to mammals, at least acutely.

The primary risk of molinate to birds and mammals is chronic risk related to reproductive toxicity. The risk assessment for EC products indicate that all uses pose a potential risk of impairing reproduction in all types of mammals. The Agency does not have an accepted method to quantitatively assess chronic risk from application of granular product on soil, but considering the potential level of risk predicted for EC products, potential chronic risk is expected for granular products as well.

Numerous EPA guideline studies and non-guideline studies from the open literature provide consistent evidence that molinate is very toxic to the male and female reproductive systems in rodents. In male rats, observed effects include testicular lesions and degeneration, abnormalities in spermatozoa, and decreased circulating testosterone levels. In female rats, observed effects include ovarian lesions, enlarged ovaries, delayed sexual development, increased abortions, and decreased fecundity. Ellis *et al.* (1998) and Jewell *et al.* (1998) both found that the metabolite molinate sulfoxide causes similar reproductive toxicity in the male rat as does parent molinate, but at even lower doses. They concluded that molinate is bioactivated in rodents through transformation into molinate sulfoxide. Therefore, molinate sulfoxide, which is also an environmental degradation product of parent molinate, could add to the reproductive toxicity of molinate to mammals.

These findings are consistent with molinate, or molinate sulfoxide, being an endocrine disruptor. Ellis *et al* (1998) state that "the association of the initial sperm lesion to the stage of spermatogenesis dependent on testosterone was suggestive of molinate inducing the effects by a perturbation of testosterone synthesis, release, or action at the dependent site within the testes." Wickramarante *et al.* (1998) propose that, in rodents, molinate inhibits the synthesis of estrogen and testosterone, and this interference of hormone production impairs normal processes of reproduction controlled by these hormones, such as vaginal opening in females and sperm production in males.

The amendments to the Food Quality Protection Act (FQPA) and the Safe Drinking Water Act (SDWA) mandate or support the development of a screening program that will determine whether pesticides and certain contaminants of drinking water sources "may have an effect in humans that is similar to an effect produced by a naturally-occurring estrogen, or other such endocrine effect as the Administrator may designate." Very early in its deliberations, EPA's Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) determined that there was both a strong scientific basis and feasibility, considering time and resource constraints, to expand the scope of the screening program to include the androgen- and thyroid hormone systems, and to include evaluations of the potential impacts on wildlife as well as on human health. EPA is developing a screening and testing program which incorporates these modifications.

Based on the adverse findings reported above, EFED recommends that, when testing protocols currently being considered under the Agency's Endocrine Disruptor Screening Program (EDSP) have been validated, molinate be subjected to more definitive testing to better characterize effects related to endocrine disruption.

In Appendix K, the Agency presents a refined terrestrial risk assessment for the application of molinate on rice through application to floodwater. This assessment is applicable to EC applications that are made directly to the floodwater and to aerial application of granular products into flooded rice fields. The assessment predicts risk to an herbivorous bird (the Canada goose), an herbivorous mammal (the muskrat), and a carnivorous mammal (the mink). Exposure is modeled based on predicted daily intake of molinate from residues in food and drinking water. The model shows that, for all three species, exposure to molinate will be below levels that are acutely toxic, but for the two mammals species, exposures are above levels that causes adverse reproductive effects. Thus, the Agency concludes that application of molinate into floodwater poses a potential chronic risk to mammals that are associated with aquatic habitats. The chronic risk for the goose could not be assessed because data on the reproductive toxicity of molinate to birds are not available. Avian reproduction testing with the bobwhite quail and the mallard are required.

Information on the toxicity of molinate to non-target terrestrial plants is limited to one vegetative vigor study which was classified as supplemental. Based on this study, molinate appears to pose minimal risk to non-target terrestrial plants from exposure through spray drift. New phytotoxicity studies providing core data need to be submitted to improve this assessment.

Appendices:

A. Use Profile
B. Physical/Chemical Properties Data
C. Ecological Toxicity Assessment
D. Environmental Fate Assessment and Guideline Summaries
E. Detailed Water Assessment
F. Detailed Risk Quotients
G. Incident Lists
H. Endangered Species
I. References
J. Risk Characterization
K. Refined Terrestrial Risk Assessment

Appendix A. Use Profile

The only crop for which molinate is registered is rice. It is used to control barnyardgrass, sprangletop, broadleaf signalgrass, and various other nonaquatic weeds. The maximum per application rates of products containing molinate range from 3 to 5 lb ai/A, and the maximum per season application rates range from 6 to 9 lb ai/A. Products may be applied two or three times per growing season. Application may be by aircraft or ground equipment. Molinate is currently marketed under the brand names Ordram and Arrosolo, the later of which contains both molinate and propanil as dual active ingredients. Table 1 gives information on the use of individual products.

Table 1. Use information for products containing molinate.

Product name (formulation type)	Application timing and method	Max. per application rate (lb ai/A)	Max per season rate (lb ai/A).	Max. number of applications per season
Arrosolo 3-3E (EC)	On emerged weeds, preflood or postflood after draining	3	9	3
Ordram 8E (EC)	Preplant with soil incorporation (PPI), postemergence preflood, postemergence at flood, and postemergence post flood.	4	6	2
Ordram 15G and 15GM (granular)	Preplant preflood with soil incorporation (water seeded rice in all regions) and preplant postflood (water seeded rice in Southern region only).	4	9	3
Ordram 15G and 15GM (granular)	Postflood postemergence.	5	9	3

Rice in the United States is grown primarily in two regions. One region, hereafter called the "Southern region", consists of the Gulf Coast of Texas and Louisiana and the Mississippi River Valley in Louisiana, Mississippi, Arkansas, and Missouri. Approximately 2,500,000 acres of rice are grown in this region annually. The second region is the Sacramento Valley and San Joaquin Valley in California, where approximately 500,000 acres of rice are grown annually. Use of molinate is widespread in both regions. For the years 1988 through 1997, molinate was applied on average to approximately 40% (1,200,000 acres) of all rice acreage planted in the United States (2,992,000 acres). Labels with products containing molinate restrict its use to the following states: Arkansas, California, Louisiana, Mississippi, Missouri, Tennessee, and Texas.

Approximately 80-85% of rice grown in the Southern region is "dry-seeded", meaning seeds are sowed and grown in dry seed beds for several weeks before flooding. If there is no rainfall, fields are irrigated with a small volume of water (i.e. flushed) to promote seed germination. The remaining 15-20% of rice production in this area, mainly in southern Louisiana, is "water-seeded", meaning that germinated seeds are aerially applied to water in flooded fields. Molinate may be applied to fields before or after they are flooded. EC products are typically applied before flooding. Arrosolo is commonly applied to control emerged weeds before flooding, and ORDRAM 8E is typically applied as a pre-plant incorporated application to water-seeded rice prior to flooding. Granular products are typically used for applications applied after flooding. Arrosolo may also be applied to flooded fields to control weeds that emerge out of the water. With water seeded rice in the Southern region, fields are drained a few days after seeding, and then reflooded several days later after the rice has sprouted. Granular molinate products may be applied at either flood, but most often would be applied after the permanent flood is established since draining the field would cause the efficacy of the application to be lost.

In California, the majority of rice production (98%) is water-seeded with a continuous flood. Unlike the Southern region, in California molinate is almost always applied as a granule to water in flooded fields. A small percentage of rice farmers in California uses "pin-point flood" culture, in which case molinate may be applied as a liquid to dry-ground before fields are flooded. California state regulations prevent rice farmers from discharging tailwater from rice fields for 28 days after application.

Appendix B. Chemical and Physical Properties

Pesticide Name: Molinate
Chemical Name: S-Ethyl hexahydro-1H-azepine-1-carbothioate
P.C. Number: 041402
CAS Number: 2212-67-1

Parameter	Guideline Number	Value or Description	Reference
Color	63-2	Colorless (Pure active); bright orange (Technical)	40237203
Physical State	63-3	Clear liquid (Pure active and Technical)	40237203
Odor	63-4	"Sweetish, reminiscent of sulfur-containing compounds" (Pure active); "Decaying cabbage, reminiscent of sulfur-containing compounds" (Technical)	40237203
Melting Point	63-5	N/A (material is a liquid at room temperature)	40237203
Boiling Point	63-6	136.5°C at 10 torr (Pure active)	40237203
Solubility	63-8	Water: 970 mg/L at 25°	00149370
Vapor Pressure	63-9	0.71 Pa; 5.3×10^{-3} mm Hg/Torr (Pure active)	40593304
Henry's Law Constant	None	1.3×10^{-6} m^3-atm/g-mol	Calculated
Dissociation constant (pKa)	63-10	N/A (material does not dissociate)	40237203
Octanol/water Partition Coefficient (K_{ow})	63-11	average 756 at ambient temperature (Pure active); Log K_{ow}: 2.88	40593304
pH	63-12	7.12 at 20°C (Pure active); 7.47 (Technical)	40237203

Appendix C. Ecological Toxicity Assessment

Ecological Toxicity Summary

On an acute basis, molinate is practically nontoxic to birds and slightly toxic to mammals. Molinate is a reproductive toxicant in mammals, with a chronic NOAEL for ecologically relevant effects at 5 ppm. The chronic toxicity to birds is unknown. Most studies indicate that the molinate is slightly toxic to freshwater and saltwater fish on an acute basis, although a couple of studies indicate that it is highly toxic. Carp are particularly sensitive to subchronic exposure of molinate, with LC_{50}'s from 2-3 exposure studies of approximately 0.2 ppm. The reported chronic NOAEL for fish is 390 ppb, but this value may underestimate the toxicity of molinate because it came from a test which did not assess reproductive effects. Molinate is moderately to highly toxic to both freshwater and saltwater crustaceans on an acute basis. The chronic NOAEL is 110-380 ppb for freshwater crustaceans and 25.6 ppb for saltwater crustaceans. Molinate is slightly toxic to estuarine mollusks. For an herbicide, molinate is not particularly toxic to nontarget plants. Based on vegetative vigor effects, molinate may harm terrestrial plants at an exposure of 0.22 lb/A or more. The EC_{50}'s for sensitive aquatic plants are 3.3 ppm for vascular plants and 0.22 ppm for algae. All toxicity values are given in terms of active ingredient.

a. Toxicity to Terrestrial Animals

i. Birds, Acute and Subacute

An acute oral toxicity study using the technical grade of the active ingredient (TGAI) is required to establish the toxicity of molinate to birds. The preferred test species is either mallard duck (a waterfowl) or bobwhite quail (an upland game bird). Results of this test are shown below.

Acute Oral Toxicity to Birds

Species	% ai	LD_{50} (mg/kg)	Toxicity Category	MRID No. Author/Year	Study Classification[a]
Mallard *(Anas platyrhynchos)*	98.8	>2250[b]	Practically nontoxic	Acc. # 258924 Beavers, 1984	Core

[a] Core studies satisfy test guideline requirements; supplemental studies are scientifically sound, but do not satisfy guideline requirements.
[b] Neither mortality nor adverse effects were observed at any test level.

Since the LD_{50} is greater than 2000 mg/kg, molinate is classified as practically nontoxic to avian species on an acute oral basis. The guideline (71-1) is fulfilled (Acc. No. 258924).

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

Subacute Dietary Toxicity to Birds

Species	% ai	5-Day LC50 (ppm)[a]	Toxicity Category	MRID No. Author/Year	Study Classification
Northern bobwhite quail *(Colinus virginianus)*	98.8	> 5620[b]	Practically nontoxic	Acc. # 258924 Beavers, 1984	Core
Mallard duck *(Anas platyrhynchos)*	98.8	>5620[c]	Practically nontoxic	Acc. # 258924 Beavers, 1984	Core
Mallard duck *(Anas platyrhynchos)*	72.3 (Ordram 6E)	21,100 (15,300 ppm ai)	Practically nontoxic	Acc. # 246020 Beliles *et al.*, 1965	Supplemental[d]

[a] Test organisms observed an additional three days while on untreated feed.
[b] Mortality at 1780 ppm and 3160 ppm were 10% and 30%, but none of these mortalities was attributed to the test substance.
[c] No mortality was observed at any of the test levels.
[d] Study was supplemental because a formulated product was tested.

Since the LC_{50}'s are greater than 5000 ppm, molinate is classified as practically nontoxic to avian species on a subacute dietary basis. The guideline (71-2) is fulfilled (Acc. No. 258924).

ii. Birds, Chronic

Avian reproduction studies using the TGAI are required for all pesticides with outdoor uses. Data on the effects of molinate on the reproduction of birds was previously listed as "reserved", but is now required. These data are especially important since mammalian studies indicate that molinate can cause reproductive toxicity. Avian reproduction studies with the mallard and the bobwhite are required. The guideline (71-4) is not fulfilled.

iii. Mammals, Acute and Chronic

For molinate, the rat toxicity data obtained from the Agency's Health Effects Division (HED) will substitute for wild mammal testing. These toxicity values are reported below.

Acute Toxicity to Mammals

Species	% ai	LD_{50} (mg/kg)	Toxicity Category	MRID/Acc. No.
Rat (*Rattus norvegicus*)	96.0	549	Slightly toxic	247547
Rat (*Rattus norvegicus*)	99.5	*male:* 584 *female:* 660	Slightly toxic	
Rat (*Rattus norvegicus*)	69.3 (Ordram)	940 (651 mg ai/kg)	Slightly toxic	250520
Rat (*Rattus norvegicus*)	69.3 (Ordram)	852 (590 mg ai/kg)	Slightly toxic	250520
Rat (*Rattus norvegicus*)	71 (Ordram 6-E)	*male:* 794 (534 mg ai/kg) *female:* 681 (484 mg ai/kg)	Slightly toxic	
Rat (*Rattus norvegicus*)	10 (Ordram)	>5000 (>500 mg ai/kg)	Practically nontoxic	249409

The results indicate that molinate is slightly toxic to small mammals on an acute oral basis. Results from chronic and subchronic rat studies pertinent to ecological effects are tabulated below.

Subchronic and Chronic Toxicity to Mammals

Species	% ai	Test Type	Toxicity Value	Affected Endpoints	MRID/Acc. No.
Rat (*Rattus norvegicus*)	99.5	13-week feeding	NOEL=700 ppm LOEL=1400 ppm	Decreased organ weight, histological changes	002264
Rat (*Rattus norvegicus*)	99.5	13-week feeding	NOEL=160 ppm LOEL=320 ppm	Ovarian vacuolation	002264
Dog	99.5	13-week feeding	NOEL=900 ppm LOEL=1800 ppm	Increased thyroid weight	002264
Rat (male)		Fertility study, 5 days, 5 weeks, and 10 weeks	NOEL=0.2 mg/kg/day (4 ppm) LOEL=4 mg/kg/day (80 ppm)	Decreased number, viability and mobility of sperm, increased sperm abnormalities, decreased number of implants and fetuses, increased pre-implantation loss.	Acc. No. 245675
Rat	Technical	3-month inhalation	NOEL not determined LOEL=2.2 mg/m^3	Testicular degeneration, abnormal spermatozoa	Acc. No. 241965
Rat	Technical	3-month inhalation	NOEL not determined LOEL=2.2 mg/m^3	Decreased number of implantations and fetuses	Acc. No. 241965
Rat	86.6	90-day neurotoxicity	NOEL not determined LOEL=50 ppm	Body weight, food consumption and utilization	MRID 43270701
Mouse	97.6	18-month carcinogenicity	NOEL=10 ppm LOEL=100 ppm	Testicular degeneration	MRID 41809201, 43037801
Rat		Developmental toxicity	NOEL=44 ppm LOEL=700 ppm	Increase in runting	MRID 41473401
Rat		Developmental toxicity	NOEL=400 ppm LOEL=4000 ppm	Increased abortions, decreased maternal weight gain, increased maternal liver wt, delayed fetal development	MRID 14021015
Rabbit	98.8	Developmental toxicity	NOEL=20 mg/kg/d (~660 ppm) LOEL=200 mg/kg/d (~6600 ppm)	Increased abortions, decreased maternal body weight gain, increase liver weight, reduced ossification of the sternbrae.	MRID 001474-30
Rabbit	98.1	Male fertility	NOEL=40 mg/kg/d (~1320 ppm) LOEL=80 mg/kg/d (~2640 ppm)	Atypically sperm	MRID 425613-01
Rat	97.6	2-generation reproduction	*Maternal:* NOEL=6 ppm LOEL=50 ppm *Repro:* NOEL=6 ppm LOEL=50 ppm	Vacuolation/hypertrophy of the ovary Decreased fecundity, vocuolation/hypertrophy of ovary, ovarian lesions in offspring	MRID 41333402
Rat		2-generation reproduction	*Parental:* NOEL=5 ppm LOEL=10 ppm *Repro:* NOEL=5 ppm♂/ 20 ppm♀ LOEL=10 ppm♂/	Increased sperm abnormalities Lesions in ovary, increased sperm abnormalities, decreased % pups born alive	MRID 44403201

Subchronic and Chronic Toxicity to Mammals

Species	% ai	Test Type	Toxicity Value	Affected Endpoints	MRID/Acc. No.
Rat	Technical	3-generation reproduction	NOEL>12.6 ppm	–	231331
Rat	Technical	2-year feeding/ carcinogenicity	NOEL not determined LOEL<12.6 ppm	Increased organ and testes weight	231327 and 236576
Rat	97.6	2-year feeding/ carcinogenicity	*Reproductive:* NOEL=7 ppm LOEL=40 ppm *Neurotoxicity:* NOEL < 7 ppm LOEL = 7 ppm	Ovarian lesions, degeneration with atrophy of testes and decreased testes weight at 300 ppm. Degeneration/demethylaOon in the sciatic nerve and atrophy/reserve cell hyperplasia in the muscle.	MRID 41815101, 43037801, and 43116302
Rat	96.8	Neurotoxicity	*Mat:* NOEL=300 ppm LOEL=700ppm *Repro:* NOEL=700ppm LOEL=1000ppm	Decreased body weight gain and food consumption Increased gestarioo length, decreased litter size, decreased percent of male pups, decrease number of pups born alive, and death of all pups by day 4 post partum.	MRID 4338202
Rat		22-day *post partum partum partum*	NOEL not determined LOEL=300 ppm	Delayed vaginal opening	MRID 44373601

Molinate shows a clear pattern of causing reproductive toxicity in rodents. Numerous studies involving different routes of exposure (dietary, inhalation, and injection) show that molinate exposure damages testes and ovaries and reduces fertility in males and females. Studies also show that sexual development in offspring is impaired. Although the mechanism of action is uncertain, these results are consistent with molinate possibly being an endocrine disruptor. In addition to reproductive and developmental effects, molinate has been shown to be a neurotoxin Neurotoxic effects have been observed in offspring following *in utero* exposure at dose levels at or below the maternal NOAEL. Studies with rabbits and dogs suggest that nonrodent species are considerably less sensitive to the reproductive toxicity of molinate than are rodents.

For the purpose of the risk assessment for wild mammals, the two-generational study with the rat (MRID 4440320) established the NOAEL as 5 ppm and the LOAEL as 10 ppm for male mammals. For female mammals, a second 2-generational study with the rat (MRID 41333402) established the NOAEL and LOAEL as 6 ppm and 50 ppm, respectively. These NOAEL and LOAEL values are based on endpoints that are known to be ecologically significant, including reduced number and survival of offspring (i.e., fertility).

Published literature provides further evidence of the reproductive toxicity of molinate. Jewell *et al.* (1998) found that *ip* administration of molinate at doses of 200 to 400 mg/kg produced tissue damage in the testes of male rats. The testes in the rats of the 400 mg/kg showed severe atrophy, weighing less than half of the testes of control rats, and were almost completely absent of germ cells. Although this study did not look at reproduction, the results indicate that these rats became essentially infertile. Similar effects were observed in rats that were administered molinate sulfoxide, a primary metabolite of molinate, suggesting that the toxic moiety is molinate sulfoxide or another metabolite that is produced further down the metabolic pathway. The authors concluded that reproductive toxicity of the sulfoxide metabolite exceeds that of the parent.

Ellis et al. (1998) found similar effects on reproduction, but at lower doses, when they administered molinate and molinate sulfaxide to male rats for a duration of 7 days. When administered at 40 mg/kg/day (approximately 800 ppm) molinate produced a sperm lesion and caused markedly decreased concentrations of circulating and testicular testosterone. Morphological changes in the testes were observed at higher doses (140 mg/kg/day). Administration of the metabolite molinate sulfoxide at 10 mg/kg/day (approximately 200 ppm) or more produced a similar sperm lesion and caused markedly decreased plasma and testicular concentrations. The results provide further evidence that metabolic activation of molinate, which involves the oxidation of the molinate sulfur, results in testis damage and reproductive impairment.

iv. Insects

A honey bee acute contact study using is not required for molinate because its use only on rice, a crop which is not associated with much honey bee exposure. Therefore, testing of molinate for nontarget insect toxicity is not required.

b. Toxicity to Freshwater Animals

i. Freshwater Fish and Amphibians, Acute and Subchronic

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

Acute Toxicity of Technical Molinate to Freshwater Fish

Species/ (Flow-through or Static)	% ai	96-hour LC50 (ppm)	Toxicity Category	MRID/Acc. No. Author/Year	Study Classification
Rainbow trout *(Oncarhynchus mykiss)* flow-through	96.8	20 (17-27)	Slightly toxic	MRID 43337603 Kent *et al.*, 1994	Core
Rainbow trout *(Oncorhynchus mykiss)* static	98.6	0.21 (0.16-0.29)	Highly toxic	MRID 40098001 Mayer and Ellersieck, 1986	Core
Rainbow trout *(Oncorhynchus mykiss)* static	99	6.97 (5.21-9.34)	Moderately toxic	Acc. No. 246020 Sleight *et al.*, 1970	Supplementary
Rainbow trout *(Oncorhynchus mykiss)* static	97.8	1.3 (0.896-1.88)	Moderately toxic	Acc. No. 246020 Beliles *et al.*, 1983	Supplementary
Bluegill sunfish *(Lepomis macrochirus)* flow-through	96.8	23.1 (18-32)	Slightly toxic	MRID 43337602 Kent *et al.*, 1994	Core
Bluegill sunfish *(Lepomis macrochirus)* static	98.6	0.32 (0.19-0.53)	Highly toxic	MRID 40098001 Mayer and Ellersieck, 1986	Core
Bluegill sunfish *(Lepomis macrachirus)* static	99	18.8 (16.7-21.1)	Slightly toxic	Acc. No. 246020 Sleight *et al.*, 1970	Supplementary
Bluegill sunfish *(Lepomis macrochirus)* static	97.8	29 (20.4-39.7)	Slightly toxic	Acc. No. 246020 Beliles *et al.*, 1983	Supplementary
Catfish (unknown species)	Technical	13.0 (10.6-16.0)	Slightly toxic	Acc. No. 246020 McGowan, 1972	Supplementary
Fathead minnow (*Pimephales promelas*) static	99	26.0 (20.5-32.9)	Slightly toxic	Acc. No. 246020 Sleight *et al.*, 1970	Supplementary
Carp (*Cyprinus corpio*) static	Technical	42.8 (32-56)	Slightly toxic	Acc. No. 246020	Supplementary
Goldfish (*Carrassius auratus*)	97.8	30 (16.2-55.5)	Slightly toxic	Acc. No. 246020 Beliles *et al.*, 1983	Supplementary

Below are toxicity results for formulated products of molinate.

Acute Toxicity of Formulated Products of Molinate to Freshwater Fish

Species/ (Flow-through or Static)	% ai	96-hour LC50 (ppm)	Toxicity Category	MRID/Acc. No. Author/Year	Study Classification
Rainbow trout *(Oncorhynchus mykiss)* static	90.3 (Ordram 8E)	19.5 (9.8-31) (17.6 mg ai/L)	Slightly toxic	MRID 41613603 Tapp *et al.*, 1990	Core
Rainbow trout, stealhead form *(Oncorhynchus mykiss)*, static	90.3 (Ordram 8E)	14 (4.7-23.3)	Slightly toxic	Finlayson and Faggella, 1986	Unreviewed (Open literature)
Chinook salmon *(Oncorhynchus tshawytscha)*	90.3 (Ordram 8E)	13 (10.8-15.2)	Slightly toxic	Finlayson and Faggella, 1986	Unreviewed (Open literature)
Bluegill sunfish *(Lepomis macrochirus)* static	90.3 (Ordram 8E)	24 (18-33) (21.7 mg ai/L)	Slightly toxic	MRID 41613601 Sankey *et el.*, 1990	Core
Channel catfish *(Ictalurus punctatus)*	90.3 (Ordram 8E)	34 (20-48)	Slightly toxic	Finlayson and Faggella, 1986	Unreviewed (Open literature)
Striped bass *(Morone saxatilis)*	90.3 (Ordram 8E)	8.1 (6.4-9.8)	Slightly toxic	Finlayson and Faggella, 1986	Unreviewed (Open literature)
Mosquito fish *(Gambusio affinis)*	71.0 (Ordram 6E)	26 (18 mg ai/L)	Slightly toxic	MRID 00084743 Bullock, 1968	Supplementary

The acute toxicity of molinate to fish is uncertain because of the unusually wide range of reported toxicity values. The majority of the studies place the toxicity of molinate in the "slightly toxic" category (>10 to 100 ppm); however, two supplemental studies place it in the "moderately toxic" category (>1 to 10 ppm), and two studies reported in the EPA reference manual of Mayer and Ellersieck (1986) place it in the "highly toxic" range (0.1 to 1 ppm). These data indicate that the rainbow trout or the striped bass is the most sensitive species tested for acute toxicity, although under subchronic exposure the common carp might be even more sensitive (see below). Because of the large discrepancy in reported toxicity values, both the minimum value for the rainbow trout (0.21 mg ai/L) and the mean of the six LC_{50} values from studies with rainbow trout (10.3 mg ai/L) will be used in the risk assessment for freshwater fish. These data fulfill the requirements of guideline 72-1 (MRIDs 43337602, 43337603, 41613601, 41613603, 40098001, Acc. No. 246020).

Other studies with a formulated product have shown that subchronic exposure (21-28 days) to molinate can cause mortality in fish at concentrations lower than those that are toxic at acute exposure. The mechanism of the subchronic mortality appears to be induced anemia (Kawatsu, 1977). Finlayson and Faggella (1986) concluded that the mortality of an estimated 7,000 to 30,000 common carp in the Colusa Basin Drain in California from 1981 through 1983 could be attributed to high molinate concentrations resulting from drainage of water from rice fields. The following table summarized finding of subchronic toxicity of fish by molinate.

43

Subchronic Toxicity to Freshwater Fish

Species/ (Flow-through or Static)	% ai	Subchronic LC50 (ppm)	NOAEL (ppm ai)	LOAEL (ppm)	Endpoint effected	MRID/Acc. No. Author/Year
Common carp (*Cyprinus carpio*)	90.3 (Ordram 8-EC)	0.21 (28-day)	0.09	0.13	Survival, hematocrit and hemoglobin levels	Finlayson and Faggella, 1986
Common carp (*Cyprinus carpio*)		0.18 (21-day)	0.032			Kawatsu, 1977
Channel catfish (*Ictalurus punctatus*)	90.9 (Ordram 8E)	6.1 (4.5-8.1)	0.88	1.57	Behavior, hematocrit and hemoglobin levels	Miller 1984 Acc. No. 258924
Channel catfish (*Ictalurus punctatus*)	90.3 (Ordram 8-EC)	>8.6	1.7	2.6	Hematocrit and hemoglobin levels	Finlayson and Faggella, 1986
Bluegill sunfish (*Lepomis mocrochirus*)	90.9 (Ordram 8E)	>6.05	6.05	–[2]	None	Miller 1984 Acc. No. 258924

[1] These toxicity categories were established for acute toxicity.
[2] No adverse effects were observed at any test concentration.

These results show that exposure to molinate concentrations as small as 0.13 ppm for 28 days can cause significant declines in hematocrit and hemoglobin levels, signifying anemia, which can lead to mortality of fish. The study with the channel catfish found that hematocrit and hemoglobin levels returned to normal by day 42 of the recovery period.

Heath *et al.* (1997) studied mortality and sublethal effects in the fathead minnow in response to acute exposure to molinate. The results from this study are somewhat unreliable because a problem with low dissolved oxygen compromised the test of molinate toxicity. Increased mortality and slowed growth were observed in fish exposed to 83 μg/L and 9700 μg/L of molinate, but these responses were not dose-related and could have been caused by the low DO conditions. A reduction in swimming response was observed in fish exposed to a concentration near the LC_{50} (9700 μg/L), but not in fish exposed to a concentration that approximated molinate levels in the Colusa drain (83 μg/L). Neither concentration level resulted in observable effects on acetylcholinesterase activity or critical thermal minimum and maximum levels. Finally, in two trials testing fish water collected from the Colusa Basin Drain, mortality was at low background levels and fish showed no adverse sublethal effects. The water samples were taken from the Colusa Basin Drain on May 21 and June 6, 1994, a time of the year of peak use of molinate on rice. This paper concluded that levels of molinate that currently occur in Colusa Basin Drain (after the imposition of mandatory water-holding periods on rice fields) cause no acute or measurable sublethal effects in fish.

The table below gives results of tests of the toxicity Ordram:Propanil 3:3E, a formulated product containing propanil as well as molinate. The percent active ingredients of this product were not specified.

Acute Toxicity of Ordram:Propanil 3:3E to Freshwater Fish

Species/ (Flow-through or Static)	96-hour LC50 (ppm)	Toxicity Category	MRID No. Author/Year	Study Classificanoo
Rainbow trout *(Oncorhynchus mykiss)* static	8.3 (5.6-18)	Moderately toxic	41613604	Core
Bluegill sunfish *(Lepomis macrochirus)*	14 (11-18)	Slightly toxic	41613602	Core

These results indicate that Ordram:Propanil 3:3E is slightly to moderately toxic to freshwater fish on an acute basis.

One study is available on the toxicity of molinate to amphibians. Sanders (1970, Acc. No. 246020, Reference No. 25) tested the acute toxicity of molinate to tadpoles of the Fowler's toad (*Bufo woodhousii fowleri*), and determined the 96-hr LC_{50} to be 14 mg/L. The percent purity of the test material is unknown. It appears from these data that the toxicity of molinate to amphibians is comparable to the toxicity to fish.

ii. Freshwater Fish, Chronic

A freshwater fish early life-stage test using the TGAI is required for molinate because the end-use product may be applied directly to water, and the following conditions are met: (1) water monitoring data show that the pesticide is continuously presence in water over several days, (2) some aquatic acute LC_{50} and EC_{50} values are less than 1 mg/L, and (3) the EEC in water is equal to or greater than 0.01 of acute LC_{50} and EC_{50} values. Furthermore, a supplemental study with the mysid (MRID 43976801) indicates that molinate is toxic to early life-stages of aquatic organisms at concentrations considerably lower than toxic to later life-stages (MRID 43976801).

Early Life-Stage Toxicity to Freshwater Fish under Flow-through Conditions

Species, Study Duration	% ai	NOAEL (ppb)	LOAEL (ppb)	MATC[1] (ppb)	Endpoints Affected	MRID No. Author/Year	Study Classification
Rainbow trout *(Oncorhynchus mykiss)*, 60 days	99	390	830	570	Survival	40657801 McAllister 1987	Supplemental[2]

[1] MATC is defined as the geometric mean of the NOAEL and LOAEL.
[2] This study does not fulfill the guideline requirements because the dilution water had excessive hardness and pH, the time to hatch was not measured, the raw data were not provided, and incomplete information was provided on test methodology.

Based on supplemental study, survival of early life stages of freshwater fish will begin to be affected at molinate concentrations between 390 and 830 μg ai/L. It should be noted that this study does not assess the effects of molinate on the reproduction of fish. Although the test guideline (72-4) has not been fulfilled, a new fish early life-stage study is not required because information on chronic toxicity will be provided by the required fish life-cycle study (see below).

A freshwater fish life-cycle test using the TGAI is required for molinate because the end-use product is intended to be applied directly to water and both of the following triggers are met: (1) the EEC is equal to or greater than one-tenth of the NOAEL in the fish early life-stage and the invertebrate life-cycle test, and (2) studies of other organisms indicate the reproductive physiology of fish may be affected. The reproductive toxicity of molinate has been clearly demonstrated in mammalian studies, and this toxicity also may be expressed in other vertebrates, including fish. The preferred test species is fathead minnow. The test guideline (72-5) is not fulfilled.

iii. Freshwater Invertebrates, Acute

A freshwater aquatic invertebrate toxicity test using the TGAI is required to establish the toxicity of molinate to aquatic invertebrates. The preferred test species is *Daphnia magna*. Results of this test are tabulated below.

Acute Toxicity to Freshwater Invertebrates

Species, Study Type	% ai	EC_{50} (ppm ai)	Toxicity Category	MRID No. Author/Year	Study Classification
		Technical			
Waterflea (*Daphnia magna*), static	"Technical"	*48-hr:* 19.4 (15.2-25.5)	Slightly toxic	Acc. # 246020 Vilkas and Hutchinson, 1977	Core
Waterflea (*Daphnia magna*)	Technical	*26-hr:* 0.70 (0.46-1.05)	Highly toxic	MRID 05001465 Crosby and Tucker, 1966	Supplemental[1]
Amphipod[2] (*Gammarus lacustris*)	98.6	*48-hr:* 7.6 (6.1-9.5)	Moderately toxic	MRID 05009242 & 40098001 Mayer and Ellersieck, 1986	Supplemental
		96 hr: 4.5 (3.5-5.8)			
Stonefly[2] (*Pteronorcys spp.*)	98.6	*96 hr:* 0.34 (0.24-0.47)	Highly toxic	MRID 40098001 Mayer and Ellersieck, 1986	Supplemental
Moina australiensis (an Australian cladoceran), static	Technical	*48 hr:* 2.40 (1.42-4.18)	Moderately toxic	Julli and Krassoi, 1995	Supplemental (Open literature)
		8-day: 0.30 (0.16-0.57)	Highly toxic		
		Formulated Product			
Waterflea (*Daphnia magna*), static	91.2 (Ordram 8E)	4.7 (4.3-5.3) (4.3 ppm ai)	Moderately toxic	MRID 41613605 Farrelly and Hamer, 1989	Core

[1] Study is supplemental because the exposure period was only 26 hours.
[2] Study was conducted with mature organisms.

The majority of the studies classify molinate as moderately to highly toxic to freshwater invertebrates on an acute basis, although one older study would classify it as slightly toxic. The stonefly EC_{50} of 0.34 mg ai/L will be used for the risk assessment to freshwater invertebrates. An 8-day study with *Moina australiensis* found an EC_{50} value that was approximately an order of magnitude less than that found in the 48-hr toxicity study. This indicates that subacute exposure of molinate is more toxic to freshwater invertebrates than is acute exposure. A similar phenomenon has been observed in fish. The guideline (72-2) is fulfilled (MRID 41613605, Acc. No. 246020).

iv. Freshwater Invertebrate, Chronic

A freshwater invertebrate life-cycle test using the TGAI is required for molinate because the end-use product may be applied directly to water, and the following conditions are met: (1) water monitoring data show that the pesticide is continuously presence in water over several days, (2) some aquatic acute LC_{50} and EC_{50} values are less than 1 mg/L, and (3) the EEC in water is equal to or greater than 0.01 some of the acute LC_{50} and EC_{50} values. Furthermore, a supplemental study with the mysid (MRID 43976801) indicates that molinate is toxic to early life-stages of aquatic organisms at concentrations considerably lower than toxic to later life-stages (MRID 43976801). The preferred test species is the waterflea.

Life-Cycle Toxicity to Freshwater Invertebrates

Species, test type	% ai	NOAEL (ppm)	LOAEL (ppm)	MATC[1] (ppm)	Endpoints Affected	MRID No. Author/Year	Study Classification
Waterflea (*Daphnia magna*)	97.5	0.38	0.90	0.59	Reproduction and growth (length)	40657802 Forbis 1987	Core[2]
Moina australiensis (an Australian cladoceran), static	Tech	0.11 (8-day)	0.29 (8-day)	0.18 (8-day)	Reproduction	Julli and Krassoi, 1995	Supplemental (Open literature)

[1] Defined as the geometric mean of the NOAEL and LOAEL.
[2] Upgraded from supplemental to core (see EPA memo for bar code D259942)

The risk assessment will be based on core data, which shows that molinate can impair the growth and reproduction of freshwater invertebrates at concentrations of 0.90 mg/L or greater. The NOEL was established at 0.38 ppm. Supplemental data for *Moina australiensis* indicate that some freshwater crustaceans are more sensitive to molinate than is the standard test specis, *Daphnia magna*. The test guideline for an aquatic invertebrate life cycle study (GLN 72-4b) has been fulfilled (MRID 40657802).

c. Toxicity to Estuarine and Marine Animals

i. Estuarine and Marine Fish and Invertebrates, Acute

Acute toxicity testing with estuarine/marine fish and invertebrates is required because the use of molinate on rice in coastal areas is expected to result in the active ingredient reaching this environment. The preferred test species are the sheepshead minnow, the mysid and the eastern oyster. Results of these tests are tabulated below.

Acute Toxicity to Estuarine/Marine Fish and Invertebrates

Species, Type of Study	% ai.	96-hour EC50 or LC50 (ppm ai)	Toxicity Category	MRID No. Author/Year	Study Classification
Sheepshead minnow *(Cyprinodon variegatus)*, Flow-through	96.8	13-24[a]	Slightly toxic	MRID 43337604 Kent *et al.*, 1994	Supplemental[b]
Sheepshead minnow *(Cyprinodon variegatus)*, Static	98.8	13 (7.8-22)	Slightly toxic	Acc. # 258924 Ward, 1984	Supplemental[c]
Eastern oyster *(Crassostrea virginica)*, Static embryo-larvae	96.8	27.1 (25.0-29.4)	Slightly toxic	MRID 43337601 Kent *et al.*, 1994	Core
Mysid *(Americamysis bahia)* static	96.8	2.5 (1.8-3.4)	Moderately toxic	MRID 43337605 Kent *et al.*, 1994	Core
Mysid *(Americamysis bahia)* static	98.8	0.76 (0.13-1.00)	Highly toxic	Acc. # 258924	Core

[a] Observed mortality was 0% at 13 ppm and 70% at 24 ppm.
[b] The LC_{50} could not be established because mortality occurred at only one test level.
[c] This study does not fulfill the guideline requirements because insolubility was observed at the two highest test levels, fish were larger than recommended, and temperature was not properly controlled.

Since the LC_{50} for the mysid is 0.1 and 1.0 ppm, molinate is classified as highly toxic to estuarine/marine crustaceans on an acute basis. Molinate is only slightly toxic to estuarine/marine fish and immature mollusks. The guidelines for shrimp and mollusks (72-3b and 72-3c) are fulfilled (MRIDs 43739801 and 43603305, respectively). Although the guideline for estuarine/marine fish (72-3a) is not fulfilled, but supplemental data (MRID 43337604, Acc. No. 258924) and core data for the toxicity of Ordram 8E (MRID 416136-07) together provide adequate information on the acute toxicity of molinate.

Results of toxicity testing of formulated products with marine/estuarine species are given in the table below. The results indicate that the formulated products show similar toxicity to the active ingredient for fish and crustaceans, but appear to have somewhat greater toxicity to mollusks.

48

Acute Toxicity of Formulated Products to Estuarine/Marine Fish and Invertebrates

Species, Type of Study	Formulation	96-hour EC50 or LC50 (ppm formulation)	Toxicity Category	MRID No. Author/Year	Study Classification
Sheepshead minnow *(Cyprinodon variegotus)*, Static	Arrosolo 3-3E[1]	17 (9.4-30)	Slightly toxic	MRID 41613608 Tapp *et al*., 1990	Core
Sheepshead minnow *(Cyprinodon variegotus)*, Static	Ordram 8E[2]	12 (11-34)	Slightly toxic	MRID 416136-07 Tapp *et al*., 1990	Core
Eastern oyster *(Crassostrea virginica)*, Flow-through shell deposition	Arrosolo 3-3E[1]	4.5 (4.2-4.8)	Moderately toxic	MRID 41705302	Supplemental
Eastern oyster *(Crassostrea virginica)*, Flow-through shell deposition	Ordram-8E[2]	5.3 (4.7-6.2)	Moderately toxic	MRID 41705301	Supplemental
Mysid (*Americamysis bahia*), static	Arrosolo 3-3E[1]	7.6 (5.7-10.0)	Moderately toxic	MRID 41613610 Williams *et al*., 1990	Core
Mysid (*Americamysis bahia*), static	Ordram-8E[2]	3.4 (2.6-4.4)	Moderately toxic	MRID 41613609 Williams *et al*., 1990	Core

[1] Arrosolo 3-3E contains 33.5% molinate and 34% propanil.
[2] Ordram 8E contains 90.3% molinate.

ii. Estuarine and Marine Invertebrate, Chronic

An estuarine/marine invertebrate life-cycle toxicity test using the TGAI is required for molinate because the end-use product may be applied directly to the estuarine/marine environment or expected to be transported to this environment from the intended use site, and any of the following conditions are met: (1) the pesticide is intended for use such that its presence in water is likely to be continuous or recurrent regardless of toxicity, (2) any aquatic acute LC50 or EC50 is less than 1 mg/l, (3) the EEC in water is equal to or greater than 0.01 of any acute LC50 or EC50 value, or, (4) the actual or estimated environmental concentration in water resulting from use is less than 0.01 of any acute LC50 or EC50 value and any of the following conditions exist: studies of other organisms indicate the reproductive physiology of fish and/or invertebrates may be affected, physicochemical properties indicate cumulative effects, or the pesticide is persistent in water (e.g., half-life greater than 4 days). The preferred test species is the mysid. Results of this test are tabulated below.

Chronic Toxicity to Estuarine/Marine Invertebrates

Species, Type of Study	% ai	28-day NOAEL (ppb ai)	28-day LOAEL (ppb ai)	MATC[1] (ppm ai)	Most Sensitive Endpoints	MRID No. Author/Year	Study Classification
Mysid (*Neomysis mercedis*), Flow-through early life-stage test	tech	25.6	45.2	34.0	Larvae survival	MRID 43976801 Bailey 1993	Supplemental[2]

[1] Defined as the geometric mean of the NOAEL and LOAEL.
[2] This study is supplemental due to guideline deviations in hardness and pH, no time-to-hatch data, no raw data submitted, and incomplete information of test methodology.

Based on measured concentrations, molinate inhibited the growth of mysids at concentrations of 6.15 µg/L and greater. The NOAEL for growth was 3.09 µg/L. Reproduction of mysid was impaired at a concentration of 45.4 µg/L. The test guideline (72-4) is not fulfilled.

d. Toxicity to Plants

i. Terrestrial Plants

Terrestrial plant testing is required for molinate because it is an herbicide with non-residential terrestrial use patterns, and it may be applied aerially, is volatile (vapor pressure = 5.3 x 10^{-3} mg Hg/Torr at 25°C), and may pose hazards to endangered or threatened plant species. The required testing consists of seedling emergence and vegetative vigor tests with ten crop species. Six of the species must be dicotyledonous and represent at least four families. One of these species must be soybean (*Glycine max*) and a second must be a root crop. The remaining four species must be monocotyledonous and represent at least two families. One of these species must be corn (*Zea mays*). Tier I tests (GLN 122-1) may be conducted to measure the response of plants, relative to a control, at a test level that is equal to the highest use rate (expressed as lbs ai/A) or three times the EEC for nontarget areas. Tier II tests (GLN 123-1) are required for any test species that shows a reduction in response equal to or greater than 25% in the Tier I tests.

Tier II tests measure the response of plants, relative to a control, and five or more test concentrations. A tier II phytotoxicity study with Ordram 8E, a TEP containing 91.4% molinate, has been submitted to the Agency (MRID 41613611). The seedling emergence portion of this test was classified as invalid and cannot be used to assess risk. The results of the vegetative vigor portion of this study are tabulated below.

Effects of Ordram 8-E (91.4% Molinate) on the Vegetative Vigor of Nontarget Terrestrial Plants (Tier II), Based on Farmer and Canning, 1990 (MRID 41613611).

Species	EC_{25} (lbs ai/A)	EC_{10} (lb ai/A)[a]	Most Sensitive Endpoint Affected	Study Classification
Corn (monocot)	>4.0	1.4 (0.74-2.7)	Visual assessment	Supplemental[c]
Winter wheat (monocot)	>4.0	>4.0	Visual assessment	Supplemental[c]
Wild oat (monocot)	>4.0	2.9 (1.0-45)	Visual assessment	Supplemental[c]
Purple nutsedge (monocot)	>4.0	>4.0	Visual assessment	Supplemental[c]
Sugar beet (dicot, root crop)	>4.0	1.3 (0.63-2.6)	Visual assessment	Supplemental[c]
Soy bean (dicot)	0.22 (0.15-0.29)	0.05 (0.03-0.78)	Visual assessment	Supplemental[c]
Oilseed rape (dicot)	2.5 (1.6-4.9)[b]	0.32 (0.15-0.54)[b]	Visual assessment	Supplemental[c]
Teaweed (dicot)	1.3 (1.0-1.6)	0.62 (0.44-0.81)	Visual assessment	Supplemental[c]
Velvetleaf (dicot)	0.42 (0.31-0.53)	0.13 (0.08-0.19)	Visual assessment	Supplemental[c]
White mustard (dicot)	0.66 (0.41-1.0)	0.06 (0.02-0.12)	Visual assessment	Supplemental[c]

[a] EC_{10} values are reported in lieu of NOAEL values, which were not determined for the visual damage assessment. For plant dry weights, the study report gave NOAEL values, but not EC_x values. For every species tested, the NOAEL value for plant dry weights was greater than the EC_{10} for the visual damage assessment.

[b] The EC_{25} and EC_{10} values reported for oilseed rape are for 14 days after treatment because heat damage to plants prevented data from being collected for 28 days after treatment.

[c] This study is supplemental because EC values were not calculated for percent emergence or dry weight, visual assessments were not conducted in control plants, and the progression of application rates was 4-fold rather than 2-fold.

For Tier II vegetative vigor soybean is the most sensitive species (based on supplemental data). Monocot species do not appear to be sensitive to vegetative vigor effects of molinate. The test guidelines (123-1a and 123-1b) are not fulfilled.

ii. Aquatic Plants

Terrestrial Tier II studies are required for all low dose herbicides (those with the maximum use rate of 0.5 lbs ai/A or less) and any pesticide showing a negative response equal to or greater than 50% in Tier I tests. The following species should be tested at Tier II: *Pseudokirchneria subcapitata* (formerly *Selanastrum capricornutum*), *Lemna gibba*, *Skeletonema costatum*, *Anabaena flos-aquae*, and a freshwater diatom.

51

Results of Tier II toxicity testing on the technical/TEN material are tabulated below.

Toxicity to Aquatic Plants (Tier II)

Species	% ai	EC_{50} (ppm)	NOAEL (ppm)	MRID No. Author/Year	Study Classification
Vascular Plants					
Duckweed *Lemna gibba*	99	3.30	0.84	MRID 41702702 Thompson *et al.*, 1990	Core
Nonvascular Plants					
Green algae *Pseudokirchneria subcapitata*	99	0.22 (4-day)	0.17 (4-day)	MRID 41613612 Smyth *et al.*, 1990	Core
Marine diatom *Skeletonema costatum*	99	4.3 (4-day)	0.94 (4-day)	MRID 41613613 Smyth *et al.*, 1990	Core
Freshwater diatom *Navicula pelliculosa*		10 (4-day)	4.5 (4-day)	41702703	Core
Blue-green algae *Anabaena flos-aquae*		9.48	0.95	41702701	Supplemental

The Tier II results indicate that *Pseudokirchneria subcapitata* is the most sensitive aquatic plant, with an EC_{50} of 0.22 ppm. The guideline (123-2) is fulfilled for duckweed, green algae, marine diatoms, and freshwater diatoms (MRID 41702702, 41613613, 41613613, and 41702703), but not for bluegreen algae.

e. Fish and Wildlife Mortality Incidents

Finlayson and Faggella (1986) investigated the cause of large fish kills that occurred in the Colusa Basin Drain in north-central California, an agricultural drain that runs through an intensive rice-growing area. They report that an estimated 7,000 to 30,000 carp died annually in this drain between 1981 and 1983. No fish kills were observed in 1984 to 1987. They determined the 28-day LOEL and LC_{50} for carp to be 0.13 and 0.21 ppm, respectively. Water monitoring of the Colusa Basin Drain showed that peak residue values in the years 1981 through 1983 exceeded the carp LOEL and approached or exceeded the carp LC_{50}, whereas peak values during 1984 through 1986 remained below the carp LOEL and LC_{50}. Significantly, primarily carp were killed in this drain, while other species present such as bass and catfish were not affected. Laboratory studies have shown that carp are particularly sensitive to the anemic effects of molinate, whereas other species, such as the channel catfish (Finlayson and Faggella, 1986) and bluegill sunfish (Miller, 1984) are relatively insensitive. Furthermore, Finlayson and Faggella (1986) showed that molinate exposure significantly reduces hemoglobin and hematocrit levels in carp, and found that carp collected from the Colusa Basin Drain in 1983 had reduced hemoglobin and hematocrit on June 15, following a period of high molinate exposure. Thus, while there is no evidence from tissue analysis, circumstantial evidence suggest that molinate was likely the primary causal factor of the large fish kills in the Colusa Basin Drain. It should be noted that continued residue monitoring of this drain has shown that peak residues were reduced substantially following the imposition of mandatory water-holding periods for rice farmers beginning in 1990.

The Environmental Incident Information System contains two incidents of fish kills that could be attributed to molinate. In one incident in 1978, thousands of dead carp were observed in the a toe drain area on the Yolo Bypass in Yolo County, California (Incident # B0000-215-06). Analysis of water samples detected molinate at a concentration of 60 ppb. Fish were too decomposed for tissues to be analyzed. Although molinate cannot be confirmed as the causal factor, the similarities of this incident to the kills of carp mentioned above suggest that it could have been caused by molinate toxicity.

A second incident possibly attributed to molinate occurred in Bayou Macon in West Carroll Parish, Louisiana, in 1991 (Incident # I000109T). This incident involved an unknown number of dead fish of "multiple species". It occurred in a bayou that is lined on both sides by cotton and rice fields. Water samples revealed molinate concentrations of 15-20 ppb. Although this concentration is not thought to be enough to be lethal to fish, the condition of the fish indicated that they were killed several days prior to the incident being reported, and molinate residues could have been higher at that time. No analysis of fish tissue was conducted since the fish were too decomposed. There is too little evidence to conclude that this fish kill was or was not caused by molinate.

Appendix D. Environmental Fate Assessment and Guideline Summaries

Environmental Fate Assessment

Zeneca has submitted many documents pertaining to the environmental fate and transport of molinate. While the data contained in these documents are generally deficient in terms of compliance with Subdivision N guidelines, the weight of evidence from the submitted studies and the monitoring data together satisfy all environmental fate and transport guidelines and provide a relatively consistent picture of the environmental fate and transport of molinate. Detailed summaries for each environmental fate guideline are presented in Attachment 1. Zeneca also provided details about specific surface water intakes that EFED listed in the drinking water assessment. Drinking water issues are addressed in Appendix E.

In MRID 44956602, data were presented for aerobic soil metabolism, anaerobic soil metabolism, simulated rice field studies (including plant uptake), and leaching-adsorption-desorption. The data from this document are included below.

Based on the submitted environmental fate and transport studies and the monitoring data, the route(s) of dissipation of molinate are, in descending order of importance, (1) volatility, (2) reversible partitioning to soil, (3) indirect photolysis of molinate to 4-keto molinate formed when molinate desorbs into the paddy water, (4) degradation leading to formation of many degradates at low percentages, (5) plant uptake, and (6) release of rice water from treated fields into surface water.

There are some inconsistencies between the laboratory and field results for molinate. In general, molinate is more persistent in the laboratory than in the field. The registrant claims that the basis for this difference is the occurrence of volatility in the field and not the laboratory. This is supported by the general decrease in half-lives when observing laboratory studies, greenhouse and outdoor contained studies, and field dissipation studies.

Molinate is stable to hydrolysis and direct photolysis, and does not appear to degrade rapidly under aquatic conditions in the laboratory. However, indirect photolysis may be occurring in the field. The metabolite 4-keto molinate was detected in all surface water samples in CA where parent molinate was detected, and was approximately 10-30 % (one sample contained 50 %) of total molinate load. In the Southern region, 4-keto molinate levels in water of 10-50 % of detected parent molinate have also been observed. The degradate 4-keto molinate may be occurring from both indirect photolysis and aquatic metabolism studies, since it did not reach 30 % of applied molinate in any of the metabolism studies. In the aquatic metabolism studies, molinate appeared to volatilize and reversibly partition to clay and organic matter. Up to about 20 % of applied molinate was present as degradates that did not individually reach significant levels (10 % of applied).

Based on batch equilibrium studies, molinate and the degradates hexamethyleneimine and molinate sulfoxide are moderately mobile to very mobile in the environment. The USGS (Majewski and Capel, Open-File Report 94-0506) cites Seiber et al. (1983) and Soderquist et al. (1977) as saying that the percent of molinate lost from rice paddy water by volatilization were 35 % in 4 days and 78 % in 7 days, respectively. This is consistent with the Henry's Law constant of 1.3×10^{-6} m^3-atm/g-mol. In the field, applied molinate that did not volatilize tended to partition reversibly to sediment within a 3-day period, but the application rates could not be confirmed in some studies. Therefore, EFED is reasonably certain about the route(s) of dissipation of molinate in the environment.

EFED has reviewed surface and ground water monitoring data for molinate and has found high detections and high frequencies of detections where rice is grown. In surface water in California, maximum levels of 43.7 ug/L have been observed following the holding periods. High levels of 100-332 ug/L have been observed in the Southern region where there are no required holding periods. This would appear to be inconsistent with the apparently rapid rate of volatility from the field. However, this may be associated with releases of tailwater from fields soon after application.

In ground water, molinate has been detected at levels ranging from 0.005-1.5 ug/L. Most of the detections did not exceed 0.056 ug/L (Arkansas, Mississippi, and California), but there were two higher detections of 0.11 ug/L in Texas and 1.5 ug/L in Missouri. Based on the persistence in aquatic metabolism studies, EFED expects persistence of molinate in ground water if it reaches ground water.

Guideline Summaries

i. Degradation

Abiotic Hydrolysis (161-1)

(^{14}C)Molinate, at 100 ppm, was stable to hydrolysis at pH values of 5, 7, and 9. The test solutions were incubated in darkness for 30 days at 25°C and 40 °C.

The hydrolysis (161-1) data requirement is fulfilled (MRID 40817901).

Photolysis in Water (161-2)

Unlabeled molinate (89.8 ppm) was stable to direct photolysis in sterile aqueous pH 7 buffer solutions that were continuously irradiated with artificial light at 25 ±1°C for 14 days. The light source was a Heraeus Suntest xenon arc lamp fitted with a UV filter to remove wavelengths below 290 nm. The light source had a spectrum similar to sunlight and an average integrated light intensity of 508 watts/m^2, which was calculated to be more than a 30-day irradiation under a clear summer sky at approximately 38°N.

The photolysis in water (161-2) data requirement is fulfilled (MRID 41599301).

Photodegradation on Soil (161-3)

Radiolabeled molinate, at the equivalent of 5 lbs ai/A (337 μg/6 cm^2), did not degrade significantly under dark or irradiated conditions at 25 °C when applied to dry films (0.4 mm thickness) of Biggs clay soil (pH 5.5, 1 % OC). The irradiated samples received the equivalent of 30 days of natural sunlight (3 days of a xenon lamp) filtered to remove wavelengths of <290 nm. Material balances were 98 ± 3 % in the dark controls and 97 ± 2 % in the irradiated samples. One unidentified photoproduct was found at ≤2 % of applied. More than 92 % of applied radioactivity was extractable from the soil, and unextracted residues did not exceed 3 % of applied.

The photodegradation in soil (161-3) data requirement is fulfilled (MRID 42396501).

Photodegradation in Air (161-4)

The photodegradation in air (161-4) data requirement is not required because molinate is stable to direct photolysis.

Aerobic Soil Metabolism (162-1)

The aerobic soil metabolism data requirement was waived on 4/12/90 because molinate is only used on rice, an aquatic crop. However, molinate is also labeled for use on dry seeded rice. Therefore, an aerobic soil metabolism study was required in the 1999 RED dated 8/18/99.

In response to the 1999 RED, the registrant submitted an aerobic soil metabolism study (MRID 44956602). The half-life in the study was 51 days (r^2=0.84, F=31, p=1.4 x 10^{-3}), but EFED notes that material balance was below 90 % of applied by one week and decreased to about 32-35 % of applied by 12-32 weeks (end of study). The registrant attributed the poor material balance to volatility of molinate caused by the rigorous extraction procedure necessary for removal of bound residues that increased to 29.3 % of applied by 32 weeks. This explanation is consistent with the fact that the portion of molinate that does not volatilize immediately reversibly binds to sediment immediately. There were no degradates formed at 10 % of applied or greater. The aerobic soil metabolism data requirement is satisfied for molinate even though the material balances were low.

The registrant also submitted a literature study that provided supplemental information on the dissipation of molinate in both non-flooded (aerobic) and flooded (anaerobic) soils. The title of the study was "Degradation of the Herbicide Molinate in Soils, Iwai, Y. and S. Kowatsuka, J. Pesticide Sci. 7:487-497, 1982." This study was conducted on Japanese soils that were aerobic or flooded in separate experiments. Radiolabeled molinate was applied to Anjo (kaolinitic clay), Nagano (montmorillonitic clay), and Tochigi (volcanic ash) soils from Japan. Samples were taken at 0, 10, 20, 40, and 80 days. The application rate was 10 ppm on a dry weight basis. GC/MS was used to identify degradation products and CO_2 was trapped and quantified. Raw data were not provided, so EFED read approximate values from graphs.

Molinate degraded more rapidly under aerobic conditions than flooded (anaerobic) conditions. Under aerobic conditions, the half-lives were 8, 20, and 25 days in Anjo, Nagano, and Tochigi soils. As expected CO_2 formation was much higher under aerobic conditions than under flooded conditions. CO_2 increased to 40 % of applied by 40 days in the Anjo soil, and approximately 20 % in the Nagano and Tochigi soils. Non-extracted soil residues (remaining after MeOH extraction) increased to approximately 20 % in all soils. The metabolites 4-oxo-molinate, 4-OH molinte, 2-oxo-molinate, and molinate-acid did not exceed 20 % of applied in the study as a group. The only metabolites that increased to approximately 10 % were 4-oxo-molinate and 2-oxo-molinate. Molinate sulfoxide peaked at 3.7 % of applied in the Tochigi soil at day zero (maximum of any soil) and decreased to 0.1-0.3 % of applied by 80 days. HMI peaked at 2.6 % of applied in the Tochigi soil at day zero (maximum of any soil) and declined to 0.1 % of applied by 80 days. The Eh ranged from +600-670 mv in the upland soil studies. The study authors provided graphs that showed limited degradation under sterile conditions as compared to non-sterile conditions.

<u>Anaerobic Aquatic Metabolism (162-3)</u>

As a result of the registrant's responses for MRID 41421801 (DP Barcode D259945, 30-day response), the additional anaerobic aquatic metabolism study (MRID 44956603), the simulated rice field study (MRID 44956602), and consistent results in the aquatic field dissipation studies below, EFED now considers the anaerobic aquatic metabolism guideline (162-3) to be satisfied for molinate and metabolites. When applied in the field, molinate rapidly volatilizes and reversibly sorbs to sediment with some degradation. The difference in half-lives for this guideline (6.7-130 days) may be attributed to the fact that the longest half-life (130 days) was in the laboratory study and the other half-lives (6.7-11 days) were associated with studies conducted in the greenhouse and in open air, allowing more volatility.

In the 1999 RED, EFED considered the anaerobic aquatic metabolism study submitted for review (MRID 41421801) to be unacceptable but upgradable. The registrant was required to demonstrate that anaerobic conditions were present during the incubation. No data were reported for redox potential, dissolved oxygen, or pH of the sediment:water systems. The large amount of CO_2 formed (approximately 50% of the applied radioactivity was evolved as CO_2 by 365 days) would indicate that anaerobic conditions were not maintained during the study. In addition, the registrant was required to provide information on whether molinate residues were stable during frozen storage in soil (sediment samples were stored frozen for an unspecified length of time before extraction and analysis).

The registrant response (DP Barcode D259945) did not provide any specific information on the redox potential, dissolved oxygen, or pH of the sediment water systems. However, the registrant correctly noted that degradates that would normally be found under <u>anaerobic</u> conditions were found in the <u>anaerobic</u> aquatic metabolism study. They also noted that degradates that would normally be found under <u>aerobic</u> conditions were found in the <u>aerobic</u> aquatic metabolism study. However, they were incorrect in their assertions about the formation of CO_2 formed in the study.

They stated that increased levels of CO_2 were not formed except one flask (#24) at day 95, based on Table A-VI. However, Table A-VI shows that CO_2 generally increased to an average of 1.79 % of applied by 23 days, and the later sampling intervals showed average CO_2 levels of 5.8-12.7 % of applied between intervals and a total of 45.5 % of applied by 365 days (end of study). These high levels of CO_2 are not indicative of anaerobic conditions.

In response to the 1999 RED, the registrant also provided data that demonstrated stability of molinate and metabolites in soil and water for an appropriate time frame for the study. Parent molinate was stable for up to 7 months, and most metabolites were stable for up to 12 months. Carboxy-molinate was stable for up to 2 months in water. Only three of the samples were stored for longer than 2 ½ months.

[Ring-2-^{14}C]molinate (radiochemical purity 98%) at 5.1 ug/g soil, degraded slowly in flooded clay loam soil systems that were incubated in darkness in the laboratory at 30°C for 365 days under a slight positive pressure (1 psi) of nitrogen gas (MRID 41421801). The calculated half-life was 130 days (r^2=0.96, F=410, and p=7.7 x 10^{-14}. Degradates identified in both the floodwater and the soil were 4-hydroxymolinate, molinate acid, 4-oxomolinate, 3-hydroxymolinate, N–formyl-hexamethyleneimine (N-formyl-HMI), molinate alcohol, methyl molinate, 2-oxomolinate, and 3-oxomolinate. Up to 17 different [^{14}C]residues were isolated from the floodwater; however, none comprised more than 0.026 ppm (0.5% of the applied). However, no more than 9.3 % of applied molinate was present as metabolites at any time in the study. Volatilized radioactivity trapped in the foam plugs was 21.7-25.7% of the applied by 365 days posttreatment, with the rate of evolution decreasing with time. Greater than 90%of the volatilized radioactivity was molinate, with methyl molinate as the only other compound detected in volatility traps. $^{14}CO_2$ was a maximum of 40.9-45.4% at 365 days posttreatment. During the study, material balances ranged from 85.3-97.4%.

Under anaerobic aquatic conditions, radiolabeled [^{14}C]molinate, at a nominal concentration of 3.5 ppm, dissipated with a total system half-life of 11 days (r^2= 0.89, F=16.2, P=5.7 x 10^{-2}) in flooded Biggs clay loam sediment that was incubated outdoors at 37 ± 3°C (99 °F) for up to 56 days (MRID 44956603). All reported data are the means of duplicates. The minor degradates, 2-keto Ordram, 2-OH Ordram, 3-OH Ordram, 4-OH Ordram, 4-keto Ordram, N-formyl HMI, Ordram sulfoxide, HMI, Carboxy-Ordram, and Caprolactam were each present at ≤5.6% of the applied radioactivity during the incubation period. Total degradates (polar and non-polar) were 17.9 % of applied at 7 days, 12.5 % 21 days, and 5.6 % at 56 days posttreatment. Nonextractable [^{14}C]residues accounted for 7.9% of the applied radioactivity at 7 days posttreatment, were a maximum of 34.6% at 21 days, and were 28.3% at 56 days. The distribution ratio (reviewer-calculated) of [^{14}C]residues between the sediment and water phases was 1.05:1 at 7 days posttreatment, 5.2:1 at 21 days posttreatment, and 8.4:1 at 56 days posttreatment. Volatile [^{14}C]residues were not determined.

In a simulated rice field study conducted in a greenhouse using water with 4 ppm of molinate (MRID 44956602), the main compartments that contained residues of molinate (as radioactivity) were water and sediment. The total system half-life was 6.7 days (r^2=0.95, F=19.5, p=1.4 x 10^{-1}), which is consistent with observed field half-lives. In water, 19.7 % of applied molinate was found at 7 days after treatment. However, by 14 days, only 1.9 % of applied was in the water phase. Extractable soil residues increased from 16.9 % at 7 days to 21.7 % of applied by 14 days. Soil bound residues increased from 5.9 % at 7 days to 10.3 % at 14 days. Total volatiles (including CO_2, organic volatiles, and chamber rinse) reached 7.3 % at 7 days and 18.9 % of applied by 14 days. Total molinate residues in rice roots and shoots reached 2.2 % by 7 days and 7.2 % by 14 days. Even though the material balance was poor in the study (52-60 %), the study provides supplemental information about the relative routes of dissipation of molinate in the environment.

Under anaerobic conditions, only 29 % of molinate degraded by 80 days in the Tachigi soil, leading to an estimated half-life (EFED) of 137 days (Iwai and Kowatsuka, 1982, previously cited). This is consistent with the half-life in the anaerobic aquatic study (MRID 41421801). However, shorter half-lives of 40 and 70 days were observed in the Nagano and Anjo soils, respectively. CO_2 and non-extracted soil residues did not exceed 10 % of applied in any of the soils. The metabolites 4-oxo-molinate, 4-OH molinte, 2-oxo-molinate, and molinate-acid did not exceed 20 % of applied in the study as a group. The only metabolite that increased to approximately 10 % was molinate acid, which stayed between 5-10 % of applied at 10-80 days in the Nagano soil. In the Anjo soil, 4-OH molinate and molinate acid increased to approximately 4 % each by 80 days, but no degradates were observed above 1 % of applied in the Tochigi soil. Levels of molinate sulfoxide and HMI were similar with maximum amount of 2.4 % of applied which declined to 0.1-0.7 % of applied by 80 days. The Eh ranged from +354-594 mv in the soils until 30, 60, and 15 days after preincubation in the Anjo, Nagano, and Tochigi soils, respectively. The Eh after these days were -200 mv or less (Imai and Kowatsuka, 1982).

Aerobic Aquatic Metabolism (162-4)

The aerobic aquatic soil metabolism data requirement is satisfied with the combination of MRID's 41421802 and 44956603. In the 1999 RED, EFED concluded that a half-life for molinate could not be determined because less than 50% of the applied material had degraded by the time the laboratory study was terminated (MRID 41421802). As a result, the long-term behavior of molinate in natural aerobic aquatic systems could not be predicted with certainty from the results of this study. However, the registrant submitted an aerobic aquatic metabolism study conducted outdoors (MRID 44956603) that showed consistent results with field dissipation studies and laboratory greenhouse studies conducted to simulate field studies.

[Ring-2-^{14}C]molinate (radiochemical purity 95-98%) at 4.2 ug/g soil, degraded with an observed half-life of >30 days in flooded clay soil that was incubated under a slight pressure of oxygen and 5 cm of water in darkness at 30 °C for 30 days (MRID 41421802, **laboratory study**). Total [^{14}C]molinate was 86.8% of the applied radioactivity immediately posttreatment, and declined to

59

65.52% of the applied radioactivity by 30 days. During the study, [^{14}C]residues associated with the soil layer increased from 44 to 62% of the applied radioactivity, and [^{14}C]residues associated with the floodwater decreased from 51 to 24%. Four degradates were identified in both the soil and floodwater at <10% of applied. These included molinate sulfoxide (maximum 8.8% of the applied radioactivity at 14 days posttreatment, distributed 1:4 between the soil and the floodwater, respectively), hexamethyleneimine (HMI) (maximum of 9.6% in the floodwater at 7 days posttreatment; distributed 1:27 between the soil and the floodwater, respectively), caramel chloride (maximum of 1.6% at 7 days posttreatment), and 3-keto molinate (maximum of 0.84% at 1 day posttreatment). Three degradates were identified only in the floodwater. These included S-ethyl-5-carboxypentyl thiocarbamate, 4-keto molinate, and carboxy methyl molinate at ≤0.8%. There were four unidentified metabolites observed at ≤0.25% of the applied. $^{14}CO_2$ comprised 0.96% of the applied radioactivity by 30 days and volatile molinate comprised 7.2% at 30 days. Unextracted radioactivity increased from 0.77% immediately posttreatment to 1.23-2.39% at 1-30 days posttreatment. Material balances ranged from 84.57-95.27%.

Under aerobic aquatic conditions, radiolabeled [^{14}C]molinate, at a nominal concentration of 3.5 ppm, dissipated in water with a reviewer-calculated half-life of 5.6 days ($r^2 = 0.99$, F=410, P=3.1 x 10^{-2}) in flooded Biggs clay loam sediment that was incubated **outdoors** at 35 ± 2°C (95 °F) for up to 56 days (MRID 44956603). All reported data are the means of duplicates. All data represent water phase samples (no sediment phase was prepared for aerobic aquatic samples). The minor degradates, 2-keto Ordram, 2-OH Ordram, 3-OH Ordram, 4-OH Ordram, 4-keto Ordram, N-formyl HMI, Ordram sulfoxide, HMI, Carboxy-Ordram, and Caprolactam were each ≤3.8% of the applied radioactivity during the incubation period. Total degradates (polar and non-polar) were 19.7 % of applied at 7 days, 15.8 % 21 days, and 11 % at 56 days posttreatment. Volatile [^{14}C]residues were not determined.

ii. Mobility

Leaching and Adsorption/Desorption (163-1)

The registrant has provided three leaching-adsorption-desorption studies that were reviewed and considered to be acceptable. These included studies for parent molinate (MRID 40749701), molinate sulfoxide (MRID 41835103), and hexamethyleneimine (MRID 41835102). The leaching-adsorption-desorption data requirement is satisfied for molinate and the degradates molinate sulfoxide, and hemethyleneimine. In the 1999 RED, EFED stated that if additional degradates are formed in significant quantities in the required aerobic soil metabolism study, leaching-adsorption-desorption data will be required for these degradates. There were no significant degradates in the aerobic soil metabolism study (MRID 44956602) submitted in response to the RED , and therefore the 163-1 data requirement is satisfied for molinate and all degradates.

Also in response to the 1999 RED, the registrant has submitted additional soil adsorption data on parent molinate in four soils (found in MRID 44956602). The registrant has already submitted acceptable studies on parent molinate, and the data are generally consistent between the acceptable study in the RED and the recently-submitted study. Therefore, no DER was written for this study. In the recently-submitted study, the Freundlich Kads values ranged from 0.72-3.03 ml/g. Adsorption was related to pH (r^2=0.70), clay (r^2=0.84), and organic carbon (r^2=0.95).

Based on batch equilibrium studies, molinate was very mobile to mobile in Keeton sandy loam, Manteca sandy loam, Columbia loamy sand, Biggs clay soil, and a clay loam aquatic sediment from the Colusa canal in California (Table 2). Adsorption was correlated with %organic matter (r^2=0.70) and % clay (r^2=0.93); it was not correlated with pH (r^2=0.16). The soil:0.1 N calcium chloride solution slurries (2.5:10 ratio) were equilibrated in darkness at 20.5 °C for 1 hour during adsorption and for 1.5 hours for desorption. Solution concentrations were 0.0159, 0.164, 1.51, and 14.9 µg/mL. Molinate was stable in the samples during the study.

Table 2. Soil mobility data for molinate (MRID 40749701).

Soil	% OM	Clay	pH	Kads	n	r^2	Koc[1] (ads)	Kdes	n	r^2	Koc[1] (des)
Keeton sandy loam	0.5	9.8	7.7	0.741	1.26	0.99	252	1.14	1.34	0.99	388
Columbia loamy sand	1.9	5.8	7.8	1.35	1.12	0.99	121	1.73	1.17	0.99	155
Manteca sandy loam	2.2	10.6	7.5	2.04	1.09	0.99	158	2.70	1.07	0.99	209
Biggs clay	1.7	50.0	5.5	1.95	1.04	0.99	195	2.94	1.09	0.99	294
Colusa Canal sediment	1.3	36.6	7.7	1.57	1.04	0.99	206	1.78	1.17	0.99	233

[1] Koc was calculated using the equation: % organic carbon = % organic matter/1.7. If you only have %OM from the soils characterization information, convert to %OC using the relationship

%OC = %OM / 1.724
where 1.724 is the Van Bemmelen factor.

Hexamethyleneimine
DER 163-1
MRID 41835102

Based on batch equilibrium studies, the molinate degradate hexamethyleneimine was very mobile to moderately mobile in sandy loam, silt loam, loam, and clay soils, and in a clay sediment. Freundlich Kads values ranged from 1.64 to 7.23 mL/g, and desorption values

61

ranged from 1.13 to 9.22 mL/g (Table 3). Adsorption was strongly correlated with cation exchange capacity (CEC; $r^2 = 0.93$), but was not correlated with %OM ($r^2 = 0.24$) or pH ($r^2 = 0.32$). The study was conducted using a soil:solution ratio of 1:5 at concentrations of 0.014, 0.133, 1.34, and 13.2 µg/mL hexamethyleneimine in 0.01 M calcium chloride solution and a 4 hour equilibration period. Hexamethyleneimine did not degrade during the study, and material balances following desorption ranged from 83 to 97% of the applied.

No K_{oc} values were reported because neither adsorption or desorption were related to soil organic carbon. (MRID 41835102)

Table 3. Soil mobility data for Hexamethyleneimine (MRID 41835102).

Soil	% OM	CEC	pH	Kads[1]	n	r^2	Kdes	n	r^2
Atterbery silt loam	3.0	19.2	5.6	5.62	1.10	0.99	6.1	1.27	0.99
Sorrento loam	3.9	17.3	6.8	4.51	1.07	0.99	4.6	1.30	0.99
Visalia sandy loam	0.8	7.6	7.4	1.64	1.08	0.99	1.13	1.56	0.98
Biggs clay	2.3	31.5	6.1	7.23	1.04	0.99	9.22	1.53	0.98
Colusa Canal sediment	2.2	24.4	7.5	5.69	1.04	0.99	6.44	1.15	0.99

[1] Koc values were not reported because neither adsorption or desorption were related to soil organic carbon.

Molinate sulfoxide
DER 163-1
MRID 41835103

Based on batch equilibrium studies, molinate sulfoxide was very mobile to moderately mobile in sandy loam, silt loam, loam, and clay soils, and in a clay sediment, with Freundlich Kads values of 0.78 to 2.81 mL/g (Table 4). Desorption values ranged from 0.93 to 3.53. Adsorption was strongly correlated with cation exchange capacity (CEC; $r^2 = 0.84$), but was not correlated with %OM or pH. The study was conducted using a soil:solution ratio of 3:10 for the sandy loam soil (1:5 for the other soils) at concentrations of 0.018, 0.177, 1.74, and 17.2 µg/mL molinate sulfoxide in 0.01 M calcium chloride solution and a 4 hour equilibration period. Molinate sulfoxide did not degrade during the study, and material balances following desorption ranged from 93 to 100% of the applied. No K_{oc} values were reported because neither adsorption or desorption were related to soil organic carbon. (MRID 41835103)

62

Table 4. Soil mobility data for molinate sulfoxide (MRID 41835102).

Soil	% OM	CEC	pH	Kads[1]	n	r^2	Kdes	n	r^2
Atterbery silt loam	3.0	19.2	5.6	2.26	1.05	0.99	3.03	1.11	0.99
Sorrento loam	3.9	17.3	6.8	1.86	1.06	0.99	2.51	1.11	0.99
Visalia sandy loam	0.8	7.6	7.4	0.78	1.02	0.99	0.934	1.06	0.99
Biggs clay	2.3	31.5	6.1	2.81	1.01	0.99	3.53	1.04	0.99
Colusa Canal sediment	2.2	24.4	7.5	1.88	1.02	0.99	2.64	1.04	0.99

[1] Koc values were not reported because neither adsorption or desorption were related to soil organic carbon.

Laboratory and Field Volatility

In the Phase 4 EFED document dated 6/10/91, EFED did not require laboratory and field volatility data because the vapor pressure of 5.3 x 10^{-3} mm Hg suggests that molinate is volatile. The calculated Henry's Law constant of 1.3 x 10^{-6} m^3-atm/g-mol also supports this conclusion, as well as the published literature (Mabury et al., 1996, Deuel et al., 1978, Ross and Sava, 1986, Seiber et al., 1989, and Soderquist et al., 1977 as quoted by Johnson and Lavy, 1995,). EFED will not require dedicated studies to determine the extent of volatility in the laboratory. Volatility in the field is addressed in field dissipation studies.

Terrestrial and Aquatic Field Dissipation (164-1, 164-2, 164-3)

In the 1999 RED, EFED required three new terrestrial/aquatic field dissipation studies to cover the use of molinate in dry-seeded and water-seeded rice in California, Arkansas, and southwestern Louisiana. These studies were required to address rice production practices where they are conducted and all routes of dissipation in the field (e.g. biological degradation, chemical degradation, air sampling over space and time for molinate volatility, the volume and concentrations of water that are released from the rice fields, and the amount of molinate that remains in the field. EFED further required the registrant to submit protocols for each study. Combination/tank mix dissipation data (164-4) were also required in the previous RED since molinate is formulated as a product with propanil.

In MRID 44926502, the registrant responded by saying that molinate volatility is adequately understood and field volatility measurements will not add any new information. Based on the new information presented in the responses (MRID 44956602) and incorporated under the individual guidelines, the air monitoring data in California, and the two tank mix studies conducted in Texas and Mississippi (MRID's 44970002 and 44970003) for molinate and propanil (see below), EFED no longer requires additional environmental fate guideline studies for molinate.

Air monitoring has been conducted in California both in the field and in a town approximately one mile from treated fields. Maximum concentrations of molinate in air in the field were approximately 48 ppb and 1.17 ppb in the town of Maxwell, California. The USGS (Majewski and Capel, Open-File Report 94-0506) cites Seiber et al. (1983) and Soderquist et al. (1977) as saying that the percent of molinate lost from rice paddy water by volatilization were 35 % in 4 days and 78 % in 7 days, respectively. This is consistent with the Henry's Law constant of 1.3×10^{-6} m^3-atm/g-mol.

The registrant has submitted terrestrial field dissipation studies for molinate in Arkansas, Texas, and California. The application rate for both 8E and 15G molinate in the Arkansas study could be confirmed, but only the 8E molinate application rate could be confirmed in the Texas study. Only four percent of the applied 15G molinate in Texas was confirmed. Also, only 10 % of applied 8E or 15G molinate was confirmed in the California studies. Therefore, no meaningful half-lives could be calculated where the application rate was not confirmed. In general, molinate appeared to volatilize and partition to sediment in the rice paddies, but no route of dissipation could be confirmed since the recoveries in the field were low.

Arkansas–MRID 40391706

Molinate was applied at 4 lbs ai/A as Ordram 8-E and incorporated, followed by immediate planting of rice. After 42 days, the soil was flooded and 15G molinate was applied at 5 lbs ai/A. The half-lives for 8E in soil and 15G in soil and water were 6.3 days, 7.3 days, and <2 days, respectively. Maximum percent recoveries for both formulations were 100 and 73 %, respectively. There were some limited detections to 6-12 inches of depth in the study.

Texas–MRID 40391707

Molinate was applied at 4 lbs ai/A as Ordram 8-E to a 1-acre field of sandy clay loam soil (0.5% organic matter, pH 6.0, soil not further characterized) located near Brookshire, Texas. The pesticide was applied and incorporated, and then the field was planted to rice on the day of application that day. After 40 days posttreatment, the site was flooded. The site was treated with 5 lbs ai/A of Ordram 15-G. On September 22 (42 days posttreatment), the site was treated (aerial) with molinate (Ordram 15-G, 15% G, Stauffer) at 5 lb ai/A. The site was drained 42 days later.

The half-life in soil from the 8-E formulation was 5 days ($r^2=0.7$, 100 % recovery). However, no meaningful half-life could be calculated for the 15-G formulation since the maximum percent recovery was only 4 %. In response, the registrant stated that no soil samples were taken immediately after application, and that water analysis was inadequate to confirm the application rate. However, based on the results of all the data from submitted guideline studies and monitoring data, the 164-1,2,3 data requirements are satisfied.

California-MRID 41421803

Field plots of clay soil (21% sand, 25% silt, 54% clay, 2.7% organic matter, pH 6.1, CEC 33.7 meq/100 g) located near Durham, California, were flooded (4-inch depth) on July 5, 1988; planted to rice on July 7; and aerially-treated with molinate formulated either as Ordram 8-E or Ordram 15-G at 5 lbs ai/A/application (10 lbs ai/A total) on July 15 and 22 (Figure 1). The plots were not cultivated after treatment, and the flood water was maintained at a 4-inch depth until it was drained from the plots 81 days after the second molinate application.

Meaningful half-lives in soil and water could not be calculated since the application rate could not be confirmed. The maximum percent recoveries were about 10 %. However, it appeared that molinate was more persistent in soil when applied as 15-G. This is probably because the granules would be likely to sink to the bottom of the water, where they would interact with sediment and reduce the amount of probable volatility loss. Based on the results of all the data from submitted guideline studies and monitoring data, the 164-1,2,3 data requirements are satisfied.

Tank-Mix Aquatic Field Dissipation Studies (164-4)

Since the application rate of molinate and propanil could not be confirmed in the Mississippi and Texas studies, the tank mix aquatic field dissipation studies (MRID's 44970002 and 44970003) do not satisfy the 164-4 data requirement by themselves. However, given the weight of evidence provided by laboratory, greenhouse, and field dissipation studies, it is clear that molinate rapidly volatilizes into the atmosphere and reversibly partitions to sediment. Therefore, the 164-4 data requirement is considered to be satisfied and no further aquatic field dissipation data are required for molinate.

<u>Bioaccumulation</u>

Molinate residues accumulated in bluegill sunfish exposed to 0.10 ppm of molinate for 25 days, with maximum mean bioconcentration factors of 29x, 140x, and 72x for edible (muscle, skin, skeleton), nonedible (fins, heads, internal organs), and whole fish tissues, respectively. Five degradates were identified in the fish tissues: molinate sulfoxide, carboxymolinate, molinate sulfone, 4-keto molinate, and 4-hydroxymolinate; none were present at greater than 10% of the total residues. Depuration was gradual, with 75-90% of the accumulated [14C] residues eliminated from the fish tissues by day 14 of the depuration period. The exposure phase of the study was terminated after 25 days because the fish exhibited increasing mortality (4 out of the original 120 individuals died) and abnormal behavior (loss of equilibrium, quiescence, and lying on the bottom of the exposure chamber). The 7-day LC50 had been estimated to be 8.2 mg/L, which was 82 times the exposure level. (MRID 40593303)

Appendix E. Detailed Water Assessment for Ecological Effects and Drinking Water

Areas of Rice Production Assessed

Molinate is applied only to rice that is grown in California and in the southeastern/south-central states of Missouri, Arkansas, Tennessee, Louisiana, Mississippi, and Texas (Southern region). Since there are no labels for molinate use on rice in Florida, EFED did not address the limited Florida rice production in Palm Beach and Hendry Counties.

Sources of Monitoring Data

To obtain both ground and surface water concentrations for the purpose of risk assessment, EFED has received monitoring data from the USGS, the State of Arkansas Department of Pollution Control and Ecology, the City of Sacramento, CA, the State of California Department of Environmental Regulation, and the State of Texas. Some of these data were provided in the EPA STORET database. EFED used monitoring data for the drinking water assessment since the data were available for the areas where molinate is applied except for Tennessee, where only 3,000-5,000 acres of rice are grown in Lake County. Also, EFED has no official models to generate estimated environmental concentrations (EECs) from pesticide use on aquatic crops. EFED has conducted a state-by-state regional assessment since molinate is applied only in California and in the south central/south eastern states of Arkansas, Louisiana, Missouri, Texas, and Tennessee.

Adjustment of Parent Molinate Concentrations for Degradates

Adjustment of parent molinate concentrations in ground water and surface water for degradates was necessary since there was no monitoring for any degradates with the exception of the photoproduct 4-keto molinate, which is discussed below. To determine which molinate metabolites are of toxic concern, EFED and HED held a meeting of the HED MARC (Metabolism and Review Committee) on 10/31/2000. At the MARC meeting, EFED provided a list of metabolites that have been detected or have the potential to be detected in the aquatic laboratory and field dissipation studies. The metabolites that were determined to be of concern include molinate sulfoxide, molinate sulfone, 3-keto and 4-keto molinate, hydroxy molinate (2, 3, and 4), molinate acid (carboxymethyl molinate), and ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate).

The environmental fate studies did not contain adequate data on all metabolites of concern. Some information on the molinate sulfoxide, 4-keto molinate, hydroxy molinate (2, 3, and 4), and molinate acid (carboxymethyl molinate) was available in relevant laboratory and field studies. However, no meaningful estimates of exposure for molinate sulfone, 3-keto molinate, or ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate) could be determined based on the submitted environmental fate studies. Even though adequate information on some of these metabolites was not available, EFED does not expect significant formation of these metabolites in water. This is based on the fact that volatility is the primary route of dissipation for molinate, and the other metabolites are formed in relatively low amounts (<10 % of applied) with the exception of 4-keto molinate.

To obtain the percent of molinate acid and molinate sulfoxide degradates relative to parent molinate at each time interval, EFED used the results of aquatic field dissipation studies for dry-seeded rice (MRID 41421803) and water-seeded rice (MRID 41421804) that included information on parent molinate and these two degradates. EFED added the residues of the two degradates for each time interval, divided the total by the initial parent molinate residue for the first and second applications as appropriate, and multiplied by 100. The average percent of parent molinate was 9.4 % for dry-seeded rice and 11 % for water-seeded rice, leading to adjustment factors of 1.094 and 1.11, respectively. To account for 2-, 3-, and 4-hydroxy molinate, the EEC's may be increased by another 14.7 % (average percent observed in an aerobic aquatic metabolism laboratory study, MRID 44956603). The use of a laboratory study was necessary because no metabolites other than molinate acid and molinate sulfoxide were analyzed for in the aquatic field dissipation studies.

EFED is accounting for 4-keto molinate by adding 30 % of parent molinate estimates to the monitoring data. In a recent publication (Pesticides and Pesticide Degradation Products in Stormwater Runoff: Sacramento River Basin, California, Water Resources Bulletin, Volume 32, Issue 5, October, 1996, pp. 953-964), the photoproduct 4-keto molinate was recently observed to be found in surface water. This study was conducted in the Sacramento Basin below the confluence of the Colusa Drain and the Sacramento River and extended downstream from the City of Sacramento (p. 962). Four-keto molinate was detected in California at 10-30 % (one detection of 50 %) of parent molinate in every sample where molinate was detected in surface water from storm water runoff. In the Southern region, 4-keto molinate levels in water of 10-50 % of detected parent molinate have also been observed.

As a result of the additional information on degradates presented above, the EEC's can be adjusted by factors of 1.54 for dry-seeded rice and 1.56 for water-seeded rice, respectively. EFED recommends using the 1.56 adjustment factor for both California and the Southern Region for both surface and ground estimates of parent molinate. Table 1 contains a summary of the degradates and the justification for the different factors associated with each.

Table 1. Metabolite Adjustment Factors for Surface and Ground Water Monitoring Data for both Ecological and Drinking Water Exposures.[1]

Metabolite	Study ID	Percent of parent at time interval[2]	Value used	Comments
Hydroxy molinate (2-,3-,4-), treated as sum	MRID 44956603 Aerobic Aquatic	mean--14.7 SD--20.4 CV--170 %	14.7 % for CA and Southern Region	0-21 day sampling intervals used in calculations.
Molinate sulfoxide and acid, treated as sum	MRID 41421803 and 41421804 Aquatic Field Dissipation	8 EC formulation mean--9.4 SD--16.1 CV--170 % 15G formulation mean--11 SD--15.3 CV--140 %	11 % for CA and Southern Region	Calculated for each interval if parent was detected in the studies.
Molinate sulfone, 3-keto molinate, and (S-ethyl-5-carboxypentyl thiocarbamate)	no data from laboratory or field studies		0[3]	
4-keto molinate	USGS article[4]		30 % (CA and Southern Region)	4-keto molinate was detected at 10-50 % of detected molinate in both CA and Southern Region . EFED used 30 % because most values were ≤30 %.
Adjustment Factor for both California and Southern Region			1.56 (1+ 56 % as decimal)	

[1] EFED adjusted the monitoring data because it only contained information on parent molinate and the degradate 4-keto molinate. Based on the 10-31-00 HED MARC meeting, the degradates in the table were considered to be of concern.
[2] EFED divided the amount of degradate at each time interval by the amount of parent present and multiplied by 100 to obtain the percent of parent as the degradate.
[3] These compounds were either not looked for or not found in aerobic aquatic metabolism or aquatic field dissipation studies. However, volatility is the primary route of dissipation (Sieber, et al., 1989, Soderquist, et al., 1977). Therefore, EFED believes that the estimate of 56 % of parent molinate as toxic degradates is a reasonable estimate for all toxic residues.
[4] Domagalski, J. 1996. Pesticides and Pesticide Degradation Products in Stormwater Runoff: Sacramento River Basin, California. American Water Resources Association, Water Resources Bulletin, Vol. 32, No.5.

Aquatic Exposure Assessment for Ecological Effects

For ecological exposure in California, Mississippi, Louisiana, and Texas, EFED identified the body of water in each rice-producing state with the maximum observed concentration of parent molinate residues. EFED then used the maximum concentration for that year as estimates acute exposure, and the time-weighted annual (January-December) and seasonal (May-July) means as estimates of chronic exposure. For Arkansas, EFED used a different approach because the 1995 monitoring data were survey data for bayous, creeks, and rivers instead of targeted data to a small number of water bodies. For acute exposure in Arkansas, EFED took the maximum concentration from bayous, creeks, and rivers from the 1995 monitoring data. For chronic exposure in Arkansas, EFED calculated the upper 95th percentile value for each type of water body. Since there was no apparent monitoring data in Missouri and Tennessee, EFED did not specifically address ecological risk in these states because it is unlikely that higher concentrations of parent molinate will be observed than in Mississippi or Arkansas (100-332 ug/L). Table 2 below provides the EEC's for parent molinate that were used for ecological risk.

In Table 2, the maximum concentrations ranged from 43.7-332 ug/L (68.2-519 ug/L for parent and metabolites). The annual and seasonal means and the upper 95th percentiles of parent molinate ranged from 1.5-32.4 ug/L (2.3-45.9 ug/L for parent and metabolites). Concentrations were generally higher in the Southern Region because California has a drier climate and required holding periods to prevent release into surface water.

Table 2. Surface Water Levels from Monitoring Data used for Ecological Risk Assessment.

State	Location	Year	Frequency of Detection (Range of detection limits)	Parent Molinate			Parent + degradates of concern including adjustment factor (See Table 1 for justification of adjustment factor)		
				Maximum Concentration (ug/L)	Time-Weighted Annual Mean Concentration (ug/L)	Time-Weighted Seasonal (May-July) Mean Concentration (ug/L)	Maximum Concentration (ug/L)	Time-Weighted Annual Mean Concentration (ug/L)	Time-Weighted Seasonal (May-July) Mean Concentration (ug/L)
California	Colusa Drain	1996	27/35 (0.5, 1 ug/L)	43.7	4.8	12.1	68.2	7.5	18.9
Mississippi	Bogue Phalia River	1996	23/25 (0.004 ug/L)	100	7.5	29.0	156	11.7	45.2
Louisiana	Tensas River	1997	15/27 (0.004 ug/L)	32	1.5	6.0	49.9	2.3	9.4
Texas	White's Bayou	1994	18/21 (0.004 ug/L)	200	7.9	32.4	312	12.3	50.5
State	Location	Year	Frequency of Detection (Range of detection limits)	Maximum Concentration (ug/L)	Upper 95th percentile of concentrations (ug/L)	Upper 95th percentile of concentrations (ug/L)	Maximum Concentration (ug/L)	Upper 95th percentile of concentrations (ug/L)	Upper 95th percentile of concentrations (ug/L)
Arkansas	Bayous	1995	35/47 (0.005-0.02 ug/L)	47.2	29.4	29.4	73.6	45.9	45.9
	Creeks	1995	23/67 (0.005-0.02 ug/L)	332.7	17.4	17.4	519	27.1	27.1
	Rivers	1995	27/67 (0.005-0.02 ug/L)	45.7	10.7	10.7	71.3	16.7	16.7

Drinking Water Assessment

Drinking Water from Ground Water

EFED did not run the SCI-GROW2 ground water model because it is inappropriate for rice. SCI-GROW2 assumes vulnerable soils with a shallow water table, but rice fields require impermeable layers to hold the floodwater. Also, SCI-GROW2 does not directly take into account the volatility of a given compound. Therefore, EFED based its assessment on monitoring data.

To provide estimates of dietary exposure from ground water used as drinking water, EFED is recommending the use of 0.056 ug/L for acute, chronic, and cancer assessment for parent molinate and 0.087 ug/L for total toxic residues of molinate. The 0.056 ug/L concentration was the maximum observed in recent USGS monitoring data from California and the Southern Region (Mississippi and Arkansas). Some of the wells in which detections were observed were drinking water wells. There were higher detections that were either due to runoff to open wells (0.56-29 ug/L) or from data of unknown quality or relevance (Missouri and Texas, 1.5 and 0.11 ug/L, respectively). In monitoring conducted by the State of Louisiana, there are also non-detections (LOD 0.11 ug/L) reported in 12 wells located near rice production,. However, other details such as total depth and depth of well casings were not available to interpret these non-detections. In Texas, there were no detections in the Trinity River Basin in recent USGS monitoring. However, EFED notes that if rice production increases, levels in ground water could approach the 0.11 ug/L detection in older monitoring.

The registrant also cited the same data that EFED cited with the exception of the 1.5 ug/L detection. There are no recent detections of parent molinate in ground water in the Trinity River Basin in Texas, and no monitoring for any degradates. In MRID 44970001, the registrant argues that EFED should recommend a maximum ground water value of 0.01 ug/L for dietary exposure assessment. This conclusion is based on a lower limit of detection in the non-detections (0.01 ug/L) and predominance of non-detections. However, even the more recent monitoring data show detections at up to five times this amount, and therefore do not support this conclusion.

In response to information obtained from the USA Rice Federation, additional ground water monitoring was also submitted. According to the submission dated June 2nd, 2000, 50 wells in Louisiana have been sampled for parent molinate residues in 1995, 1997, 1998, and 1999 with no detections (LOD <0.011 ug/L). In a 7/5/2000 fax from Larry LeJeune of the Louisiana Department of Agriculture and Forestry, 12 of the 50 wells are near rice production. However, details such as analytical procedures and depth of wells and well screens were not provided. Therefore, it is impossible to use this information in a drinking water assessment at this time.

Drinking Water from Surface Water

Calculation of Dietary Estimates

At the request of the Health Effect Division (HED), EFED provided maximum values for acute dietary assessment and time-weighed annual means (January-December) for chronic and cancer dietary assessment. In addition, EFED provided time weighted seasonal (May-July) means for any chronic concerns that may be caused by shorter exposure times. The May-July period of time contains the maximum concentrations in surface water because this is the application period of molinate, and paddy water can be released into surface water following application under some conditions.

Percentile

The EFED scientist used the @percentile function in Lotus 123 to find the upper 95th percentile of the data for a given site. The data were sorted by descending concentrations and the @percentile function was used [@percentile(0.95,data range)].

Annual and Seasonal Means

EFED used the above monitoring information to estimate drinking water concentrations in California and the Southeastern U.S. The monitoring data available for this assessment were censored by different detection limits depending on the source of the data. When data are below the limit of detection (LOD), they are reported as non-detects. As a result, EFED calculated upper bounds of parent molinate exposure by using the limit of detection for non-detects and lower bounds by using zero for non-detects. The upper and lower bounds of parent molinate exposure are presented for each location below and the true exposure is between the two bounds.

EFED calculated annual means and seasonal (May-July) means to capture both long-term and shorter-term exposure, respectively. The May-July means represent the peak concentrations associated with application time and the time intervals immediately following application. The data were sorted by water body and by year, and checked for duplicate samples for each day. If duplicate samples were present, they were averaged for that day and only the average was used in the analysis. For annual means, the time weights for the first sample were calculated by determining the time difference between January 1st and the first sample, followed by half the difference between the first and second samples [ex. 90 days plus (date of second sample- date of first sample)/2]. The time weight for the last sample was calculated by determining the difference between December 31st and the last sample in a given year for each water body, followed by adding half-the time difference between the last and next-to-last sample [ex. 120 days + (date of last sample minus the date of next-to-last sample)/2]. After that, the time weights for the intervals in between (example is second sampling interval) were calculated by the formula [(date of third interval minus date of first interval)/2]. The time weights were summed, and added to 365 days for non-leap years and 366 days for leap years. The time weights were multiplied by the observed detections (when present) and by the limit of detection (LOD) for non-detections. The annual mean was calculated by dividing the sum of the weights*concentrations and weights*LOD by the sum of the weights.

For seasonal means, the data for the sampling intervals of May-July for each year were considered. The time weights for the first sample were calculated by determining the time difference between May 1st and the first sample, followed by half the difference between the first and second samples [ex. 6 days +(date of second sample minus date of first sample)/2]. The time weight for the last sample was calculated by determining the difference between July 31st and the last sample in May-July for each water body, followed by adding half-the time difference between the last and next-to-last sample [ex. 5 days + (date of last sample minus date of next-to-last sample)/2]. After that, the time weights for the intervals in between (example is second sampling interval) were calculated by the formula [(date of third interval - date of first interval)/2]. The time weights were summed to 92 days since there are 92 days in the months of May, June, and July for both leap and non-leap years. The time weights were multiplied by the observed detections (when present) and by the limit of detection for non-detections. The seasonal mean was calculated by dividing the sum of the weights*concentrations and weights*LOD by the sum of the weights.

The percent error associated with the use of censored data was calculated for each annual and seasonal mean to estimate the amount of uncertainty in the monitoring data. The greater the error, the greater the uncertainty associated with each estimate. The percent error is affected by the amount of non-detections versus total samples, the total number of samples, the time distribution of the data, and the specific limit(s) of detection. When more samples are present over a wider period of time, there is more confidence in the analysis of the data, especially for calculating annual means. This is because wider time intervals around a given sampling interval tend to add more weight to a given sampling interval. Potential skewing of the calculated means can result from this. To calculate the percent error, the means using the limit of detection for non-detections and means using zero for non-detections were calculated. The formula [(LOD mean-zero mean)*100/LOD mean] was used.

Table 3 below provides the estimates of dietary exposure from parent molinate and the residues of toxic concern. Details about each group of intakes is provided below Table 3.

The surface water intakes with the highest exposure are Sacramento and West Sacramento. Maximum concentrations of parent molinate ranged from 1.52-2.13 ug/L, and annual and seasonal mean concentrations ranged from 0.29-0.54 ug/L. The intakes on the Mississippi and Atchafalaya Rivers in Louisiana had similar maximum parent molinate concentrations of 0.109-0.117 ug/L and annual and seasonal mean concentrations of 0.014-0.057 ug/L. Arkansas, Mississippi, Missouri, and Tennessee have no surface water intakes in rice-production areas, and therefore no exposure in drinking water from surface water. Table 10 below lists the Atchafalaya intakes and populations.

Table 3. Monitoring EECs for parent molinate and residues of concern that may be used for acute, chronic, and cancer risk assessment for molinate.

Location (Source of Data) [Population]	Frequency of Detection (Range of detection limits)	Parent Molinate			Adjustment Factor for degradates of concern[3]	Parent + degradates of concern (See Table 1 above).		
		Maximum Concentration (ug/L)	Annual Means (ug/L)[1]	May-July Seasonal Means (ug/L)[2]		Maximum Concentration (ug/L)	Annual Means (ug/L)	May-July Seasonal Means (ug/L)
Sacramento, California (Upper 95th percentile of parent molinate levels in raw water from the Sacramento River after holding periods (1991-2000 data), [pop. 374,600][4]	65/117 (0.1 ug/L)	1.52	0.29	0.39	1.56	2.37	0.45	0.61
West Sacramento, California (Upper 95th percentile of parent molinate levels in raw water from the Sacramento River after holding periods (1991-2000 data) adjusted for the percent flow data at City of Sacramento, [pop. 30,000][4]	65/117 (0.1 ug/L)	2.13	0.41	0.54	1.56	3.32	0.64	0.84
Arkansas, Mississippi, Missouri, and Tennessee (no surface water intakes in rice-production areas)	Not Applicable	0	0	0	1.56	0	0	0

76

New Orleans Area (Upper 95th percentile of parent molinate levels in raw water from 1996-1999 USGS data in the Mississippi River at St. Francisville, LA), [pop 1.21 million][5]	13/58 (0.004 ug/L)	0 117	0.014	0.050	1.56	0.18	0.022	0.078
St. Mary Parish, Louisiana Intakes at Atchafalaya River (Upper 95th percentile of parent molinate levels in raw water from 1996-1999 USGS data at Melville, LA), [pop. 61,374][5]	15/57 (0.004 ug/L)	0.109	0.018	0.057	1.56	0.17	0.028	0.089
Lake Anahuac, Texas, (from dilution calculations) [pop. 1,960][6]	20/20 (0.004 ug/L)	0.073	0.0029[7]	0.0023[7]	1.56	0.114	0.005[7]	0.004[7]

[1] Time-weighted annual mean concentrations were requested by the Health Effects Division.

[2] Time-weighted seasonal (May-July) mean concentrations. May-July is the highest exposure period for molinate. EFED provided these to the Health Effects Division for any chronic effects that may be caused by shorter-term exposure to molinate.

[3] Based on a meeting between EFED and the HED MARC committee, EFED calculated an adjustment factor of 1.56 for the parent molinate monitoring data to account for degradates of concern (See Table 1 above).

[4] The City of West Sacramento gets all of their water from the Sacramento River, while the City of Sacramento gets 71.4 % of their water from the Sacramento River and 28.6 % from the American River. EFED divided the Sacramento concentrations by 71.4 % to estimate concentrations for West Sacramento. Even though West Sacramento gets more molinate in their water, they do not get taste and odor complaints as does Sacramento. The two cities are investigating this discrepancy.

[5] The intakes below the USGS sampling points at St. Francisville in the Mississippi River and at Melville in the Atchafalaya River are located at diluted portions of both rivers, and both rivers are channelized. There are no significant downstream sources of water to dilute the residues further. As a result, EFED expects concentrations similar to the estimates at these intakes. The annual means using zero for non-detections for 1996, 1998, and 1999 were at or below the limit of detection, while the means calculated using the limit of detection were above the limit of detection, indicating additional uncertainty in these estimates for these locations.

[6] White's Bayou drains rice fields directly into Lake Anahuac, a drinking water supply for 1,960 people. However, there are other sources of water for this intake and EFED does not know the exact proportions. Also, rice production along White's Bayou has declined by approximately two-thirds since the year the data were generated (1994).

[7] These estimates have additional uncertainty because they are below the lowest detection limit of 0 004 ug/L.

California

In California, only the cities of Sacramento and West Sacramento receive any rice drainage in their drinking water. As a result, EFED is restricting the California drinking water assessment to these locations.

Sacramento

The City of Sacramento (pop. 374,600) has monitored for molinate and thiobencarb (another rice herbicide) since 1982 because of taste and odor problems in treated water. Beginning in 1991, rice farmers were required to hold the tailwater from rice fields for up to 28 days prior to release to surface water. As a result, the estimates of maximum, annual mean, and seasonal mean concentrations have decreased by factors of approximately 12, 3, and 7, respectively. The taste and odor problems have declined significantly at Sacramento.

EFED has modified previous estimates of surface water concentrations at Sacramento to include the 2000 monitoring data at Sacramento. Sacramento gets their drinking water from the intake that is below the confluence of the American and Sacramento Rivers. They receive approximately 71.4 % of their water from the Sacramento River, based on the average volume percentages from 1991-2000. The percent of uncertainty associated with assigning the limit of detection (0.1 ug/L) to non-detections because of censored data ranged from 0-97.3 and 0-89 % for annual and seasonal (May-July) means for 1991-2000, the years of monitoring after the holding periods were implemented. Figures 1, 2, and 3 below are graphical representations of the monitoring data at the City of Sacramento. Figure 1 includes the maximum yearly concentrations that were observed following implementation of the holding periods. Figures 2 and 3 include the upper and lower bounds of exposure for annual and seasonal means for specific years, respectively. The upper bound represents the mean calculated using the limit of detection for samples reported as non-detections and the lower bound represents zero (0) used for samples reported as non-detections. The upper 95th percentile of maximum parent molinate concentrations was 1.52 ug/L. Using the limit of detections for non-detections, the upper 95th percentiles of the annual and seasonal means of parent molinate were 0.29, and 0.39 ug/L, respectively. Using zero for non-detections, the upper 95th percentiles of annual and seasonal mean concentrations of parent molinate were 0.28 and 0.38 ug/L, respectively, which are almost identical to the limit of detection 95th percentiles. Tables 4 and 5 below provide details of the monitoring data at Sacramento from 1982 to 2000. Tables 4 and 5 also provide the annual means and seasonal means for each year, respectively.

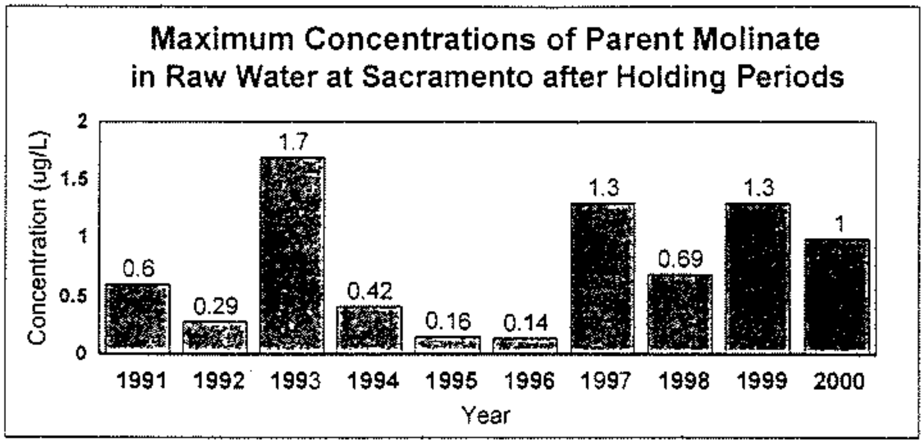

Figure 1. Maximum Concentrations of Parent Molinate in Raw Water at Sacramento after Holding Periods.

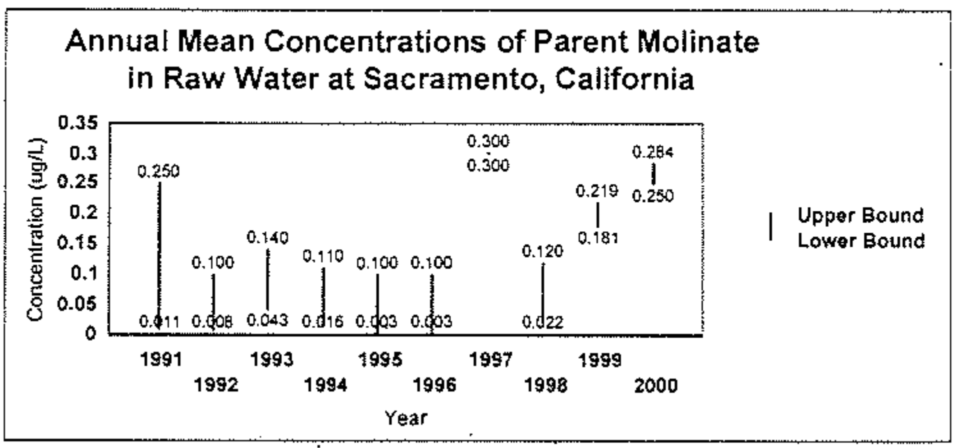

Figure 2. Annual Mean Concentrations of Parent Molinate in Raw Water at Sacramento After Holding Periods.

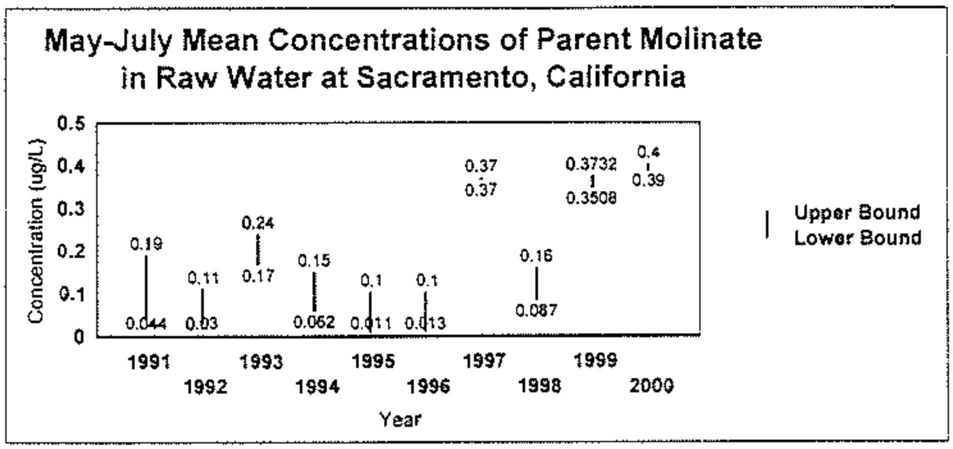

Figure 3. May-July Mean Concentrations of Parent Molinate in Raw Water at Sacramento After Holding Periods.

80

Table 4. Time Weighted Annual Means of City of Sacramento Monitoring Data for Molinate from the Sacramento River Water Treatment Intake and from Finished Tap Water (Spreadsheets entitled rice82.wk1-rice98.wk1, rice99.123, rice2000.123).

	Raw Water				Finished Water[3]		Time-weighted Annual Means of Raw Water Data using zero for non-detections (ug/L)	Time-Weighted Annual Means of Raw Water data using LODs for non-detections (ug/L)	Percent Error due to censored data (LOD means-0 means)/LOD means *100
Year	**Number of Samples, (Sampling Period)**	**Number of Detections (LOD in ug/L)**	**Maximum Detections (ug/L)**	**Percent Detections**	**Number of Samples**	**Number of Detections (LOD in ug/L)**			
1982[1]	16 (May-July)	13 (<0.3,1.5)	16	81.3	13	0 (<0.1,0.3)	1.26	1.41	10.6
1983[2]	61 (April-July)	37 (<0.3)	4	60.7	5	0 (<0.05, 0.1, 0.12, 0.3)	0.018	0.36	95.0
1984[2]	75 (April-July)	71 (<0.1)	14.5	94.6	10	0 (<0.1)	0.59	0.67	11.9
1985[2]	78 (April-June)	62 (<0.1)	13.2	79.5	5	0 (<0.1)	0.71	0.74	4.1
1986[2]	62 (April-July)	59 (<0.1)	14	95.2	2	0 (<0.1)	0.52	0.55	5.5
1987[1]	49 (May-June)	44 (<0.1)	5.7	89.8	1	0 (<0.1)	0.34	0.37	8.1
1988[1]	46 (May-June)	44 (<0.1)	4.8	95.7	1	0 (<0.1)	0.38	0.42	9.5
1989[**]	43 (April-June)	37 (<0.1)	2.6	86.0	0	0 (<0.1)	0.19	0.23	17.4
1990[1]	42 (April-Sept.)	33 (<0.1)	6.5	78.6	0	0 (<0.1)	0.28	0.35	20.0

1991[1]	17 (May-June)	8 (<0.1,0.5)	0.6	47.1	0	0 (<0.1)	0.011	0.25	95.6
1992[1]	18 (May-June)	7 (<0.1)	0.29	39.0	0	0 (<0.1)	0.075	0.10	25.0
1993[1]	17 (May-June)	12 (<0.1)	1.7	70.5	0	0 (<0.1)	0.043	0.14	69.3
1994[1]	9 (May-June)	5 (<0.1)	0.42	55.6	0	0 (<0.1)	0.016	0.11	85.5
1995[1]	13 (May-June)	2 (<0.1)	0.16	15.4	0	0 (<0.1)	0.0027	0.10	73.0
1996[1]	10 (May-June)	3 (<0.1)	0.14	30	0	0 (<0.1)	0.0031	0.10	96.9
1997[1]	10 (May-June)	10 (<0.1)	1.3	100	0	0 (<0.1)	0.3	0.30	Not calculated since there were 100 % detections
1998[1]	7 (May-June)	4 (<0.1)	0.69	57.1	0	0 (<0.1)	0.022	0.12	81.7
1999[1]	8 (May-June)	7 (<0.1)	1.3	87.5	0	0 (<0.1)	0.18	0.22	17.6
2000[1]	8 (May-June)	7 (<0.1)	1.0	87.5	0	0 (<0.1)	0.25	0.28	12.8
Upper 95th percentile of annual means before mandatory water holding period (1982-1990)							1.04	1.14	8.8 (overall)
Upper 95th percentile of annual means after mandatory holding period (1991-2000)							0.28	0.29	3.4 (overall)
Upper 95th percentile of maximum values before mandatory holding period (1982-1990)							15.4	15.4	Not Applicable
Upper 95th percentile of maximum values after mandatory holding period (1991-2000)							1.52	1.52	Not Applicable

[1] Includes Sacramento River data only since this was the only data presented
[2] Includes Village Marina in 1985 and both Village and Riverside marine in 1986 since data were presented.
[3] Chlorination converts parent molinate to the metabolite molinate sulfoxide. Because the City of Sacramento only analyzes for parent molinate in treated water, no detections are expected in treated water.

82

Table 5. Time Weighted Seasonal Means (May-July) of City of Sacramento Monitoring Data for Molinate from the Sacramento River Water Treatment Intake and from Finished Tap Water (Spreadsheets entitled rice82.wk1-rice98.wk1, rice99.123, rice2000.123).

	Raw Water				Finished Water[3]		Time-weighted Seasonal Means (May-July) of Raw Water Data using zero for non-detections (ug/L)	Time-Weighted Seasonal Means (May-July) of Raw Water Data using LODs for non-detections (ug/L)	Percent Error due to censored data (LOD means-0 means)/LOD means *100
Year	Number of Samples, (Sampling Period)	Number of Detections (LOD in ug/L)	Maximum Detections (ug/L)	Percent Detections	Number of Samples	Number of Detections (LOD in ug/L)			
1982[1]	16 (May-July)	13 (<0.3,1.5)	16	81.3	13	0 (<0.1,0.3)	3.02	3.12	3.2
1983[2]	60 (April-July)	36 (<0.3)	4	60.0	5	0 (<0.05, 0.1, 0.12, 0.3)	0.36	0.58	37.9
1984[1]	73 (April-July)	71 (<0.1)	14.5	97.3	10	0 (<0.1)	2.34	2.37	1.3
1985[2]	68 (April-June)	62 (<0.1)	13.2	91.2	5	0 (<0.1)	1.81	1.85	2.2
1986[2]	60 (April-July)	59 (<0.1)	14	98.3	2	0 (<0.1)	1.81	1.82	0.6
1987[1]	49 (May-June)	44 (<0.1)	5.7	89.8	1	0 (<0.1)	0.97	0.98	1.0
1988[1]	46 (May-June)	44 (<0.1)	4.8	95.7	1	0 (<0.1)	1.18	1.19	0.8
1989[2]	42 (April-June)	37 (<0.1)	2.6	88.1	0	0 (<0.1)	0.54	0.56	3.6
1990[1]	37 (April-Sept.)	33 (<0.1)	6.5	89.2	0	0 (<0.1)	1.11	1.13	1.8

1991[1]	17 (May-June)	8 (<0.1,0.5)	0.6	47.1	0	0 (<0.1)	0.044	0.19	76.8
1992[3]	18 (May-June)	7 (<0.1)	0.29	39.0	0	0 (<0.1)	0.03	0.11	72.7
1993[1]	17 (May-June)	12 (<0.1)	1.7	70.5	0	0 (<0.1)	0.17	0.24	29.2
1994[3]	9 (May-June)	5 (<0.1)	0.42	55.6	0	0 (<0.1)	0.062	0.15	58.7
1995[3]	13 (May-June)	2 (<0.1)	0.16	15.4	0	0 (<0.1)	0.011	0.10	89.0
1996[1]	10 (May-June)	3 (<0.1)	0.14	30	0	0 (<0.1)	0.013	0.10	87.0
1997[1]	10 (May-June)	10 (<0.1)	1.3	100	0	0 (<0.1)	Not Calculated (100 % detections)	0.37	Not Calculated (100 % detections)
1998[1]	7 (May-June)	4 (<0.1)	0.69	57.1	0	0 (<0.1)	0.087	0.16	45.6
1999[1]	8 (May-June)	7 (<0.1)	1.3	87.5	0	0 (<0.1)	0.35	0.37	6.0
2000[1]	8 (May-June)	7 (<0.1)	1.0	87.5	0	0 (<0.1)	0.39	0.40	3.2
Upper 95th percentile of means before mandatory water holding period (1982-1990)							2.75	2.82	2.5 (overall)
Upper 95th percentile of means after mandatory holding period (1991-2000)							0.38	0.39	2.6 (overall)
Upper 95th percentile of maximom values before mandatory holding period (1982-1990)							15.4	15.4	Not Applicable
Upper 95th percentile of maximum values after mandatory holding period (1991-2000)							1.52	1.52	Not Applicable

[1] Includes Sacramento River data only since this was the only data presented

[2] Includes Village Marina in 1985 and both Village and Riverside marine in 1986 since data were presented.

[3] Chlorination converts parent molinate to the metabolite molinate sulfoxide. Because the City of Sacramento only analyzes for parent molinate in treated water, no detections are expected in treated water.

84

West Sacramento

For West Sacramento, California, EFED learned that the city gets ALL of their water from the Sacramento River. To adjust for the source of water, EFED used the maximum concentration, and the annual and seasonal mean estimates for the City of Sacramento, divided the estimates by the average percent of Sacramento River that Sacramento receives (71.4 % from 1991-2000), and multiplied by 100. This approach was taken based on personal communication with Ron Myers of the City of Sacramento. Even though West Sacramento gets more molinate and thiobencarb in their water, they do not get taste and odor complaints. The two cities are investigating this discrepancy.

The percent of uncertainty for West Sacramento is the same as the City of Sacramento because the City of Sacramento data were used. The upper 95th percentile of maximum raw water concentrations of parent molinate was 2.13 ug/L. Using the LOD of 0.1 for non-detections, the upper 95th percentile concentrations of the annual mean and seasonal means of parent molinate are 0.41 and 0.54 ug/L, respectively. Using zero (0) for non-detections, the upper 95th percentiles of annual mean and seasonal means for parent molinate are 0.39, and 0.53 ug/L, respectively.

Arkansas, Mississippi, Missouri, and Tennessee

Arkansas, Mississippi, Missouri, and Tennessee have no surface water intakes in rice production areas, and therefore, no dietary exposure from surface water containing molinate is expected in these states.

Louisiana

For Louisiana, EFED divided the state into two populations that receive rice drainage in their surface water. This included the population that gets their drinking water from the Mississippi River (pop. 1.21 million between Donaldsonville and the Gulf, including New Orleans; 26 % of the Louisiana population), and the populations in St. Mary's Parish that are potentially exposed from levels in the Atchafalaya River (pop. 61,374). Monitoring data were available for the Mississippi and Atchafalaya Rivers in Louisiana, and EFED used the estimated concentrations for dietary exposure assessment for the populations with surface water intakes downstream. Tables 6 and 7 below provide details of the monitoring data for the Mississippi River intakes from 1996-1999, including annual and seasonal means, respectively. Tables 8 and 9 below provide details of the monitoring data for the Atchafalaya River intakes from 1996-1999, including annual and seasonal means, respectively.

Mississippi River Intakes

For the Mississippi River intakes, EFED found monitoring data for 1995, 1996, 1997, 1998, and 1999 at St. Francisville, Louisiana, which is upstream of the intakes. Only the 1996, 1997, 1998, and 1999 data contained samples from the times molinate would be expected to be present (spring and summer). The upper 95th percentile of the maximum concentrations from 1996-1999 for acute exposure for parent molinate was 0.117 ug/L. For chronic exposure, EFED also calculated annual and seasonal means of parent molinate for 1996-1999 and provided them to HED. Using the limit of detections for non-detections (upper bound exposure), the upper 95th percentiles of the annual and seasonal means were 0.018 and 0.057 ug/L, respectively. Using zero for non-detections (lower bound exposure), the upper 95th percentiles of annual and seasonal mean concentrations were 0.015 and 0.051 ug/L, respectively, and are almost identical to the limit of detection 95th percentiles. Tables 3 and 4 above provide details of the monitoring data at St. Francisville from 1996-1999. They also provide the annual means and seasonal means for each year, respectively. For annual means and seasonal means, the percent of uncertainty associated with assigning the limit of detection to non-detections because of censored data ranged from 21-49 % and 2-23 %, respectively. EFED notes that the annual means using zero for non-detections for 1996, 1998, and 1999 were at or below the limit of detection, while the means calculated using the limit of detection were above the limit of detection. This indicates additional uncertainty in these estimates.

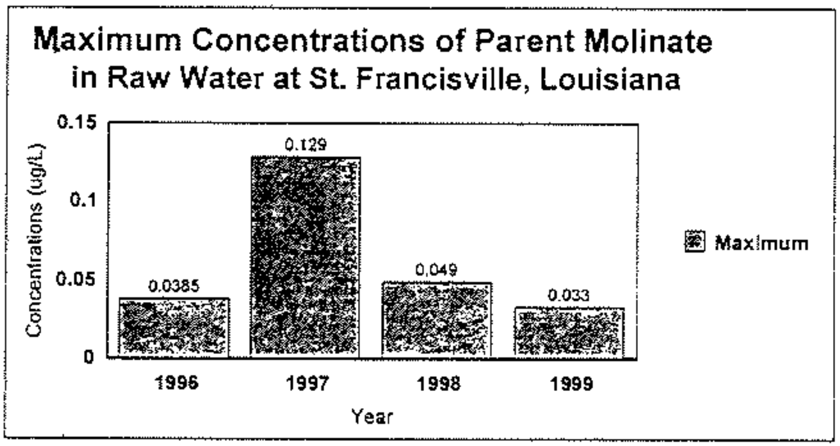

Figure 4. Maximum Concentrations of Parent Molinate in Raw Water at St. Francisville, Louisiana.

86

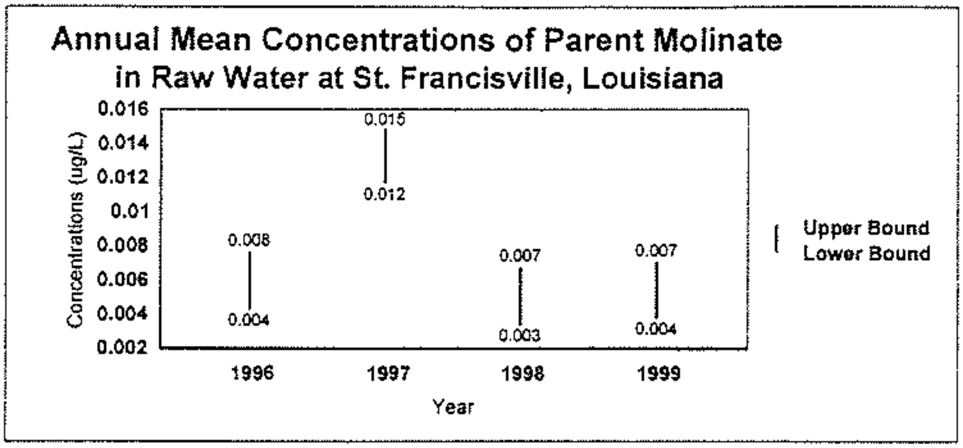

Figure 5. Annual Mean Concentrations of Parent Molinate in Raw Water at St. Francisville, Louisiana.

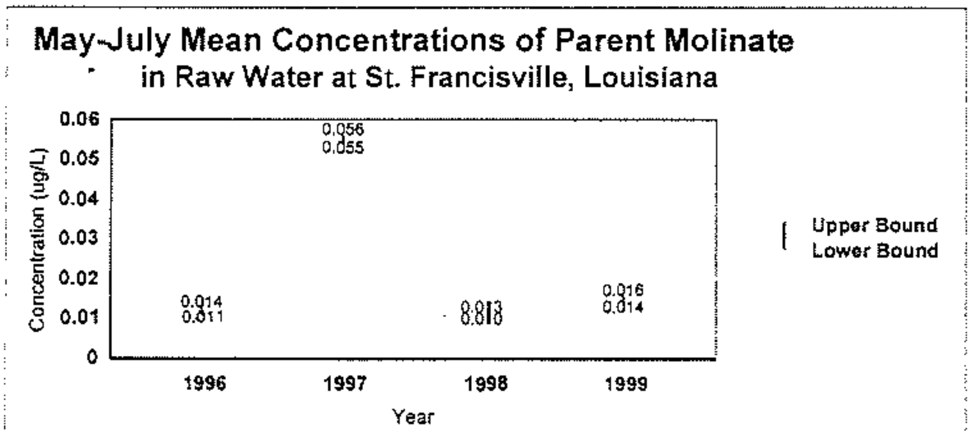

Figure 6. May-July Mean Concentrations of Parent Molinate in Raw Water at St. Francisville, Louisiana.

87

Table 6. Annual Means of Molinate for the Mississippi River in the State of Louisiana (**Spreadsheet file name St. Francisville no duplicates.123**).

Location (ID No.)	Year (dates of sampling)[1]	# Samples	# Detections (LOD<0.004 ug/L)	Percent Detections	Maximum Detections (ug/L)	Annual Means (with zero for non-detections)	Annual Means (using LOD of 0.004 ug/L for non-detections)	Percent Error due to censored data (LOD means-0 means)/LOD means *100
Mississippi River (7373420)	1996 (February-November)	13	4	31	0.13	0.009	0.012	25
Mississippi River (7373420)	1997 (January-December)	14	4	31	0.13	0.012	0.015	20
Mississippi River (7373420)	1998 (January-December)	16	3	18.8	0.049	0.003	0.007	49
Mississippi River (7373420)	1999 (January-December)	15	3	20	0.033	0.004	0.007	46
Upper 95th percentiles (1996-1999)					0.117	0.011	0.014	21.4

[1] Only two samples were taken in 1995 in the Mississippi River. They were taken in October and December.

88

Table 7. Seasonal Means of Molinate for the Mississippi River in the State of Louisiana (Spreadsheet file name St. Francisville no duplicates.123).

Location (ID No.)	Season (May-July)	# Samples	# Detections (LOD <0.004 ug/L)	Percent Detections	Maximum Detections	Seasonal Means (with zero for non-detections)	Seasonal Means (using LOD of 0.004 ug/L for non-detections)	Percent Error due to censored data (LOD means-0 means)/LOD means *100
Mississippi River (7373420)	1996	7	3	43	0.13	0.022	0.024	8.3
Mississippi River (7373420)	1997	4	3	75	0.13	0.055	0.056	1.8
Mississippi River (7373420)	1998 (January-September)	16	3	18.8	0.049	0.010	0.014	28.6
Mississippi River (7373420)	1999 (January-September)	15	3	20	0.033	0.013	0.016	18.8
Upper 95th percentile values (1996-1999)					0.117	0.049	0.050	2

[1] Only two samples were taken in 1995 in the Mississippi River. They were taken in October and December.

89

Atchafalaya River Intakes

For the Atchafalaya River intakes, EFED found monitoring data for 1995, 1996, 1997, 1998, and 1999 at Melville, Louisiana, which is upstream of the intakes. Only the 1996-1999 data contained samples from the times molinate would be expected to be present (spring and summer). For acute exposure, the upper 95[th] percentile of the peak concentrations of parent molinate from 1996-1999 was 0.105 ug/L. For chronic exposure, EFED calculated annual and seasonal means for 1996-1999 and provided them to HED. Using the limit of detections for non-detections (upper bound exposure), the 95[th] percentiles of the annual and seasonal means are 0.015 and 0.051 ug/L, respectively. Using zero for non-detections (lower bound exposure), the 95[th] percentiles of annual and seasonal mean concentrations of parent molinate were 0.011 and 0.49 ug/L, respectively, and are almost identical to the limit of detection 95[th] percentiles. Figures 7, 8, and 9 below are graphical representations of the monitoring data at Melville, Louisiana. Figure 7 provides the maximum concentrations for each year. Figures 8 and 9 include the upper bound and lower bound of annual mean and seasonal mean exposures for specific years, respectively. The upper bound represents the mean calculated using the limit of detection for non-detections and the lower bound represents zero (0) used for non-detections. For annual and seasonal means, the percentages of uncertainty associated with assigning the limit of detection to non-detections because of censored data was 13-52 % and 2-21 %, respectively. Tables 8 and 9 below provide details of the monitoring data for the Atchafalaya River intakes from 1996-1999, including annual and seasonal means, respectively. Table 10 contains the list of intakes that are potentially exposed from surface water in the Atchafalaya River.

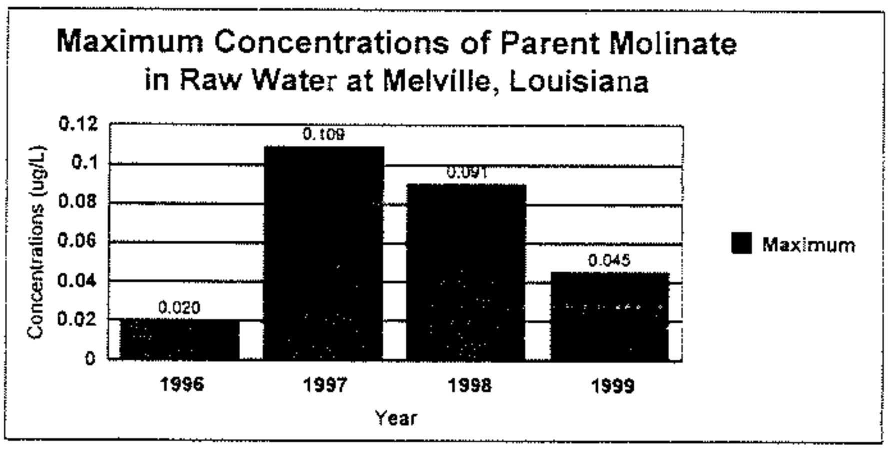

Figure 7. Maximum Concentrations of Parent Molinate in Raw Water at Melville, Louisiana.

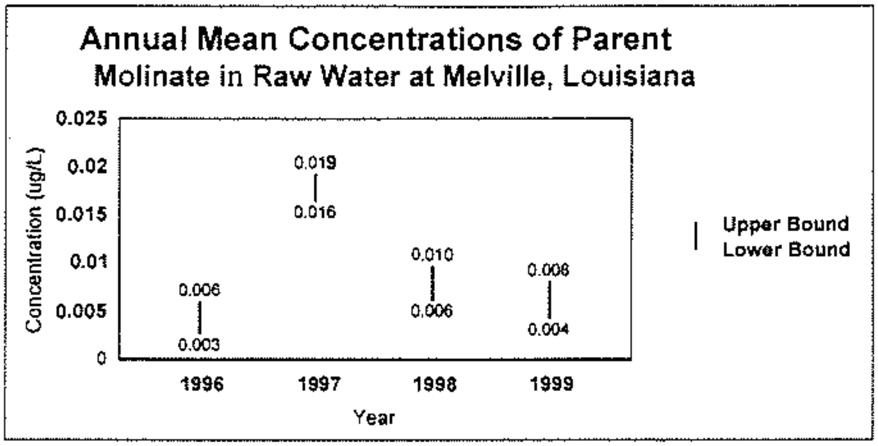

Figure 8. Annual Mean Concentrations of Parent Molinate in Raw Water at Melville, Louisiana.

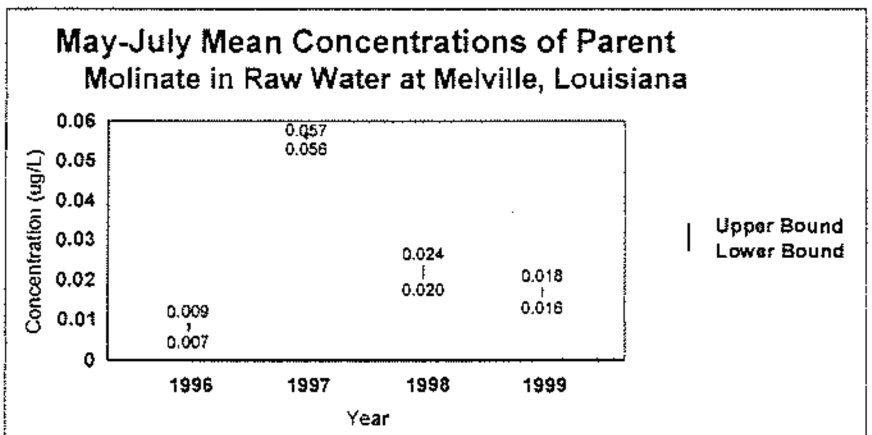

Figure 9. May-July Mean Concentrations of Parent Molinate in Raw Water at Melville, Louisiana.

Table 8. **Annual Means of Molinate in the Atchafalaya River in the State of Louisiana (Spreadsheet file name Melville no duplicates.123).**

Location (ID No.)	**Year (dates of sampling)[1]**	**# Samples**	**# Detections (LOD<0.004 ug/L)**	**Percent Detections**	**Maximum Detections (ug/L)**	**Annual Means (with zero for non-detections)**	**Annual Means (using LOD of 0.004 ug/L for non-detections)**	**Percent Error due to censored data (LOD means-0 means)/LOD means *100**
Atchafalaya River (7381495)	1996 (February-November)	12	3	25	0.02	0.003	0.006	50
Atchafalaya River (7381495)	1997 (January-December)	16	5	31	0.109	0.016	0.019	14
Atchafalaya River (7381495)	1998 (January-December)	14	3	21	0.091	0.006	0.010	34
Atchafalaya River (7381495)	1999 (January-December)	15	3	20	0.045	0.004	0.008	43
Upper 95th percentiles (1996-1999)					0.105	0.015	0.018	17

[1] Only two samples were taken in 1995 in the Atchafalaya River. They were taken in October and December.

Table 9. Seasonal Means (May-July) of Molinate in the Atchafalaya River in Louisiana (Spreadsheet file name Melville no duplicates.123).

Location (ID No.)	Season (May-July)	# Samples	# Detections (LOD <0.004 ug/L)	Percent Detections	Maximum Detections	Seasonal Means (with zero for non-detections)	Seasonal Means (using LOD of 0.004 ug/L for non-detections)	Percent Error due to censored data (LOD means-0 means)/LOD means *100
Atchafalaya River (7381495)	1996 (February-November)	12	3	25	0.02	0.007	0.009	22
Atchafalaya River (7381495)	1997 (January-December)	16	5	31	0.109	0.056	0.057	2
Atchafalaya River (7381495)	1998 (January-December)	14	3	21	0.091	0.020	0.024	17
Atchafalaya River (7381495)	1999 (January-December)	15	3	20	0.045	0.016	0.018	11
Upper 95th percentiles (1996-1999)					0.105	0.051	0.057	11

[1] Only two samples were taken in 1995 in the Atchafalaya. They were taken in October and December.

93

Table 10. Surface Water Intakes in Louisiana that are Potentially Exposed to Molinate in the Atchafalaya River (from the Safe Drinking Water Information System (http://www.epa.gov/OGWDW/dwinfo/la.htm).

Drinking Water Supply	Parish	Source of Water	Population
Berwick-Bayou Vista WW C	St. Mary	Bayou Teche and Atchafalaya River[1]	12,135
City of Franklin WS	St. Mary	Bayou Teche and Atchafalaya River[1]	10,001
Morgan City Water System	St. Mary	Atchafalaya River and Lake Palourde[2]	15,500
Patterson Water System	St. Mary	Atchafalaya River	4,500
St. Mary Parish Water System Comm #1	St. Mary	Bayou Boeuf[3]	4,800
St. Mary Parish WW District # 5	St. Mary	Six Mile Lake (part of Atchafalaya River)	6,500
St. Mary Parish WW District #6	St. Mary	Atchafalaya River	7,938
Total Population			61374

[1] These utilities use the Atchafalaya River in periods of low water levels in Bayou Teche to maintain a positive water flow in Bayou Teche. Bayou Teche flows into the Atchafalaya River near Morgan City.
[2] According to the USGS in Louisiana, at present Morgan City draws their water only from the Atchafalaya River.
[3] Owned by St. Mary Parish WW District #3.

Texas

The only intake found to receive molinate residues was Anahuac, Texas. At this location, White's Bayou drains rice fields into Lake Anahuac, which is a drinking water source for 1,960 people (Town website: http://www.lone-star.net/excite/AT-texasmallquery.html). . However, EFED realizes that other sources of water that do not receive rice drainage are used to supplement the lake. Also, rice production along White's Bayou has declined by approximately two-thirds since the year the data were generated (1994). As a result, the predicted EEC's are probably higher than actual exposure. EFED has no information on the proportion of water from the other source and from rice fields and the number of days Lake Anahuac receives rice drainage so that the estimates of drinking water concentrations can be refined.

For 1994, EFED found monitoring data for White's Bayou, an agricultural drain, and Lake Anahuac, a drinking water supply. In Lake Anahuac, there is limited sampling with one detection in 1994. Therefore, EFED used dilution calculations to estimated dietary exposure at this location. To calculate EEC's for Lake Anahuac, EFED factored in the flow rates and concentrations in White's Bayou and the approximate volume of the lake. EFED has learned that the lake has a diameter of approximately 2.8 miles and an average depth of about 4 feet.

To obtain a maximum concentration for acute exposure in Lake Anahuac, EFED multiplied the concentrations (ug/L) at each sampling time by the flow rate (cfs) to determine a maximum loading from White's Bayou. The 200 ug/L concentration was not included because it was only estimated, not confirmed, and therefore had higher uncertainty than the other concentrations. After determining the maximum loading event (May 17, 1994), the flow rate (186 cfs) was converted to liters/day (4.34×10^8 L/day), divided by the estimated volume of the lake (1.8×10^{10} L), and multiplied by the concentration at the time interval (3.1 ug/L). This led to an estimated peak concentration of 0.073 ug/L in Lake Anahuac.

To obtain average concentrations for chronic exposure in Lake Anahuac, EFED calculated estimates of both annual and seasonal (May-July) exposure using a similar procedure. For the annual mean concentration, EFED multiplied the concentrations * flow rates in White's Bayou for each sampling interval. These products were time-weighted to obtain a loading factor in ug/second. The loading factor (22.83 ug/second) was multiplied by 86, 400 seconds/day to obtain a daily loading, and multiplied by 27 to convert the loading from a cubic feet basis to a liter basis. This was done because the volume of the lake was calculated in liters. This led to an average loading of 5.33×10^7 ug/day, which was divided by the estimated volume of the lake (1.8×10^{10} L). The annual mean concentration of molinate in Lake Anahuac was estimated to be 0.0029 ug/L. The 200 ug/L concentration was not included because it was only estimated, not confirmed, and therefore had higher uncertainty than the other concentrations. Also, the 3/15/94 data were not used because a flow rate was not available. For seasonal means of exposure (May-July), the procedure for annual mean exposure was used except that only the sampling intervals for May-July were used in the analysis. The loading factor was 17.67 ug/second, and the average loading was 4.12×10^7 ug/day. The estimated seasonal mean concentration was 0.0023 ug/L for Lake Anahuac. EFED notes that the estimates of mean concentrations are below the limit of detection (0.004 ug/L). These concentrations would likely be reduced since Lake Anahuac receives water from an additional source that receives no rice drainage.

Registrant's Response to Previous Water Assessments

The registrant has also provided drinking water assessments for molinate (MRID 44791001). Both the registrant and EFED have cited the same data in their drinking water assessments, except for the fact that EFED included a STORET search that included monitoring that was conducted by the State of Arkansas. The registrant has also calculated time-weighted annual means (January-December) for each monitoring location and year combination, but did not calculate time-weighted seasonal (May-July) means. EFED identified all known surface water intakes that are downstream of the detections in the different rivers in rice-producing regions. The registrant summarized water treatment practices and the effect of water treatment on molinate residues in their water assessment.

Effect of Water Treatment on Molinate Residues in Raw Water

If there are detectable molinate residues in water, the efficiency of removal of molinate during drinking water treatment will determine the residues of molinate in the finished water. EFED has received laboratory studies on the efficiency of parent molinate removal. These studies simulated the entire City of Sacramento (CA) water treatment process. When chlorination was used as a oxidant, the majority of parent molinate was present as molinate sulfoxide, which still has the carbamate functional group. Potassium permanganate appeared to be a more effective oxidant for molinate, degrading almost all parent molinate to a non-carbamate degradate. However, because the extent of use of oxidants other than chlorine is uncertain, because there are differences in water treatment practices between surface water intakes, and because conventional treatment using chlorine results in molinate conversion to the equally toxic metabolite molinate sulfoxide, EFED recommends using the raw water concentrations of parent molinate in a drinking water assessment.

Information Provided by the USA Rice Federation

The USA Rice Federation confirmed EFED's previous conclusion that there are no surface water intakes in the Delta in Mississippi and Missouri. For rice in Missouri, the drainage flows into the St. Francis River and eventually into the Mississippi River at Helena, Arkansas. The rice federation also provided the proportion of dry-seeded and water-seeded rice production by state, which was consistent with EFED's previous conclusions. The water retention and release facts also provided useful information. The surface water data in Louisiana from quarterly sampling in the years 1992-1999 are consistent with the USGS data that have been recently obtained. Surface water concentrations were observed up to 30 ppb in surface water that is not used for drinking water.

Assumptions, Certainties, Uncertainties, and Limitations

Water Treatment

Most drinking water facilities with surface water intakes located downstream of rice production have some uncertainty about their water treatment processes. The registrant has submitted a document (MRID 44926503) that includes drinking water treatment for several intakes that are either near rice production or downstream of rice production. With the exception of an intake that uses potassium permanganate as an oxidant, the listed drinking water facilities use only chlorination as an oxidative process. However, the intake that uses potassium permanganate as an oxidant does not appear to receive rice drainage, and therefore the information on the non-exposed intake has no bearing on the risk assessment. Because chlorination purportedly transforms molinate to a toxic sulfoxide degradate, the majority of parent molinate present in raw water would still be present as the toxic metabolite molinate sulfoxide after treatment. The registrant claims that conventional water disinfection practices degrade molinate. They are correct in saying that PARENT molinate is degraded with chlorination, but predominantly to the toxic metabolite molinate SULFOXIDE. If the registrant has additional information about the effect of water treatments other than oxidants such as potassium permanganate, then it should be submitted.

EFED has received molinate-specific laboratory studies that simulate water treatment at Sacramento, CA. However, the efficiency of water treatment practices to remove toxic residues of molinate may vary significantly between intakes. Variables such as spiking rates of oxidants, size of the distribution system, and storage/treatment times may provide different pesticide removal efficiencies. Therefore, using the results of one intake's treatment may not be accurate for another intake.

The water treatment practices at the Mississippi and Atchafalaya River intakes was not provided by the registrant. EFED is assuming that chlorination is the only oxidative treatment at these intakes.

Use of Monitoring Data

EFED is very certain about the drinking water conclusions for California, Missouri, Tennessee, and Arkansas for parent molinate. EFED is less certain about the Mississippi and Atchafalaya River intakes in Louisiana because of fewer years of monitoring data (4 years or less) compared to California (19 years). EFED is uncertain about the extent of exposure at Anahuac, Texas because the amount of water from other sources and the number of days that Lake Anahuac receives rice drainage is unknown.

The amount of the degradate 4-keto molinate exposure in the use season is uncertain. The Domagalski article states that between 10-30 % of detected molinate was present in the Sacramento River in California. However, this study was conducted in January, and molinate is applied in May-June primarily. The study author speculates that the higher levels of 4-keto molinate were a result of the longer time available for photolysis to occur. The degradate 4-keto molinate never reached significant levels (10 % of applied) in the laboratory or field studies. Also, none of the studies showed DIRECT photolysis, where a pesticide absorbs the light and degrades. Any formation of 4-keto molinate at high levels must be resulting from INDIRECT photolysis, where other organic substances pass the energy from sunlight to molinate.

The use of monitoring data to assess dietary exposure creates uncertainties. Monitoring data are not available everywhere for all uses of a given compound. In a given year, it is highly likely that peak concentrations are missed since sampling is not always conducted on a daily schedule or over the time necessary to detect peaks. Also, peak concentrations are not likely to be detected unless sampling is conducted in a stratified sampling pattern in highly vulnerable sites. Sampling is also not necessarily representative of the entire year unless sampling is conducted over a year. Since monitoring data are dependent on the weather in a particular year, data may not always be available for enough years to cover the range of weather in a given area of application. The associated information to interpret monitoring information, such as amount of use and the area treated in a watershed, the timing and amount of rainfall events that drive runoff events, and specific cultural practices are not always available. Inclusion of data from an area where no pesticide is applied tends to bias estimates of exposure downward when considered with data from use areas. In analyzing these data, efforts were made to only include data from areas where molinate was known to have been used.

Estimation of degradate concentrations based on field and laboratory studies

Estimation of degradate concentrations in surface water based on laboratory and field studies introduces uncertainties because levels of degradates relative to parent compound vary with time. Degradate concentrations are lowest relative to parent compounds immediately following the application and increase with time. As a result, no single adjustment factor for monitoring data will perfectly represent the contribution of degradates to ecological and drinking water exposure. However, the 1.56 factor is an average number that will reasonably represent the contribution of degradates for both ecological and drinking water exposure. Monitoring for all residues of concern is the only certain method to assess exposure.

Most of the monitoring data were for parent molinate only and not the degradates. Only some of the USGS monitoring data contained any information on the 4-keto molinate degradate. No monitoring data on the other degradates of concern was available. As a result, EFED has attempted to account for the presence of degradates in surface and ground water by incorporating data from aquatic field dissipation and an aerobic aquatic metabolism study from the laboratory. However, these studies did not include any information on molinate sulfone, 3-keto molinate, or ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate). However, volatility is the primary route of dissipation and the other metabolites are formed in relatively low amounts with the exception of 4-keto molinate. As a result, EFED does not expect significant formation of these metabolites in water.

The potable water studies provided highly variable estimates of the dietary contribution of the molinate sulfoxide and molinate acid degradates. The adjustment factors for 8 EC and 15G molinate were 1.094 (0-50 % total degradates observed) and 1.11 (0-48 % of total degradates observed), respectively. Therefore, some monitoring may be required for those intakes with EEC's close to the Drinking Water Level of Comparison.

Time-weighting of monitoring data

Time-weighting of monitoring data introduces uncertainties. In the case of molinate, the time-weighting of data over a year from seasonal data was conducted based on a request by the Health Effects Division (HED). While this approach leads to a consistent time basis for means of data, calculating an annual mean from seasonal data creates uncertainties in the final estimates due to extrapolation. The detections or lack of detections at the first sampling interval are extended to the time between January 1st and the first sampling interval. Also, the detections or lack of detections at the last sampling interval are extended to the time between December 31st and the last sampling interval. Non-detections at the beginning and end sampling intervals tend to bias the final estimates downward, while high detections at the end sampling intervals tend to bias the final estimates upward. Also, relatively few years of data are available for most molinate use areas, with the exception of the Sacramento River where extensive data (19 years) were available. This adds some uncertainty to our assessment.

Use of dilution calculations

Since Lake Anahuac was the only intake for which dilution calculations were used, additional uncertainties exist for this location. Dilution calculations assume instantaneous distribution throughout the receiving water body, which can be relevant with shallow, well-mixed water bodies that do not stratify, such as Lake Anahuac. Also, increasing time tends to lead to uniform concentrations in the receiving water body. However, many factors can increase error when this assumption is used, including gradients in water temperature and salt concentrations and the presence of channelization that tend to localize concentrations of a pesticide. The location of the intake relative to the source water body can influence how much pesticide actually reaches the intake. If an intake is located near the source water body or in an area with high localized concentrations, the concentrations in drinking water may be higher than estimated. If an intake is located further away from the source water body or in an area where the pesticide does not localize, the concentration in drinking water may be less than estimated. In addition, extrapolation of concentrations and flow rates from the source water body to longer time intervals is a possible source of error. For molinate in White's Bayou (source water body), the flow rates were expressed as cubic feet/second. These flow rates were extrapolated to cubic feet/day for the calculations, which assumes that the same flow rate occurs over an entire day. The concentrations in White's Bayou were also extrapolated to an entire day, when they actually represent a point in time.

Appendix F. Risk Quotients

Risk characterization integrates the results of the exposure and ecotoxicity data to evaluate the likelihood of adverse ecological effects. The means of this integration is called the quotient method. For this method, risk quotients (RQs) are calculated by dividing exposure estimates by acute and chronic ecotoxicity values:

RQ = EXPOSURE/TOXICITY

RQs are then compared to OPP's levels of concern (LOCs). These LOCs are criteria used by OPP to indicate potential risk to nontarget organisms and the need to consider regulatory action. The criteria indicate that a pesticide used as directed has the potential to cause adverse effects on nontarget organisms. LOCs currently address the following risk presumption categories: (1) **acute risk**--potential for acute risk exists; regulatory action may be warranted in addition to restricted use classification, (2) **acute restricted use**--the potential for acute risk which may be mitigated through restricted use classification, (3) **acute endangered species**--endangered species may be adversely affected; regulatory action may be warranted, and (4) **chronic risk**--the potential for chronic risk exists; regulatory action may be warranted. Currently, EFED does not perform assessments for chronic risk to plants, acute or chronic risks to nontarget insects, or chronic risk from granular/bait formulations to birds or mammals.

The ecotoxicity test values (i.e., measurement endpoints) used in the acute and chronic risk quotients are derived from required studies. Examples of ecotoxicity values derived from short-term laboratory studies that assess acute effects are: (1) LC_{50} (fish and birds), (2) LD_{50} (birds and mammals), (3) EC_{50} (aquatic plants and aquatic invertebrates), and (4) EC25 (terrestrial plants). Examples of toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are: (1) LOAEL (birds, fish, and aquatic invertebrates), (2) NOAEL (birds, fish and aquatic invertebrates), and (3) MATC (fish and aquatic invertebrates). For birds and mammals, the NOAEL is generally used as the ecotoxicity test value in assessing chronic effects, although other values may be used when justified. For fish and aquatic invertebrates, the MATC (defined as the geometric mean of the NOAEL and LOAEL) is used as the ecotoxicity test value when the most sensitive endpoint in the toxicity test is growth, but the NOAEL is used when the most sensitive endpoint is production of offspring or survival.

Risk presumptions, along with the corresponding RQs and LOCs, are tabulated below.

a. Risk Presumptions, RQ's, and LOC's

Terrestrial Animals		
Risk Presumption	RQ	LOC
Acute Risk	EEC[1]/LC50 or LD50/sqft[2] or LD50/day[3]	0.5
Acute Restricted Use	EEC/LC50 or LD50/sqft or LD50/day (or LD50 < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC50 or LD50/sqft or LD50/day	0.1
Chronic Risk	EEC/NOAEL	1

[1] abbreviation for Estimated Environmental Concentration (ppm) on avian/mammalian food items

[2] $\frac{\text{mg/ft}^2}{\text{LD50 * wt. of bird}}$ [3] $\frac{\text{mg of toxicant consumed/day}}{\text{LD50 * wt. of bird}}$

Aquatic Animals		
Risk Presumption	RQ	LOC
Acute Risk	EEC[1]/LC50 or EC50	0.5
Acute Restricted Use	EEC/LC50 or EC50	0.1
Acute Endangered Species	EEC/LC50 or EC50	0.05
Chronic Risk	EEC/MATC or NOAEL	1

[1] EEC = (ppm or ppb) in water

Plants		
Risk Presumption	RQ	LOC
	Terrestrial and Semi-Aquatic Plants	
Acute Risk	EEC[1]/EC25	1
Acute Endangered Species	EEC/EC05 or NOAEL	1
	Aquatic Plants	
Acute Risk	EEC[2]/EC50	1
Acute Endangered Species	EEC/EC05 or NOAEL	1

[1] EEC = lbs ai/A
[2] EEC = (ppb/ppm) in water

b. Exposure and Risk to Nontarget Terrestrial Animals

i. Birds

The acute risk quotients could not be determined for EC products because definitive avian acute dietary LC_{50} values have not been established for molinate. In avian acute dietary tests conducted with the bobwhite and the mallard, no mortality was observed with test concentrations as high as 5620 ppm. Application of molinate as an EC spray, with a maximum application per-application rate of 4 lb ai/A, is predicted to result in concentrations on wildlife food items not greater than 960 ppm. Even for the maximum seasonal application rate of 9 lb ai/A, with the assumption of no dissipation of residues between applications, the maximun concentration is predicted to be no greater than 2160 ppm. Therefore, spray applications of molinate on rice are predicted to pose minimal acute risk to birds. However, based on the available data, the margin of safety is not great enough to rule out the potential of acute hazard to threatened and endangered birds and reptiles that feed on short grass. These species could possibly be affected if they feed within rice fields after post-emergent applications since they might feed on the newly emerged rice plants.

Molinate also may be applied to rice as granules in preplant incorporated (PPI) or postflood applications. Birds may be exposed to granular pesticides ingesting granules when foraging for food or grit. They also may be exposed by other routes, such as by walking on exposed granules or drinking water contaminated by granules. The Agency assesses risk to birds based on three bodyweights: 1000 g (e.g., a waterfowl), 180 g (e.g., an upland game bird) and 20 g (e.g., a songbird). The number of lethal doses (LD_{50}'s) that are available within one square foot immediately after application (LD_{50}/ft^2) is normally used as the risk quotient for granular products. Since PPI applications are soil incorporated by discing or harrowing, only 15% of the granules are assumed to be available on the soil surface. For postflood applications, 100% of the granules are assumed to be available. For this use, the assessment is based on exposure to unincorporated granules on the levees and berms.

The acute risk quotients could not be determined for granular products because definitive avian acute oral LD_{50} values have not been established for molinate. In an acute oral toxicity study with the mallard, no mortality or adverse effects were observed at the maximum test dose of 2250 mg ai/kg. In the following table, this dose is converted to mg ai/individual (based on bodyweight) and compared to the amount of AI that would be exposed in one square foot of application area.

Avian Toxicity and Exposure for Applications of Granular Products on Rice.

Rate in lbs ai/A (application method)	Proportion of Pesticide Left on the Surface	Body Weight (g)	LD_{50} (mg/individual)	Amount AI per ft^2
4 (Preplant incorporated)	0.15	20	>44.6	6.25
4 (Preplant incorporated)	0.15	180	>401	6.25
4 (Preplant incorporated)	0.15	1000	>2,230	6.25
4 (Preplant, postflood)	1.0	20	>44.6	41.6
4 (Preplant, post flood)	1.0	180	>401	41.6
4 (Preplant, postflood)	1.0	1000	>2,230	41.6
5 (Postflood, postemergence)	1.0	20	>44.6	52.1
5 (Postflood, postemergence)	1.0	180	>401	52.1
5 (Postflood, postemergence)	1.0	1000	>2,230	52.1
9 (Maximum seasonal rate)	1.0	20	> 44.6	93.7
9 (Maximum seasonal rate)	1.0	180	> 401	93.7
9 (Maximum seasonal rate)	1.0	1000	> 2,230	93.7

For preplant incorporated applications, the amount of molinate available in one square foot is well below the maximum dose tested in the laboratory which yielded no adverse effects. The same is also true for a single postflood application with the exception of small birds, for which the amount of molinate available in one square foot is only slightly greater than the maximum laboratory dose which yielded no effects. Since this dose was the highest dose tested, it is unknown how much greater of dose would be required to cause mortality. The predicted esposure based on the maximum seasonal application rate, which gives the upper bound of risk from multiple applications, is also greater than the maximum laboratory dose. The Agency concludes that use of granular molinate poses minimal acute risk to all birds when used in PPI applications and to medium to large birds when used in postflood applications. Mortality of small birds from a single postflood application or from repeated applications cannot be ruled out based on the current data, but this risk is likely to be minor because (1) most of the granules applied postflood would fall into water and thus be unavailable to small birds and (2) a relatively large number of granules would need to be consumed to reach the lethal dose, which us unlikely for small birds.

A chronic avian risk assessment cannot be conducted for molinate at this time because data from avian reproduction studies have not been submitted to the Agency. However, studies in mammals have shown that molinate poses a chronic risk because of its toxicity to the reproductive system. The reproductive systems of birds and mammals are similar enough to suspect that damage to avian reproductive system may also occur. Therefore, until reproductive data on birds can be reviewed, the chronic risk to birds should be assumed.

ii. Mammals

EC Products

Estimating the potential for adverse effects to wild mammals is based upon EEB's draft 1995 SOP of mammalian risk assessments and methods used by Hoerger and Kenaga (1972) as modified by Fletcher *et al.* (1994). The concentration of molinate in the diet that is expected to be acutely lethal to 50% of the test population is determined by dividing the rat LD_{50} by the proportion of body weight consumed. A risk quotient is then determined by dividing the EEC by this derived concentration. Risk quotients are calculated for three separate weight classes of mammals (15, 35, and 1000 g), each presumed to consume four different kinds of food (grass, forage, insects, and seeds). This risk assessment is applicable for risk associated with preflood applications only. The acute risk quotients for broadcast applications of nongranular products are tabulated below.

Mammalian Acute Risk Quotients for Application of EC Products on Rice, Based on a Rat LD_{50}.
Part I: Herbivores and Insectivores.

Rate in lbs ai/A (Application method)	Body Weight (g)	% Body Weight Consumed	Rat LD50 (mg/kg)	EEC (ppm) Short Grass	EEC (ppm) Forage & Small Insects	EEC (ppm) Large Insects	Acute RQ[1] Short Grass	Acute RQ[1] Forage & Small Insects	Acute RQ[1] Large Insects
4 (unincorp.)	15	95	549	960	540	60	1.66***	0.93***	0.10*
	35	66	549	960	540	90	1.15***	0.65***	0.11*
	1000	15	549	960	540	90	0.26**	0.15*	0.02
3 (preflood, unincorpor.)	15	95	549	720	405	45	1.25***	0.70***	0.08
	35	66	549	720	405	45	0.87***	0.49**	0.05
	1000	15	549	720	405	45	0.20**	0.11*	0.01
9 (max. rate per season)	15	95	549	2160	1215	135	3.74***	2.10***	0.23**
	35	66	549	2160	1215	135	2.60***	1.46***	0.16*
	1000	15	549	2160	1215	135	0.59***	0.33**	0.04

[1] RQ = EEC (ppm) / LD50 (mg/kg)/ % Body Weight Consumed

*** RQ exceeds LOC for acute or chronic risk
** RQ exceeds LOC for restricted use
* RQ exceeds LOC for endangered species

109

Part II. Granivores

Rate in lbs ai/A (Application method)	Body Weight (g)	% Body Weight Consumed	Rat LD50 (mg/kg)	EEC (ppm) Seeds	Acute RQ[1] Seeds
4 (unincorp.)	15	21	549	60	0.02
	35	15	549	60	0.02
	1000	3	549	60	<0.01
3 (preflood, unincorpor.)	15	21	549	45	0.02
	35	15	549	45	0.01
	1000	3	549	45	<0.01
9 (max. rate per season)	15	21	549	135	0.05
	35	15	549	135	0.04
	1000	3	549	135	0.01

[1] $RQ = \frac{\text{EEC (ppm)}}{\text{LD50 (mg/kg)/ \% Body Weight Consumed}}$

*** RQ exceeds LOC for acute or chronic risk
** RQ exceeds LOC for restricted use
* RQ exceeds LOC for endangered species

For a single unincorporated application of EC product, risk quotients range from <0.01 to 1.7 when the maximum use rate is 4 lb ai/A, and <0.01 to 1.25 when maximum use rate is 3 lb ai/A. These results indicate that certain mammals may have some acute risk from exposure to molinate. The level of exposure, and thus the risk, will vary depending on application method. Applications to emerged weeds are predicted to pose the highest risk to some mammals. Postflood applications may also pose a risk because some mammals, such as the muskrat, may feed on the young emerged rice plants after they are sprayed. Also, spraying of flooded rice fields, would result in exposure of to the dry ground areas on the levees and around the field edges, especially if spraying is done aerially.

Risk quotients for the maximum application rate per season are given to provide an upper bound estimate of risk from repeated application. These risk quotients overestimate risk because they do not account for the dissipation of residues between applications. If the dissipation of residues could be quantified, the risk quotients for multiple applications would be somewhere in between those for a single application and those for the maximum rate per season. The conclusions based on the per-season risk quotients are generally the same as for a single application, namely potential risk to certain types of small mammals.

Pre-plant incorporated (PPI) applications, in which the pesticide is applied to bare soil which is then mixed to a depth of 2 inches, would result in a much reduced exposure to mammals. Based on the relatively low risk quotients for unincorporated applications, it appears unlikely that PPI applications would pose risk to mammals. If the active ingredient were to be mixed evenly in the top 2 inches of soil, an application of 4 lb ai/A would yield a soil concentration of 4.4 ppm. This is less than even the chronic rat NOAEL (5 ppm), which is expected to be much less than the acute NOAEL. Therefore, PPI applications are predicted to pose minimal risk to mammals.

Mammalian Chronic Risk Quotients for Single Application of EC Products on Rice, Based on the Rat NOAEL.

Application Rate in lbs ai/A (Application method)	Food Items	Maximum EEC[1] (ppm)	NOAEL (ppm)	Chronic RQ (EEC/NOAEL)
4 (unincorporated)	Short grass	960	5	192
	Tall grass	440	5	88
	Broadleaf plants/Insects	540	5	108
	Seeds	60	5	12
3 (preflood, unincorpor.)	Short grass	720	5	144
	Tall grass	330	5	66
	Broadleaf plants/Insects	405	5	81
	Seeds	45	5	9
9 (Max. rate per season)	Short Grass	2160	5	432
	Tall Grass	990	5	198
	Broadleaf plants/Insects	1215	5	243
	Seeds	135	5	27

[1] Based on Fletcher without degradation.

The risk assessment shows that a single application of EC products of molinate on rice poses potential chronic risk to all types of mammals due to reproductive toxicity. The risk quotients for the maximum rate per season (9 lb ai/A) gives the upper bound of risk quotients for multiple applications. These risk quotients are overestimations because are based on no dissipation of residues between applications. (This dissipation could not be quantified with the currently available data). The actual risk quotient for repeated application would be somewhere between those for a single application and those for the maximum rate per season.

Granular Products

Mammalian species also may be exposed to granular pesticides by ingesting granules. They also may be exposed by other routes, such as by walking on exposed granules and drinking water contaminated by granules. The number of lethal doses (LD50's) that are available within one square foot immediately after application can be used as a risk quotient (LD50's/ft^{2}) for the various types of exposure to bait pesticides. Risk quotients are calculated for three separate weight classes of mammals: 15 g, 35 g and 1000 g.

The acute risk quotients for broadcast applications of granular products are tabulated below.

Mammalian Acute Risk Quotients for Granular Products on Rice, Based on a Rat LD_{50} of 549 mg/kg.

Rate in lbs ai/A (Application method)	Proportion of Pesticide Left on the Surface	Body Weight (g)	Acute RQ[1] (LD50/ft²)
4 (Preplant incorporated)	0.15	15	0.76*
		35	0.33
		1000	0.011
4 (Preplant, postflood)	1.0	15	5.06*
		35	2.17*
		1000	0.076
5 (Postflood, postemergence)	1.0	15	6.32*
		35	2.71*
		1000	0.095
9 (Max. per season rate)	1.0	15	11.38*
		35	4.88*
		1000	0.17

[1] $LD_{50}/ft^2 = \frac{\text{App. Rate (lbs ai/A)} * (453{,}590\ \text{mg/lbs}/43{,}560\ \text{ft}^2\text{/A})}{\text{LD50 mg/kg} * \text{Weight of Animal (kg)}}$

* RQ exceeds acute risk LOC

For all uses of granular products, the acute risk quotient exceeds the acute risk LOC (0.5) for at least some of the mammals assessed. For preplant incorporated use, the LOC is exceeded for only mammals of small body weight, whereas for postflood (unincorporated) uses, the LOC is exceeded for medium-sized mammals as well. Risk quotients based on the maximum per-season rate of 9 lb ai/A, which give the upper bound of the risk quotient for repeated applications, also exceed the LOC for small and medium-sized mammals. While flooding is expected to reduce exposure to mammals, exposed granules are expected to be present on the levees in and around the rice fields, which could lead to exposure to mammals. Currently, EFED has no procedure for assessing chronic risk to mammalian species for granular products.

iii. Insects

Currently, EFED does not quantitatively assess risk to nontarget insects. However, since the use of molinate on rice is not expected to result in appreciable exposure to bees, little risk to bees is expected.

c. Exposure and Risk to Nontarget Freshwater Aquatic Animals

Note: Risk to aquatic organisms was assessed by comparing observed monitoring levels to acute and chronic toxicity levels. This assessment was not based on risk quotients; however, risk quotients for aquatic organisms are provided below.

i. Fish

The risk assessment for freshwater fish is uncertain because of the large discrepancy among the toxicity data. The minimum acute LC_{50} obtained for a freshwater fish was 0.21 ppm for the rainbow trout. This value was reported in a summary report of F&WS studies (Mayer and Ellersieck, 1986, MRID 40098001). This value is questionable, however, since two other core studies with the rainbow trout yielded LC_{50}'s of 20 ppm and 19.5 ppm (MRID 43337603 and 41613603, respectively). Furthermore, the LC_{50} value of 210 ppb is less than a chronic NOAEL determined in an early life-stage study with the rainbow trout (390 ppb, MRID 40657801). The LC_{50} reported in Mayer and Ellersieck (1986) for the bluegill sunfish was also almost two orders of magnitude lower than those reported in other core studies. The reason for the discrepancy in the findings are not apparent. In this aquatic risk assessment, the rainbow trout acute LC_{50} value of 0.21 ppm that was reported in Mayer and Ellersieck (1986) will be used as a conservative screen. When this assessment does not indicate minimal risk, then a second assessment will be conducted based on the mean value of the six studies with the rainbow trout (10.3 ppm). Data for tadpoles (Sanders,1970; Acc. No. 246020) indicate that assessments based on the higher toxicity threshold for the rainbow trout are also appropriate for protection of amphibians.

The risk assessment to freshwater fish is complicated by the finding that the common carp is much more sensitive to subchronic exposure than acute exposure to molinate. Published studies for carp have reported a 21-day subchronic LC_{50} of 180 ppb (Kawatsu, 1977) and a 28-day LC_{50} 210 ppb (Finlayson and Faggella, 1986), compared to a 96-hr LC_{50} of 42,280 ppb (Acc. No. 246020). The mortality observed in the subchronic studies is apparently related to reduced hemoglobin and hematocrit levels. These findings are consistent with the observation of mortality of large numbers of carp in the Colusa Basin Drain in California from 1981 through 1983, a time when peak molinate residues equal or exceeded 200 ppb. Thus, the LC_{50} of 180 ppb will be used as a toxicity threshold for assessing exposure to molinate at levels that are sustained for 21 days or longer.

In California at this time, molinate does not appear to pose an acute risk to freshwater fish or amphibians. Molinate concentrations have been monitored in the rivers and waterways that drain the rice-growing areas of central California. In the early 1980's, molinate concentrations in the Colusa Basin Drain were as high as 340 ppb and may have been responsible for large kills of carp (Finlayson and Faggella, 1986). However, water monitoring data collected from rivers and agricultural drains since 1990, when mandatory holding periods were imposed for water on rice fields, show that water concentrations have remained well below levels that are acutely or subchronicly toxic to fish. Since 1990, the peak concentrations measured in water from the Sacramento River at the water treatment intake at Sacramento, California was 6.5 ppb. The State of California Department of Pesticide Regulation conducted water monitoring of the Sacramento River, Colusa Drain, and Sutter River. The peak molinate residue detected from 1995 and 1997 was 43.7 ppb in the Colusa Drain. The USGS also monitored for molinate in the Colusa Drain and the Sacramento River at Freeport between 1996 and 1998 as part of their NAWQA program.

The peak molinate concentration was 19.2 ppb from the Colusa Drain. All of these peak concentrations are below the conservative estimate of the freshwater fish 96-hr LC_{50} (210 ppb), the 21-day LC_{50} (180 ppb), and the chronic freshwater fish NOAEC (390 ppb). Acute risk is not exceed the acute risk LOC, but because peak monitoring values exceed one-tenth the LC_{50}, risk exceeds the LOC for considering restricted use classification. **Therefore, the Agency concludes that the use of molinate on rice in California, under current water management practices, does not pose an acute risk to freshwater fish. This conclusion is further supported by the findings of Heath *et al.*** (1997) (see **Appendix C** for **a discussion of these findings).**

Molinate concentrations in the Southern region are generally higher than in California, and may pose some acute risk to freshwater fish. We examined recent monitoring data from various sources for rivers, creeks and bayous in rice-growing areas of Arkansas, Mississippi, Louisiana, and Texas. Seasonal means during the primary molinate use period (May through July) were no more than 32.4 ppb for parent molinate and 50.5 ppb for parent plus degradates, which are below the acute risk threshold. However, peak concentrations in some creeks, bayous, and small rivers were occasionally much higher and sometimes approached or exceeded toxic levels. The highest levels of parent molinate observed in the data were 332.7 ppb from a creek in Arkansas, 200 ppb from White's Bayou in Texas, and 100 ppb from the Bogue Phalia River in Mississippi. The highest levels of parent molinate plus predicted degradates were 519 ppb from a creek in Arkansas, 312 ppb from White's Bayou in Texas, and 156 ppb from the Bogue Phalia River in Mississippi (See Appendix E and Section V of EFED RED Chapter). Based on the minimum estimate of the acute toxicity to the rainbow trout, the acute risk LOC is exceeded when concentrations exceed 105 ppb. As shown in Fig. A and B below, residues of parent molinate greater than 100 ppb occurred only during spikes in concentrations with a duration of only a few days.

In laboratory studies, 50% mortality was predicted to occur when common carp are exposed to concentrations of approximately 200 ppb for 21 to 28 days consecutive days (Finlayson and Faggella, 1986; Kawatsu, 1977). This mortality is the result of anemia that develops after relatively long-term exposure to molinate. Exposure for 14 days at molinate concentrations up to 350 ppb did not result in any significant mortality (Finlayson and Faggella, 1986). Based on monitoring data, residues do not persist above 200 ppb for more than a few days. Thus, carp are not likely to be exposed to toxic levels of molinate for adequate periods of time for anemia to develop.

Use of molinate in the southern region has the potential to pose acute and subchronic risk to freshwater fish. The only potential risk is to sensitive fish in small streams and tributaries that receive a substantial amount of drainage from rice fields. Fish in these habitats may be at risk, but only during episodes of peak concentrations. The risk is great enough to exceed the LOC for consideration of a restricted use classification and to pose a concern for threatened and endangered species.

The chronic risk assessment for freshwater fish cannot be conducted at this time because no data are available on the effects of molinate on fish reproduction. A fish life-cycle study must be submitted to the Agency since this is the only guideline study that assesses effects on fish reproduction. If the reproductive toxicity that is exhibited in mammals is also exhibited in fish, then the life-cycle study could show toxic effects at levels much lower than those detected by the fish early life-stage study. **In the absence of these data, possible chronic risk to freshwater fish must be assumed.**

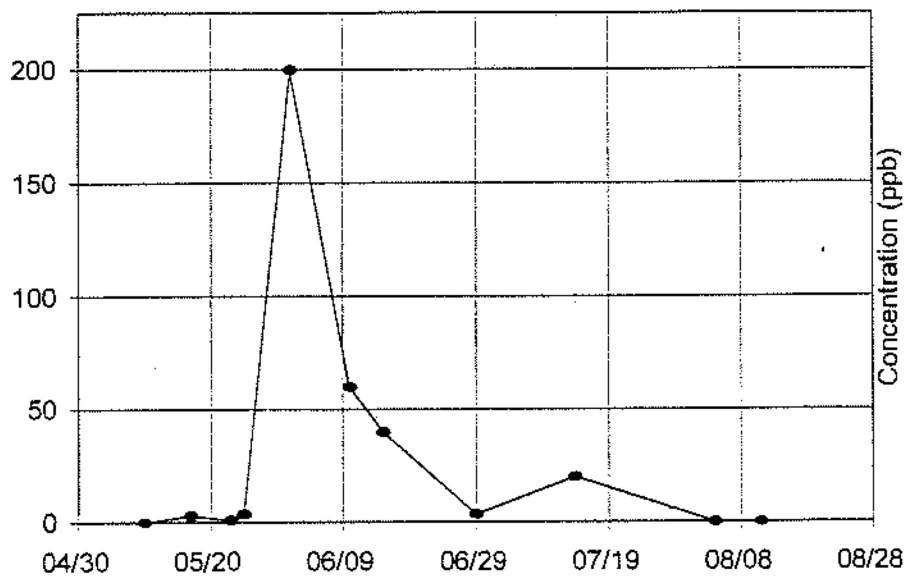

Fig. 1. Molinate concentrations in the White's Bayou at Anahuac, Texas, in 1994.

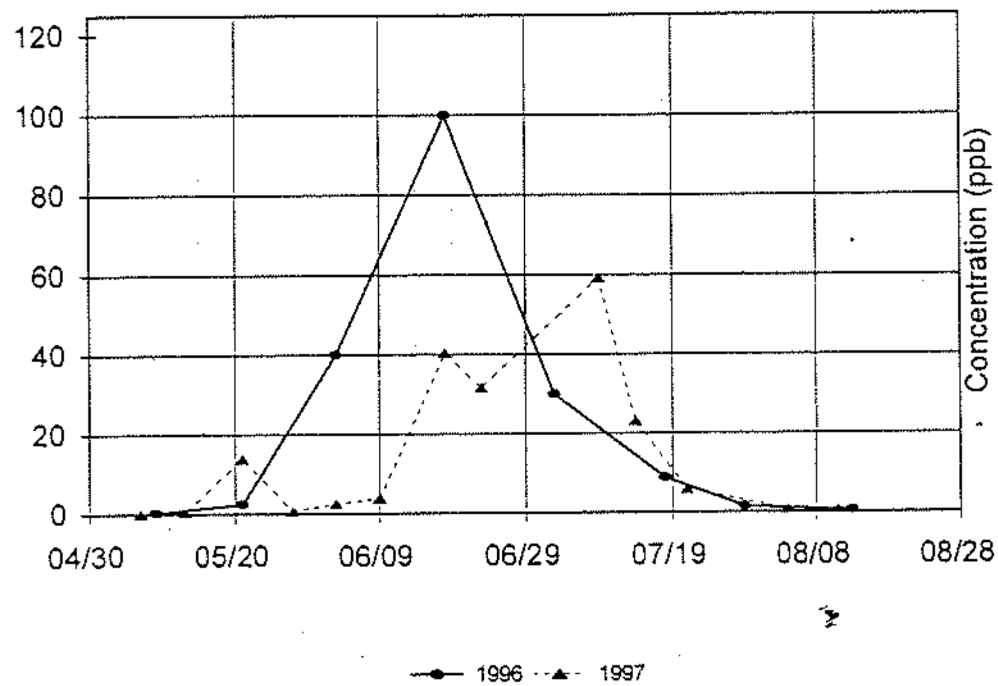

Fig. 2. Molinate concentrations in the Bogue Phalia River, Mississippi.

ii. Freshwater Invertebrates

In California, use of molinate poses minimal acute risk to freshwater invertebrates. Monitoring data indicate that, since mandatory holding periods were imposed in 1990, water concentrations have remained well below levels that are acutely or subchronicly toxic to invertebrates. Since 1990, the peak concentration measured in water from the Sacramento River at the water treatment intake at Sacramento was 6.5 ppb. The State of California Department of Pesticide Regulation has sampled water from the Sacramento River, Colusa Basin Drain, and Sutter River. The peak molinate residue detected from 1995 and 1997 was 43.7 ppb in the Colusa Basin Drain. The USGS also monitored for molinate in the Colusa Basin Drain and the Sacramento River at Freeport between 1996 and 1998 as part of their NAWQA program. The peak molinate concentration was 19.2 ppb from the Colusa Basin Drain. All of these peak concentrations are below the minimum 48-hr LC_{50} for freshwater invertebrates of 340 ppb. Observed levels are also below the chronic NOAEL's for the waterflea (380 ppb) and *Moina australiensis* (110 ppb). Risk does not exceed the acute risk LOC, but because peak monitoring values exceed one-tenth the LC_{50}, risk exceeds the LOC for considering restricted use classification. **Therefore, the Agency conclude that the use of molinate on rice in California, under current water management practices, poses an acute risk to freshwater invertebrates which warrants consideration of a restricted use registration.**

The reported chronic NOAEL's were 380 ppb for the waterflea and 110 ppb *Moina australiensis*. However, the acute data indicate that the stonefly (*Pteronarcys spp.*) is a more sensitive species. The acute LC_{50} of the stonefly (340 ppb) is in fact less than the chronic NOAEL for the waterflea and *Moina australiensis*. Therefore, a chronic NOAEL value was predicted for the stonefly based on the acute LC_{50} and the acute-to-chronic ratio. Based on the acute and chronic data for *Moina australiensis*, the acute-to-chronic ratio for the toxicity of molinate to freshwater invertebrates is 21.8 (2.40 ppm/0.11 ppm). This yields a predicted chronic NOAEL for the stonefly of 15.6 ppb. The peak monitoring value from the Sacramento River (6.5 ppb) does not exceed this predicted NOAEL, indicating minimal risk of chronic effects to invertebrates in this river. The peak monitoring levels from the Sutter River (16.4 ppb) and the Colusa Basin Drain (43.7 ppb) exceed the predicted NOAEL for the stonefly, but not the NOAEL's for the waterflea or *Moina australiensis*. The time-weighted mean concentration, based on measurements of molinate in the Colusa Basin Drain from April through July, were 10.3 ppb, 12.1 ppb, and 8.08 ppb in 1995, 1996, and 1997, respectively (Memorandum: Drinking Water Assessment for Molinate, D252252, 2 February 1999). The 12.1 ppb level was misreported as 16.8 ppb in the February 1999 memorandum. Thus, in 1996, the seasonal mean concentration exceeded the predicted NOAEL for the stonefly, but not the two measured NOAEL's. **Therefore, the Agency concludes that the use of molinate on rice in California poses a chronic risk to freshwater invertebrates in small rivers and drains. This conclusion is uncertain because it is based a predicted chronic toxicity level for the stonefly, but is not confirmed by the actual chronic data for other species.**

Molinate concentrations in the Southern region are generally higher than in California, and may pose some acute risk to freshwater invertebrates. We examined recent monitoring data from various sources for rivers, creeks and bayous in rice-growing areas of Arkansas, Mississippi, Louisiana, and Texas. Seasonal mean during the primary molinate use period (May through July) were no more than 29 ppb. However, peak concentrations in some creeks, bayous, and small rivers are occasionally much higher and sometimes approached or exceeded acutely toxic levels. The highest recorded levels were 333.7 ppb from a creek in Arkansas, 200 ppb from White's Bayou in Texas, and 100 ppb from the Bogue Phalia River in Mississippi. Based on the acute toxicity to the stonefly, the acute risk LOC is exceeded when concentrations exceed 170 ppb. Residues in small creeks and bayous can briefly exceed 170 ppb (see Fig 1). In larger rivers, such as the Yazoo River and Big Sunflower River in Mississippi, and the Tensas River in Louisiana, monitoring data indicate that molinate residues remain well below levels that would be acutely toxic to freshwater invertebrates.

Chronic risk to invertebrates is uncertain because chronic toxicty data are not available for the stonefly, which is the most sensitive species based on acute data. As discussed above, predicted chronic NOAEL for the stonefly of 15.6 ppb. The peak measured concentration of molinate in many of the creeks, bayous, and small rivers exceed this predicted NOAEL. In the Bogue Phalia River in Mississippi, even the seasonal mean concentrations exceeded the predicted NOAEL in 1996, 1997, and 1998 (Memorandum: Drinking Water Assessment for Molinate, D252252, 2 February 1999). Furthermore, peak molinate concentrations recorded in a creek in Arkansas and a bayou in Texas also exceed the actual NOAEL for *Moina australiensis*. Therefore, molinate concentrations in the Southern region pose a chronic risk to aquatic invertebrates.

In conclusion, use of molinate on rice in the Southern region poses a risk to freshwater invertebrates. The risk is primarily due to sublethal chronic effects, but there may be some mortality from acute exposure in creeks, bayous, and small rivers during periods of exceptionally high molinate concentrations.

d. Estuarine and Marine Animals

In California, the only estuarine habitats that are likely to be exposed to significant residues of molinate are bays near San Francisco which receive water from the Sacramento River and San Juaquin River. These rivers drain all of the rice-growing region in California. Stringent regulation requiring the retainment of floodwater from rice fields have greatly reduced concentrations of molinate occurring in the Sacramento-San Joaquin Delta since 1985 (Bailey, 1993). Since 1990, the maximum detection of molinate in monitoring data for the Sacramento River was 6.5 ppb (City of Sacramento monitoring data from the Sacramento River water treatment intake, 1990). For the San Joaquin River, the maximum detection was only 0.145 ppb (monitoring data of the State of California Pesticide, 1993). These concentrations are well below the lowest acute LC_{50} for estuarine fish (sheepshead minnow, 1200 ppb) or estuarine invertebrates (mysid, 760 ppb). Because concentrations in the coastal estuaries would be no greater than concentrations in the rivers that feed them, **the Agency concludes that use of molinate on rice in California poses minimal acute risk to marine/estuarine fish and invertebrates.**

In the Southern region, rice is grown in Louisiana and Texas is often near estuaries or the Gulf of Mexico. The Agency does not have water monitoring data for molinate from estuaries. Therefore, the acute risk assessment for marine and estuarine fish and invertebrates will be based on concentrations measured in freshwater habitats of Louisiana and Texas.The maximum detection of molinate in these states was 200 ppb from White's Bayou at Anahuac, Texas (Fig. 1). Mean concentrations for the season of high molinate use, May through July, were also calculated based on monitoring data for the Tensas River in Louisiana. The highest seasonal mean was 5.89 ppb in 1997. The peak molinate detection in this river was 32 ppb. Molinate concentrations are likely to be lower in estuaries than in rivers because of dilution caused by tidal flux and mixing with seawater.

The lowest acute LC_{50} for effects of molinate on an estuarine fish was 12 ppm (12,000 ppb). The lowest acute LC_{50} obtained for a marine or estuarine invertebrate is 760 ppb for the mysid. Based on this value, the acute risk LOC would be exceeded if concentrations reach 380 ppb. As stated above, the maximum measured concentration in Texas and Louisiana was 200 ppb. Monitoring data indicate that molinate concentrations in the estuarine and marine habitats of Texas and Louisiana will remain well below concentrations that would be toxic to estuarine or marine fish, and slightly below levels toxic to marine and estuarine invertebrates.

In conclusion, use of molinate on rice in the Southern region is predicted to pose minimal acute risk to marine and estuarine fish. It is not predicted to pose acute risk to marine and estuarine invertebrates, but would pose enough risk to warrant consideration of restricted use classification and to cause concern for threatened and endangered species.

The Agency considers the information currently available on chronic toxicity of molinate to estuarine and marine organisms to be inadequate for conducting a risk assessment at this time. Mammalian toxicity data indicate that the primary chronic effect of molinate in vertebrates is reproductive toxicity. Mammalian studies indicate that molinate and the metabolite molinate sulfoxide are both are potent reproductive toxicants and produces effects that are consistent with it being an endocrine disruptor (Jewel *et al.*, 1998, Ellis *et al.*, 1998). The only data available on chronic toxictiy is from a published literature study which did not assess reproduction. **In the absence of adequate data, the Agency must assume the potential for chronic risk to estuarine and marine fish and invertebrates because of reproductive impairment.**

e. Exposure and Risk to Nontarget Plants

i. Terrestrial and Semi-aquatic Areas

The EFED does separate risk assessments for two categories of nontarget plants, terrestrial and semi-aquatic. Non-target terrestrial plants inhabit non-aquatic areas which are generally well drained. Non-target plants inhabit low-lying semi-aquatic areas that are usually wet, although they may be dry during certain times of the year. Plants in both the terrestrial and semi-aquatic areas are exposed to pesticides from runoff, drift, and volatilization. They differ, however, in that plants in terrestrial areas are assumed to be subjected to sheet runoff, whereas plants in semi-aquatic areas are assumed to be subjected to channelized runoff.

For non-target terrestrial plants, EFED typically assumes a scenario in which plants are exposed from sheet runoff or channelized runoff. However, use of molinate on rice is not expected to result in significant exposure to nontarget terrestrial and semiaquatic plants from runoff. Rice fields are always bordered by a dike or temporary berm which would prevent runoff from leaving the field. These structures do have a gate or opening for the release of water from the field, but this water is normally channeled into a drain, stream, or river. Outflow from rice fields therefore will not normally enter dry-land and wetland habitats where plants occur.

Use of molinate on rice will expose nontarget plants through spray drift. Spray drift, and thus exposure to nontarget plants, will be negligible when molinate is applied as a granule. The Agency assumes that spray drift from liquid (EC) formulations of molinate results in EECs that are 5% and 1% of the application rate for aerial and ground applications, respectively. Risk quotients for nonendangered plants were calculated by dividing EEC based on spray drift exposure by the vegetative vigor EC_{25} for the most sensitive of the test species. Risk quotients for EC formulations are tabulated below.

Risk Quotients for Nonendangered Terrestrial Plants from a Single Application of EC Products on Rice, Based on the EC_{25} for Soybean.

Application rate in lbs ai/A (Application method)	Vegetative Vigor EC25 (lbs ai/A)	Exposure from Drift (lbs ai/A)		Risk Quotient	
		Ground (1%)	Aerial (5%)	Ground	Aerial
4 (unincorporated)	0.22	0.04	0.2	0.18	0.91
3 (preflood, unincorporated)	0.22	0.03	0.15	0.14	0.68

Risk quotients for molinate (EC products) do not exceed the LOC for nonendangered plants (1). Use of granular products of molinate is expected to pose minimal risk to nontarget terrestrial plants because exposure from runoff and spray drift is expected to be minimal. **Therefore, the Agency concludes that the use of molinate on rice will pose minimal risk to nonendangered nontarget terrestrial plants. However, this conclusion is uncertain because it is based on incomplete phytotoxicity data.**

Because of the greater concern for protection of threatened and endangered species, risk quotients for threatened and endangered terrestrial plants are normally based on the NOAEL for phytotoxicity. However, in the supplemental vegetative vigor study (MRID 416136-11), NOAEL's were not determined for the most sensitive endpoint, visual assessment, because control plants were not rated for phytotoxic symptoms. The Data Evaluation Record for this study reports the EC_{10} values in lieu of NOAEL's for the visual assessment endpoint. Thus, the endangered species RQs for molinate are based on EC_{10} values. Because of this, the risk quotients for threatened and endanger terrestrial plants, tabulated below, are very uncertain.

Risk Quotients for Threatened and Endangered Terrestrial Plants from a Single Application of EC Products on Rice, Based on the EC_{10} for Soybeans.

Application rate in lbs ai/A (Application method)	Vegetative Vigor EC25 (lbs ai/A)	Exposure from Drift (lbs ai/A)		Risk Quotient	
		Ground (1%)	Aerial (5%)	Ground	Aerial
4 (unincorporated)	0.05	0.04	0.20	0.80	4.0
3 (preflood, unincorporated)	0.05	0.03	0.15	0.60	3.0

Risk quotients for molinate (EC products) exceed the LOC for threatened and endangered plants (1) for aerial applications, but not for ground applications. Use of granular products of molinate is expected to pose minimal risk to nontarget terrestrial plants because exposure from runoff and spray drift is expected to be minimal. **Therefore, the Agency concludes that aerial spray applications of molinate to rice will pose a risk to threatened and endangered nontarget terrestrial plants, hut granular and ground spray applications will not. These conclusions are uncertain because data on the phytotoxicity of molinate are supplemental and incomplete.**

ii. Aquatic Areas

Exposure to nontarget aquatic plants may occur through runoff and spray drift from adjacent treated sites. A risk assessment for aquatic vascular plants was performed using duckweed (*Lemna gibba*) as a surrogate species. A risk assessment for nonvascular aquatic plants was performed using green algae (*Pseudokirchneria subcapitata*), which was the most sensitive nonvascular species tested. Exposure to aquatic plants was based on actual measurements from water monitoring in creeks, bayous, and rivers from rice-growing areas of California, Arkansas, Mississippi, Louisiana, and Texas.

Molinate does not appear to be very toxic to vascular aquatic plants (duckweed EC_{50}=3.3 ppm). Molinate concentrations are expected to at least one order of magnitude below levels toxic to vascular plants in both California and the southern region. Molinate is more toxic to nonvasular plants. The lowest EC_{50} obtained was 220 ppb for green algae. Concentrations above this level would result in a risk above the level of concern. In California, monitoring data indicates that, with the current management practices, molinate concentrations in creeks, drains, and rivers do not exceed 50 ppb. In the southern region, molinate concentrations may occasionally will approach or exceed the EC_{50}. However, these high concentrations appear to be rare and only occur during concentration spikes that only last a few days (see Fig. 1). It is expected that algae concentrations would recover quickly from any damage done during these brief spikes, and that the impact on the ecosystem would be minimal. Furthermore, because of dilution, these high levels are not seen in the larger rivers and waterways.

In conclusion, use of molinate on rice is expected to pose minimal risk to aquatic plants when used in California. Use of molinate in the southern region does pose a risk to algae, but only during brief periods of peak exposure.

5. Threatened and Endangered Species

Risks from molinate exceed LOC for threatened and endangered (T&E) mammals due to acute and chronic effects. Molinate does not pose an acute risk to T&E birds, but likely poses a chronic risk to these species due to reproductive toxicity. Use of molinate in the Southern region poses a risk to T&E species of freshwater fish, freshwater invertebrates, and marine and estuarine invertebrates. However, under the current water management practices, use in California will pose minimal risk to T&E aquatic species. Finally, aerial spray application of molinate poses a risk to T&E nontarget terrestrial plants due to effect of spray drift.

The Agency has developed a program (the "Endangered Species Protection Program") to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that will eliminate the adverse impacts. At present, the program is being implemented on an interim basis as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989), and is providing information to pesticide users to help them protect these species on a voluntary basis. As currently planned, the final program will call for label modifications referring to required limitations on pesticide uses, typically as depicted in county-specific bulletins or by other site-specific mechanisms as specified by state partners. A final program, which may be altered from the interim program, will be described in a future Federal Register notice. The Agency is not imposing label modifications at this time through the RED. Rather, any requirements for product use modifications will occur in the future under the Endangered Species Protection Program.

Appendix G. Fish and Wildlife Mortality Incidents

Finlayson and Faggella (1986) investigated the cause of large fish kills that occurred in the Colusa Basin Drain in north-central California, an agricultural drain that runs through an intensive rice-growing area. They report that an estimated 7,000 to 30,000 carp died annually in this drain between 1981 and 1983. No fish kills were observed in 1984 to 1987. They determined the 28-day LOEL and LC50 for carp to be 0.13 and 0.21 ppm, respectively. Water monitoring of the Colusa Basin Drain showed that peak residue values in the years 1981 through 1983 exceeded the carp LOEL and approached or exceeded the carp LC50, whereas peak values during 1984 through 1986 remained below the carp LOEL and LC50. Significantly, primarily carp were killed in this drain, while other species present such as bass and catfish were not affected. Laboratory studies have shown that carp are particularly sensitive to the anemic effects of molinate, whereas other species, such as the channel catfish (Finlayson and Faggella, 1986) and bluegill sunfish (Miller, 1984) are relatively insensitive. Furthermore, Finlayson and Faggella (1986) showed that molinate exposure significantly reduces hemoglobin and hematocrit levels in carp, and found that carp collected from the Colusa Basin Drain in 1983 had reduced hemoglobin and hematocrit on June 15, following a period of high molinate exposure. Thus, while there is no evidence from tissue analysis, circumstantial evidence suggest that molinate was likely the primary causal factor of the large fish kills in the Colusa Basin Drain. It should be noted that continued residue monitoring of this drain has shown that peak residues were reduced substantially following the imposition of mandatory water-holding periods for rice farmers beginning in 1990.
The Environmental Incident Information System contains two incidents of fish kills that could be attributed to molinate. In one incident in 1978, thousands of dead carp were observed in the a toe drain area on the Yolo Bypass in Yolo County, California (Incident # B0000-215-06). Analysis of water samples detected molinate at a concentration of 60 ppb. Fish were too decomposed for tissues to be analyzed. Although molinate cannot be confirmed as the causal factor, the similarities of this incident to the kills of carp mentioned above suggest that it could have been caused by molinate toxicity.

A second incident possibly attributed to molinate occurred in Bayou Macon in West Carroll Parish, Louisiana, in 1991 (Incident # I000109T). This incident involved an unknown number of dead fish of "multiple species". It occurred in a bayou that is lined on both sides by cotton and rice fields. Water samples revealed molinate concentrations of 15-20 ppb. Although this concentration is not thought to be enough to be lethal to fish, the condition of the fish indicated that they were killed several days ago, and molinate residues could have been higher at that time. No analysis of fish tissue was conducted since the fish were too decomposed. There is too little evidence to conclude that this fish kill was or was not caused by molinate.

Appendix H. Threatened and Endangered Species

Risks from molinate exceed the LOC for threatened and endangered (T&E) mammals due to acute and chronic effects. Molinate does not pose an acute risk to T&E birds, but likely poses a chronic risk to these species due to reproductive toxicity. Use of molinate in the Southern region poses a risk to T&E species of freshwater fish, freshwater invertebrates, and marine and estuarine invertebrates. However, under the current water management practices, use in California will pose minimal risk to T&E aquatic species. Finally, aerial spray application of molinate poses a risk to T&E nontarget terrestrial plants due to effect of spray drift.

The Agency has developed a program (the "Endangered Species Protection Program") to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that will eliminate the adverse impacts. At present, the program is being implemented on an interim basis as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989), and is providing information to pesticide users to help them protect these species on a voluntary basis. As currently planned, the final program will call for label modifications referring to required limitations on pesticide uses, typically as depicted in county-specific bulletins or by other site-specific mechanisms as specified by state partners. A final program, which may be altered from the interim program, will be described in a future Federal Register notice. The Agency is not imposing label modifications at this time through the RED. Rather, any requirements for product use modifications will occur in the future under the Endangered Species Protection Program.

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Appendix J. Risk Characterization

Summary of Risk Assessment

Note: Conclusions of ecological risk are based on a screening level assessment. In the past, these risks would have been characterized as "high" acute or chronic risk. However, recognizing the uncertainty in the ability of a screening level assessment to quantify the level or significant of risk, the EFED is changing the wording of the conclusions when exceeding the LOC is based solely on screening level risk assessment. This change does not reflect a change in the risk assessment process, or alter the criteria of exceeding the LOC's. Also, it does not change the other presumptions of risk, including those related to restricted use and endangered species.

Drinking Water

- Molinate has been detected frequently in surface water adjacent to rice growing areas and downstream from rice growing areas in California, Arkansas, Mississippi, Louisiana, and Texas. No detections have been observed in Missouri, and monitoring data are not available in Tennessee. There is very limited rice production in Tennessee. Intakes for a number of drinking water utilities, some of which serve large populations, are located downstream of areas where molinate is used.

- EFED has received molinate-specific laboratory studies that simulate water treatment at Sacramento, CA. In these studies, disinfection using chlorination (2.5 ppm) converted parent molinate to molinate sulfoxide, a toxic metabolite (Ross, 1983, DP Barcode D267629). An analysis of the water treatment plants in the molinate use area and impacted downstream areas indicate that chlorination was used as a disinfectant except for a plant using potassium permanganate as an additional oxidant (MRID 44926503). However, the efficiency of water treatment practices to remove toxic residues of molinate may vary significantly between intakes. Variables such as spiking rates of oxidants, size of the distribution system, use of aeration, and storage/treatment times may provide different pesticide removal efficiencies. Therefore, using the results of one intake's treatment may not be accurate for another intake.

- As a result of the holding periods that are possible because of a dryer climate, the levels in surface water in California are generally lower than in the Southeast.

- In ground water, molinate has been detected at levels ranging from 0.005-1.5 ug/L. Most of the detections did not exceed 0.056 ug/L (Arkansas, Mississippi, and California), but there were two higher detections ranging from 0.11 ug/L in Texas and 1.5 ug/L in Missouri. Based on the persistence in aquatic metabolism studies, EFED expects persistence of molinate in ground water if it reaches ground water.

Terrestrial Organisms

- Risk to mammalian reproduction (highly certain).
- Risk of reproductive impairment is assumed but uncertain in birds. EFED needs additional data for confirmation.
- Molinate is a likely endocrine disruptor in rodents. Additional data are needed to confirm endocrine disruption in non-mammalian animals.
- Minimal risk to terrestrial plants (uncertain, additional data needed for confirmation).

Aquatic Organisms--California

- Minimal acute risk to fish, amphibians, and aquatic invertebrates (high certainty).
- Chronic risk to freshwater invertebrates that live in agricultural drains and small rivers is predicted but with low certainty, since chronic toxicity was based on the acute:chronic ratio and not direct measurements.
- Risk of reproductive impairment is assumed but uncertain in freshwater fish. EFED needs additional data for confirmation.
- Minimal risk to estuarine areas because estuaries are distant from use sites (moderate certainty).
- Minimal risk to aquatic plants (highly certainty).

Aquatic Organisms--Southern Region

- Acute risk to fish, amphibians, and aquatic invertebrates, especially in smaller water bodies subject to high exposure from rice drainage (low certainty due to highly variable toxicity data).
- Chronic risk to freshwater fish from possible reproductive effects (uncertain, additional data needed for confirmation).
- Chronic risk to freshwater invertebrates (moderate certainty, based partly on estimated chronic toxicity derived using the acute:chronic ratio).
- Acute risk to estuarine fish and invertebrates is minimal (moderate certainty).
- Chronic risk to reproductive success in estuarine fish and invertebrates is possible, but

not known due to lack of life-cycle toxicity data (uncertain, additional data needed for confirmation).

- Risk to nontarget aquatic plants (low certainty).

Terrestrial Habitats

Certainties and Uncertainties

Uncertainty in the risk conclusions stems mainly from uncertainties of the extent of exposure to terrestrial organisms from use of molinate on rice. We are certain that terrestrial organisms will be present in rice fields and will be exposed to some degree. *However, we are uncertain as to the degree that soil incorporation and flooding of fields will mitigate the exposure.* Additionally, while there is strong evidence that molinate poses a risk to mammals due to reproductive toxicity, data are lacking to confirm reproductive toxicity in birds. Chronic risk must be assumed for birds and other terrestrial organisms unless data become available that refute this conclusion.

Characterization of Terrestrial Risk

On an acute basis, molinate is classified as practically nontoxic to birds and slightly toxic to mammals. Risk quotients indicate minimal acute risk to birds, but acute risk to some types of small mammals. The more substantial risk from molinate appears to be from chronic reproductive effects. Numerous EPA guideline studies and nonguideline studies from the open literature provide consistent evidence that molinate is very toxic to the male and female reproductive systems in rodents. In male rats, observed effects include testicular lesions and degeneration, abnormalities in spermatozoa, and decreased circulating testosterone levels. In female rats, observed effects include ovarian lesions, enlarged ovaries, delayed sexual development, increased abortions, and decreased fecundity. Ellis *et al*. (1998) and Jewell *et al*. (1998) both found that the metabolite molinate sulfoxide causes similar reproductive toxicity in the male rat as does parent molinate, but at even lower doses. They concluded that molinate is bioactivated in rodents through transformation into molinate sulfoxide. Therefore, molinate sulfoxide, which is also an environmental degradation product of parent molinate, could add to the reproductive toxicity of molinate to mammals.

These findings are consistent with molinate, or molinate sulfoxide, being an endocrine disruptor. Ellis *et al* (1998) state that "the association of the initial sperm lesion to the stage of spermatogenesis dependent on testosterone was suggestive of molinate inducing the effects by a perturbation of testosterone synthesis, release, or action at the dependent site within the testes." Wickramarante *et al.* (1998) propose that, in rodents, molinate inhibits the synthesis of estrogen and testosterone, and this interference of hormone production impairs normal processes of reproduction controlled by these hormones, such as vaginal opening in females and sperm production in males.

The amendments to the Food Quality Protection Act (FQPA) and the Safe Drinking Water Act (SDWA) mandate or support the development of a screening program that will determine whether pesticides and certain contaminants of drinking water sources "may have an effect in humans that is similar to an effect produced by a naturally-occurring estrogen, or other such endocrine effect as the Administrator may designate." Very early in its deliberations, EPA's Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) determined that there was both a strong scientific basis and feasibility, considering time and resource constraints, to expand the scope of the screening program to include the androgen- and thyroid hormone systems, and to include evaluations of the potential impacts on wildlife as well as on human health. EPA is developing a screening and testing program which incorporates these modifications.

Based on the adverse findings reported above, EFED recommends that, when testing protocols currently being considered under the Agency's Endocrine Disruptor Screening Program (EDSP) have been validated, molinate be subjected to more definitive testing to better characterize effects related to endocrine disruption.

Wickramarante *et al.* (1998) reports that molinate does not cause abnormalities of sperm in the dog, rabbit, or monkey, presumably because the primary synthetic pathway of testosterone in these species is different from that of rodents. Chronic toxicity data submitted to the Agency testing the rabbit and dog also suggest that rodents are more sensitive to the reproductive toxicity of molinate than are other mammals. Even if reproductive effects to mammals are restricted to rodents, however, the ecological impacts could be major because rodents are a large component of most small mammal communities and serve as an important food source for many animals. Reproductive toxicity of molinate in species other than mammals is currently unknown. As the synthesis of estrogen and testosterone plays a fundamental role in the reproduction of all vertebrates, molinate possibly could impair reproduction in birds, reptiles, and amphibians as well. On the other hand, these groups of organisms might not be susceptible to the reproductive toxicity of molinate due to in differences their metabolic pathways. Because of this uncertainty, fulfilling the data requirement for avian reproduction testing should be a high priority. Without these data, molinate must be assumed to pose a reproductive hazard to all types of wildlife.

Molinate is used exclusively on rice. Many wildlife, especially waterfowl and wading birds, are attracted by the water on rice fields. The timing of application, in April through June, coincides with the breeding season for many terrestrial and semiaquatic vertebrates. Numerous waterfowl and wading bird species breed in flooded rice fields of California[1]. A few waterfowl and wading birds also breed in the Southern region. Some semiaquatic mammals, such as muskrats, also use

[1] Waterfowl species that breed in the California rice-growing region include the mallard, wood duck, cinnamon teal, northern shoveler, gadwall, redhead, ruddy duck, pied-billed grebe and eared grebe. Breeding wading birds include the great egret, snowy egret, green-backed heron, black-crowned night heron, Virginia rail, sora rail, common moorhen, American coot, black-necked stilt, and American avocet.

rice fields and would be breeding at this time. In addition, numerous semi-aquatic amphibians (frogs and salamanders) and reptiles (turtles and snakes) would be breeding in rice fields at this time in both California and the Southern region. Therefore, there is the potential for molinate to cause reproductive impairment in a wide variety of wildlife.

The amount of exposure to terrestrial wildlife is very much related to the application methods and cultivation practices that are used. In California, molinate is mostly applied as a granular to permanently flooded fields. Most of the granules would fall into the water and sink to the bottom of the flood water. This reduces risk since the water would make the granules less available to wildlife. They may still be consumed by ducks and geese which would feed off the bottom, but the granules in water would probably rapidly disintegrate or lose their content of active ingredient through diffusion. Wildlife would be exposed, however, to granules which fall on the levees that surround and separate rice paddies. This could lead to considerable exposure, despite of the relative small area they represent, because wildlife would likely use use these levees as travel corridors and resting sites. Birds are particularly vulnerable to poisoning by granular pesticides because the granules resemble grit particles that birds intentionally ingest to aid in digestion. Fortunately, molinate is practically nontoxic to birds on an acute basis and thus acute risk to birds is low. Granular molinate does pose some acute risk to mammals. This risk to mammals would likely be short-lived because molinate is highly volatile and would therefore dissipate relatively rapidly from unincorporated granules. Overall, the acute risk to wildlife of granular molinate does not appear to be very high.

The Agency does not have a standard method for assessing the chronic risk of granular pesticides to terrestrial organisms; however, EFED is preparing a refined risk assessment for application to flooded fields that will include chronic risk to mammals from granular applications. The degree of chronic risk to birds is uncertain because avian reproduction data are not available. If molinate produces similar reproductive effects in birds as in rodents, a substantial risk of reproductive impairment could exist, especially considering the behavior of birds to consume pesticide granules.

In the Southern region, most rice is primarily cultivated using dry-seeded methods, except in southern Louisiana and coastal Texas, where the water-seeded method is more prevalent. Pre-plant incorporated (PPI) applications, which are primarily made on water-seeded rice in this region, represents less than 5% of the total use of molinate on rice. These applications may be in either a liquid or granular formulation (Ordram 8E or Ordram 15G, respectively). Soil incorporation greatly reduces risk to terrestrial wildlife by making residues and granules unavailable to animals feeding on the surface. The risk assessment indicates that all PPI applications of molinate poses minimal risk to birds and mammals, with the possible exception of acute risk from granular application to very small mammals. Even this risk appears to be small since the risk quotient is less than one (0.76) and the availability of food on recently tilled rice fields is likely low. Since the Agency does not have an accepted risk assessment method to assess chronic risk from granular application, the chronic risk from granular PPI applications is uncertain.

Molinate may also be applied preplant to emerged weeds without soil incorporation. This type of use poses a greater risk to wildlife than PPI applications. In the Southern region, molinate can be applied preflood to emerged weeds in the product Arrosolo, which contains molinate and propanil as dual active ingredients. Arrosolo use represents about 38% of the total usage of molinate.[2] This application would also expose birds and mammals that would feed in the treated field prior to flooding, which may occur up to 5 days later. In California and the Southern region, the EC product Ordram 8E may be applied postflood to kill grass weeds that emerge out of the flood water, but this use represents only about 0.2% of the total usage of molinate.[2] The risk assessment indicates that this exposure will pose an acute and chronic risk to mammals. The acute risk to birds would be low, but chronic risk to birds is unknown. If the reproductive toxicity of molinate is similar in birds and mammals, then these applications would also pose a chronic risk to birds.

There are no incidents reported in the EIIS database involving effects on terrestrial organisms. It must be recognized, however, that the primary risk from molinate is from reproductive impairment, a adverse effect which cannot be assessed by evaluating incident reports.

Aquatic Habitats and Drinking Water

Certainties and Uncertainties

Major uncertainties exist in the ecological risk assessment. There are also some uncertainties in the drinking water assessment that are created by the use of monitoring data, calculation of annual means, the lack of taste and odor problems at West Sacramento, and the use of dilution calculations at Anahuac, Texas.

Considerable uncertainty exists in the ecological risk assessment due to the lack of complete toxicological data. Mammalian studies indicate that molinate is a potent reproductive toxicant in rodents; however, studies have not been conducted to show if this reproductive toxicity is also expressed in aquatic animals. Full life-cycle studies are also lacking for fish and estuarine crustaceans. The early life stage studies that have been conducted with these groups are not adequate because they do not assess the endpoint of reproduction. Until data are available for these groups, the Agency must assume that there is a potential risk of reproductive effects whenever there is exposure. Also, acute toxicity data for freshwater organisms was highly variable, with toxicity values from one source (Mayer and Ellersieck, 1986) being consistently lower (indicating greater toxicity) than those from other sources. Finally, the estimate of the chronic toxicity level for freshwater invertebrates is uncertain because it was extrapolated from the test species to a more sensitive species (the stone fly) using the acute-to-chronic ratio. These uncertainties decrease the certainty of the risk conclusions for aquatic organisms.

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[2] ZENECA Ag Products. 30-Day Response to the Molinate EFED Science Chapter Ecotoxicology and Water Monitoring Assessments. MRID 449265-01.

The certainty of the drinking water assessment and ecological risk assessment for aquatic organisms depends on the confidence in the available surface water monitoring data. EFED is very confident of expected surface water levels of parent molinate in California where monitoring has been extensive. EFED is also generally confident of expected levels of parent molinate in the Southern region where monitoring has been conducted, but notes that levels may vary more from year to year based on different weather conditions and the lack of required holding periods. There are also fewer years of monitoring data for this region (between 1 and 4 years) compared to California (e.g., 19 years for the City of Sacramento). However, EFED does note that the concentrations of up to 30 ug/L in USGS data from southern Louisiana are consistent with the State of Louisiana data from streams that are not used for drinking water.

The use of monitoring data to assesss dietary exposure creates uncertainties. Monitoring data are not available everywhere for all uses of a given compound. In a given year, it is highly likely that peak concentrations are missed since sampling is not always conducted on a daily schedule or over the time necessary to detect peaks. Also, peak concentrations are not likely to be detected unless sampling is conducted in a stratified sampling pattern in highly vulnerable sites. Sampling is also not necessarily representative of the entire year unless sampling is conducted over a year. Since monitoring data are dependent on the weather in a particular year, data may not always be available for enough years to cover the range of weather in a given area of application. The associated information to interpret monitoring information, such as amount of use and the area treated in a watershed, the timing and amount of rainfall events that drive runoff events, and specific cultural practices are not always available. Inclusion of data from an area where no pesticide is applied tends to bias estimates of exposure downward when considered with data from use areas. In analyzing these data, efforts were made to only include data from areas where molinate was known to have been used.

Estimation of degradate concentrations in surface water based on laboratory and field studies introduces uncertainties because levels of degradates relative to parent compound vary with time. Degradate concentrations are lowest relative to parent compounds immediately following the application and increase with time. As a result, no single adjustment factor for monitoring data will perfectly represent the contribution of degradates to ecological and drinking water exposure. However, the 1.56 factor is an average number will reasonably represent the contribution of degradates for both ecological and drinking water exposure. Monitoring for all residues of concern is the only certain method to assess exposure.

Most of the monitoring data were for parent molinate only and not the degradates. Only some of the USGS monitoring data contained any information on the 4-keto molinate degradate. No monitoring data on the other degradates of concern was available. As a result, EFED has attempted to account for the presence of degradates in surface and ground water by incorporating data from aquatic field dissipation and an aerobic aquatic metabolism study from the laboratory. However, these studies did not include any information on molinate sulfone, 3-keto molinate, or ring-opened molinate (S-ethyl-5-carboxypentyl thiocarbamate). However, volatility is the primary route of dissipation and the other metabolites are formed in relatively low amounts with the exception of 4-keto molinate. As a result, EFED does not expect significant formation of these metabolites in water.

The potable water studies provided highly variable estimates of the dietary contribution of the molinate sulfoxide and molinate acid degradates. The adjustment factors for 8 EC and 15G molinate were 1.094 (0-50 % total degradates observed) and 1.11 (0-48 % of total degradates observed), respectively. Therefore, some monitoring may be required for those intakes with EEC's close to the Drinking Water Level of Comparison.

Time-weighting of monitoring data introduces uncertainties. In the case of molinate, the time-weighting of data over a year from seasonal data was conducted based on a request by the Health Effects Division (HED). While this approach leads to a consistent time basis for means of data, calculating an annual mean from seasonal data creates uncertainties in the final estimates due to extrapolation. The detections or lack of detections at the first sampling interval are extended to the time between January 1st and the first sampling interval. Also, the detections or lack of detections at the last sampling interval are extended to the time between December 31st and the last sampling interval. Non-detections at the beginning and end sampling intervals tend to bias the final estimates downward, while high detections at the end sampling intervals tend to bias the final estimates upward. Also, relatively few years of data are available for most molinate use areas, with the exception of the Sacramento River where extensive data (19 years) were available. This adds some uncertainty to our assessment.

Since Lake Anahuac was the only intake for which dilution calculations were used, additional uncertainties exist for this location. Dilution calculations assume instantaneous distribution throughout the receiving water body, which can be relevant with shallow, well-mixed water bodies that do not stratify, such as Lake Anahuac. Also, increasing time tends to lead to uniform concentrations in the receiving water body. However, many factors can increase error when this assumption is used, including gradients in water temperature and salt concentrations and the presence of channelization that tend to localize concentrations of a pesticide. The location of the intake relative to the source water body can influence how much pesticide actually reaches the intake. If an intake is located near the source water body or in an area with high localized concentrations, the concentrations in drinking water may be higher than estimated. If an intake is located further away from the source water body or in an area where the pesticide does not localize, the concentration in drinking water may be less than estimated. In addition, extrapolation of concentrations and flow rates from the source water body to longer time intervals is a possible source of error. For molinate in White's Bayou (source water body), the flow rates were expressed as cubic feet/second. These flow rates were extrapolated to cubic feet/day for the calculations, which assumes that the same flow rate occurs over an entire day. The concentrations in White's Bayou were also extrapolated to an entire day, when they actually represent a point in time.

Characterization of Aquatic Risk

Scenarios for aquatic risks from molinate differs considerably between California and the Southern region. In California, rice is predominantly water-seeded in fields that are permanently flooded. Molinate is usually applied onto flooded fields as a granule. Rice growers are required to retain floodwater onsite for 28 days after the application of pesticides, which allows much of the pesticide residues to dissipate before the water is released. In the Southern region, most rice is dry-seeded, meaning that seeds are sown on dry ground and then flooded some time after germination. Application methods of molinate are variable; it may be applied as a liquid or granule prior to flooding or after flooding. In parts of the growing area near the Gulf Coast, especially in southern Louisiana, rice is water-seeded using a "pinpoint flood," in which the field is temporarily flooded during seeding, drained for several days as the rice sprouts, and then reflooded gradually as the rice grows. There are no mandatory retaining periods in this region. In addition, there is much more rainfall in the Southern region than in California. Heavy thunderstorms are common, and these storms quite frequently cause water to overflow the levees. The temporary levees used in this region are also subject to rupture, causing unscheduled releases of water. In general, the climate and growing practices make molinate a greater risk in the Southern region than in California.

Aquatic risk in California was much greater prior to the imposition in 1990 of mandatory holding periods for retaining water on rice fields after pesticide application. Between 1981 and 1983, peak residue levels in the Colusa Valley Drain in central California were 200 to 340 ppb, and large kills of fish, primarily carp, were common (Finlayson and Faggella, 1986). In contrast, the maximum concentration reported in this drain since 1995 was only 43.7 ppb. Reported concentrations in other waterways in California have been even lower. This risk assessment, based on these monitoring data, indicates low acute and subchronic risk to fish, and no fish kills heve been reported in recent years. Thus, it appears that mandatory holding periods have effectively mitigated the acute risk of molinate to fish in California. The holding periods are probable effective because much of the molinate residue in the flood water dissipates through volatilization prior to discharge (Mabury *et al.*, 1996). It is important that these mandatory holding periods be retained to prevent hazardous levels of molinate from returning in California.

Aquatic residue levels in the Southern region are characterized by generally low basal levels during the spring with occasional high peaks. The high peaks probably are associated with the release of flood water from rice fields. Releases that occur soon after an application of molinate, before residues have had time to dissipate, would be most problematic. Such releases could occur for several reasons: 1) overflow or levee failure due to heavy rain, 2) drainage of flood water following seeding when pinpoint flood practices are used (primarily in southern Louisiana), and (3) drainage of fields that is done as part of a management practice to control a growth abnormality in rice called straighthead. In general, however, the rice grower would try to avoid draining a field soon after application of molinate since doing so would remove the efficacy of the application. However, unscheduled releases due to heavy rainfall could occur at any time. With dry-seeded rice, some water also may be released from the field before the flood is established. Releases may be from runoff of rain water or drainage of excess water from flushes (i.e., very shallow short-term floods used to moisten the soil). This water may contain molinate residues that desorb from the soil into the water, but the volume of water released would be small. In general, it appears that the most significant contamination of molinate in aquatic habitats would occur from unscheduled releases of water from either flooded or unflooded fields resulting from heavy rain occurring soon after application of molinate. Heavy thunderstorms are common in this region in the spring, especially in the Gulf Coast region.

In the Southern region, spikes caused by release of contaminated water from rice fields may occasionally result in molinate concentrations that exceed levels that are acutely toxic to fish and aquatic invertebrates. Effects would generally be localized and limited to small shallow bodies of water. Residues in the larger rivers appear to be diluted enough to not be acutely toxic to fish or invertebrates. Only one reported fish kill in the Southern region has been associated with molinate. This kill occurred in 1991 in Louisiana in a bayou lined with rice and cotton fields. The fish kill was investigated several days after the mortality occurred, and although molinate levels of 15-20 ppb were observed in the water, it is impossible to know if the kill was the result of this pesticide, other pesticides used in the area, or other causes.

In addition to risk from acute effects, the potential for chronic effects related to reproductive toxicity and endocrine disruption is a major concern for fish and other aquatic organisms. In mammals, molinate has been shown to damage the reproduction system in males and females, apparently by inhibiting synthesis of estrogen and testosterone. Since the reproduction of fish, amphibians, crustaceans, and mollusks is also dependent on synthesis of estrogen and testosterone, molinate could cause reproductive impairment in these organisms as well. Molinate is applied mostly in the spring, which corresponds to active breeding of many fish and amphibians. As well as affecting freshwater habitats, use of molinate in the Gulf Coast region will also expose many coastal estuarine areas. Shallow coastal estuaries are often referred to as "fish nurseries" because they provide essential habitat for the reproduction of many marine and estuarine organisms, including fish, crabs, shrimp, and shell fish. Molinate, as a possible endocrine disruptor, could impair reproduction of adults, and even could interfere with the sexual development of many immature stages of fish and invertebrates which inhabit these habitats. Therefore, contamination of these habitats with molinate potentially could result in significant ecological and economical harm. Further aquatic life-cycle testing and endocrine disruption testing is very important to further assess this potential hazard.

Appendix K. Refined Terrestrial Risk Assessment

Risk to Terrestrial Wildlife from Application of Molinate to Floodwater on Rice

In this addendum, we assess the risk to terrestrial wildlife when molinate is applied as a liquid or granular to the floodwater of rice paddies. Ordram 8E, an EC product of molinate, is frequently applied directly to the irrigation water as it is pumped onto the fields (i.e., chemigation). Therefore, standard EFED risk assessment methods, which are based on EECs on plants and insects exposed from spray applications, are not appropriate for this use pattern. Furthermore, the EFED currently does not have an accepted standard method for assessing chronic risk from granular applications. With postflood applications, most of the granules will fall within the floodwater and quickly release the active ingredient into the water. Therefore, chronic risk from postflood granular applications will be assessed similarly to acute and chronic risk from application of EC products directly into irrigation water. Acute risk to mammals from exposure through dissolved molinate will also be assessed to complement the previous acute risk assessment presented in body of the RED document, although the previous assessment still should be considered as an assessment of acute risk from exposure to granules which fall on the levees and field margins.

To assess the risk of molinate dissolved in floodwater, dietary exposure models are utilized for three representative species: the Canada goose (*Branta canadensis*), the muskrat (*Ondatra zibethicus*), and the mink (*Mustela vison*). All three species are assumed to be exposed to molinate through drinking treated floodwater. Concentrations of molinate in treated floodwater are estimated based on measured obtained from three aquatic field dissipation studies (MRID's 41421803, 41421804, and 40391706). The highest instantaneous concentration is used for acute exposures and the highest 7-day time-weighted average concentration is used for chronic exposures. The highest instantaneous concentration (4.2 mg ai/L) occurred on day 111 of the field dissipation study conducted in Arkansas (MRID 40391706). The highest time-weighted average concentration (0.53 mg ai/L) occurred between days 8 and 15 of the aquatic field dissipation study in California using Ordram 8E (MRID 41421803). The Canada goose and the muskrat are herbivorous species and are assumed to feed on young emerged rice plants in the rice field. The estimate for the maximum concentration of molinate in young rice plants is derived from a Japanese plant uptake study (Imai and Kuwatsuka, 1984). The mink, a carnivorous species, is assumed to feed on aquatic organisms (e.g., fish, frogs, and crayfish) living in the rice paddy. Molinate concentrations in the mink's prey are estimated by multiplying the time-wighted average concentration by the BCF for fish.

Dietary exposures for all species are calculated by multiplying the dietary concentrations (wet weight) by the daily food and water intake rates (wet weight). Food and water intake rates specific to each species are obtained from the Wildlife Exposure Factor Handbook, Volume I (Office of Research and Development, USEPA, 1993, EPA/600/R-93/187-a). When more then one value is reported, the average is used. Since the only reported food intake rate for the Canada goose was for captive birds consuming dry grains, an intake rate was calculated for free-living birds feeding on grass. Intake rates are expressed as mg ai/kg BW per day, thereby eliminating the need to estimate body weights. Acute and chronic risk quotients are calculated by dividing the total daily intake rates (water + food) by the LD_{50} and NOAEL, respectively. Both acute and chronic toxicity values were expressed as mg ai/Kg BW. The input vales used are given in the table below.

Species	Food Intake Rate (kg food/kg BW per day)	Water Intake Rate (kg water/kgBW per day)	Acute LD_{50} (mg ai/kg BW)	Chronic NOAEL (mg ai/kg BW)
Canada Goose	0.35[a]	0.044	>2250 (mallard)	--
Muskrat	0.34	0.098	549	0.25
Mink	0.13	0.10	549	0.25

[a] Food ingestion rate for the Canada goose was calculated based on a typical metabolic rate of free-living birds (175 kcal/kg-d), energy content of grass (1.3 kcal/g wet wt.), and assimilation efficiency for geese feeding on emergent vegetation (39%). All values were obtained from the Wildlife Exposure Factors Handbook.

Acute Risk to Birds from Application of Molinate Floodwater (Chemigation)

Herbivorous Birds

The acute risk assessment for birds was based on the Canada goose. The goose was assumed to feed entirely on young rice plants from a rice paddy treated with molinate through chemigation. The maximum concentration of molinate in plant shoots was 47 mg/kg dry weight, or approximately 9.4 mg/kg wet weight. This concentration was measured in young rice plants which...[need to see paper]. The predicted daily intake of molinate from food is the peak measured concentration in rice shoots multiplied by the food intake rate for the Canada goose.

$$\text{Intake (food)} = 9.4 \text{ mg ai/kg} \times 0.35 \text{ kg/kg BW} = 3.29 \text{ mg ai/kg BW}$$

The maximum concentration of molinate measured in floodwater of the aquatic field dissipation studies was 4.2 mg/L, which occurred in the study conducted in Arkansas (MRID 40391706). This value, which represented only the parent compound, was increased by 50% to 6.3 mg ai/L to account for toxic degradates. A Potable Water Study found that the concentration of molinate degradates may be as much as 50% of the concentration of the parent (MRID's 41421803 and 41421804). The daily intake of molinate through water is calculated below.

$$\text{Intake (water)} = 6.3 \text{ mg ai/kg} \times 0.044 \text{ kg/kg BW} = 0.28 \text{ mg ai/kg BW}$$

Thus the total dietary intake is 3.29 + 0.28 = 3.57 mg ai/Kg BW. This intake is very small compared to acute toxic threshold for birds (mallard LD_{50}>2250 mg ai/kg BW). The acute risk quotient is less than 0.01, which does not exceed any acute level of concern. Therefore, chemigation applications of molinate on rice field is predicted to pose minimal acute risk to birds, including threatened and endangered species.

Carnivorous Birds

The great blue heron is used as a model species to assess risk to carnivorous birds....

Since chronic toxicity data are not currently available for birds, the chronic risk to birds from this use will be based on the mammalian chronic risk assessment (see below). The muskrat can be used to represent herbivorous birds like the Canada goose, and the mink can be used to represent carnivorous birds like the great blue heron.

Risk to Mammals from Application of Liquid or Granular Molinate to Floodwater

Herbivorous Mammals

The muskrat was used as a model species to assess risk to herbivorous mammals. As with the Canada goose, the diet of the muskrat was assumed consist entirely on young rice plants from a treated rice field. The daily intake of molinate from food is calculated below.

Intake (food) = 9.4 mg ai/kg x 0.34 kg/kg BW = 3.2 mg ai/kg BW

The acute daily intake of molinate from water is calculated below.

Intake (water) = 6.3 mg ai/kg x 0.098 kg/kg BW = 0.62 mg ai/kg BW

The total acute daily intake of molinate for the muskrat is 3.2 + 0.62 = 3.8 mg ai/kg BW. This value divided by the rat LD_{50} of 549 mg ai/kg BW yields a RQ of 0.0069. Since this RQ does not exceed any of the acute levels of concern, applications of molinate directly to floodwater of rice fields is predicted to pose minimal acute risk to herbivorous mammals, including threatened and endangered species.

Because molinate is relatively short-lived in the water column, a lower water concentration is assumed for chronic exposure. The chronic water concentration was estimated based on the highest 7-day average concentration measured in the California aquatic field dissipation studies (MRID 41421803 and 41421804). The highest average concentration was 0.53 Mg ai/L, which occurred between days 8 and 15 in the study using Ordram 8E (MRID 41421803). This value, which was a measure of only the parent compound, was increased by 50% to 0.80 mg ai/L to account for the presence of toxic degradation products.

The acute concentration for molinate in rice shoots (9.4 mg ai/kg) was also used as the estimated chronic concentration. Therefore, the chronic daily intake of molinate for the muskrat remains at 3.20 mg ai/kg BW. The chronic daily intake of molinate from water is calculated below.

Intake (water) = 0.80 mg ai/kg x 0.098 kg/kg BW = 0.078 mg ai/kg BW

The total daily intake of molinate on a chronic basis is 3.2 + 0.078 = 3.3 mg ai/kg. The chronic NOAEL for mammals, based on reproductive toxicity to the rat, is 5 ppm or approximately 0.25 mg ai/kg-day. The chronic risk quotient is 3.3/0.25 = 13. Because the RQ exceeds the chronic LOC of 1, application of molinate to flood irrigation water is predicted to pose a chronic risk to mammals.

Carnivorous Mammals

The mink was selected as a model species to assess to carnivorous mammals. The diet of the mink is assumed to consist of small aquatic animals like fish, frogs, and crayfish. The tissue concentration of molinate in these organisms is assumed to be the maximum chronic water concentration multiplied by the bioconcentration factor for fish. As before, the 7-day chronic water concentration is estimated to be 0.80 mg ai/kg (see above assessment for herbivorous mammals). The bioconcentration factor of molinate for whole fish is 72X (MRID's 4059303 and 40635101). Therefore, the tissue concentration in aquatic animals is predicted to be 0.80 x 72 = 57.6 mg ai/L. The mink consumes approximately 13% of its body weight per day. The daily intake of molinate through food is calculated below.

Intake (food) = 57.6 mg ai/kg x 0.13 kg/kg BW = 7.5 mg ai/kg BW

The acute and chronic water concentrations are the same as those used above for herbivorous mammals. For acute exposure, the daily intake through water is calculated below.

Intake (water) = 6.3 mg ai/kg x 0.10 kg/kg BW = 0.63 mg ai/kg BW

The total daily intake for acute exposure is thus 7.5 + 0.63 = 8.1 mg ai/kg BW. Dividing this exposure value by the rat LD_{50} of 549 mg ai/kg BW yields a RQ of 0.015. Since this RQ does not exceed any of the acute levels of concern, applications of molinate directly to floodwater on rice fields is predicted to pose minimal acute risk to carnivorous mammals, including threatened and endangered species.

For chronic exposure, the daily intake through food is the same as for acute exposure, 7.5 mg ai/kg BW. The daily intake for water is less than for acute exposure since a 7-day average water concentration is used. The daily intake from water for chronic exposure is calculated below.

$$\text{Intake (water)} = 0.80 \text{ mg ai/kg} \times 0.10 \text{ kg/kg BW} = 0.080 \text{ mg ai/kg BW}$$

The total daily intake for acute exposure is thus 7.5 + 0.08 = 7.6 mg ai/kg BW. Dividing this exposure value by the chronic rat NOAEL of 0.25 mg ai/kg BW yields a RQ of 30. Because the RQ exceeds the chronic LOC of 1, application of molinate to flood irrigation water is predicted to pose a chronic risk to mammals.

Summary of Risk Quotients

Wildlife Group	Model Species	Acute RQ	Chronic RQ
Herbivorous bird	Canada Goose	<0.01	--
Herbivorous mammal	Muskrat	<0.01	13[b]
Carnivorous mammal	Mink	0.015[a]	30[b]

[a] Exceeds the LOC for risk to threatened and endangered species.

[b] Exceeds the LOC for chronic risk.

Conclusions

Risks from applications of liquid and granular molinate directly to floodwater on rice fields are generally similar to those posed by other uses of molinate. Application of liquid molinate directly to floodwater (i.e., chemigation) is predicted to pose minimal acute risk to birds. Although birds would be prone to consume granules that would fall on the levees and field margins, a previous risk assessment concluded that granular applications of molinate also poses little acute risk to birds. Chronic risk to birds cannot be assessed until avian reproduction data are available. However, based on the results of the mammalian risk assessment, chronic risk to birds appears possible.

Application of EC or granular products of molinate directly to water is predicted to pose minimal acute risk, but chronic risk, to herbivorous and carnivorous mammals. A previous acute assessment found minimal risk to mammals from EC spray applications, and only some minor risk from granular applications from exposure to granules that fall on the levees and field margins.

However, the chronic risk assessment for applications to floodwater agree with previous risk assessment in predicting risk to mammals. This risk stems from the high reproductive toxicity exhibited in rodents. **This assessment concludes that aquatic rodents such as the muskrat would be at risk to reproductive effects from feeding and drinking in rice paddies treated with molinate.**

The assessment for carnivorous mammals also indicates chronic risk, but this risk conclusion is uncertain because carnivorous mammals are not rodents, and there is some evidence that the reproductive toxicity of molinate does not occur in mammals other than rodents. The activation of reproductive toxicity of molinate is dependent on a particular metabolic pathway that predominates in rodents but not in many other types of mammals . Wickramarante *et al.* (1998) found that the reproductive toxicity of molinate is relatively low in the dog, rabbit, and monkey, and the Agency testing the rabbit and dog also suggest that rodents are more sensitive to the reproductive toxicity of molinate than are other mammals.

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