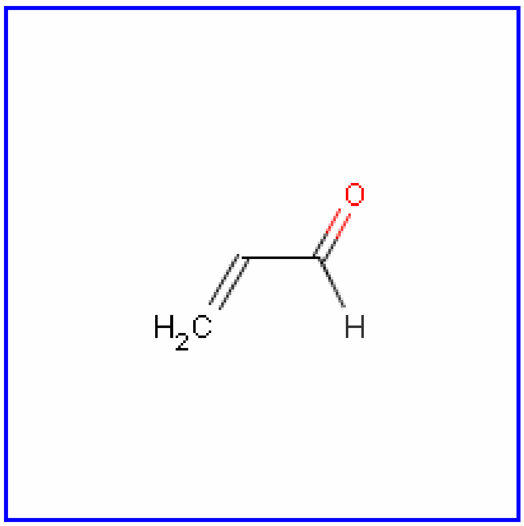
Office of Prevention, Pesticides,
and Toxic Substances

Environmental Fate and Ecological Risk Assessment for the Reregistration of Acrolein



MAGNACIDE® H
CAS 107-02-8   PC Code 000701

Prepared by: Kristina Garber, Biologist; R. David Jones, Ph.D., Senior Agronomist; Thomas Steeger, Ph.D., Senior Biologist	U.S. Environmental Protection Agency Office of Pesticide Programs Environmental Fate and Effects Division Environmental Risk Branch IV 1200 Pennsylvania Ave., NW Mail Code 7507P Washington, DC 20460
Reviewed by: Elizabeth Behl, Branch Chief	

Acknowledgements

The Environmental Fate and Effects Division would like to thank Dr. Kurt Getsinger, US Army Engineer Research and Development Center, Vicksburg, MS, Mr. Dave Sisneros, US Bureau of Reclamation, Denver, CO, and Mr. Lars Anderson, U. S. Department of Agriculture Agricultural Research Station, Davis, CA. for their contributions to the Agency's understanding of the current uses of acrolein.

Additionally, the Agency would like to thank Environment Australia Environmental Quality Division Risk Assessment and Policy Section for their willingness to share their Environmental Assessment Report on MAGNACIDE® H. Herbicide.

1 Executive Summary

1.1 Nature of the Chemical Stressor

Acrolein (CAS No. 107-02-8) registered under the trade name MAGNACIDE® H is a herbicide primarily used to remove submersed plants from irrigation canals. Acrolein is applied directly under the water's surface through a closed delivery system. The label refers the user to an "Application and Safety Manual" for directions for use. The maximum allowed treatment concentration is 15 mg/L. Water within the treatment area of canals/irrigation ditches is held at the treatment concentration for periods ranging from 30 minutes to 8 hours. Both the concentration and the treatment time may vary depending on the weed growth condition, water flow rate, temperature, and application time desired. At this time, the label does not limit the number of times an irrigation canal can be treated in a year or the period of time between treatments (a minimum reapplication interval). The label does stipulate that "*water treated with [acrolein] must be used for irrigation of fields, either crop bearing, fallow, or pasture, where the treated water remains on the field OR held for 6 days before being released into fish bearing waters or where it will drain into them*".

1.2 Conclusions Regarding Exposure

Acrolein is applied directly to water and is maintained at a targeted treatment concentration for specified periods of time. The laboratory fate properties for acrolein are not well known other than the hydrolytic reactions with water, and the physical chemical properties, (solubility, vapor pressure, and Henry's Law Constant). The primary route of degradation may be volatilization, microbial metabolism, or binding into plants by cross-linking of proteins, but insufficient data are currently available to identify which of these are the major degradation route(s) with any certainty. Volatilization is definitely a route of dissipation, but the importance of volatilization relative to other degradation routes cannot be quantified at this time. The last of these, cross-linking of proteins, is related to the pesticidal mode of action, but there are no direct data supporting it as contributing to decline of acrolein, and the extent of occurrence is uncertain and speculative.

Acrolein forms several degradates in the environment. One of these, 3-hydroxypropanal, forms abiotically, and is in equilibrium with acrolein, and thus reforms the acrolein as it dissipates by other routes. Other prominent degradates include acrylic acid, allyl alcohol, propanol, propionic acid, oxalic acid, and ultimately carbon dioxide. As is discussed below, the risk assessment is dominantly based on monitoring data. Because these monitoring studies only report the parent, it is only possible to consider the risks due to the parent acrolein at this time. This is expected to only slightly underestimate the risk since the toxicity is dominantly associated with the parent compound.

Monitoring studies show that the compound can be transported to distances of at least 61 miles beyond the initial site of application at concentrations that are still active. Estimated half-lives in these studies range from 2 to 20 hours as the pulse was tracked downstream after application. Field studies in which acrolein-treated irrigation water was applied in-furrow to agricultural fields showed that acrolein dissipated rapidly (half life of 0.25 days). Although the label stipulates that treated water must be used for irrigation or “held” for 6 days, available monitoring data demonstrate that these requirements are not effective in controlling acrolein residues in water released from the treatment area as it is frequently reaching the discharge points from irrigation systems. In addition, such requirements may be infeasible, given how acrolein is typically used to control aquatic vegetation in irrigation systems.

Based on estimated environmental concentrations calculated using Henry’s law constant and based on actual measured concentrations from field studies, acrolein volatilizes from treated waters. The volatilized acrolein in the vicinity of the treated irrigation canal water represents a source of exposure to non-target animals through inhalation.

1.3 Conclusions Regarding Effects

On an acute exposure basis acrolein is very highly toxic to freshwater fish and invertebrates, estuarine/marine invertebrates and to birds and it is highly toxic to mammals and estuarine/marine fish. Chronic exposure to acrolein resulted in reduced growth and survival in fish and reduced survival in aquatic invertebrates. Chronic exposure in mammals resulted in decreased growth in both parents and offspring. No chronic toxicity data are available for birds. Median effect concentrations for vascular and nonvascular aquatic plants are 36 and 72 µg/L, respectively. There are no guideline data available with which to evaluate the toxicity of acrolein to terrestrial plants. Available toxicity data indicate that aquatic animals are as or more sensitive to acrolein than aquatic plants. No toxicity data are available on the major degradate of acrolein, 3-hydroxypropanal.

1.4 Conclusions Regarding Potential Risks to Non-target Organisms

Based on the most sensitive species and assuming maximum treatment concentrations of 15 mg/L, the acute risk level of concern is exceeded for aquatic animals by factors of 2,142X for freshwater fish and 4,286X for aquatic-phase amphibians. The acute risk LOC is exceeded by a factor of 968X for freshwater aquatic invertebrates. For estuarine/marine animals the acute risk

LOC is exceeded by factors of 70X and 545X for fish and invertebrates, respectively. The acute risk LOC for vascular and nonvascular aquatic plants is exceeded by factors of 208X and 417X, respectively.

The potential for chronic exposure and effects of acrolein is uncertain and is highly dependent on location and treatment regimen. In situations where acrolein is applied to flowing water in only one section of an irrigation canal and relatively infrequently, acrolein residues that are not removed in irrigation water may be transported through the length of the canal and diluted by untreated water from other canals prior to discharge, resulting in short-term, rather than extended exposure. Alternatively, if acrolein is used as a routine component of a treatment regimen, it may be possible for multiple applications in multiple canals to result in exposure over a longer term. Additionally, the acute toxicity of acrolein suggests that few biological receptors would survive the initial contact with the chemical; reducing the likelihood of chronic exposure to acrolein. The available monitoring data indicate that risks to non-target organisms can extend for considerable distances in treated irrigation canals and for periods that extend beyond the actual treatment duration.

Acrolein is reputed to have an acrid odor and is irritating to mucus membranes; these combined attributes could serve as a deterrent to terrestrial animals that might drink acrolein-treated water. Although acute LOCs are not exceeded for birds and mammals that drink water, at the maximum treatment concentration, and depending on the size of the animal evaluated, the acute restricted use LOC is exceeded for both birds and mammals. Acrolein is already classified as a restricted use pesticide. Additionally, based on upper-bound estimated environmental concentrations for acrolein in the air surrounding treated canals, there is a risk of acute mortality for both birds and mammals through inhaling acrolein fumes. Terrestrial animals foraging on vegetation, seeds and insects in agricultural fields where acrolein is applied as irrigation may also experience acute mortality depending on the size of the animal and the nature of the forage material. Although the acrid odor and irritating taste of acrolein may serve to dissuade terrestrial animals from foraging in acrolein irrigated fields, there are insufficient data available at this time to discount the possibility of acute effects.

The potential chronic toxicity of acrolein to terrestrial animals is uncertain. Although there are no chronic toxicity data for birds with which to evaluate chronic toxicity, the relatively rapid dissipation of the compound once applied to treated fields is likely to limit potential chronic exposure. Multiple applications of the compound could contribute to chronic risk to terrestrial animals drinking treated water; however, repeat applications are typically done at much lower treatment concentrations than those evaluated in this assessment.

Monitoring data indicate that acrolein concentrations have been measured up to 61 miles from the point of application and up to 54 hours after application at levels that can exceed the acute risk LOC for both freshwater vertebrates and invertebrates. RQs calculated based on measurements taken near the discharge point from irrigation canals ranged up to 66 for freshwater fish and 15 for freshwater invertebrates.

A total of 13 incidents have been reported to the Agency associated with the use of acrolein from 1971 to 2004. The majority has been associated with the deaths of fish and aquatic invertebrates; one incident was reported involving aquatic birds. Although thirteen incidents have been reported, this does not preclude the possibility that non-target mortality may be occurring but is unnoticed or not reported. However, the low number of reported incidents relative to other pesticides such as some organophosphate and carbamate insecticides may also suggest that controlled application procedures have limited the extent of non-target mortality. Unless systematic efforts to collect incident data are put in place, determining a cause and effect relationship between the number of incidents and changes in management practices is not possible.

Although there are no terrestrial plant toxicity data with which to evaluate potential risk, there is an incident report of damage to an agricultural crop from the application of acrolein-treated water. It has been hypothesized that the waxy cuticle of terrestrial plants that protects them from desiccation may also serve to protect them from the toxic effects of acrolein. However, terrestrial plant toxicity tests are not available to address uncertainties associated with terrestrial plant risks; the incident report suggests however, that terrestrial plants can be vulnerable to acrolein.

1.4.1 Endangered Species

Effects on Federally-listed endangered and/or threatened species may be an important consideration for site-specific applications. **Table 1** provides a summary of potential direct effects to listed taxa. Across all taxa evaluated, there is a potential risk to listed species and to critical habitat for listed species.

Table 1. Potential listed species risks associated with direct or indirect effects due to treatment of irrigation canals with acrolein.

Listed Taxon	RQ	Direct Effects from Acute Exposures	Indirect Effects
Aquatic			
Aquatic vascular plants	1,250	Yes	Yes[6]
Freshwater invertebrates	>484	Yes	Yes[4,5]
Marine/estuarine crustaceans			
Mollusks	273	Yes	Yes[4,5]
Freshwater fish	1,071	Yes	Yes[4,5]
Marine/estuarine fish	35	Yes	Yes[4,5]
Aquatic-phase amphibians	2,143	Yes	Yes[4,5]
Terrestrial			
Semi-aquatic plants	presumed[1]	presumed[1]	presumed[2]
Terrestrial plants	presumed[1]	presumed[1]	presumed[2]
Insects	presumed[1]	presumed[1]	presumed[2]
Birds	0.47	Yes	Yes[3,4]
Terrestrial-phase amphibians	0.47	Yes	Yes[3]
Reptiles	0.47	Yes	Yes[3,4]
Mammals	0.26	Yes	Yes[3,4]

[1] No toxicity data are available to define RQ values for this exposure.
[2] Since the risks of direct effects to semi-aquatic and terrestrial plants are unknown, risks of indirect effects to organisms relying upon these plants are unknown.
[3] Direct effects to small mammals, amphibians, reptiles and birds could result in indirect effects to animals that rely upon them as food.
[4] Direct effects to aquatic animals could result in indirect effects to animals that rely upon them as food.
[5] Direct effects to aquatic plants (including unicellular and vascular) could result in indirect effects to animals that rely upon them as food.
[6] Direct effects to aquatic plants (including unicellular and vascular) could result in alterations in the plant community structure through changes in species interactions.

Table of Contents

2 Problem Formulation

The purpose of problem formulation is to provide the foundation for the environmental fate and ecological risk assessment of acrolein. It sets the objectives for the risk assessment, evaluates the nature of the problem, and provides a plan for analyzing the data and characterizing the risk.[1]

2.1 Nature of the Regulatory Action

This environmental fate and ecological risk assessment is being conducted in support of the reregistration eligibility decision for acrolein under the Federal Insecticide Fungicide and Rodenticide Act.

2.2 Stressor Source and Distribution

2.2.1 Nature of the Chemical Stressor

Acrolein is marketed by Baker Petrolite Corporation and is the active ingredient in MAGNACIDE® H Herbicide (EPA Registration Number 10707-9), a restricted use pesticide for control of submerged and floating aquatic weeds and algae in irrigation canals and irrigation reservoirs in some states.[2] The chemical was first registered as a herbicide in 1975 by BPC, but was previously registered in 1959 by Shell as Aqualin®.

A preliminary summary of physical/chemical and environmental fate/transport properties are provided in **Table 2**. Degradation and volatilization are believed to be the major pathways for dissipation of acrolein from water. Acrolein may also bind to plant material and this may serve as an additional route of dissipation from the water column.

Table 2 Chemical/Physical Characteristics of Acrolein	
Common name	Acrolein
Chemical Name	2-propenal
Pesticide type	Herbicide
Chemical class	Reactive aldehyde
CAS number	107-02-8
Empirical formula	*C3H4O1*
Molecular Mass (g/mol)	56.06

[1] USEPA 1998. Guidelines for Ecological Risk Assessment. EPA/630/R-95/002F http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=12460

[2] Baker Petrolite. 2000. MAGNACIDE® H Herbicide Product Data.

Vapor pressure	0.354 atm at 25°C
Henry's Law Constant (atm-m^3/mol)	1.95 x 10^{-4}
Solubility in water (g/L)	237.6
Log K_{ow}	0.98-1.10
PK_a/PK_b	*No data*

Acrolein is a reactive aldehyde and is considered a contact herbicide that is phytotoxic to most submersed aquatic vegetation. Contact herbicides act quickly by destroying plant cells; however, they do not kill the roots and re-application several weeks or months following the initial application may be required. Owing to its reactivity with organic matter, the chemical is not likely to persist; however, it can move considerable distances in fast moving water such as that which may be present in irrigation canals. The major degradate of acrolein is 3-hydroxypropanal.

According to the product data fact sheet for MAGNACIDE® H Herbicide, acrolein is a general cell toxicant which reacts with sulfhydryl groups in proteins. In a review of acrolein toxicity, Beauchamp *et al.*[3] attributed the toxicity of acrolein to the chemical's reaction with critical sulfhydryl groups present in proteins and peptides that play important roles in chemical reactions of living cells. Submersed aquatic plants treated with MAGNACIDE® H Herbicide are intended to gradually disintegrate into small fragments and float downstream.

Acrolein is also the active ingredient of a restricted use broad-spectrum microbiocide (MAGNACIDE® B) to control bacteria and remove hydrogen sulfide in oilfield operations; however, the use of acrolein as a biocide will not be considered in this ecological risk assessment. In addition to its use as a pesticide, acrolein is primarily used as an intermediate in the manufacture of plastics; it is also used in manufacturing perfumes, pharmaceuticals, and animal feed additives. Other sources of acrolein include its formation from the breakdown of certain pollutants in outdoor air or from burning tobacco or gasoline.

2.2.2 Overview of Pesticide Usage

Acrolein is applied directly under the water's surface through a closed delivery system. Applications are made to a treatment area at a desired treatment concentration for specific periods of time depending on the extent of aquatic plant growth conditions. Use of acrolein is typically limited to arid western states where crops are irrigated. At this time, the label does not limit the number of times an irrigation canal can be treated in a year or the period of time between treatments (a minimum reapplication interval). The label does stipulate that "*water*

[3] Beauchamp, R. O. Jr., D. A. Andjelkovich, A. D. Kligerman, K. T. Morgan, and H. d'A. Heck 1985. A Critical Review of the Literature on Acrolein Toxicity. CRC Critical Reviews in Toxicology 14: 309 – 380.

treated with [acrolein] must be used for irrigation of fields, either crop bearing, fallow, or pasture, where the treated water remains on the field OR held for 6 days before being released into fish bearing waters or where it will drain into them".

2.3 Receptors

Aquatic receptors that may be exposed to acrolein include aquatic animals (*i.e.*, freshwater and estuarine/marine fish and invertebrates, and aquatic-phase amphibians) and plants. Terrestrial receptors that may be exposed to acrolein include terrestrial and semi-aquatic wildlife (*i.e.*, mammals, birds, reptiles, and terrestrial-phase amphibians). Since acrolein is applied underwater, exposure of terrestrial plants and topical exposure of insects is not anticipated, with the exception of application of irrigation water containing acrolein to fields.

Consistent with the process described in the Overview Document[4], this risk assessment uses a surrogate species approach. Toxicological data generated from surrogate test species, that are intended to be representative of broad taxonomic groups, are used to extrapolate to potential effects of acrolein on a variety of species (receptors) included under these taxonomic groupings.

Acute toxicity data from registrant-submitted studies and open literature are used to evaluate potential effects of acrolein to the aquatic and terrestrial receptors identified in this section. This evaluation can also provide insight into indirect effects of acrolein on biotic communities due to loss of species that are sensitive to the chemical and changes in structure and functional characteristics of the affected communities.

Table 3 provides examples of taxonomic groups and the surrogate species tested to help understand potential ecological effects of acrolein to these non-target taxonomic groups.

[4] USEPA. Overview of the Ecological Risk Assessment Process in the Office of Pesticide Programs. http://www.epa.gov/oppfead1/endanger/consultation/ecorisk-overview.pdf

Table 3 Taxonomic Groups and Test Species Evaluated for Ecological Effects in Baseline Risk Assessments.	
Taxonomic Group	**Example(s) of Representative Species**
Birds[1]	Mallard duck (*Anas platyrhynchos*) Bobwhite quail (*Colinus virginianus*)
Mammals	Laboratory rat (*Rattus norvegicus*)
Insects	Honey bee (*Apis mellifera L.*)
Freshwater fish[2] and aquatic-phase amphibians	Fathead minnow (*Pimephales promelas*) African clawed frog (*Xenopus laevis*)
Freshwater invertebrates	Water flea (*Daphnia magna*)
Estuarine/marine fish	Longnose killifish (*Fundulus similis*)
Terrestrial plants[3]	Monocots) Dicots
Aquatic plants and algae[4]	Vascular plants Non-vascular plants

[1] Birds represent surrogates for amphibians (terrestrial phase) and reptiles.
[2] Freshwater fish may be surrogates for amphibians (aquatic phase).
[3] Four species of two families of monocots and six species of at least four dicot families are typically evaluated.
[4] One vascular plant and four non-vascular plants are typically evaluated.

2.3.1 Ecosystems Potentially at Risk

Aquatic ecosystems potentially at risk include the irrigation and drainage canals where acrolein is applied to control aquatic weeds, as well as return flows of treated irrigation waters into receiving rivers, streams, or lakes. For use in coastal areas, aquatic habitat also includes marine ecosystems such as estuaries. Given that the drainage canals are used as a source of irrigation water, it is assumed that these systems are primarily freshwater, whereas receiving water bodies may be either freshwater or estuarine/marine, depending on proximity to coastal areas. In addition, it should be noted that irrigation canals and drainage ditches in some areas contain water only during the growing season when they are delivering water to crops. As such, they can be dry from 3 to 6 months out of the year, depending on the area and crops being irrigated. Although some of these canals and ditches are likely to be intermittent, these aquatic systems provide viable habitat for such organisms as larval amphibians, reptiles, benthic aquatic invertebrates (including a number of emergent insects), and diapausal pelagic (*i.e.*, living in the open water) invertebrates and fish; spawning habitat for fish; and feeding habitat for piscivorous and insectivorous wildlife.

2.4 Assessment Endpoints

Assessment endpoints represent the actual environmental value that is to be protected, defined by an ecological entity (species, community, or other entity) and its attribute or characteristics.[5] For acrolein, the assessment endpoints are survival, reproduction and growth of birds, mammals, freshwater fish and invertebrates, estuarine/marine fish and invertebrates, terrestrial plants, insects, and aquatic plants and algae.

[5] *Ibid* USEPA 1998.

2.5 Conceptual Model

A conceptual model provides a written description and visual representation of the predicted relationships between the pesticide (stressor), potential routes of exposure, and the predicted effects for the assessment endpoint. The conceptual model consists of two major components: the risk hypotheses and a diagram.

2.5.1 Risk Hypotheses

For acrolein, the following ecological risk hypothesis is being employed for this baseline risk assessment:

> *Non-target aquatic animals and plants and terrestrial animals may be exposed to acrolein that is applied according to the label to control aquatic weeds in drainage and irrigation ditches. Based on available information regarding volatilization, persistence, and direct and indirect toxicity, acrolein has the potential to compromise survival and cause sub-lethal effects in non-target aquatic animals and plants, terrestrial mammals, birds and plants.*

2.5.2 Conceptual Diagram

The conceptual diagram used to depict the potential ecological risk associated with acrolein is fairly generic and assumes that as a pesticide, acrolein is capable of affecting aquatic organisms at the anticipated environmental concentrations resulting from proposed label uses. All potential routes of exposure are considered and presented in the conceptual diagrams (**Figures 1 and 2**). The conceptual model generically depicts the potential source of acrolein, release mechanisms, abiotic receiving media, biological receptor types, and effects endpoints of potential concern.

In order for a chemical to pose an ecological risk, it must reach ecological receptors in biologically significant concentrations. An exposure pathway is the means by which a contaminant moves in the environment from a source to an ecological receptor. For an ecological exposure pathway to be complete, it must have a source, a release mechanism, an environmental transport medium, a point of exposure for ecological receptors, and a feasible route of exposure. The assessment of ecological exposure pathways, therefore, includes an examination of the source and potential migration pathways for constituents, and the determination of potential exposure routes, *e.g.*, ingestion, inhalation, and dermal contact. Exposure to aquatic organisms and plants is expected from surface waters contaminated with acrolein through direct application and from treated irrigation water that flows into receiving rivers, streams, or lakes. Since acrolein is applied underwater, exposure of terrestrial plants via direct application or spray drift or contamination of plants and insect forage sources for terrestrial animals are not anticipated exposure pathways, except in cases where acrolein-treated irrigation water is applied to agricultural fields. Based on the use pattern for acrolein, the main exposure pathways for terrestrial animals are exposure via ingestion of contaminated water and inhalation of volatilized acrolein. **Figure 2** depicts the potential risk to terrestrial animals following application of acrolein-treated water to agricultural fields. More probable routes of exposure are depicted with solid lines in each of the figures while less probable routes of exposure are depicted with dashed lines.

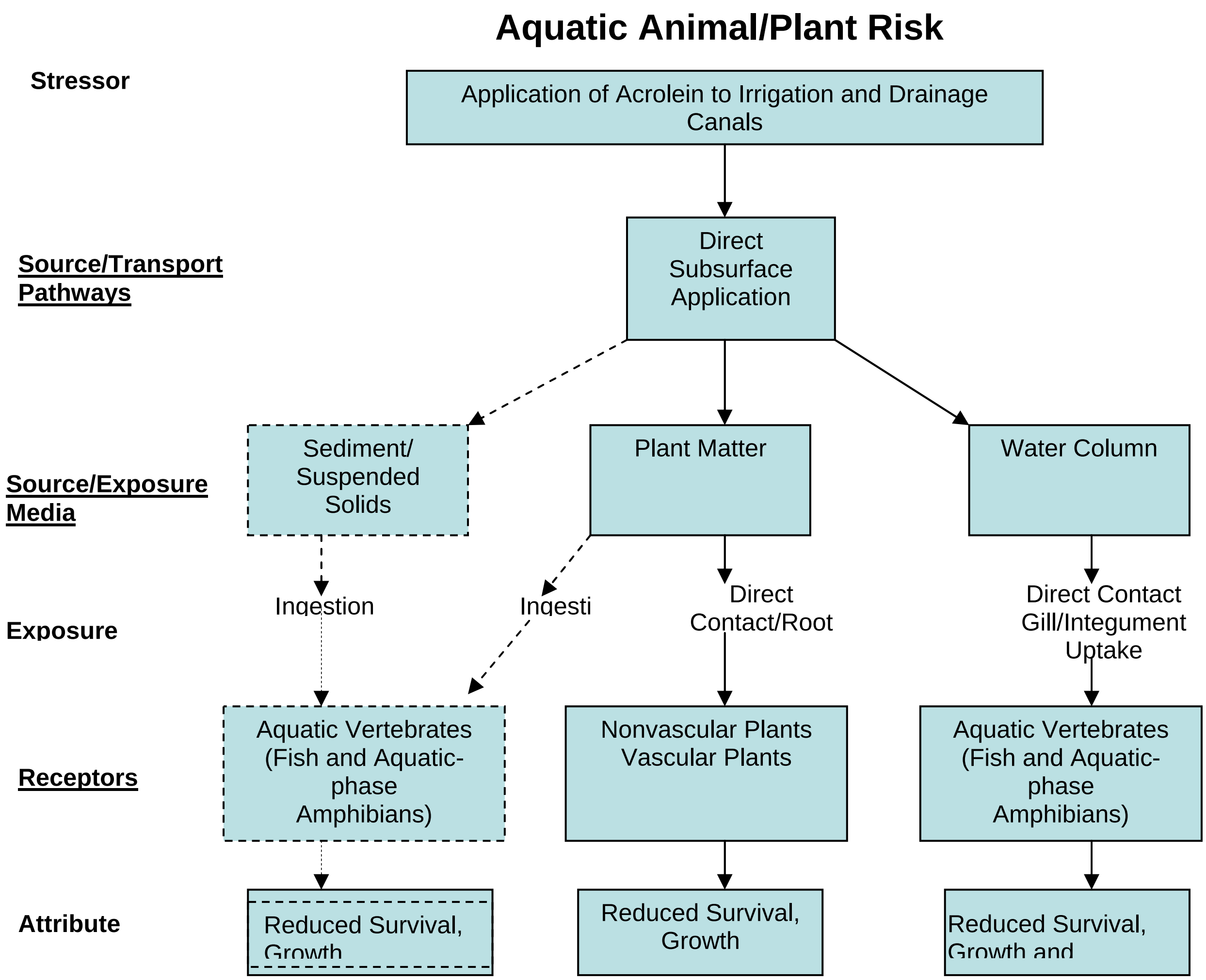


Figure 1 Ecological Conceptual Exposure Model for Aquatic Plants and Animals in a Screening-Level Risk Assessment of Acrolein Applied to Irrigation Canals and Drainage Ditches

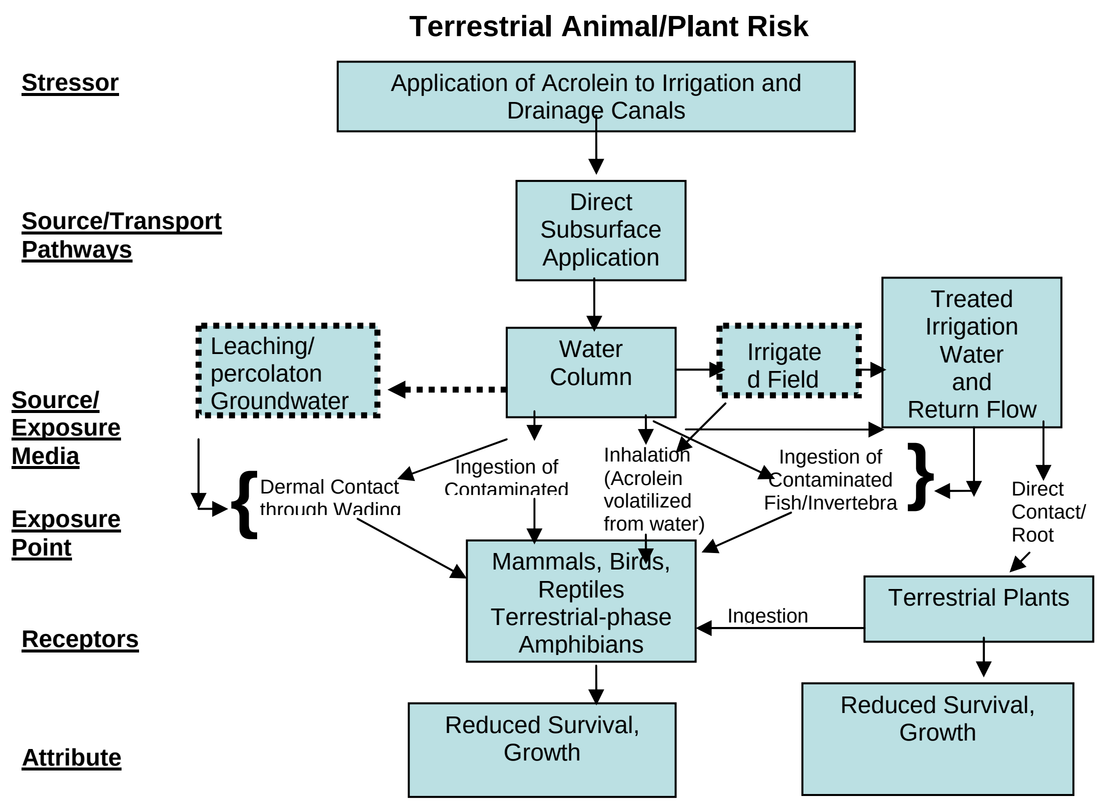


Figure 2. Ecological Conceptual Exposure Model for Terrestrial Plants and Animals in a Screening-Level Risk Assessment of Acrolein Applied to Irrigation Canals and Drainage Ditches

2.6 Analysis Plan

2.6.1 Preliminary Identification of Data Gaps and Analysis Plan

In conducting this risk assessment for acrolein, an analysis of the available data was conducted. For the aquatic ecosystem, acute toxicity data for acrolein are available for freshwater fish and invertebrates, estuarine/marine invertebrates, and aquatic algae. For the terrestrial ecosystem, acute toxicity data were identified to quantify mammalian and avian risks associated with exposure to acrolein via consumption of contaminated water. In addition, inhalation toxicity data are available to characterize risks associated with inhalation of contaminated air by mammals. Toxicity data are not available for the major degradate of acrolein, i.e., 3-hydroxypropanal; therefore, potential risks from the degradate are not considered in this assessment.

For acrolein, data sufficient for use in a quantitative risk assessment are available for freshwater fish, freshwater invertebrates, estuarine/marine fish, estuarine/marine invertebrates, algae and aquatic vascular plants. Presumably, submerged aquatic vegetation (vascular and nonvascular plants) will succumb to acrolein since they represent the targeted receptors.

The anticipated exposure pathways for terrestrial animals are oral exposure via drinking of contaminated water, and inhalation exposure of volatilized acrolein. Based on these exposure scenarios, open literature data sources were queried for acute and subacute oral and acute inhalation toxicity studies in birds and mammals. Acceptable oral toxicity studies were identified for mammals, an acute dietary study was identified for birds, and acute inhalation toxicity studies were identified for mammals; the lack of acute inhalation data in birds was treated as a data gap in this assessment. Due to potential volatilization, chronic exposure of terrestrial receptors is not anticipated. In addition, given that acrolein is applied directly below the surface of water, exposure of terrestrial plants is not anticipated except where fields are irrigated with the treated water. In situations were acrolein is applied to fields in an effort to dispose of waters containing the chemical, terrestrial plant and animal exposure is likely and potential risk of acute effects will depend on the extent to which acrolein has dissipated before reaching non-target organisms.

Since acrolein is relatively short-lived because of its volatility and reactivity, chronic exposure of aquatic and terrestrial ecosystems is likely to be limited; thus, this analysis plan focuses primarily on acute exposure.

For aquatic animals, the pathway of acrolein exposure is by direct application to water. Risks to aquatic species are based on the maximum allowable concentrations in water in irrigation canals and receiving water.

Since acrolein is applied directly below the water surface, terrestrial exposure pathways and receptors typically considered in EPA's ecological risk assessments, are not considered *i.e*., exposure of terrestrial animal food sources and plants via direct application or spray drift. Any potential exposure to terrestrial ecosystems via treated irrigation water is expected to be limited to drinking water and inhalation of volatilized acrolein at the site of application; however, an effort is made to estimate risks to terrestrial animals foraging in fields irrigated with treated water.

To assess exposure of terrestrial animals via ingestion of contaminated water, the maximum allowable concentration in irrigation canals is used in conjunction with the maximum solubility limit for acrolein.

Information on the potential ecological effects of acrolein are available from both registrant-submitted data on the technical grade active ingredient and through published open literature available through EPA's database ECOTOX[6].

Risks are estimated based on a deterministic (point estimate) approach, where a single point estimate of toxicity is divided by an upper and lower bound exposure estimate to calculate a risk quotient (RQ). The acute RQ values for each taxonomic group identified as an assessment endpoint is compared to the Agency's Levels of Concern (LOCs). LOCs serve as criteria for categorizing potential risk to non-target organisms. RQ values are calculated in the risk estimation section for each endpoint, and characterization and interpretation of risk is described in the risk description. Risks for each taxonomic group are described based on available lines of evidence from open literature data on acrolein. In addition, a preliminary assessment of listed species of concern is also included.

2.6.1.1 Measures of Effect and Exposure

This section describes the tools and methods used to conduct the analysis of the pesticide described in the analysis plan for acrolein. Each assessment endpoint requires one or more measures of ecological effect, which are measurable changes in the attribute of an assessment endpoint in response to a stressor, such as the Bobwhite quail acute oral LD_{50}. It also requires measures of exposure, which are the measures of stressor existence and movement in the environment and their contact or co-occurrence with the assessment endpoint. Examples include the maximum foliar residues on food items for birds.

Table 3 should provide a summary of the assessment endpoints previously identified along with the measure of effects and exposure and should be tailored for the chemical being evaluated.

[6] U.S. Office of Research and Development National Health and Environmental Effects Research Laboratory Mid-Contnent Ecology Division ECOTOXicology Database http://cfpub.epa.gov/ecotox/

Table 2. Assessment Endpoints and Measures of Ecological Effects and Exposure for Acrolein.			
Taxonomic Group	**Assessment Endpoint (Abundance)**	**Surrogate Species and Measures of Ecological Effect[1]**	**Measures of Exposure**
Birds[2]	Survival	Bobwhite quail acute oral LD_{50} Bobwhite quail and mallard duck subacute dietary LC_{50}	Maximum residues on food items (foliar)
	Reproduction and growth	Bobwhite quail and mallard duck chronic reproduction NOAEC and LOAEC (no studies available)	
Mammals	Survival	Laboratory rat acute oral LD_{50}	
	Reproduction and growth	Laboratory rat oral reproduction chronic NOAEC and LOAEC	
Freshwater fish[3]	Survival	Fathead minnow African clawed frog	Peak EEC[4]
	Reproduction and growth	Fathead minnow chronic (early life-stage) NOAEC and LOAEC	60-day average EEC[4]
Freshwater invertebrates	Survival	Water flea (and other freshwater invertebrates) acute EC_{50}	Peak EEC[4]
	Reproduction and growth	Water flea chronic (life cycle) LOAEC	21-day average EEC[4]
Estuarine/marine fish	Survival	Longnose killifish acute LC_{50}	Peak EEC[4]
	Reproduction and growth	Typically a chronic (early life-stage) NOAEC and LOAEC (no data available)	60-day average EEC[4]
Estuarine/marine invertebrates	Survival	Eastern oyster acute EC_{50} and mysid acute LC_{50}	Peak EEC[4]

Table 2. Assessment Endpoints and Measures of Ecological Effects and Exposure for Acrolein.			
Taxonomic Group	**Assessment Endpoint (Abundance)**	**Surrogate Species and Measures of Ecological Effect[1]**	**Measures of Exposure**
	Reproduction and growth	Typically a mysid chronic NOAEC and LOAEC (no data available)	21-day average EEC[4]
Terrestrial plants[5]	Survival and growth	Monocot and dicot seedling emergence and vegetative vigor $EC_{25,}$ EC_{05}, and NOAEC values	Estimates of runoff and spray drift to non-target areas
Insects	Survival (not quantitatively assessed)	Honeybee acute contact LD_{50} (no study available)	Maximum application rate
Aquatic plants and algae	Survival and growth	Algal and vascular plant (i.e., duckweed) EC_{50} and NOAEC values for growth rate and biomass measurements	Peak EEC

[1] If species listed in table represent most commonly encountered species from registrant-submitted studies, risk assessment guidance indicates most sensitive species tested within taxonomic group are to be used for baseline risk assessments.
[2] Birds represent surrogates for amphibians (terrestrial phase) and reptiles.
[3] Freshwater fish may be surrogates for amphibians (aquatic phase).
[4] One in 10-year return frequency.
[5] Four species of two families of monocots - one is corn, six species of at least four dicot families, of which one is soybeans.

LD_{50} = Lethal dose to 50% of the test population; NOAEC = No observed adverse effect concentration; LOAEC = Lowest observed adverse effect concentration; LC_{50} = Lethal concentration to 50% of the test population; EC_{50}/EC_{25} = Effect concentration to 50%/25% of the test population.

3 Use Characterization

3.1 Herbicidal Uses

MAGNACIDE® H Herbicide (EPA Reg. No. 10707-9), is one of two registered pesticide products containing acrolein. According to aquatic resource managers (personal communication Kurt Getsinger, US Army Engineer Research and Development Center, Vicksburg, MS; Dave Sisneros, US Bureau of Reclamation, Denver, CO; Lars Anderson, US Department of Agriculture Agricultural Research Station, Davis, CA), there are over 50 million acres of irrigated agriculture in the US, most of which (88%) occur in the Western states. A major portion of the Western irrigation canal system was designed and built by the US Bureau of Reclamation (USBR), mostly in conjunction with major river diversions and reservoirs. In addition to water delivery and drainage canals, the system comprises water storage and irrigation reservoirs (providing potable water, fish and wildlife habitat, and recreational activities) and hydroelectric generation capacity. In many cases, the primary delivery systems have state-owned/operated components as well (*e.g.* California Department of Water Resources). Most secondary conveyance systems are managed by local irrigation districts, which have "on the ground" responsibilities for aquatic weed management. In California alone, there are more than 300 such districts; this vast irrigation system consists of approximately 150,000 miles of canals, laterals, and drains, and services the production of over 250 different crops. California's Central Valley, the Columbia Basin Project in Washington State, and the Snake River Valley in Idaho are major centers of water withdrawal for irrigation. Irrigated agriculture accounts for billions of dollars in the US economy on an annual basis (over $20 billion in California alone).

Herbicides are currently the most widely used technique for controlling submersed weeds in irrigation canal systems of the Western US. While some non-chemical alternatives are employed to control submersed weeds in irrigation canals (drag-lines, harvesters, chaining, excavation during drawdown, hand-removal, grass carp) herbicides are the most practical, efficacious and cost effective technique in the majority of these systems. Most of the chemical weed control is provided through the use of copper containing herbicides (and algaecides) and acrolein applications, and to a far lesser extent by xylene treatments.

Major canals and smaller laterals comprise the largest proportion of irrigation systems and have the greatest weed management requirements. Usually 100% broad-spectrum weed control is desired from April through October. However, in some southern parts of the western states, irrigation is continuous throughout the year which makes seasonal dewatering/ mechanical maintenance very difficult. For example, some irrigation districts in the southwestern US maintain water within their conveyance system throughout the year, requiring continuous aquatic weed and algae control via integrated pest management strategies.

Submersed plants and algae generally cause the most severe weed problems in the western irrigation systems restricting water flow and delivery capacity. The primary target species is the vascular submersed plant, sago pondweed (*Potamogeton pectinatus*). Secondary targets include horned pondweed (*Zannichellia palustris*), Eurasian watermilfoil (*Myriophyllum spicatum*), coontail (*Ceratophyllum demersum*), and hydrilla (*Hydrilla verticillata*). Western milfoil (*Myriophyllum hippuroides*) appears to be increasingly problematic as well. Algae (primarily filamentous species) are commonly found in many of the irrigation systems year round and tend to impact water quality, causing taste and odor problems.

In contrast, drainage canals (drains) and water storage reservoirs have different and less intensive weed management requirements. Demand for weed control in drains is less frequent, with the primary objective to provide adequate, unimpeded conveyance of seasonal flood waters as well as sufficient flows of some irrigation return water (tail water). Furthermore, by reducing weed infestation in drains, propagules of invasive species (seeds, turions, etc) may be prevented from infesting downstream sites that receive irrigation wastewater, such as rivers and reservoirs.

Negative impacts of submersed weeds on irrigation systems include: a) reduced water delivery capacity; b) clogged pumps and structures (increasing maintenance costs); c) ruptured canals and canal failures; d) increased seepage and loss of water; e) flooding events; f) increased water costs; g) degradation of water quality; and h) weed dispersal to downstream supply canals and receiving waters (*e.g.* lakes, reservoirs, rivers, and wetlands).

The revised use closure memo for acrolein (**Appendix A**), states that the registrant, Baker Petrolite, intends to support the use of MAGNACIDE® H in irrigation canals, ditches, along with use in retention ponds/reservoirs. In addition, the registrant is supporting the use of MAGNACIDE® B in oil fields; however, this assessment focuses on the herbicidal use and does not address the potential ecological risks associated with the use of acrolein as a biocide. MAGNACIDE® H Herbicide is a restricted use pesticide used for the control of submersed and floating weeds and algae in irrigation systems. Baker Petrolite requires all applicators to complete a training/certification program and applicators must attend a refresher course at least once every three years.

According to the MAGNACIDE® H application and safety manual[7], which is referenced on the pesticide label, and the use closure memo, effective treatment concentrations in irrigation systems are as high as 15 mg/L, with application times (exposure periods) ranging from 30 minutes to 8 hours. Water treated with MAGNACIDE® H Herbicide must be used for irrigation of fields, either crop bearing, fallow or pasture, where the treated water remains on the field or held for 6 days before being released into fish bearing waters or where it will drain into them. Washington State has Special Local Needs labels where holding times as low as 48 hours are

[7] Baker Petrolite. 2005. MAGNACIDE® H Herbicide Application and Safety Manual. Manual Revision Date: March 2005.

used. Although the label specifies that water should be held for 6 days if not used to irrigate fields, the label does not specify how or where water is to be held.

The amount of MAGNACIDE® H Herbicide required to treat an irrigation system is primarily determined by the volume of water and weed density, although water velocity, temperature and quality are considered. The effectiveness of the herbicide is determined by its concentration and exposure time. Higher weed densities decrease flow and restrict contact time with submersed vegetation due to poor mixing of the water column. Additionally, acrolein is less soluble in cooler water and plant susceptibility is reduced; therefore, higher weed densities and lower water temperatures require higher concentrations and/or longer exposure periods for the herbicide.

The spatial extent of the treatment area is dependent on a number of parameters which are specified in the MAGNACIDE® H application and safety manual[4], and other parameters that are system-specific. For example, the manual specifies a treatment duration (in hours) for a volumetric flow rate (in cubic feet per second, or cfs) (**Table 4**. For an irrigation canal that is approximately 10 feet wide and 3.5 feet deep, one can calculate the downstream extent of treatment for a given flow rate. Some representative treatment distances are provided in the table below. These distances represent the lengths of canals that are expected to contain acrolein residues up to the treatment concentration. Thus, at a treatment duration of 1 hour, the treated area of a canal with a flow rate of 50 cfs would be roughly 10 feet wide, 3.5 feet deep, and 1 mile long, assuming no diversions.

Table 4 Treatment duration and extent of treatment area at two different flow rates, i.e., 50 and 120 cfs.

Treatment Duration (Hours)	Distance downstream of point of application (Flow rate of 50 cfs)	Distance downstream of point of application (Flow rate of 120cfs)
1	1.0 miles	2.3 miles
2	2.0 miles	4.7 miles
4	4.0 miles	9.3 miles
8	8.0 miles	18.7 miles

Acrolein is applied from pressurized containers using a stream of industrial grade nitrogen, supplied from a separate cylinder (**Figure 3**), to force the acrolein through a metering device. The nitrogen is also intended to minimize the presence of oxygen since oxygen will degrade the hydroquinone stabilizer co-formulated with acrolein to limit its polymerization. Acrolein is distributed below the surface of the water through a 15-m (50-ft) injection hose using nitrogen pressure settings ranging from 6 to 60 psig.

MAGNACIDE® H is registered for use in 15 states in the Great Plains or West: Arizona, California, Colorado, Idaho, Kansas, Montana, Nebraska, Nevada, New Mexico, North Dakota, Oregon, South Dakota, Utah, Washington, and Wyoming. The registrant, Baker Petrolite Corporation, has provided information on how acrolein is used in all these states except Kansas (MRID 46976913). The maximum single application rate used during the year at each irrigation system is most often 8 ppm but applications at 15 ppm commonly occur (reported in at least one irrigation district in 9 of 15 of these states). The number of applications in each irrigation system varied from 1 to 20 with 4 to 6 applications being used most commonly. Application intervals as short as 7 days are reported but 14 to 21 days are more typical. In some irrigation systems applications are more frequent but at lower concentrations required to control the lower weed density (some users refer to this as "chemical mowing"[8]). In California, the state with the most irrigation systems that reported use, the most common number of applications is two. Reported treatment durations ranged from 1 to 12 hours with 4 hours being the common application duration.

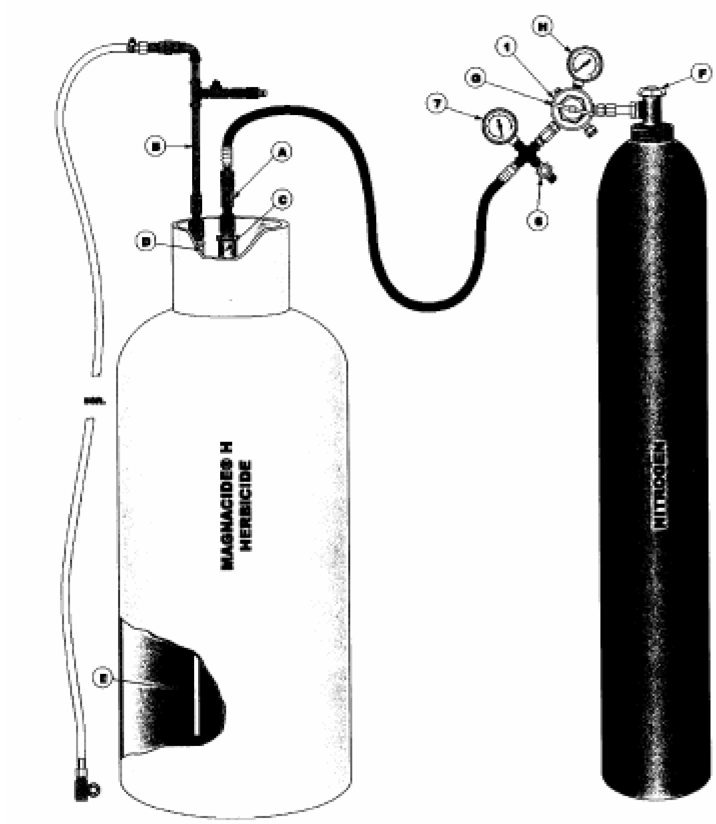


Figure 3 Pressurized MAGNACIDE H canister and Delivery Tubing along with Compressed Nitrogen Cylinder.

3.2 Non-herbicidal Uses

Acrolein is also used and produced by industry for non-herbicidal purposes. Information on industrial disposal and/or releases of acrolein was obtained from the Toxics Release Inventory

[8] Personal communication, Hugh MacEachen, Columbia Basin Irrigation District, January 2007

(http://www.epa.gov/tri/). The Toxics Release Inventory (TRI) is a publicly available EPA database that contains information on toxic chemical releases and other waste management activities reported annually by certain covered industry groups as well as federal facilities. This inventory was established under the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) and expanded by the Pollution Prevention Act of 1990. Inventory data were analyzed using the Statistical Analysis System (SAS Institute, Release 8.02, Cary, NC); output from the analysis is in **Appendix B**. **Figure 4** depicts TRI data from 1988 through 2004 and indicates that the lowest reported total annual disposal/release occurred in 1989 (88,042 lbs). Annual disposals/releases increased annually thereafter until it peaked at 545,452 lbs in 2001 after which time reported disposals/releases declined. In 2004, a total of 284,480 lbs were released. Across all seventeen years, Texas released the highest amount (2,512,765 lbs) representing 58% of the total followed by Mississippi with 459,709 lbs representing roughly 11% of the total. North Carolina (247,398 lbs), Georgia (194,026 lbs), Minnesota (180,093 lbs) and Illinois (168,815 lbs) accounted for 5.7%, 4.5%, 4.2%, and 3.9% and of the total, respectively. Therefore, these 6 Midwestern states accounted for 87% of the reported industrial acrolein disposals/releases in the TRI. Industrial disposal/release of acrolein in western states where acrolein is used as a herbicide, accounted for less than 1% of the total industrial release of acrolein during the seventeen year reporting period.

Within states where acrolein is used as an herbicide and where there are also data on industrial releases (California, Oregon, Kansas and Nebraska), industrial releases have fluctuated from 2002 to 2004 (**Figure 5**). The states with the least amount of industrial releases have been California and Oregon

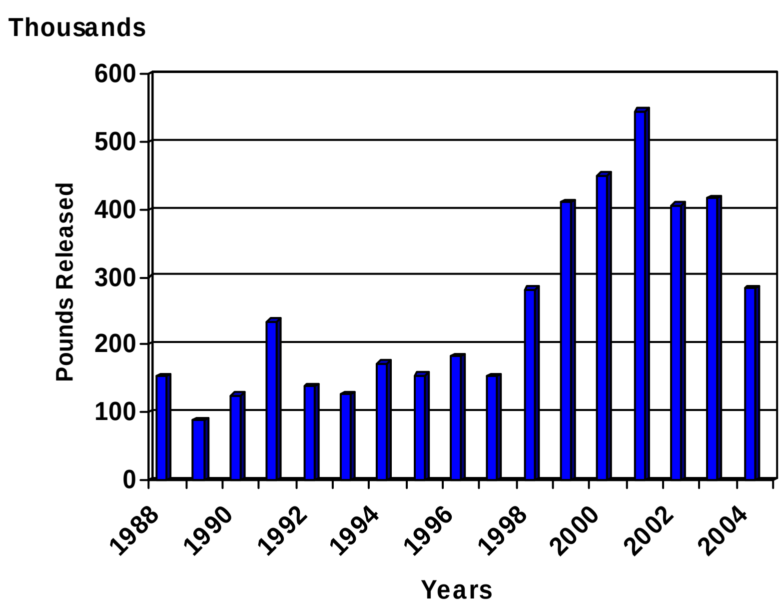


Figure 4 Total annual industrial release of acrolein reported in the Toxic Release Inventory 1988 - 2004.

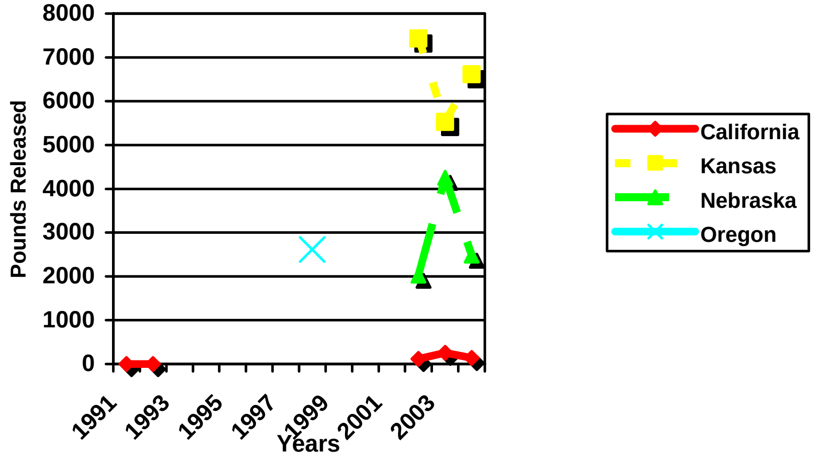


Figure 5. Industrial releases of acrolein by year in California, Kansas, Nebraska and Oregon based on Toxic Release Inventory.

4 Environmental Fate Characterization

The environmental fate of acrolein, or 2-propenal, is not well described based on current environmental fate data. Available data (**Table 5**) indicate potential for acrolein to reach natural surface water bodies which receive water from discharge water from irrigation canals. Volatilization, microbial metabolism, and possibly binding into plant material, are potential major routes of dissipation but it is not clear which of these routes may dominate in the environment and under what conditions.

No data are currently available to substantiate that binding into the plant material could be a route of dissipation for acrolein. However, acrolein's pesticidal mode of action involves cross-linking biological macromolecules, through interaction with sulfhydryl groups (Ghilarducci and Tjeerdema, 1995), *i.e.* the amino acid cysteine in proteins, and may also interact with nucleic acids. This cross-linking should 'use up' the acrolein as it kills plants and algae in the irrigation canal. This notion is at least somewhat supported in that the label recommends higher use rates for greater weed densities in the treated canals. At this time, however, the nature and extent of this route is highly uncertain and speculative in nature. Note that this 'cross-linking' is different from the surface absorption which is usually described in fate assessments for pesticides. Cross-linking involves the formation of covalent bonds between acrolein and the plant proteins and is essentially not reversible, whereas surface adsorption involves van der Waals binding as is fully reversible.

Acrolein is a highly reactive molecule. It must be stabilized with hydroquinone, or it will exothermically self-polymerize in the presence of air and ultra-violet light, or temperatures higher than 150ºC (Ghilarducci and Tjeerdema, 1985). Acrolein is a liquid at 25 ºC but has a vapor pressure of 0.354 atm at the same temperature (Smith 1962), and will rapidly volatilize if not kept in a closed container (Ghilarducci and Tjeerdema, 1985). Acrolein is also very soluble in water, at 237.6 g/L at 25°C (MRID 40840602). This high solubility tends to mitigate the volatilization tendency somewhat, as indicated by the measured Henry's constant of 1.9×10^{-4} $atm \cdot m^3 mol^{-1}$ (MRID 47008401; Salma, 2001; Smith, 1962).

Acrolein does not follow ideal behavior, as the measured partial pressures are about twice what would be predicted from Raoult's Law. The Henry's Law constant (K_{Hen}) varies according to temperature according to the **Equation 1** where t is temperature in degrees Celsius. This suggests that acrolein may be undergoing a reversible dimerization reaction in aqueous solution. Acrolein does form a dimer through the addition of one acrolein across the double bond of a second forming 3,4-dihydro-2H-pyran-2-carboxaldehyde.

$$Eq.1 \quad K_{Hen} = 5.561 - 781(177 - t)$$

Following are brief descriptions of the available fate data and some of the available monitoring data which describe acrolein occurrence in the environment.

Table 5 Environmental fate properties of acrolein		
Parameter	**Value**	**Source**
Molecular Mass (g/mol)	56.06	Baker Hughes 2005
Vapor pressure (atm)	0.354 at 25°C	Smith, 1962
Henry's Law Constant (atm-m^3/mol)	1.93×10^{-4}	MRID 47008401
Solubility in water (g/L)	237.6	MRID 40840602
Log K_{ow}	0.98-1.10	Hansch and Leo 1995; MRID 40840604
pH 7 hydrolysis half-life (days)	1.55 @ pH 7.2	MRID 409454-01
Equilibrium Constant with 3-hydroxypropanal	10.4 ± 5.7 @ 25°C	MRID 409454-01

4.1 Abiotic Degradation

4.1.1 Hydrolysis

Acceptable data are available to characterize the hydrolysis of acrolein. Acrolein does not undergo hydrolytic degradation in aqueous solution, but rather goes into equilibrium with a hydration product, 3-hydroxypropanal, where water has added to the double bond (MRID 40945401). At 25°C, the equilibrium constant for this reaction is 10.4 ± 5.7 and appears to be independent of pH. The observed rate of reaction varies with pH, with half-lives of 92, 37, and 19 hours at pH values of 5.28, 7.19 and 8.92, respectively. Because the rate of reaction does not vary directly with the hydrogen ion concentration, it suggests that the hydration reaction proceeds by more than one mechanism. In natural waters, rates appear to be about an order of magnitude faster than in pure water indicating there are components in the natural water that catalyze the reaction.

4.1.2 Photolysis

No currently acceptable data are available to characterize the rate of photolysis for acrolein in water. This is a significant data gap in our understanding of the environmental fate properties of acrolein.

4.2 Biotic Degradation

4.2.1 Microbial Metabolism

Submitted data provide evidence that acrolein does indeed degrade by both aerobic and anaerobic metabolism. However, available studies were not sufficient to quantify degradation rates, although the parent has an observed DT_{50} of about one day. Both an aerobic aquatic (MRID 43227101) and anaerobic aquatic metabolism study (MRID 42949201) had evidence of both oxidation and reduction processes occurring in the test systems as oxidative and reductive degradates were produced. Degradates formed by oxidation include acrylic acid, propionic acid, oxalic acid and carbon dioxide. Allyl alcohol, a reduction product, was also seen in both studies. Both reduction and oxidation products can occur in these test systems as there is a redox gradient between the water column and the bottom sediment, with the water column generally being relatively more oxidized than the bottom sediment. The abiotic degradate 3-hydroxypropanal was identified as a minor degradate, as well as 3-hydroxypropionic acid, which probably formed by oxidation of the aldehyde. **Table 6** lists the degradates and the maximum percentage of the nominal parent concentrations by study type.

Table 6. Maximum percentage of the nominal concentration of degradates formed from acrolein by abiotic and metabolic degradation processes. The time after experiment initiation that maximum occurred is in parentheses.

Degradate	Hydrolysis	Aerobic Aquatic Metabolism	Anaerobic Aquatic Metabolism
Acrylic acid	--	19% (2 d)	38.0% (1 d)
Allyl alcohol	--	8% (0 d)	16.7% (1 d)
Propionic acid	--	20% (2 d)	63.5% (8 d)
Oxalic acid	--	2% (2 d)	49.3% (30 d)
Bicarbonate	--	39% (5 d)	89.3% (30 d)
3-hydroxypropanal	90.9% (all pH's)*	--	7.2% (1 d)
3-hydroxypropionic acid	--	9% (2 d)	3.6% (1 d)
Propanol	--	21% (1 d)	9.2% (1 d)
Glyceric acid	--	1% (5 d)	--

* estimated concentration at equilibrium

4.2.2 Adsorption/Desorption

No acceptable data are available for estimating desorption coefficient (K_d) values for acrolein. Qualitative information can be used from the metabolism studies and chemical properties of acrolein to identify the potential adsorption/desorption of acrolein. In the aerobic and anaerobic aquatic metabolism studies cited above, acrolein was not identified in the sediment of the test vessels. This suggests that acrolein does not partition into sediment to any significant extent. In addition, the very high solubility (237 g/L at 25°C) would indicate a very low tendency to absorb to sediment.

4.3 Monitoring Data

MAGNACIDE Monitoring Program for the State of Nebraska (MRID 46976905). This study was conducted in 8 canals in five irrigation districts in Nebraska in 1982. Chemical analysis was made both with the colorimetric dinitrophenylhydrazine (DNPH) and a polarographic procedure. Applications of between 0.5 and 5 mg/L of acrolein were made to irrigation canals and the pesticide was monitored downstream to the discharge point from the irrigation canal.

Dissipation half-lives were estimated for this study based on the peak concentration in the plume as it moved downstream, by identifying the maximum concentration measured at each site, and noting the time after the start of application that this concentration occurred. The DT_{50} was then estimated from these values using linear regression on log-transformed data and assuming a first-order dissipation model. In some cases, two applications were made to the canal with the second application made downstream of the first application. For some irrigation systems, this made it difficult to interpret the data because the pulses from the two applications overlapped to some extent. Half-lives were estimated for seven of the eight canals and ranged from 2 to 9.8 h.

In five of the eight canals, acrolein was found in measurable concentrations just upstream from the discharge of the irrigation system. In the 2832 lateral of the Farmer's Irrigation District, the concentration of acrolein near the discharge from the canal was 1150 µg/L and was diluted to 20 µg/L in the receiving water body, the Nine Mile Canal. In the Meeker Canals of the Frenchman-Cambridge Irrigation District, acrolein was found at 230 µg/L at 27 h after application and after traveling 31 mi. In the Red Willow Canal of the Frenchman-Cambridge Irrigation District, the drain discharges to a dry creek which is a tributary to the Republican River. Discharge from the canal, containing up to 410 µg/L of acrolein could potentially then travel undiluted to the river, although no measurements were made beyond the discharge point from the canal (**Table 7**).

In a companion study, reported with the Nebraska monitoring data, acrolein dissipated below the detection limit of 10 µg/L during transit across a 0.15-mi long irrigation ditch in a bean field. As a result of this study, the registrant recommended diversion of irrigation water into holding ponds or onto irrigated crops to avoid discharge of irrigation water containing acrolein. Note that while the current labels recommend, 6-day or 2-day holding times (SLN labels), depending on the State, the label states that water treated must be used for irrigation of fields or held, although it does not indicate how the water is to be held.

Table 7 Acrolein movement in Nebraska irrigation canals. Canals marked with an asterisk had detectable concentrations at the drainage point from the canal.					
Irrigation Canal	Nominal Application Concentration (µg/L)	Time for last Detection (hours)	Furthest Detected Distance from Application Site (mi)	Concentration at Furthest Detected Distance (µg/L)	Dissipation Half-life† (hours)
Red Willow*	2400	23	15	410	9.8
Meeker*	2400	27	31	230	**
Franklin Main	1900	12	16	700	2.8
Farwell*	4000	27	11	310	6.6
Bone Lateral	500	8	7.3	170	3.9
Airport Lateral	500	7	6.2	34	2.0
2165 Lateral*	3200	8	6.5	54	3.8
2832 Lateral*	4900	5	3	1150	5.2

* Sites marked with an asterisk had acrolein measured at the discharge point of the irrigation canal.

** Dissipation occurred but rate half-life could not be estimated.

† Dissipation half lives were estimated by using the peak concentrations and occurrence time at each sampling site as the pulse of acrolein moved downstream.

Washington State Monitoring Program (MRID 47008404). The primary purpose of this study was "to provide data to substantiate the viability of a lower, more realistic holding restriction for treated water in the state of Washington." The study was conducted from June 24, to July 10, 1986. Seven applications were made to four canals, East Low Canal, Potholes East Canal, Roza Main Canal, and Town Ditch Canal with a similar protocol to that used for the Nebraska study (MRID 46976905). Of the seven applications to these four sites, four could be resolved into separate plumes traveling downstream. A dissipation half-life could not be calculated from one of these four because of an unspecified volume of dilution from irrigation return flow entering the canal between the application zone and the irrigation canal discharge. Application rates ranged from 1 to 3 mg/L. When dissipation half-lives could be estimated they were, in general, somewhat longer than in Nebraska but still less than 1 d, ranging from 12 to 19 h (**Table 8**). In all cases measurable concentrations of acrolein were found in the discharge from the canals.

Acrolein was found in the Scootenay Wasteway at 50 µg/L, one-half mile below the end of the East Low Canal and 61 miles from the application site, but had dissipated below the detection limit 3.5 mi downstream before discharging into the Scootenay Reservoir. Water containing acrolein from the Potholes East Canal containing 0.36 µg/L acrolein was found in a stilling pond at 0.28 µg/L after first passing through the P.E.C. 66 Power Plant. It was not, however, found in the Columbia River, 100 ft downstream from the pond. The Roza Main Canal had different discharge points for the first and second applications (Coral Creek, 22.8 mi downstream from application site) and third applications (Sulphur Creek, 17.8 mi downstream from application site). Both of these creeks were monitored just above their confluence with the Yakima River, and in neither case was there detectable acrolein. The Town Ditch drains into the Badger Wasteway which was monitored 0.5 mi from where Town Ditch enters, and also it had no detectable acrolein.

In a companion study, irrigation water from the East Low Canal containing 1.2 mg/L acrolein was diverted down a 0.2 mi long furrow. The acrolein concentration decreased to 0.25

µg/L at the end of the furrow. Irrigation water at the same concentration from the Potholes East Canals diverted through a furrow in an onion field dropped to 0.52 µg/L after traveling 0.1 miles down the furrow. Baker Performance Chemicals concluded in their report that "if irrigation districts are unable to pond treated water for the required holding time, then diverting the wave of treated water onto irrigated crops near the wasteways can be viewed as a reasonable alternative. If no weed or algae control is desired near the wasteway, the districts can also move their applications further upstream in the canals."

Table 8. Acrolein movement in Washington irrigation canals. Canals marked with an asterisk had detectable concentrations at the drainage point from the canal.

Irrigation Canal	Nominal Application Concentration (µg/L)	Time for last Detection (h)	Furthest Detectioni Distance from Application Site (mi)	Concentration at Furthest Detected Distance Site (µg/L)	Dissipation Half-life (h)
East Low*	1500	23	61	50 †	19.9
Potholes East, 1st application*	1500	26	35	410 ††	12.2
Potholes East, 2nd application*	1600	5	21	280 ††	**
Roza Main, app 1 *	770	27	64	80	13.6
Roza Main, app 2*	980	24	23	80	***
Roza Main, app 3 *	990	7	18	160	**
Town Ditch*	3000	26	20	20	‡

*Sites marked with an asterisk had acrolein measured at the discharge point of the irrigation canal
** Dissipation occurred but rate half-life could be estimated from data set.
*** Application overlapped 1st application, and dissipation rate could not be estimated
† Concentration is the receiving water body just past the discharge from the canal.
†† Last measured values was in a stilling pond 1 mi downstream from the discharge of the canal into the PEC 66 Power Plant, just above the Columbia River.
‡ Dissipation estimate could not be made due to dilution from incoming return flow

Washington Department of Agriculture, 2004. Data were provided to OPP by Washington State Department of Agriculture for 2004 NPDES monitoring of applications of acrolein to irrigation canals in 3 irrigation districts in the state. Ancillary data on application locations and collection and analytical methods have been received but could not be reviewed in time to be considered in this document. Consequently, these data only provide supplemental information on the occurrence of acrolein in irrigation systems; however, these monitoring data are useful for characterizing applications of acrolein to irrigation canals in Washington State (**Table 9**). Samples were taken at the point of compliance (POC) which is a sampling point near but not necessarily at the point of discharge from the canal. The POC is the location at which sampling is done for NPDES permit compliance sampling and "are at 'natural waters' where surface water courses existed prior to the alteration of water drainage and creation of reclamation and irrigation projects (State of Washington, Department of Ecology, 2002). In practice, the POC may be some distance upstream from the actual drainage point because of constraints of accessibility.[9] Sampling data that were provided indicate that many of the application events in 2004 resulted in non-detections of acrolein at the POC (data not shown); however, at locations where detections did occur at the POC, acrolein was detected at levels exceeding the state's NPDES permit level of 21 µg/L. The data indicate that acrolein moved many miles (>65 miles) downstream in irrigation canals and still exceeded 21 µg/L for periods of time greater than 48 hours after upstream applications of acrolein. For applications of acrolein in Washington State, a 48 hour holding period is required for treated waters before reaching receiving water bodies outside the irrigation system.

Kern County Water Storage District (MRID 47008403*).* Irrigation water containing the full treatment rate of acrolein was used to irrigate two fields: a vineyard (by furrow irrigation) and an alfalfa field (by flood irrigation). Samples were analyzed using differential pulse polarography (DPP) from the initial time of application until the point of dissipation across the irrigated field. DPP as utilized by Baker Petrolite differentiates between active acrolein and its degradates down to the parts per billion level. An initial concentration of 10.8 mg/L in the vineyard had dissipated below the detection limit after transport 600 ft down the furrow, 2 hrs after the irrigation water was applied. In the alfalfa field, an initial mean concentration of 4.0 mg/L was below the detection limit 400 ft away from the application point about 2 hrs after the termination of application. The detection limit was reported as 10 µg/L; however, no values less than 100 µg/L are reported in the study and the lowest calibration standard was 1 mg/L, so the reported detection limit in this study is questionable. The authors' conclusion was "The above data supports the premise that irrigating dry fields is a viable means of dissipating MAGNACIDE H when it is not possible to contain the treated water within the system for six days."

Air Monitoring, Kern Delta Irrigation District (MRID 47008407). An air monitoring study was conducted in 2005 associated with an application to the Kern Island Canal in the Kern Delta Water District in California in August, 2005. This data can be used to estimate exposure via inhalation. The application of 3.9 ppm was started at 7:30 in the morning and continued for 4 hours. Six air monitoring stations were set up on both banks, four on the windward side and 2 on the downwind side of the canal, within 150 ft of the injection point. A control air monitoring site was placed upstream and upwind of the application site. Analytical methods for the air samples were not reported. Air samples were also collected concurrently by the California Air Resources Board; the results from these samples were not available. The upwind samples on the upwind bank ranged from 28 to 36 $\mu g/m^3$ the values increasing with distance downstream from the application point. The downwind samples were 92 and 120 $\mu g\ m^3$ with the lower value parallel to the application point and the higher value 52 feet downstream. Because concentrations were still rising with distance downstream, it is conceivable that higher air concentration would have been seen further downstream. This would be supported by concurrent measurements of the concentration in the treated canal where concentrations increased from the application point to at least 867 feet downstream, the furthest downstream measurements were made in water. This apparent increase is likely do to incomplete mixing of acrolein in the canal.

---

[9] Personal communication, Wendy Sue Wheeler, Washington State, Department of Ecology, December, 2005.

Table 9. Occurrence of acrolein at the point of application (POA) and the point of compliance (POC) of irrigation systems sampled by the Washington Department of Agriculture.					
Description of Location	**Acrolein conc. (µg/L) at POA**	**Distance between POA and POC (miles)**	**Duration of Application (hours)**	**Time between app. and sampling at POC (h)**	**Acrolein Conc. (µg/L) at POC**
Quincy (3 Gates)	650	64.3	8	53	1.0
South (Esquatzel Wasteway)	2600	13.6	6	14	1.0
South (Wahluke Branch 5 Wasteway 1)	3900	14.8	4	23	1.1
Quincy (5th Section Canal)	790	68.1	8	53	1.5
Quincy (5th Section Canal)	2850	26.1	1.8	54	1.5
South (Esquatzel Wasteway)	2600	7.0	3	9	2.2
Quincy (78-8)	790	67.1	8	56	2.4
Quincy (78-8)	2620	24.6	6	33	2.4
Quincy (3 Gates)	790	64.3	8	52.9	2.9
South (Potholes East 16.4 Wasteway)	5200	12.8	3	31	3.1
South (Esquatzel Wasteway)	2600	7.0	3	11	5.6
Quincy (78-8)	790	67.1	8	53	8.3
South (Potholes East 16.4 Wasteway)	3600	19.6	4	24	9.3
South (Wahluke Branch 5 Wasteway 1)	3900	7.7	4	13	12.1
South (Esquatzel Wasteway)	2600	2.6	3	18	14.6
South (Esquatzel Wasteway)	2600	2.6	3	20	15.0
Quincy (5th Section Canal)	2620	26.1	3	10	21.7
Quincy (5th Section Canal)	790	68.1	8	56	23.2
Quincy (W61L lateral)	790	66.1	8	52	23.5
Quincy (Farm Unit 88)	2620	17.9	6	26	29.2
South (Potholes East 16.4 Wasteway)	3600	19.6	4	26	36.1
South (Wahluke Branch 5 Wasteway 1)	3900	7.7	4	15	62.5
Quincy (5th Section Canal)	650	68.1	8	54	67.2
Quincy (3 Gates)	2620	14.9	3	16	117
South (Wahluke Branch 5 Wasteway 1)	5200	9.1	3	18	225
South (Wahluke Branch 5 Wasteway 1)	5200	13.4	3	23	254

4.4 Terrestrial Exposure Assessment

The estimated environmental concentration (EEC) values for residues on food and feed items used for terrestrial exposure are derived from the Kenaga nomograph, as modified by Fletcher *et al.* (1994), based on a large set of actual field residue data. The upper limit values from the nomograph represent the 95th percentile of residue values from actual field measurements (Hoerger and Kenaga, 1972). The Fletcher *et al.* (1994) modifications to the Kenaga nomograph are based on measured field residues from 249 published research papers, including information on 118 species of plants, 121 pesticides, and 17 chemical classes. These modifications represent the 95^{th} percentile of the expanded data set. Risk quotients are based on the most sensitive LC_{50} and NOAEC for birds (in this instance, bobwhite quail) and LD_{50} for mammals (based on lab rat studies).

In order to estimate risks resulting from acrolein treated irrigation waters to terrestrial mammals and birds inhabiting and eating in irrigated fields, it is necessary to calculate the application rate of acrolein to a field in units of lbs a.i./A. This calculation requires conversion from the concentration of acrolein in irrigation water (mg/L) to the amount of acrolein that could potentially remain on the foliage after an irrigation event. Note that this method is relevant when sprinkler irrigation is used so that the irrigation water is applied to the foliage. Dietary exposure (other than drinking water) should not be a concern for flood or furrow irrigation as there is little contact of the irrigation water with the above ground foliage. In order to accomplish this estimate, a measure of the amount of irrigation water that sticks to the crop is required. CINTCP is a parameter used in the Pesticide Root Zone Model (PRZM) that defines the maximum interception storage of a crop. This parameter estimates the amount of rainfall (in cm) that is intercepted by a fully developed plant canopy and retained on the plant surface. CINTCP values for crops with light, moderate and maximum canopy densities are listed in table 5-4 of the PRZM manual (0.0-0.15 cm). The CINTCP for orchard is estimated as a conservative value of 0.40 cm. To calculate the volume (cm3) of irrigation water sticking to the foliage the area of a unit field, 1 ha or 1 x 10^{-9} cm^2) is multiplied by the CINTCP value (cm). The result is then converted into units of L. The volume of irrigation water sticking to the crop on a 1 ha field is then multiplied by the concentration of acrolein in the irrigation water (mg/L).This results in an estimate of the mass of acrolein (mg) applied to a 1 ha field. The units of mg/ha are converted to lbs/A. In order to provide conservative estimates of risk, the CINTCP value for orchards was utilized to estimate exposures to terrestrial mammals and birds consuming food in fields receiving irrigation water containing various concentrations of acrolein (see **Appendix D** for calculations).

4.4.1 Foliar Dissipation Half-life

In the absence of data, OPP relies on a default foliar dissipation half-life of 35 days to estimate potential residues on terrestrial animal forage items. However, given the volatility and reactivity of acrolein, the default value of 35 days is not reasonable. Given the uncertainties due to the single study and the quality of that study, a 1-day foliar dissipation half-life is used. While rates of acrolein dissipation on foliage cannot be quantified at this time, given the rates of dissipation seen in the field studies and the laboratory metabolism studies. It is expected that this value will be conservative relative to the usual rate of foliar dissipation of acrolein in the environment.

4.4.2 Terrestrial Estimated Environmental Concentrations

Terrestrial upper-bound and mean EECs (**Tables 10 and 11, respectively**) were derived for a generic crop using the equivalent single application rate, calculated according to the method described in section 4.4 above (using CINTCP). Uncertainties in the terrestrial EECs are typically associated with a lack of data on interception and subsequent dissipation from foliar surfaces.

Table 10. T-REX calculated upper-bound EECs for food residues irrigated with water containing acrolein. Application rate of 5.35 lbs a.i./A was used, corresponding to 15 mg/L acrolein in water.

Food Type	Dietary Based (ppm) (mammals and birds)	Dose Based (mg/kg-bw) (mammals)			Dose Based (mg/kg-bw) (birds)		
	All Size Classes	Small (15 g)	Medium (35 g)	Large (1000 g)	Small (15 g)	Medium (35 g)	Large (1000 g)
Short Grass	1284.0	1224.20	846.08	196.17	1462.35	833.89	373.34
Tall Grass	588.5	561.09	387.79	89.91	670.24	382.20	171.12
Broadleafplants/sm insects	722.25	688.61	475.92	110.34	822.57	469.06	210.01
Fruits/pods/lg insects	80.25	76.51	52.88	12.26	91.40	52.12	23.33
Seeds (granivore)	80.25	17.00	11.75	2.72	91.40	52.12	23.33

Table 11. T-REX calculated mean EECs for food residues irrigated with water containing acrolein. Application rate of 5.35 lbs a.i./A was used corresponding to 15 mg/L acrolein in water.

Food Type	Dietary Based (ppm) (mammals and birds)	Dose Based (mg/kg-bw) (mammals)			Dose Based (mg/kg-bw) (birds)		
	All Size Classes	Small (15 g)	Medium (35 g)	Large (1000 g)	Small (15 g)	Medium (35 g)	Large (1000 g)
Short Grass	454.75	432.01	300.14	68.21	518.42	295.59	131.88
Tall Grass	192.60	182.97	127.12	28.89	219.56	125.19	55.85
Broadleafplants/sm insects	240.75	228.71	158.90	36.11	274.46	156.49	69.82
Fruits/pods/lg insects	37.45	35.58	24.72	5.62	42.69	24.34	10.86
Seeds (granivore)	37.45	7.86	5.62	1.12	42.69	24.34	10.86

4.4.3 Estimated Environmental Concentrations for Inhalation

Because acrolein is volatile and because inhalation toxicity data are available for mammals, estimates have been made for acrolein concentration in air. Concentrations of acrolein in air are estimated by two methods. First, field study data are available where acrolein has been measured in the air immediately surrounding a treated canal, at and just downstream from the application point (MRID 47008407) where acrolein was maintained in the canal water at 3.99 mg/L. The highest measured value in the air was 120 $\mu g \cdot m^{-3}$ which is equal to 1.2×10^{-4} $mg \cdot L^{-1}$. Alternatively an upper-bound estimate on the air concentration can be made by assuming that the air over the sides of the canal is in equilibrium with the canal water. The Henry's Law Constant (1.95×10^{-4} atm·m^3·mol^{-1}) can then be used to estimate the concentration in the air over the water. Using the maximum treatment concentration of 15 mg/L in the canal water, the corresponding air concentration would be 118 mg·m^{-3} which is equivalent to 1.18×10^{-1} mg·L^{-1}. The results of the second method are approximately a factor of 1000 greater than that measured in the air during the field study.

These concentrations were used to calculate vapor inhalation doses (VID) for four organisms, a rat, a mallard duck, a ring-bill gull, and a songbird (**Table 12**) according to the method outlined in Sunzenauer *et al.,* 2004. The justification for the selection of these four species is in the Section 6.3.1 and 6.3.2 of this document. The VID was calculated for each species as follows. First, a respiration rate in liters per minute (l·min^{-1}) was estimated using allometric equations relating the respiration rate to body weights for mammals and birds (Equations are footnoted in **Table 12**.) These rates are multiplied by three to approximate the field respiration rate. The respiration rates are then multiplied by an exposure duration of 4 hours (240 min) to estimate the V_{inh}, the volume of air inhaled during the exposure event. Four hours was the duration of application in the field study discussed earlier and the most common application event duration. Air concentration, C_{air} in mg/L was then multiplied by the inhaled volume V_{inh} in liters and divided by the body weight in kg to calculate VID in mg/kg.

Table 12. Calculated Vapor Inhalation Doses (VID)for a mammal and three birds.

Species	body weight (kg)	respiration rate[1](l·min^{-1})	inhaled volume[2] (l)	lower bound VID[3] (mg·kg^{-1})	upper bound VID (mg·kg^{-1})
Rat	0.350	0.491	118	4.04×10^{-2}	3.97×10^{1}
Mallard	1.580	1.21	291	2.21×10^{-2}	2.17×10^{1}
Gull	0.350	0.380	91.1	3.12×10^{-2}	3.07×10^{1}
Songbird	0.020	0.0419	10.1	6.03×10^{-2}	5.93×10^{1}

1) $R_{rate} = 284(BW)^{0.77}x3/1000$ (birds); $R_{rate} = 379(BW)^{0.80}x3/1000$ (mammals)
2) $V_{inh} = R_{rate}$ x ED; ED = exposure duration of 240 m (4 h)
3) VID = C_{air}*V_{inh}/BW; lower bound $C_{air} = 1.2 \times 10^{-4}$ mg·L^{-1}; upper bound $C_{air} = 1.18 \times 10^{-1}$ mg·L^{-1};

5 Ecological Effects Characterization

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

5.1 Categories of Acute Toxicity

In general, acute toxicity categories for acrolein ranging from "practically nontoxic" to "very highly toxic" have been established for aquatic organisms based on LC_{50} values (**Table 13**), terrestrial organisms based on LD_{50} values (**Table 14**), and avian species based on LD_{50} values (**Table 15**). Subacute dietary toxicity for avian species is based on the LC_{50} values (**Table 16**).

Table 13. Categories for aquatic animal acute toxicity based on median lethal concentration in milligrams per liter (parts per million).

LC_{50} (mg a.i./L)	Toxicity Category
<0.1	Very highly toxic
0.1–1	Highly toxic
>1–10	Moderately toxic
>10–100	Slightly toxic
>100	Practically non-toxic

Table 14. Categories for mammalian acute toxicity based on median lethal dose in milligrams per kilogram body weight (parts per million).

LD_{50} (mg a.i./kg)	Toxicity Category
<10	Very highly toxic
10–50	Highly toxic
51–500	Moderately toxic
501–2000	Slightly toxic
>2000	Practically non-toxic

Table 15. Categories of avian acute oral toxicity based on median lethal dose in milligrams per kilogram body weight (parts per million).	
LD_{50} (mg a.i./kg)	**Toxicity Category**
<10	Very highly toxic
10-50	Highly toxic
51-500	Moderately toxic
501-2000	Slightly toxic
>2000	Practically non-toxic

Table 16. Categories of avian subacute dietary toxicity based on median lethal concentration in milligrams per kilogram diet per day (parts per million).	
LC_{50} (mg a.i./kg)	**Toxicity Category**
<50	Very highly toxic
50–500	Highly toxic
501–1000	Moderately toxic
1001–5000	Slightly toxic
>5000	Practically non-toxic

Data defining the toxicity of acrolein to aquatic and terrestrial organisms were obtained from registrant submitted studies, studies conducted by EPA and other government agencies, and from open literature studies identified through an ECOTOX[10] literature search. The ECOTOXicology database (ECOTOX) is a source for locating single chemical toxicity data for aquatic life, terrestrial plants and wildlife. ECOTOX was created and is maintained by the U.S.EPA, Office of Research and Development (ORD) , and the National Health and Environmental Effects Research Laboratory's (NHEERL's) Mid-Continent Ecology Division (MED). ECOTOX is a unique web system which includes toxicity data derived predominately from the peer-reviewed literature, for aquatic life, terrestrial plants, and terrestrial wildlife, respectively.

In cases where literature studies yielded lower values (*i.e.* more conservative) than values in studies submitted by the registrant, literature data were used to supplement data available for defining the toxicity of acrolein. For consistency and clarity, organisms are referred to by their common names within this document. For scientific names corresponding to the common names referenced in this document, refer to **Tables 17 – 20**.

10 *Ibid* U.S. Office of Research and Development

5.2 Aquatic Effects Characterization

5.2.1 Acute Effects to Animals

Toxicity data are available to describe the acute toxicity of acrolein to freshwater fish, aquatic-phase amphibians and aquatic invertebrates as well as estuarine/marine fish and invertebrates (**Table 17**). The Office of Pesticide Programs has worked closely with the Office of Water to identify and analyze available toxicity data on acrolein in order to establish the most sensitive organism for ecological risk assessment in support of the reregistration eligibility decision on acrolein under FIFRA and in the development of Aquatic Life Criteria under the Clean Water Act. Based on available data acrolein is classified as very highly toxic to freshwater fish and invertebrates and estuarine/marine invertebrates and is highly toxic to estuarine/marine fish on an acute exposure basis

There are several 96-h LC_{50} values available from submitted data, EPA studies and from the open literature (identified in ECOTOX) to describe the acute toxicity of acrolein to freshwater fish and amphibians. The most conservative value identified to describe the toxicity of acrolein to freshwater vertebrates is a 96-h LC_{50} of 7 µg a.i./L for larval African clawed frog (*Xenopus laevis)* (Holcombe *et al.* 1987). Supplemental data submitted by the registrant using guideline test species indicate that the 96-hr LC_{50} of acrolein (96.4% a.i.) to bluegill sunfish (*Lepomis macrochirus)*, and rainbow trout (*Oncorhynchus mykiss)*, under flow-through is 22.4 and <31 µg a.i./L, respectively (MRIDs 415132-01 and 415132-03). The most sensitive endpoint used to assess the acute toxicity of acrolein to freshwater fish is the 96-hr LC_{50} for fathead minnow (*Pimephales promelas)*, of 14 µg a.i./L (Geiger *et al*. 1990; Holcombe *et al*. 1987); for aquatic-phase amphibians, the most sensitive endpoint is the African clawed frog 96-h LC_{50} of 7 µg a.i./L.

Acute toxicity data for freshwater invertebrates are available for waterflea (*Daphnia magna)*; the 48 hour EC_{50} values for immobilization are <31 and 57 µg a.i./L, based on two submitted studies. Additional values describing the acute toxicity acrolein to freshwater invertebrates (e.g. midge) were identified in the ECOTOX literature search; however, these values were greater, *i.e*., less sensitive, than those submitted by the registrant. The most sensitive endpoint used to assess the acute toxicity of acrolein to freshwater invertebrates is (<) 31 µg a.i./L.

Acute toxicity data on acrolein for estuarine/marine fish are available for longnose killifish (*Fundulus similis)*, and sheepshead minnow (*Cyprinodon variegates)*. The results of an EPA study indicated that the 48-h LC_{50} value for longnose killifish is 240 µg a.i./L; the 96-h LC_{50} for sheepshead minnow is 428 µg a.i./L. Therefore, the most sensitive endpoint used to assess the acute toxicity of acrolein to estuarine/marine fish is the 48-hr LC_{50} value for longnose killifish.

Acute toxicity data for estuarine/marine invertebrates are available for Eastern oyster (*Crassostrea virginica)*, brown shrimp (*Penaeus aztecus)*, and mysid shrimp (*Americamysis bahia)*. The reported 96-h EC_{50} values for Eastern oyster are 55 and 106 µg a.i./L. Data available for brown and mysid shrimp are 48-h EC_{50} of 100 µg a.i./L, and a 96-h L C_{50} of 500 µg a.i./L, respectively. The most sensitive endpoint used to assess the acute toxicity of acrolein to estuarine/marine invertebrates is 55 µg a.i./L.

Table 17. Summary of submitted ACUTE toxicity data for aquatic animals exposed to acrolein. ECOTOX literature search identified data which are more conservative than registrant submitted data. These data are also included in this table. Additional acute toxicity data are available; however, data which were greater than submitted data (or data with MRID numbers) were not included in this table.

Species (common name)	Measure of Effect	End-point	Duration (hours)	Mean concentration, units in µg a.i./L (95% c.i.)	Test substance (% a.i.)	Study Classification	Ref. (MRID)
Freshwater Fish and Amphibians							
Xenopus laevis (African clawed frog)	Mortality	LC_{50}	96	7 (6-8)	N/A	Supplemental	Holcombe *et al.* 1987*
Pimephales promelas (fathead minnow)	Mortality	LC_{50}	96	14 (8-25)	N/A	Supplemental	Holcombe *et al.* 1987*
Pimephales promelas (fathead minnow)	Mortality	LC_{50}	96	14	97		Geiger *et al*. 1990*
Catostomus commersoni (white sucker)	Mortality	LC_{50}	96	14 (8-25)	N/A	Supplemental	Holcombe *et al.* 1987*
Oncorhynchus mykiss (Rainbow Trout)	Mortality	LC_{50}	96	16 (14-19)	N/A	Supplemental	Holcombe *et al.* 1987*
Pimephales promelas (fathead minnow)	Mortality	LC_{50}	96	19.5 (17.3-22.0)	>99	N/A	Geiger *et al.* 1988*
Lepomis macrochirus (Bluegill Sunfish)	Mortality	LC_{50}	96	22.4 (20.2-24.8)	96.4	Supplemental	415132-01
Rainbow Trout *Oncorhynchus mykiss*	Mortality	LC_{50}	96	<31	96.4	Supplemental	415132-03
Coho salmon *Oncorhynchus kisutch*	Mortality	LC_{50}	96	68	N/A	N/A	452051-07
Freshwater Invertebrates							
Water Flea *Daphnia magna*	Immobility	EC_{50}	48	<31	96.4	Supplemental	415132-02
Water Flea	Mortality	LC_{50}	48	57 (20-99)	99	Supplemental	05008271

Table 17. Summary of submitted ACUTE toxicity data for aquatic animals exposed to acrolein. ECOTOX literature search identified data which are more conservative than registrant submitted data. These data are also included in this table. Additional acute toxicity data are available; however, data which were greater than submitted data (or data with MRID numbers) were not included in this table.							
Species (common name)	**Measure of Effect**	**End-point**	**Duration (hours)**	**Mean concentration, units in µg a.i./L (95% c.i.)**	**Test substance (% a.i.)**	**Study Classification**	**Ref. (MRID)**
Estuarine/Marine Fish							
Longnose killifish *Fundulus similis*	Mortality	LC_{50}	48	240	100	Acceptable	402284-01
Sheepshead minnow *Cyprinodon variegatus*	Mortality	LC_{50}	96	428	94.7	Supplemental	432252-02
Estuarine/Marine Invertebrates							
Eastern oyster *Crassostrea virginica*	Shell Growth	EC_{50}	96	55	100	Acceptable	402284-01
Brown Shrimp *Penaeus aztecus*	Immobility	EC_{50}	48	100	100	Acceptable	402284-01
Eastern oyster *Crassostrea virginica*	Shell Deposition	EC_{50}	96	106 (73-183)	94.69	Supplemental	431643-02
Mysid shrimp *Americamysis bahia*	Mortality	LC_{50}	96	500 (390-650)	94.69	Supplemental	431643-01
* Data value identified in ECOTOX literature search.							

5.2.2 Chronic Effects to Animals

Chronic data are available on acrolein for the fathead minnow, flag fish (*Jordanella floridae),* and water flea. Data are available from an EPA fish lifecycle study on fathead minnow; the NOEC from this study is 11.4 µg a.i./L. Other toxicity data for fathead minnow indicate that the NOEC for growth and survival are 14 and 35 µg a.i./L, respectively. Additional data from chronic exposures of flag fish to acrolein indicate a NOEC for growth of 32 µg a.i./L. In an EPA study, three generations of waterflea were exposed to flow-through concentrations of acrolein for 3 weeks, yielding a NOEC for survival of 7.1 µg a.i./L (MRID 05008271) (**Table 18**). Therefore, the most sensitive endpoints used to assess the chronic toxicity of acrolein to freshwater vertebrates and invertebrates are NOEC values of 11.4 and 7.1 µg a.i./L, respectively.

No data are available to estimate the chronic toxicity of acrolein to estuarine/marine fish or invertebrates. These missing data represent data gaps that prevent the characterization of the chronic toxicity of acrolein to these aquatic animals.

TABLE 18. Summary of submitted chronic toxicity data for aquatic animals exposed to acrolein.							
Species (common name)	Measure of Effect	End-point	Duration (days)	Mean concen-tration (µg a.i./L)	Test substance (% a.i.)	Study Classifi-cation	Ref. (MRID)
Freshwater Fish							
Fathead minnow *Pimephales promelas*	Growth and reproduction	NOEC	32	9.1	N/A		Sabourin 1986*
Fathead Minnow	Survival of newly hatched fry	NOEC	60	11.4	99	Supplemental	05008271
Fathead Minnow	Survival	NOEC	32	14	97		Spehar 1989*
Flagfish *Jordanella floridae*	Survival and Growth	NOEC	32	16	97		Spehar 1989*
Freshwater Invertebrates							
Water Flea *Daphnia magna*	Survival	NOEC	3 generations	7.1	99	Supplemental	05008271
* Data value identified in ECOTOX literature search.							

5.2.3 Aquatic Plants (freshwater and estuarine/marine)

Acute toxicity data are available for four species of non-vascular plants (**Table 19**). Tier 2 toxicity tests using green algae (*Pseudokirchneriella subcapitatum*), blue-green algae (*Anabaena flos-aquae*), freshwater diatom (*Navicula pelliculosa*) and marine diatom (*Skeletonema costatum*) exposed separately to acrolein for 5 days (MRIDs 426209-01, 426209-02, 426209-03 and 426209-05). The most sensitive species tested is the marine diatom, which has an EC_{50} for reduction of cell density of 28 µg a.i./L

Acrolein toxicity data are available for a freshwater vascular plant, duckweed (**Table 19**; the NOEC is 25 µg a.i./L and the EC_{50} is 72 µg a.i./L .

Table 19. Summary of submitted toxicity data for aquatic plants exposed to acrolein.							
Species (common name)	**Measure of Effect**	**End-point**	**Duration (hours)**	**Mean concentration, units in µg a.i./L**	**Test substance (% a.i.)**	**Study Classification**	**Ref. (MRID)**
Marine Diatom *Skeletonema costatum*	Cell density	EC_{50}	120	28	95	Supplemental	42620903
		NOEC		25			
Blue-green Algae *Anabaena flos-aquae*	Cell density	EC_{50}	120	36	95	Acceptable	42620901
		NOEC		12			
Green Algae *Pseudokirchneriella subcapitatum*	Cell density	EC_{50}	120	44	95	Acceptable	42620905
		NOEC		25			
Freshwater Diatom *Navicula pelliculosa*	Cell density	EC_{50}	120	47	95	Acceptable	4260902
		NOEC		25			
Duckweed *Lemna gibba*	Frond number	EC_{50}	14 days	72	95	Supplemental	42620904
		NOEC		25			

5.3 Terrestrial Effects Characterization

5.3.1 Mammals

5.3.1.1 Acute toxicity

Acrolein is highly toxic to mammals on an acute oral exposure basis. The acute oral LD_{50} for male and female rats (*Rattus norvegicus*) is 10.3 and 11.8 mg/kg, respectively (**Table 20**). Sublethal signs of toxicity included lethargy, hypothermia, changes in respiration and weight loss.

Acrolein is also reported to be a skin/mucous membrane and eye (lacrimator) irritant. Although not typically considered in ecological risk assessments, the volatility of acrolein results in a potential mode of exposure. The inhalation LC_{50} for acrolein is 17 mg/m^3/4 hours rats, respectively. For assessment of the risks from inhalation from acrolein, this was converted to a dose based toxicity value. To estimate this value, first, the respiration rate for the rat was estimated. This used the same equation for respiration rate as was used to estimate the acrolein inhalation exposure in Section 4.4.3, except the factor of three for estimating the field respiration rate was omitted:

$$R_{rate} = 379(BW)^{0.80}x3/1000$$

In this equation, BW is the body weight, which is 0.350 kg for the rat. The resulting respiration rate is 0.164 L/min. Since the toxicity test was conducted for 4 h (240 min). The volume of air inhaled during the test was 39.3 L. Multiplying this volume by the concentration of acrolein maintained during the test and dividing by the body weight gives the acrolein inhalation LD_{50} : 2.02 mg·kg^{-1}.

5.3.1.2 Chronic toxicity

In a 2-generation reproduction study using rats, the LOAEL for acrolein parental toxicity is 6 mg/kg/day based on decreases in body weight and in food consumption as well as histological changes in the stomach, including edema, cysts, diverticulum of glandular mucosa, hemorrhage and ulcers. The NOAEL for parental toxicity is 3 mg/kg/day. The LOAEL for offspring toxicity is also 6 mg/kg/day based on body weight decrease in the F_1 generation. The NOAEL for offspring toxicity is 3 mg/kg/day (**Table 20**).

5.3.2 Birds

5.3.2.1 Acute Toxicity

Acrolein is very highly toxic (LD_{50} <10 mg/kg) to birds on an acute oral exposure basis (**Table 20**). Male mallard ducks (*Anas platyrhynchos*) dosed with 92% acrolein resulted in an LD_{50} of 9.1 mg/kg a.i. Observed sub-lethal effects included regurgitation, slow responses, ataxia, geotaxia, imbalance, phonation, wing tremors, running and falling, asthenia (weakness), myasthenia (muscular debility) and withdrawal. Sublethal effects were observed at 3.3 mg/kg treatment levels (TRID 4702140-75). Another acceptable study with mallard duck indicates that oral dosing with 95.09% acrolein resulted in a LD_{50} of 28 (18-38) mg a.i./kg-bw. Sublethal effects that were observed included: lethargy, stumbling, anorexia, high head holding, difficulty swallowing, wing-beat convulsions, dyspnea (labored breathing), and tremors. Gross necropsies of birds that died during the treatment period revealed hemorrhagic intestines and testes. Body weight and food consumption reductions were noted (MRID 421833-01). Data for a supplemental study of the oral toxicity of 92% acrolein to bobwhite quail resulted in a LD_{50} of 19 mg /kg (MRID 92001003). The most sensitive endpoint used to assess the acute oral toxicity of acrolein is 9.1 mg a.i./kg-bw.

Table 20. Summary of submitted toxicity data for terrestrial organisms exposed to acrolein.

Species (common name)	Measure of effect	End-point	Mean Concentration (C.I.)	Test Substance (% a.i.)	Study Classification	Reference (MRID)
Birds						
Mallard duck *Anas platyrhynchos*	Mortality	LD_{50}	9.11 mg a.i./kg (6.32-13.1)	92	Acceptable	(TRID) 470214075 117668
Bobwhite quail *Colinus virginianus*	Mortality	LD_{50}	19 mg/kg	92	Supplemental	92001003
Mallard duck *Anas platyrhynchos*	Mortality	LD_{50}	28 mg a.i./kg-bw (18-38)	95.09	Acceptable	421833-01
Mammals						
Laboratory rat *Rattus norvegicus*	Mortality	LD_{50}	Males: 10.3 (6.4-16.7) mg/kg Females: 11.8 (7.9-17.6) mg/kg	96.58	Acceptable	412570-01
	Parental and offspring effects (growth)	NOAEL	3 mg/kg/day	96.05-96.72	Acceptable	418691-01
		LOAEL	6 mg/kg/day			

In order to assess the risk to birds from inhalation, it is necessary to estimate the inhalation LD_{50} for acrolein from other data as no direct measurements of acrolein inhalation toxicity are available for birds. The strategy used is outlined in Sunzenauer *et al.* 2004. The strategy has four steps, as discussed in detail below: 1) estimate an oral LD_{50} for a 350 g bird from the available avian oral LD_{50} data, 2) estimate a factor (Q_a/Q_m) that accounts for differences in lung transfer efficiency for birds and mammals, 3) estimate the avian inhalation LD_{50} for a representative bird using Q_a/Q_m using the avian oral LD_{50} estimates and mammalian inhalation LD_{50} and oral LD_{50} data, and 4) estimate avian inhalation LD_{50}s for other avian species of interest.

This overall calculation uses the assumption that the ratio of oral LD_{50} to inhalation LD_{50} is the same for birds and mammals, but also makes an adjustment to account for differences in lung surface area and lung alveolar cell layer thickness between mammals and birds. In order to make this adjustment, it is necessary that the bird and mammal have the same body weight. The mammalian test species that has both oral and inhalation toxicity data is the Norway rat, which has a typical adult body weight of 350 g, so the calculation requires a 350-g bird. Ring-bill gulls are a common semi-aquatic species that would be found in the vicinity of irrigation canals where acrolein is used, and whose body weight ranges from 200 to 500 g, making it a suitable as the surrogate bird species for these calculations. The first step then is to estimate an oral toxicity dose for a 350 g ring-bill gull. The oral LD_{50}s for a ring-bill gull and a songbird were estimated from the using the equation:

$$LD_{50(\text{oral, A})} = LD_{50(\text{oral, mallard})} (BW_A/BW_{\text{mallard}})^{(1.15-1)}$$

where $LD_{50(\text{oral, A})}$ is the adjusted toxicity for the new species, $LD_{50(\text{oral, mallard})}$ is the measured LD_{50} for mallard ducks (9.1 $mg \cdot kg^{-1}$), BW_A is the body weight of the new species (*e.g.,* ring bill gull BW=0.35 kg), and BW_{mallard} is the body weight for the mallard (1.58 kg). The resulting oral LD_{50} for the ring-bill gull is 7.25 $mg \cdot kg^{-1}$.

The second step is to calculate a factor, Q_a/Q_m, which accounts for the differences in the rate that pesticides pass through lung tissue of avian species (Q_a) compared to mammalian species (Q_m). This method is based on the differences in lung surface area and lung tissue thickness, and is calculated for avian and mammalian species of the same body weight, as discussed above. In this case, that body weight is 350 g, which the typical mass of the Norway rat, and is the mammalian species for which there are inhalation toxicity data. The equations for bird lung surface area and thickness are

$$SA = 60.6BW^{0.883}$$

and

$$Th = 116.51BW^{0.044}$$

For mammals the equations for lung surface area and thickness are

$$SA = 52.1BW^{0.883}$$

and

$$Th = 237.66BW^{0.090}$$

The flux rate through the lung (Q) is then assumed to be the ratio of surface area to lung tissue thickness, *i.e.*, SA/Th. and is 10688/151 = 70.9 for a 350 g bird (Q_a) and 9188/403 = 22.8 for a mammal (Q_m) at the same weight. The ratio Q_a/Q_m is then 3.11 for 350 g species.

The third step is estimating the avian inhalation LD_{50} from the oral LD_{50} estimated in step 1. The formula for this is:

$$LD_{50(inh,\ gull)} = LD_{50\ (or,\ gull)} / (LD_{50(or,\ rat)} * (\ Q_a/Q_m) / LD_{50(inh,rat)})$$

The oral LD_{50} for the gull is divided by the ratio of the oral LD_{50} to the inhalation LD_{50} for the rat, which has been adjusted by multiplying by the ratio Q_A/Q_m which was estimated in step 2. As the rat acute oral LD_{50} is 10.3 $mg{\cdot}kg^{-1}$ and the rat inhalation LD_{50} is 2.02 $mg{\cdot}kg^{-1}$, the resulting inhalation LD_{50} for the gull is 7.25/(10.3*3.11/2.02) = 0.45 $mg{\cdot}kg^{-1}$. This value is in **Table 21.**

The final step is to estimate inhalation LD_{50}s for other avian species of interest for the risk assessment using the same allometric equation used in step 1 for adjusting the acute oral LD_{50}s for differences in body size, except in this case the reference species is the ring-billed gull rather than the mallard. Three species were chosen for the assessment, the mallard was chosen for assessment of risk from inhalation exposure as it is an aquatic bird and it is also the source of the acute oral toxicity data for birds. A 20-g songbird was chosen as representative of small avian species which are more likely to be susceptible to toxic chemicals, and a 350 g ring-bill gull was chosen to represent medium-sized birds and because the calculations first require estimation of the toxicity for a bird of the same weight as the mammalian organism which is a rat, which are typically 350 g. The adjusted inhalation LD_{50} for the mallard and songbird are in **Table 21.**

Table 21. LD_{50} for representative birds estimated from the acute oral LD_{50} for mallard duck and the adjusted rat inhalation LD_{50}. Calculations are described in the text.

Species	Body weight (g)	Oral LD_{50} ($mg{\cdot}kg^{-1}$)	Inhalation LD_{50} ($mg{\cdot}kg^{-1}$)
mallard	1580	9.1	0.574[3]
ring-bill gull	350	7.25[1]	0.458[2]
songbird	20	4.72[1]	0.298[3]

[1]oral $LD_{50(oral,\ A)} = LD_{50(oral,\ mallard)}(BW_A/BW_{mallard})^{(1.15-1)}$
[2] inhalation $LD_{50(inh,\ gull)} = LD_{50\ (or,\ gull)} / (LD_{50(or,\ rat)} * Fre / LD_{50(inh,rat)})$, Fre calculation is in text)
[3] adjusted $LD_{50(inh)}$ for mallard and songbird: $LD_{50(inh,A)} = LD_{50(inh,\ gull)}(BW_A/BW_{gull})^{(1.15-1)}$

5.3.2.2 Subacute Toxicity

No data are available to evaluate the subacute dietary toxicity (LC_{50}) of acrolein to birds either through registrant-submitted data or through a search of the open literature contained in ECOTOX.

5.3.2.3 Chronic Toxicity

No data are available to evaluate the chronic toxicity of acrolein to birds either through registrant-submitted data or through a search of the open literature contained in ECOTOX.

5.3.3 Insects

No data are available with which to evaluate the acute toxicity of acrolein to beneficial insects either through registrant-submitted data or through a search of the open literature contained in ECOTOX.

5.3.4 Plants

No data are available with which to quantitatively evaluate the toxicity of acrolein to terrestrial plants either through registrant-submitted data or through a search of the open literature contained in ECOTOX.

6 Risk Characterization

6.1 Risk Estimation

A means of integrating the results of exposure and ecotoxicity data is called the quotient method. For this method, risk quotients (RQs) are calculated by dividing exposure estimates by ecotoxicity values, both acute and chronic (**Equation 2**).

$$Equation\ 2. \quad RQ = \frac{EEC}{Toxicity}$$

Risk quotients are then compared to OPP's levels of concern (LOCs). These LOCs are criteria used by OPP to indicate potential risk to non-target organisms and the need to consider regulatory action. Exceedance of the LOC indicates that a pesticide used as directed has the potential to cause adverse effects on non-target organisms. LOCs currently address the following risk presumption categories: (1) **acute** - potential for acute risk to Federally unlisted species is high, regulatory action may be warranted in addition to restricted use classification (2) **acute restricted use** - the potential for acute risk is high, but this may be mitigated through restricted use classification (3) **acute listed species** - the potential for acute risk to endangered (Federally listed) species is high, regulatory action may be warranted, and (4) **chronic risk** - the potential for chronic risk is high, regulatory action may be warranted. Currently, EFED does not perform assessments for chronic risk to plants and acute or chronic risks to non-target insects.

The ecotoxicity test values (*i.e.*, measurement endpoints) used in the acute and chronic risk quotients are obtained from the results of required studies. Examples of ecotoxicity values from the results of short-term laboratory studies that assess acute effects are: (1) median lethal concentrations (LC_{50}) (fish and birds) (2) median lethal doses (LD_{50}) (birds and mammals) (3) median effects concentrations (EC_{50}) (aquatic plants and aquatic invertebrates) and (4) first quartile effects concentration (EC_{25}) (terrestrial plants). Examples of toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are: (1) lowest observed adverse effect concentration (LOAEC) (birds, fish, and aquatic invertebrates) and (2) no observed adverse effect concentration (NOAEC) (birds, fish and aquatic invertebrates). For birds, mammals, and all aquatic organisms, the NOAEC is the ecotoxicity test value used in assessing chronic risk. Other values may be used when justified. Risk presumptions, along with the corresponding RQs and LOCs, are summarized in **Tables 22** through **24.**

Table 22. Risk presumptions for terrestrial animals (birds and wild mammals)		
Risk Presumption	**RQ**	**LOC**
Acute High (Non-listed) Risk	EEC[1]/LC_{50} or LD_{50}/ft^2 or LD_{50}/day[3]	0.5
Acute Restricted Use	EEC/LC_{50} or LD_{50}/ft^2 or LD_{50}/day (or LD_{50} < 50 mg/kg)	0.2
Acute Endangered (Listed) Species	EEC/LC_{50} or LD_{50}/ft^2 or LD_{50}/day	0.1
Chronic Risk	EEC/NOAEC	1

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

[2] $\frac{mg/ft^2}{LD_{50} * \text{wt. of bird}}$ [3] $\frac{\text{mg of toxicant consumed/day}}{LD_{50} * \text{wt. of bird}}$

Table 23. Risk presumptions for aquatic animals		
Risk Presumption	**RQ**	**LOC**
Acute High (Non-listed) Risk	EEC[1]/LC_{50} or EC_{50}	0.5
Acute Restricted Use	EEC/LC_{50} or EC_{50}	0.1
Acute Endangered (Listed) Species	EEC/LC_{50} or EC_{50}	0.05
Chronic Risk	EEC/NOAEC	1

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

Table 24. Risk presumptions for plants		
Risk Presumption	**RQ**	**LOC**
	Terrestrial and Semi-Aquatic Plants	
Acute High (Non-listed) Risk	EEC[1]/EC_{25}	1
Acute Endangered (Listed) Species	EEC/EC_{05} or NOAEC	1
	Aquatic Plants	
Acute (Non-listed) Risk	EEC[2]/EC_{50}	1
Acute Endangered (Listed) Species	EEC/EC_{05} or NOAEC	1

[1] EEC = lbs ai/A

[2] EEC = (µg/L or mg/L) in water

6.1.1 Aquatic Animals

6.1.1.1 Acute Risk

At the maximum treatment rate of 15 mg/L, acrolein concentrations in the treatment area would exceed acute risk LOCs (RQ≥0.5) for freshwater vertebrates by factors of 2,142X and 4,286X for fish and aquatic-phase amphibians, respectively (**Table 25**). Although aquatic invertebrates are less sensitive than fish and aquatic-phase amphibians to acrolein, the acute risk level of concern for freshwater invertebrates is exceeded by a factor of 968X. For estuarine/marine animals, the acute risk LOC for fish is exceeded by a factor of 70X using the sheepshead minnow as a surrogate while the acute risk LOC for invertebrates is exceeded by a factor of 546X based on the toxicity of acrolein to the Eastern oyster. If the RQ for estuarine/marine fish had been based on the most sensitive species tested, *i.e.*, longnose killifish 96-hr LC_{50}=240 µg/l, the acute risk LOC would be exceeded by a factor of 125X. Therefore, based on laboratory animal toxicity testing, it is likely that aquatic animals in water treated with acrolein at15 mg/L will exhibit acute mortality. Even though sensitivity to acrolein is based on 48 to 96-hr toxicity data, the maximum treatment rates for acrolein with 4 to 6-h treatment times are considered likely to inflict high non-target mortality on an acute exposure basis. Treatment concentrations would have to be less than 0.35 µg/L not to exceed the acute risk to endangered/threatened species LOC (RQ≥0.05) for aquatic animals.

Table 25. Acute risk quotient (RQ) values for aquatic animals

Species	Toxicity Endpoint (µg/L)	EEC (µg/L)	Risk Quotient EEC/Toxicity
Fathead Minnow *Pimephales promelas*	14	15,000	1,071[a]
African clawed frog *Xenopus laevis*	7	15,000	2,143[a]
Water Flea *Daphnia magna*	<31	15,000	>484[a]
Sheepshead Minnow *Cyprinodon variegatus*	428	15,000	35[a]
Eastern Oyster *Crassostrea virginica*	55	15,000	273[a]

[a] Exceeds acute risk (RQ≥0.5), restricted use (RQ≥0.1) and acute risk to endangered species (RQ≥0.05) levels of concern.

As expected, aquatic plants are particularly sensitive to acrolein. RQ values for nonvascular and vascular aquatic plants exceed the acute risk LOC by factors of 417X and 208X, respectively (**Table 26**). RQ values exceed the acute risk to endangered species LOC (RQ≥1.0) for nonvascular and vascular plants by factors for 1,250X and 600X, respectively.

Table 26. Acute risk quotient (RQ) values for aquatic animals			
Species	**Toxicity Endpoint (µg/L)** **EC_{50}** **NOEC**	**EEC** **µg/L**	**Risk Quotient** **EEC/EC_{50}** **EEC/NOEC**
Blue-green Algae *Anabaena flos-aquae*	36 12	15,000	417 1,250
Duckweed *Lemna gibba*	72 25	15,000	208 600

Exceeds acute risk level of concern (RQ≥1.0).
Exceeds the acute risk to endangered species level of concern (RQ≥1.0).

Data were provided by Washington State Department of Agriculture for 2004 National Pollution Discharge Elimination System (NPDES) monitoring of applications of acrolein to irrigation canals in 3 irrigation districts in the state. These monitoring data are useful for characterizing applications of acrolein to irrigation canals in WA State and associated risks to aquatic wildlife (**Table 27**). Monitoring data indicate that irrigation canals contain acrolein residues (254 µg/L) that exceed the acute risk LOC for freshwater fish and aquatic-phase amphibians by factors as high as 36X and 73X, respectively (**Table 27**). Freshwater invertebrate RQs exceed the acute risk LOC by factors as high as over 16X based on these monitoring data. Peak monitoring concentrations (254 µg/L) exceed the acute risk LOC for nonvascular and vascular plants by factors of 7X and 3.5X, respectively. Monitoring data collected 54 hrs post-treatment (67 µg/L) exceed the acute risk LOC for freshwater fish and aquatic-phase amphibians by factors as high as 9.6X and 19X, respectively, and exceed the acute risk LOC for freshwater invertebrates by over 4.3X.

Table 27. Acute RQ values for acrolein from measured values at NPDES POC locations at Washington State irrigation districts. Source: Washington State Department of Agriculture.

Description of Location	Acrolein conc. (µg/L) at POA	Distance between POA and POC (miles)	Duration of Application (hours)	Time (hours) between application at POA and sampling at POC	Acrolein Conc. (µg/L) at POC	FW Fish RQ[1]	FW Amphibian RQ[1]	FW Invert-ebrate RQ[1,2]	E/M Fish RQ[2]	E/M Invert-ebrate RQ[2]
Quincy (3 Gates)	650	64.3	8	53.3	1	**0.07[a]**	**0.14[a]**	0.03	0.00	0.02
South (Esquatzel Wasteway)	2600	13.6	6	13.9	1	**0.07[a]**	**0.14[a]**	0.03	0.00	0.02
South (Wahluke Branch 5 Wasteway 1)	3900	14.8	4	22.75	1.1	**0.08[a]**	**0.16[a]**	0.04	0.00	0.02
Quincy (5th Section Canal)	790	68.1	8	53.3	1.5	**0.11[a]**	**0.21[a]**	0.05[a]	0.00	0.03
Quincy (5th Section Canal)	2850	26.1	1.8	54.5	1.5	**0.11[a]**	**0.21[a]**	0.05[a]	0.00	0.03
South (Esquatzel Wasteway)	2600	7	3	9	2.2	**0.16[a]**	**0.31[a]**	**0.07[a]**	0.01	0.04
Quincy (78-8)	790	67.1	8	56.5	2.4	**0.17[a]**	**0.34[a]**	**0.08[a]**	0.01	0.04
Quincy (78-8)	2620	24.6	6.1	32.9	2.4	**0.17[a]**	**0.34[a]**	**0.08[a]**	0.01	0.04
Quincy (3 Gates)	790	64.3	8	52.9	2.9	**0.21[a]**	**0.41[a]**	**0.09[a]**	0.01	**0.05[a]**
South (Potholes East 16.4 Wasteway)	5200	12.8	3	30.8	3.1	**0.22[a]**	**0.44[a]**	**0.10[a]**	0.01	**0.06[a]**
South (Esquatzel Wasteway)	2600	7	3	11	5.6	**0.40[a]**	**0.80[c]**	**0.18[a]**	0.01	**0.10[a]**
Quincy (78-8)	790	67.1	8	53.4	8.3	**0.59[c]**	**1.19[c]**	**0.27[a]**	0.02	**0.15[a]**
South (Potholes East 16.4 Wasteway)	3600	19.6	4	24	9.3	**0.66[c]**	**1.33[c]**	**0.30[a]**	0.02	**0.17[a]**
South (Wahluke Branch 5 Wasteway 1)	3900	7.7	4	13.25	12.1	**0.86[c]**	**1.73[c]**	**0.39[a]**	0.03	**0.22[a]**
South (Esquatzel Wasteway)	2600	2.6	3	18.5	14.6	**1.04[c]**	**2.09[c]**	**0.47[a]**	0.03	**0.27[a]**
South (Esquatzel Wasteway)	2600	2.6	3	20.5	15	**1.07[c]**	**2.14[c]**	**0.48[a]**	0.04	**0.27[a]**
NPDES maximum daily limit = 21 µg/L										
Quincy (5th Section Canal)	2620	26.1	3	9.5	21.7	**1.55[c]**	**3.10[c]**	**0.70[c]**	**0.05[a]**	**0.39[a]**
Quincy (5th Section Canal)	790	68.1	8	56.4	23.2	**1.66[c]**	**3.31[c]**	**0.75[c]**	**0.05[a]**	**0.42[a]**
Quincy (W61L lateral)	790	66.1	8	51.6	23.5	**1.68[c]**	**3.36[c]**	**0.76[c]**	**0.05[a]**	**0.43[a]**
Quincy (Farm Unit 88)	2620	17.9	6.3	26	29.2	**2.09[c]**	**4.17[c]**	**0.94[c]**	**0.07[a]**	**0.53[c]**

South (Potholes East 16.4 Wasteway)	3600	19.6	4	26	36.1	**2.58** [c]	**5.16** [c]	**1.16** [c]	**0.08** [a]	**0.66** [c]
South (Wahluke Branch 5 Wasteway 1)	3900	7.7	4	15.25	62.5	**4.46** [c]	**8.93** [c]	**2.02** [c]	**0.15** [a]	**1.14** [c]
Quincy (5th Section Canal)	650	68.1	8	54.1	67.2	**4.80** [c]	**9.60** [c]	**2.17** [c]	**0.16** [a]	**1.22** [c]
Quincy (3 Gates)	2620	14.9	3	16.1	117	**8.36** [c]	**16.71** [c]	**3.77** [c]	**0.27** [a]	**2.13** [c]
South (Wahluke Branch 5 Wasteway 1)	5200	9.1	3	17.83	225	**16.07** [c]	**32.14** [c]	**7.26** [c]	**0.53** [c]	**4.09** [c]
South (Wahluke Branch 5 Wasteway 1)	5200	13.4	3	22.6	254	**18.14** [c]	**36.29** [c]	**8.19** [c]	**0.59** [c]	**4.62** [c]
Maximum application rate					15000	**1071.43** [c]	**2142.86** [c]	**483.87** [c]	**35.05** [c]	**272.7 3** [c]

[1]Toxicity values are as follows: FW fish, 14 **µg/L**; FW amphibian 7 ppb; FW invertebrate, <31 **µg/L**; E/M Fish 428 **µg/L**; E/M invertebrate 55 **µg/L**.
[2]RQ values for FW invertebrates are < value in table.
POA = Point of Application; POC = Point of Compliance
[a] exceeds acute risk to Federally-listed species level of concern (RQ≥0.05)
[c] exceeds acute risk to non-listed species level of concern (RQ≥0.5)

Additional monitoring data (MRID 469769-05) from Nebraska indicate that at an initial treatment concentration of 2.4 mg/L, acrolein was detected 27 hours post-treatment and 31 miles from the application site at 230 μg/L. At this concentration, the acute risk LOC for aquatic vertebrates and invertebrates would be exceeded by factors of 66X and 15X, respectively. At treatment concentrations of 0.5 mg/L, monitoring conducted 6.2 miles from the application site 7 hours post-treatment revealed acrolein concentrations of 34 μg/L. Even at this reduced application rate, measured acrolein concentrations exceed the acute risk LOC for aquatic animals by as much as 9.7X.

Similar monitoring data were obtained by Washington State in their effort to substantiate less restrictive holding times. These data indicate that treatment rates of 1.5 mg/L resulted in acrolein concentrations as high as 410 μg/L after 26 hours post-treatment and at a distance of 35 miles from the point of application. After a treatment concentration of 0.98 mg/L, acrolein concentrations 24 hrs post-treatment and 23 miles away from the point of application were 80 μg/L. In both cases, although acrolein concentrations had dissipated substantially from initial treatment levels, sufficient acrolein was in the water column to exceed acute risk levels of concern. Based on these monitoring data, RQ values for aquatic vertebrates would exceed the acute risk LOC by factors ranging between 23X to 117X.

6.1.1.2 Chronic Risk

Given that the maximum treatment concentrations exceed acute median lethal concentrations by several orders of magnitude, it is reasonable to believe that most aquatic animals in treated waters will be killed by current maximum treatment concentrations of acrolein. NPDES monitoring data also indicate that acrolein concentrations in treated areas are sufficient to result in RQ values that exceed acute risk LOCs and that acute mortality for aquatic organisms is likely. Acrolein is typically applied to flowing water in irrigation canals and the combination of flow through and dilution with untreated water may render chronic exposure to acrolein unlikely. However, monitoring data collected up to 48 hours post-treatment indicate acrolein concentrations are sufficient to result in RQ values that exceed acute risk LOC for aquatic animals. The acute toxicity of acrolein makes it likely that few biological receptors would be present to exhibit chronic effects. For the sake of discussion though, 60-day average acrolein concentrations could not exceed 9.1 μg/L and remain below the chronic risk LOC for freshwater fish. Similarly, the 21-day average concentration could not exceed 7 μg/L and remain below the freshwater invertebrate chronic risk LOC. The extent to which acrolein would remain present in the treated area under flowing water conditions for periods of 21 or 60 days and whether there would be any receptors left after treatment are uncertain given that treatment concentrations are likely to kill most aquatic organisms (plants and animals) on an acute exposure basis.

6.1.2 Terrestrial Animals

Acrolein is reported to be irritating to mucous membranes, eyes and skin and may invoke an avoidance response; however, there are insufficient data to dismiss the possibility that both birds and mammals may continue to feed/drink along the margins (shorelines) of treated areas. Typically, EFED evaluates potential risk to terrestrial animals by calculating RQ values based on exposure through consumption of treated plants, insects and seeds. Although acrolein is a direct subsurface application to water and terrestrial plants are not initially treated with acrolein, the label explicitly requires that treated water is to be applied to fields and thus, terrestrial organisms will be exposed to acrolein-treated water. Screening-level ecological risk assessments do not typically take drinking water exposure into account; however, terrestrial animals could potentially drink water from treated irrigation canals. In order to assess potential risks, dose-based exposures are estimated for several mammalian and avian species, including mink, river otter, spotted sandpiper, belted kingfisher, herring gull, osprey, mallard duck, great blue heron and bald eagle. Species body weight data are consistent with the Wildlife Exposure Factors Handbook (USEPA 1993) (**Tables 28 and 29**).

EECs are derived by considering the maximum treatment rate of acrolein (15 mg/L) and the drinking water intake (normalized for body weight) for each of the mammalian and avian species mentioned above. Normalized drinking water intakes (*DW*) for mammals and birds are calculated based on **Equations 3 and 4,** respectively (USEPA 1993). In these equations, *BW* represents the body weight (in kg) of the animal for which the drinking water intake is being assessed. Resulting units of *DW* are L/kg-bw/day. To derive a dose-based exposure concentration of acrolein, the *DW* values for mammals and birds are multiplied by 15 mg/L, the maximum potential concentration of acrolein in the drinking water. The resulting dose-based EEC is in units of mg acrolein/kg-bw/day. It is assumed that the animal drinks exclusively from treated canal water and that 100% of drinking water consumed by an animal in a day contains acrolein at a concentration of 15 mg/L.

$$Eq.3 \quad DW = \left(0.099 * BW^{0.09}\right) / BW \quad (mammals)$$

$$Eq.4. \quad DW = \left(0.059 * BW^{0.67}\right) / BW \quad (birds)$$

Acute and chronic dose-based exposures to mammals are considered. Due to a lack of chronic toxicity data for birds, only acute, dose-based exposures to birds are considered. Available dose-based toxicity values are adjusted for the weights of the animal tested (*e.g.* laboratory rat and mallard duck) and of the animal for which the risks are being assessed (*e.g.* mink, bald eagle, etc.). These adjustments are made according to **Equations 5 and 6** (USEPA 2006), where: AT = adjusted toxicity value; LD_{50} or NOAEL = endpoint reported by toxicity study; TW = body weight of tested animal (350 g rat; 1580 g mallard duck); AW = body weight of assessed animal; x = Mineau scaling factor (default value of 1.15 used). For mammals, the measured LD_{50} for rats used to assess acute risks is 10.3 mg/kg (MRID 412570-01); and the measured NOAEL for rats used to assess chronic risks is 3 mg/kg/day (MRID 418691-01). To assess acute risks to birds, the measured LD_{50} for mallard is 9.11 mg/kg (MRID 117668).

$$Eq.5 \quad AT = \left(LD_{50}\ or\ NOAEL\right)\left(\frac{TW}{AW}\right)^{0.25} \quad (mammals)$$

$$Eq.6 \quad AT = LD_{50}\left(\frac{AW}{TW}\right)^{(x-1)} \quad (birds)$$

Based on the maximum treatment rate for acrolein (15 mg/L), dose-based acute RQ values exceed the acute risk LOC for Federally-listed endangered/threatened mammals and birds consuming only acrolein-treated drinking water (**Tables 28 and 29**). Although no acute risk LOC is exceeded for non-listed mammals or birds, the acute risk LOC for endangered species (RQ>0.5) is exceeded for mammals (minks and river otters) and birds (spotted sandpiper and belted kingfisher). Therefore, there is a potential for acute risk to listed mammals and birds consuming drinking water treated with acrolein at the maximum label rate. For listed mammals, water treatment concentrations could not exceed 5.8 mg/L if RQ values are to remain below the acute endangered species LOC. For listed birds, the treatment concentration could not exceed 3.1 mg/L in order not to exceed acute risk to endangered species LOC. No chronic risk LOC is exceeded for mammals.

Table 28. Acute and chronic dose-based RQ values for mammals exposed to Acrolein through drinking water.

Mammalian Species	BW (kg-bw)	DW (L/kg-bw/d)	EEC (mg/kg-bw/d)	Adjusted Toxicity Values (mg/kg-bw)		Risk Quotients	
				Acute	Chronic	Acute	Chronic
Mink	1.0	0.099	1.485	7.92	2.31	**0.187**[1]	0.644
River otter	8.0	0.080	1.206	4.71	1.37	**0.256**[1]	0.879

[1] Exceeds the acute LOC (0.1) for listed species.

Table 29. Acute dose-based RQ values for birds exposed to Acrolein through drinking water.

Avian Species	BW (kg-bw)	DW (L/kg-bw/d)	EEC (mg/kg-bw/d)	Adjusted Toxicity Values (mg/kg-bw)	Acute RQs
Spotted Sandpiper	0.043	0.167	2.500	5.31	**0.471**[1]
Belted kingfisher	0.148	0.111	1.662	6.39	**0.260**[1]
Herring gull	1.1	0.057	0.858	8.63	0.099
Osprey	1.5	0.052	0.774	9.04	0.086
Mallard duck	1.58	0.051	0.761	9.11	0.084
Great blue heron	2.39	0.044	0.664	9.69	0.068
Bald eagle	4.65	0.036	0.533	10.71	0.050

[1] Exceeds the acute LOC (0.1) for listed species.

Table 30. Acute dose-based RQs for mammals of different size and feeding classes exposed to acrolein.			
Food Type	**Small (15 g)**	**Medium (35 g)**	**Large (1000 g)**
Application Rate: 0.534 lbs a.i.A (15 mg/L in water)			
Short Grass	**5.41**[1, 2]	**4.62**[1, 2]	**2.48**[1, 2]
Tall Grass	**2.48**[1, 2]	**2.12**[1, 2]	**1.13**[1, 2]
Broadleaf plants/sm insects	**3.04**[1, 2]	**2.60**[1, 2]	**1.39**[1, 2]
Fruits/pods/lg insects	**0.34**[2]	**0.29**[2]	**0.15**[2]
Seeds (granivore)	**0.08**	**0.06**	**0.03**
Application Rate: 0.0534 lbs a.i./A (1.5 mg/L in water)			
Short Grass	**0.54**[1, 2]	**0.46**[2]	**0.25**[2]
Tall Grass	**0.25**[2]	**0.21**[2]	**0.11**[2]
Broadleaf plants/sm insects	**0.30**[2]	**0.26**[2]	**0.14**[2]
Fruits/pods/lg insects	**0.03**	**0.03**	**0.02**
Seeds (granivore)	**0.01**	**0.01**	**<0.01**

[1] Exceeds LOC (RQ≥0.5) for acute exposures to non-listed terrestrial mammals.
[2] Exceeds LOC (RQ≥0.1) for acute exposures to listed terrestrial mammals.
Foliar dissipation half life: 1 day
Number of applications: 1
Mammalian LD_{50}: 10.30

Although acrolein is applied directly to irrigation canal water, the treated water is required to be either held for some period of time (during which residues degrade to negligible levels) or to be applied to fields as irrigation water to dissipate the acrolein. No data have been evaluated by OPP to substantiate whether the required holding times are sufficient.

Potential risks from estimated acrolein residues on terrestrial animal forage items were evaluated using TREX (1.3.1) based on an equivalent application rates ranging between 0.0535 to 0.535 lbs a.i./A and assuming a foliar dissipation half-life of 1 day. **Table 30** lists the acute dose-based RQ values for different-sized animals feeding on short grass, tall grass, broadleaf plants/small insects, fruits/pods/large insects and seeds. Risk quotients exceed the acute risk LOC for all sized mammals feeding on short grass, tall grass, broadleaf plants and small insects at the highest equivalent application rate modeled. Also at the highest application rate modeled, RQs exceed the LOC for listed species of all sizes and feeding categories, except granivores. At the lowest equivalent application rate modeled (0.0535 lbs a.i./A), the acute risk LOC is exceeded for small-sized (15 g) mammals feeding on short grasses (RQ=0.54); however, the acute risk LOC for endangered/threatened mammals is exceeded for small and intermediate (35 g) mammals feeding on short grasses, tall grasses, and broadleaf plants/small insects; for large-sized mammals the listed species LOC for acute risk is exceeded for animals feeding on short grasses alone.

Table 31 lists acute RQ values for various size birds feeding on short grasses, tall grasses, broadleaf plants/small insects and fruits/pods/large insects. Similar to the risk estimates for mammals, the acute risk LOC is exceeded for all-sized birds feeding on all forage categories except large birds (1000 g) feeding on fruits/pods/large insects at application rates of 0.54 and lbs a.i./A representing water treatment rate of 15 mg a.i./L. At an equivalent application rate of 0.05 lbs a.i./A, the acute risk LOC is exceeded for small (20 g) and medium (100 g) birds feeding on short grasses, tall grasses and broadleaf plants/small insects (RQ range 0.78 – 3.09). The acute risk to Federally-listed species LOC is exceeded across all-sized birds feeding in all forage categories except fruits/pods/large insects at application rates equivalent to 0.05 lbs a.i./A or greater. At the lowest application rate evaluated (0.005 lbs a.i./A), the acute risk to endangered species LOC is exceeded for small birds feeding on all forage categories except fruits/pods/large insects and for medium sized birds feeding on short grasses.

Table 32 lists acute RQ values for mammals via exposure through inhalation. The inhalation LC_{50} for acrolein is 18 mg/m^3/4 hours rats. The corresponding LD_{50} is 2.0 mg·kg^{-1} assuming that the rat weighs 0.350 kg and using the allometric equation for respiration rate: $R_{rate} = 379BW^{0.8}/1000$ and an exposure duration of 240 min. The field-study provides values that have actually been measured, so they represent a lower bound on the exposure used to estimate risk while the equilibrium-based EECs represent an upper-bound. Using the same acute risk levels of concern as those for oral and dietary-based risk quotients, the upper-bound equilibrium-based EECs imply the possibility of acute mortality for both birds and mammals based on upper-bound estimates for exposure to acrolein in the air. Upper-bound risk quotients for acute mortality based on inhalation exceed the acute risk LOC by factors ranging from 20 to 208X. Even based on lower-bound [measured] concentrations of acrolein in the air, the acute risk to federally-listed endangered species LOC is exceeded for small birds that might live along the treated irrigation canals. However, because volatilization from the water's surface is a time-dependent process, the water is moving, and the air in and around the canal is unbounded, it is unlikely that equilibrium would ever be approached. While it is certain that the concentrations in air can be higher than those measured in the single available study, depending on factors such as the temperature and flow rate of the water, and the rate of mixing in the atmosphere, and the treatment concentration (4 mg L^{-1}) in the field study, it would be expected that concentrations in air would be closer to this value than the equilibrium-estimated value in the great majority of cases.

Although the potential for chronic risk cannot be precluded for acrolein, there are no avian chronic toxicity data available with which to evaluate potential risk While there are chronic toxicity data for mammals, the potential for chronic risk to mammals and/or birds is considered low since acrolein residues in treated water are expected to deter most animals from consuming the water. Additionally, field monitoring studies indicate that acrolein residues in treated fields dissipate with half-lives of less than 1 day; therefore, potential chronic exposure does not appear to be likely. While multiple applications may represent a potential source of repeated applications, frequent repeat applications are conducted at much lower treatment concentrations than the maximum rate modeled in this assessment and again, the likelihood of chronic exposure is believed to be low.

Table 31. Acute dose-based RQs for birds of different size and feeding classes exposed to acrolein.			
Food Type	**Small (20 g)**	**Medium (100 g)**	**Large (1000 g)**
Application Rate: 0.535 (15 mg/L in water)			
Short Grass	**14.17**[1, 2]	**13.85**[1, 2]	**4.39**[1, 2]
Tall Grass	**17.39**[1, 2]	**6.35**[1, 2]	**2.01**[1, 2]
Broadleaf plants/sm insects	**1.93**[1, 2]	**7.79**[1, 2]	**2.47**[1, 2]
Fruits/pods/lg insects	**14.17**[1, 2]	**0.87**[1, 2]	**0.27**[2]
Application Rate: 0.0535 (1.5 mg/L in water)			
Short Grass	**3.09**[1, 2]	**1.38**[1, 2]	**0.44**[1, 2]
Tall Grass	**1.42**[1, 2]	**0.63**[1, 2]	**0.20**[1, 2]
Broadleaf plants/sm insects	**1.74**[1, 2]	**0.78**[1, 2]	**0.25**[1, 2]
Fruits/pods/lg insects	**0.19**[2]	**0.09**	**0.03**
Application Rate: 0.00535 (0.15 mg/L in water)			
Short Grass	**0.31**[1, 2]	**0.14**[2]	**0.04**
Tall Grass	**0.14**[2]	**0.06**	**0.02**
Broadleaf plants/sm insects	**0.17**[2]	**0.08**	**0.02**
Fruits/pods/lg insects	**0.02**	**0.01**	**0.00**

[1] Exceeds LOC (RQ≥0.5) for acute exposures to non-listed terrestrial birds.
[2] Exceeds LOC (RQ≥0.1) for acute exposures to listed terrestrial birds.
Foliar dissipation half life: 1 day
Number of applications: 1
Avian LD50: 9.11 (mallard duck)

Table 32. Acute risk RQs for mammals and birds via the inhalation route.					
Species	**Inhalation LD_{50}** mg·kg^{-1}	**Lower Bound VID** mg·kg^{-1}	**Upper Bound VID** mg·kg^{-1}	**Lower Bound RQ** mg·kg^{-1}	**Upper Bound RQ** mg·kg^{-1}
Rat	2.02	4.04 x 10^{-2}	3.97 x 10^{1}	0.02	**20**[2]
Mallard	0.574	2.21 x 10^{-2}	2.17 x 10^{1}	0.04	**38**[2]
Gull	0.458	3.12 x 10^{-2}	3.0.7 x 10^{1}	0.07	**67**[2]
Songbird	0.298	6.03 x 10^{-2}	5.93 x 10^{1}	**0.20**[1]	**199**[2]

[1]Exceeds LOC (RQ > 0.1) for listed birds and for restricted use for birds
[2] Exceed LOC (RQ > 0.5) for high risk to birds

6.2 Risk Discussion

Acrolein is a restricted use herbicide primarily used to remove plants from irrigation canals and ditches and its use is limited to nine western states that rely heavily on irrigation. The chemical is injected below the surface of the water through a closed system. The chemical travels down the irrigation canal as a plume defined largely by the rate of flow in the canal and duration of the application. The concentration of acrolein in treated water will depend on the initial concentration and on the dissipation rate in the channel. The highest maximum treatment concentration is 15 mg/L for up to 8 hours depending on the extent of aquatic plant growth.

Acrolein is used also to maintain weed-free irrigation canals; however, lower treatment concentrations are typically used.

The initial risk hypothesis for acrolein stated that non-target aquatic animals and plants and terrestrial animals may be exposed to acrolein that is injected underwater according to the label to control aquatic weeds in drainage canals, irrigation ditches and retention ponds/reservoirs. Additionally, acrolein may compromise survival and cause sub-lethal effects in non-target aquatic animals and plants, terrestrial mammals, birds and plants. Based on the available information, it is not possible to refute the initial risk hypothesis; at currently registered maximum treatment rates, non-target aquatic animals and plants in treated water ways and fields will be exposed to acrolein and this exposure will likely result in acute mortality of aquatic animals (vertebrates and invertebrates) and plants following a single treatment. While irrigating fields with treated water in an effort to dissipate acrolein may be effective at reducing loads to downstream receiving waters, chemigation and/or flood irrigation can potentially increase exposure to terrestrial animals that may be in irrigated fields. Exposure of terrestrial animals to acrolein in fields irrigated with treated water is sufficiently high to exceed acute risk LOCs.

Although acrolein is expected to dissipate through both biotic and abiotic degradation, volatilization and through dilution by untreated water, monitoring data indicate that acrolein residues outside of the treatment area are sufficiently high to exceed acute risk levels of concern up to 54 hours after treatment even when treatment rates are roughly 4 times lower than the maximum label rate. Other targeted monitoring indicates that acrolein detections are not uncommon outside of the treatment area.

The current label does not restrict the number of reapplications that can occur in a year. Water district personnel in Washington State indicate that canals may be treated as frequently as every 3 weeks to maintain control of aquatic plants; however, maintenance treatments are typically at considerably lower application rates than the maximum allowed treatment concentration. The extent to which acrolein will result in non-target mortality depends on the ability of applicators to restrict the movement of treated water outside of the desired treatment area. Currently the label does not provide any guidance to users on how water should be "held", whether that should be using some retention structure or simply "held" within the irrigation system (i.e. not discharged).

Acrolein can enter the environment from a broad range of anthropogenic and natural sources. Incomplete combustion and/or pyrolysis of organic materials such as forest fires and exhaust from automobiles contribute to atmospheric loading of acrolein Industrial releases of acrolein to the environment reported in the Toxic Release Inventory in 2004 totaled 284,480 lbs. Reported releases have declined by 52% since peaking at 545,452 lbs in 2001; however, these releases do not include the use of acrolein as a herbicide. It is important to note that acrolein applicators are required to participate in trainings and adhere to a standard operating procedure (application and safety manual). Applicators can monitor treatment concentrations using MAGNACIDE H Herbicide monitoring kits provided by the registrant.

6.2.1 Risks to Aquatic Organisms

The direct application of acrolein to water at the maximum application rate is likely to result in acute mortality of aquatic animals. At treatment concentrations of 15 mg/L, acute risk LOCs are exceeded for the most sensitive vertebrate and invertebrate animals by factors as high as 4,286X and 968X, respectively. Data provided by Washington State for 2004 NPDES permitting indicate that many of the application events resulted in non detections of acrolein at the point of compliance (POC) (data not shown); however, much of the data indicate that at a designated POC, acrolein was detected at levels exceeding the state's NPDES permit level of 21 µg/L, as well as at levels sufficient to result in RQs exceeding EPA's LOCs for non-listed and listed aquatic organisms. The data indicate that it is possible for acrolein to move many miles (>65 miles) downstream in irrigation canals and still exceed the NPDES permit level and levels of concern for exposures to aquatic organisms in periods of time greater than 48 hours after upstream applications of acrolein. For applications of acrolein in WA, a 48 hour holding period is required for treated waters before reaching receiving water bodies of concern. The extent to which acrolein will persist in treated areas is uncertain; however, the NPDES permit monitoring data indicate that 48-hrs after treatment, acrolein residues can exceed the acute risk LOC for fish and aquatic invertebrates by factors of 9.6X and 4.3X, respectively. Additional monitoring data collected in Nebraska and Washington State indicate that treatment concentrations at one tenth the maximum label rate can result in acrolein concentrations of 50 µg/L after 23 hours post-treatment and up to 61 miles from the actual treatment site.

Figure 6 depicts the species sensitivity distribution for aquatic vertebrates and illustrates that at the maximum treatment rate for acrolein, all of the representative species will likely be affected. The upper 95% 96-hr LC_{50} value is 84 µg/L. and falls well below the maximum rate of 15,000 µg/L and below concentrations that have been measured at POCs in the WA state monitoring data. Although aquatic invertebrates appear to be less sensitive to acrolein than fish and amphibians, **Figure 7** illustrates that once again, a major proportion of the sensitivity distribution of aquatic organism LC_{50} data fall below the maximum treatment concentrations. The upper 95% confidence limit across all of the aquatic taxa is 1,918 µg/L; the maximum application rate exceeds this value by a factor of roughly 8X.

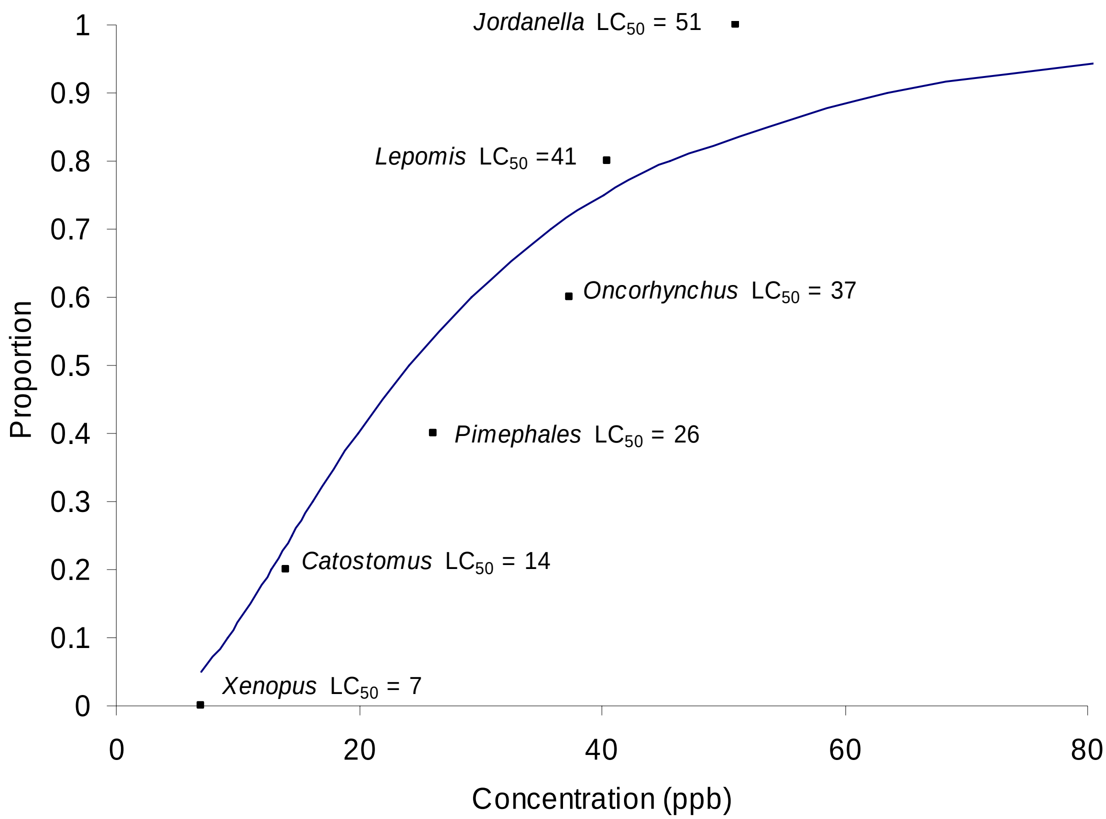


Figure 6. Distribution of measured LC_{50} values for 7 genera of fish and amphibians exposed to acrolein for 96 hours. The mean LC_{50} value for this curve is 24 µg/L and the upper 95th centile is 84 µg/L.

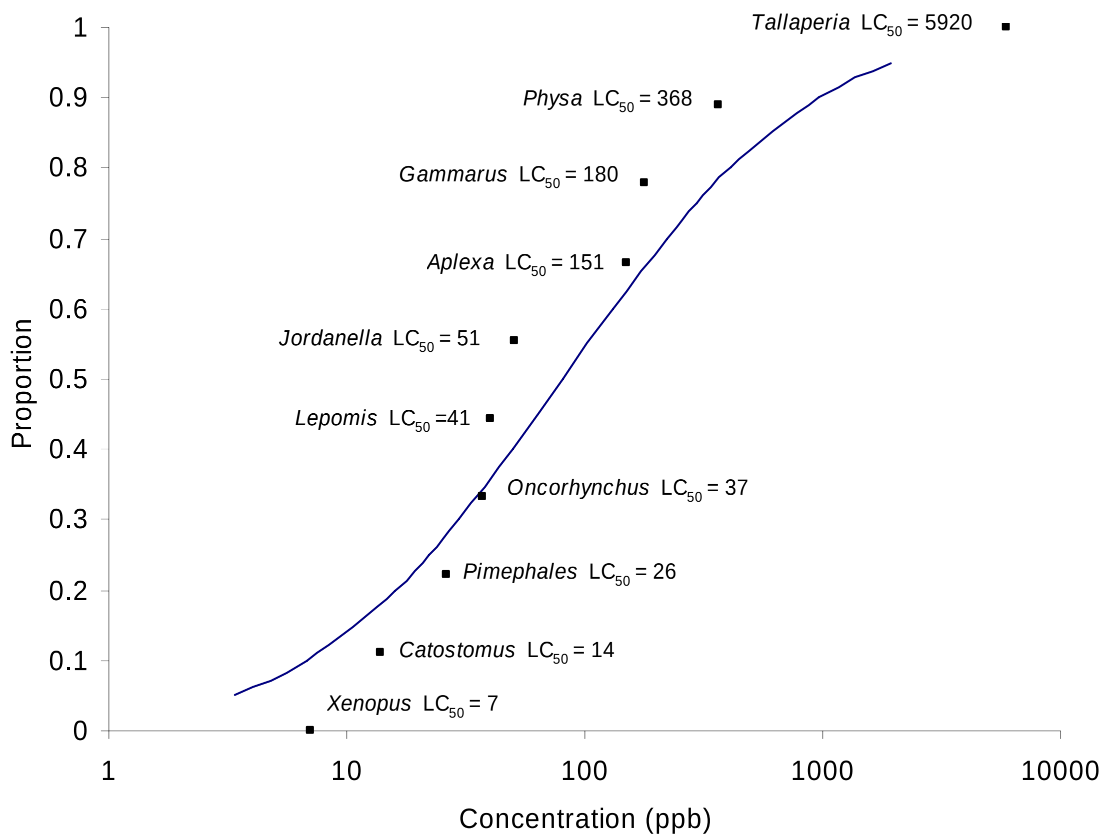


Figure 7. Distribution of measured LC_{50} values for 10 genera of freshwater organisms exposed to acrolein for 96 hours. The mean LC_{50} value for this curve is 81 µg/L and the upper 95th centile is 1,918 µg/L.

Aquatic plants used for toxicity testing were less sensitive to acrolein than the aquatic animals tested; however, acrolein is reported to be effective at killing aquatic plants. The chemical is intended not to just kill aquatic plants but accelerate their dissolution. Thus it is likely that if aquatic animals are more sensitive than aquatic plants, a significant proportion of the aquatic community would be affected in the treatment area.

The effects of acrolein are not limited to the chemical's direct toxic effect. Acrolein is intended to kill aquatic plants and the available toxicity data indicate that both vascular and nonvascular aquatic plants are vulnerable. These plants represent the basis of the aquatic food chain and the loss of this primary productivity would impact upper trophic levels that are dependent upon it as a source of food. Additionally, dissolved oxygen concentration may be impacted as photosynthesis is reduced and/or eliminated in treatment areas. According to the MAGNACIDE® H Herbicide Application and Safety Manual, acrolein is intended to not only kill but to disintegrate aquatic plants without releasing any large masses of vegetation such that organic residues from the plants travel downstream. There are studies, however, suggesting that the holdfast of aquatic plants are not killed by acrolein treatment and that there may be situations where the crown of the plant becomes draped across the bottom of the sediments. Incomplete removal of moribund plant material may increase biological oxygen demand in the treated areas and contribute to oxygen depletion. The loss of plants would also eliminate habitat for aquatic animals.

6.3 Risks to Terrestrial Organisms

6.3.1 Terrestrial Animals

Both bird and mammal acute risk LOCs are exceeded by factors as high as 28X for small birds foraging on short grasses and as high as 11X for small mammals foraging on short grasses, across a range of rates representing acrolein concentrations resulting from application of irrigation to agricultural fields. Acute risk LOCs for Federally-listed species are similarly exceeded across all application rates evaluated for small birds and mammals feeding on short grasses by factors of 142X and 54X. Potential exposure of terrestrial animals to acrolein is not limited to residues on plant and/or insect forage items in agricultural fields irrigated with acrolein. Exposure to acrolein can also occur through terrestrial animals drinking acrolein-treated water and breathing volatilized acrolein. Based on exposure through drinking water alone, acute risk LOCs for Federally-listed birds and mammals are exceeded by factors as high as 4.7X and 6.4X, respectively. Exposure via inhalation may also occur as acrolein volatilizes. Based on mammalian inhalation toxicity data and extrapolating these data to birds as discussed previously, application of acrolein to irrigation canals may result in sufficient acrolein in the air to cause acute mortality in both birds and mammals. It is unclear whether birds and/or mammals would be sufficiently deterred by the acrid properties of acrolein to effectively avoid exposure.

This assessment was conducted for terrestrial animals feeding in the treated field, drinking water from the canal near the application site, or inhaling acrolein vapour near the application site. In each case, these assessments should be protective relative to other locations away from the irrigated fields, or the application site. For the treated field, there is expected to be some exposure on the downwind side of the field due to drift of the irrigation water. However, the droplet size spectrum for irrigation tends to be quite large compared to that used for spray application of pesticides, and consequently the drift distance is relatively short. Since quantitative tools for assessing drift from irrigation are not currently available the amount of drift cannot be assessed quantitatively at this time. Drinking water exposure will be at a maximum at the application site, but may extend for substantial distances downstream, as noted in the aquatic risk assessment. Similarly inhalation exposure from volatilization from the treated canal may also extend substantial distances downstream from the treatment location, though the level will decrease as the acrolein concentration in the treated canal decreases.

In its assessment of the potential effects of acrolein to terrestrial animals, Environment Australia (2001) concluded that exposure would be limited and thus effects would be unlikely because of the following reasons:

- the potential for exposure is only short term due to the low persistence of acrolein in various compartments of the environment and the irreversible binding of any residues absorbing to soil;
- the treated water moves down the channel until it reaches the end, with concentrations in water once the plume has passed effectively returning to zero and acrolein volatilized from treated water would also be expected to dissipate rapidly in the atmosphere once the plume of treated water has passed;
- acrolein has excellent warning properties, at air concentrations well below those considered to be harmful, hence unconstrained birds and mammals exposed to acrolein-tainted air would voluntarily leave the area and voluntary ingestion of water containing acrolein to harmful levels would not be likely to occur due to the "off" taste given to the water;
- in a bioaccumulation study with various species, acrolein could not be detected in edible tissues, furthermore, a preliminary study showed that acrolein could not be recovered when directly fortified to edible fish tissue, indicating strong sorption to tissue and/or instantaneous tissue metabolism. Assuming similar adsorption and/or reaction occurs with plant tissue, acrolein is unlikely to be ingested by birds or mammals consuming fish or weeds from treated channels.

While all of these factors may represent reasonable limitations to terrestrial animal exposure, EFED has not reviewed any data to support these claims. While incident data (see below) suggest though that terrestrial animals are not particularly affected by acrolein treatments, the nature of how incident data are reported and collected do not allow them to be used to refute the occurrence of incidents. In addition, for some chemicals where bittering agents have been added to dissuade consumption by non-target animals, an animal may still consume sufficient quantities of the chemical that result in detrimental effects/death.

6.3.2 Terrestrial Plants

There are no terrestrial plant toxicity data with which to evaluate potential risks to terrestrial plants; however, there is an incident report of adverse effects to agricultural crops to which acrolein-treated water is routinely applied to dissipate the chemical. It has been hypothesized that the waxy cuticle of terrestrial plants that protects them from dehydration may also serve to protect them from the toxic effects of acrolein. However, no data have been submitted with which to evaluate this hypothesis. Residue data collected from terrestrial plants indicates dicystiene residues in terrestrial plants treated with acrolein; these data suggest that terrestrial plants are to a certain extent affected by acrolein's ability to cross-link sulfhydryl residues in proteins.

6.3.3 Review of Incident Data

A search of the EIIS (Ecological Incident Information System) database for ecological incidents (run on November 9, 2006) identified 12 reported incidents that may have involved exposures of acrolein between 1971 to 2004. Of the 12 reported incidents, 1 involved terrestrial plants, 10 involved effects to fish, amphibians and/or aquatic invertebrates and 1 involved effects to aquatic birds. Residue analysis was conducted to confirm the presence of acrolein in only one (B0000-500-87) of the reported incidents. Half of all the reported incidents occurred in California. Each of the incidents captured in the EIIS are described below. It is important to note that these incidents only reflect those reported to the Agency and may not reflect the total number of incidents that may be associated with exposure to acrolein through the use of this chemical as an herbicide.

Incidents included in EIIS are defined by a certainty index associated with the likelihood that the pesticide application described resulted in the observed incident. The certainty index defines incidents as unrelated, unlikely, possible, probable and highly probable. One note of uncertainty associated with this data base is the nature of reporting of incidents. Many more incidents may have occurred due to acrolein exposures but may not have been reported due to various factors, such as a lack of reporting, or a lack of witnessing of effects. Therefore, the lack of an incident report does not necessarily indicate an absence of incidents.

Incident I000782-001 occurred in 1992 in Pima County, AZ. This incident involved plant damage to 210 acres of squash seedlings in an agricultural area. The type of exposure was identified as absorption. MAGNACIDE® H had been applied as a flowable formulation to irrigation water according to a registered use. The seedlings were irrigated with the acrolein-treated water. The certainty index of this incident is "probable".

Incident I003351-026 occurred in 1994 in Nevada County, CA. This incident involved the mortality of 6 catfish, an unknown number of largemouth bass and 50 sunfish. Another incident (I014884-020) occurred in the same county in 2003. The incident reported mortality of over 100 bullfrogs. Whether either of these incidents resulted from registered uses of acrolein is uncertain.

The certainty index for whether these incidents likely resulted from acrolein exposure is “probable”.

Incident B0000-216-17 occurred in 1976 in Tehama County, CA. This incident involved the mortality of 1000 stickleback fish and 1000 unspecified game fish. Acrolein was applied at 0.5 ppm to irrigation and spawning channels as a registered use to remove mats of *Potamogeton sp*. and *Elodea sp*. The certainty index of this incident is “probable”.

Incident I000598-013 occurred in 1989 in Hitchcock County, NE. This incident involved the mortality of a large number of juvenile fish in Driftwood/Meeker Canal. Observations of the number of fish killed included 40,824 drum (*Aplodinotus grunniens*), 3,528 flathead catfish (*Pylodictis oilvaris*) and 6,048 gizzard shad (*Dorosoma cepedianum*). The report indicates that 47.1 gallons of MAGNACIDE® H were applied over a 3-hr time period to an irrigation canal to treat algae. The report indicates that the application was according to the recommended rate. The incident is classified as an accidental misuse. The certainty index of this incident is “highly probable”.

Incident I015594-001 occurred in 2004 in Placer County, NV. The incident report indicates that MAGNACIDE® H was applied by the Nevada Irrigation District to water in an irrigation canal as a registered use. Six hours after the MAGNACIDE® H application, golden shiners (*Notemigonus crysoleucas*) in a pond along the treated irrigation canal were showing signs of toxicity (gasping, lethargy, hemorrhaging). A total of 500 golden shiners were reported dead. The certainty index of this incident is “probable”.

Incident B0000-500-87 occurred in 1976 in Boulder County, CO. This incident involved the mortality of hundreds of brown trout (*Salmo trutta*) near Lyons in 2.4 miles of St. Vrain Creek. Lengths of affected fish ranged 2-18 inches. The report indicated that acrolein was applied to the surface of the creek as a registered use to control algae. Samples from 3 brown trout and a pint of water were analyzed for acrolein. Acrolein was detected in fish samples at 8-20 mg/kg bw. The certainty index of this incident is “highly probable”.

Incident B0000-700-01 occurred in 1977 in Josephine County, OR. The report indicated that 15.8 gallons of MAGNACIDE® H was applied to a main irrigation ditch by the Grants Pass Irrigation District in order to treat algae and moss. One mile downstream of the treatment site, the irrigation water discharged into Bloody Run Gulch, which eventually emptied into the Rogue River. The 6-day holding period for acrolein treated water, which is indicated on the MAGNACIDE® H label, was not followed. Mortality of thousands of fish and invertebrates was reported in Rogue River. This included 100 carp, 15,000 chinook salmon, 100,000 crayfish, 6,000 lamprey, 96,500 sculpin, 20,000 shiner, 74,000 sucker and 27,000 trout. The incident is classified as an accidental misuse and represents the largest reported incident involving acrolein. The certainty index of this incident is “highly probable”.

Incident B0000-231-02 occurred in 1971 in Yolo County, CA. This incident involved the mortality of thousands of unspecified species of fish. The report indicates that acrolein was applied to a portion of the irrigation system of the Yolo County Flood Control District. The incident is classified as an accidental misuse. The certainty index of this incident is “probable”.

Incident B0000-218-13 occurred in 1976 in Siskiyou County, CA. This incident involved the mortality of 1,000 steelhead trout (*Oncorhynchus mykiss*) in the Shasta River. The report indicates that MAGNACIDE® H was applied to a private irrigation ditch which emptied into the Shasta River. The incident is classified as an accidental misuse. The certainty index of this incident is “possible”.

Incident I003948-012 occurred in 1988 in Tehama County, CA. This incident involved the mortality of 8,000 salmon. It is uncertain whether the incident resulted from the registered use of acrolein. The certainty index of this incident is “probable”.

Incident B000630-001 occurred in 1986 in the Cochran Irrigation area of Reno, NV. This report involved three separate incidents of mortality of aquatic birds in MAGNACIDE® H treated irrigation waters. It is uncertain whether the incident resulted from the registered use of acrolein. The certainty index of this incident is not reported. However, the incident is plausible given the potential risks to birds from inhalation exposure discussed above.

An additional incident not captured in the EIIS database occurred in 1996 when the Talent Irrigation District in Jackson County, Oregon, applied an herbicide (MAGNACIDE® H) to an irrigation canal to control aquatic weeds and vegetation contained within the canal. The herbicide flowed from the canal into nearby Bear Creek, killing an estimated 92,000 salmon and steelhead downstream of a leaking waste gate.

As mentioned previously, these reported incidents may not reflect the actual number that may be associated with the use of acrolein as an herbicide. The data indicate that roughly one third of the reported incidents resulted from the registered use of the compound; however, the incidents involving the highest level of mortality resulted from accidental misuses. The largest loss of aquatic animals, *i.e.*, 338,600 animals killed in 1977 (B0000-700-01), resulted from an inadequate holding time. The relatively low number of incident reports combined with estimated RQ values for aquatic animals suggest that application of acrolein in most circumstances must be relatively well controlled given that it is a direct application to water. However, given the toxicity of acrolein at maximum application rates, direct contact of any aquatic animal would likely prove lethal within a relatively short period of time. Either most treated waters do not contain sufficient fauna to signal non-target mortality or aquatic/terrestrial animal deaths within a defined treatment area or are not considered and/or reported as incidents. Given that most of the treated water resides in irrigation canals that may have considerable flow rates, it is also possible that moribund animals are rapidly conveyed downstream and go unnoticed.

6.3.4 Uncertainties

6.3.4.1 Age Class and Sensitivity of Effects Thresholds

Test organism age may have a significant impact on the observed sensitivity to a toxicant. The screening risk assessment acute toxicity data for fish are collected on juvenile fish weighing between 0.1 and 5 grams. Aquatic invertebrate acute testing is performed on recommended immature age classes (*e.g.*, first instar for daphnids, second instar for amphipods, stoneflies and mayflies, and third instar for midges). Similarly, acute dietary testing with birds is also performed on juveniles, with mallard being 5-10 days old and quail 10-14 days old. The screening risk assessment has no current provisions for a generally applied method that accounts for uncertainty associated with study organism age. In so far as the available toxicity data may provide ranges of sensitivity information with respect to age class, the risk assessment uses the most sensitive life-stage information as the screening endpoint.

Additionally, this assessment does not evaluate whether acrolein could be more toxic for organisms that have lower metabolic activity. This may occur in more sensitive life stages and may render these organisms more vulnerable to chronic effects.

6.3.4.2 Lack of Effects Data for Amphibians and Reptiles

Currently, toxicity studies on terrestrial-phase amphibians and reptiles are not required for pesticide registration. Since these data are lacking, the Agency uses birds as surrogates for terrestrial-phase amphibians and reptiles. These surrogates are thought to be reflective of or protective (more sensitive) of herpetofauna or are likely to experience higher exposures based on dietary needs or behavior. Amphibians are characterized by a permeable skin. For terrestrial species, the difference between amphibians and birds and reptiles and birds is quite large. Terrestrial amphibians and reptiles are both ectothermic while birds are endothermic; birds have a higher basal metabolic rate required to maintain constant body temperature. The higher metabolic demands of birds may predispose birds to higher relative exposures. However, this does not address any potential differences in toxicity. To date, there are few controlled studies on reptile species that could be used to compare to similar studies on birds. *A priori*, there is no strong reason to think that one taxon is more or less sensitive than another. Further research is required to determine whether, in general, reptiles and terrestrial-phase amphibians are suitably represented by bird species in assessing risks.

6.3.4.3 Use of the Most Sensitive Species Tested

Although the screening risk assessment relies on a selected toxicity endpoint from the most sensitive species tested, it does not necessarily mean that the selected toxicity endpoints reflect sensitivity of the most sensitive species existing in a given environment. The relative position of the most sensitive species tested in the distribution of all possible species is a function of the overall variability among species to a particular chemical. The relationship between the sensitivity of the most tested species versus wild species (including listed species) is unknown and a source of significant uncertainty. The use of laboratory species has historically been driven by availability and ease of maintenance. A widespread comparison of species is lacking; however, even variation within a species can be quite high.

6.3.5 Federally Threatened and Endangered (Listed) Species Concerns

Section 7 of the Endangered Species Act, 16 U.S.C. Section 1536(a)(2), requires all federal agencies to consult with the National Marine Fisheries Service (NMFS) for marine and anadromous listed species, or the United States Fish and Wildlife Services (FWS) for listed wildlife and freshwater organisms, if they are proposing an "action" that may affect listed species or their designated critical habitat. Each federal agency is required under the Act to insure that any action they authorize, fund, or carry out is not likely to jeopardize the continued existence of a listed species or result in the destruction or adverse modification of designated critical habitat. To jeopardize the continued existence of a listed species means "to engage in an action that reasonably would be expected, directly or indirectly, to reduce appreciably the likelihood of both the survival and recovery of a listed species in the wild by reducing the reproduction, numbers, or distribution of the species."[11]

To facilitate compliance with the requirements of the Endangered Species Act subsection (a)(2), the Environmental Protection Agency Office of Pesticide Programs has established procedures to evaluate whether a proposed registration action may directly or indirectly reduce appreciably the likelihood of both the survival and recovery of a listed species in the wild by reducing the reproduction, numbers, or distribution of any listed species (U.S. EPA 2004). After the Agency's screening-level risk assessment is conducted, if any of the Agency's listed species LOCs are exceeded for either direct or indirect effects, an analysis is conducted to determine if any listed or candidate species may co-occur in the area of the proposed pesticide use or areas downstream or downwind that could be contaminated from drift or runoff/erosion. If determined that listed or candidate species may be present in the proposed action areas, further biological assessment is undertaken. The extent to which listed species may be at risk then determines the need for the development of a more comprehensive consultation package as required by the Endangered Species Act.

The federal action addressed herein is the proposed re-registration of pesticide product that contains the active ingredient acrolein.

[11] 50 C.F.R. § 402.02

6.3.5.1 Action Area

For listed species assessment purposes, the action area is considered to be the area affected directly or indirectly by the Federal action and not merely the immediate area involved in the action. At the initial screening level, the risk assessment considers broadly described taxonomic groups and so conservatively assumes that listed species within those broad groups are collocated with the pesticide treatment area. This means that terrestrial plants and wildlife are assumed to be located adjacent to the treated site and aquatic organisms are assumed to be located in surface water that is the treated site. The assessment also assumes that the listed species are located within an assumed area which has the relatively highest potential exposure to the pesticide, and that exposures are likely to decrease with distance from the treatment area. The use characterization section of this risk assessment presents the pesticide use sites that are used to establish initial collocation of species with treatment areas.

6.3.5.2 Taxonomic Groups Potentially at Risk

If the assumptions associated with the screening-level action area result in RQs that are below the listed species LOCs, a "no effect" determination conclusion is made with respect to listed species in that taxa, and no further refinement of the action area is necessary. Furthermore, RQs below the listed species LOCs for a given taxonomic group indicate no concern for indirect effects upon listed species that depend upon the taxonomic group covered by the RQ as a resource. However, in situations where the screening assumptions lead to RQs in excess of the listed species LOCs for a given taxonomic group, a potential for a "may affect" conclusion exists and may be associated with direct effects on listed species belonging to that taxonomic group or may extend to indirect effects upon listed species that depend upon that taxonomic group as a resource. In such cases, additional information on the biology of listed species, the locations of these species, and the locations of use sites could be considered to determine the extent to which screening assumptions regarding an action area apply to a particular listed organism. These subsequent refinement steps could consider how this information would impact the action area for a particular listed organism and may potentially include areas of exposure that are downwind and downstream of the pesticide use site.

Assessment endpoints, exposure pathways, the conceptual model addressing proposed acrolein re-registration uses, and the associated exposure and effects analyses conducted for the acrolein screening-level risk assessment are in **Sections 6** and **7.** The assessment endpoints used in the screening-level risk assessment include those defined operationally as reduced survival, reproduction, and growth for both aquatic and terrestrial animal species from direct acute and direct chronic exposures. These assessment endpoints address the standard set forth in the Endangered Species Act requiring federal agencies to ensure that any action they authorize does not reduce appreciably the likelihood of both the survival and recovery of a listed species in the wild by reducing the reproduction, numbers, or distribution of the species. Risk estimates (*i.e.*, RQs integrating exposure and effects) are calculated for broad-based taxa groups for the screening-level risk assessment and presented in **Section 8**.

Both acute endangered species and chronic risk LOCs are considered in the screening-level risk assessment to identify direct and indirect effects to taxa of listed species. This section identifies direct effect concerns, by taxa, triggered by exceeding listed species LOCs in the screening-level risk assessment with an evaluation of the potential probability of individual effects for exposures that may occur at the established listed species LOC. Data on exposure and effects collected under field conditions are evaluated to make determinations on the predictive utility of the direct effect screening assessment findings to listed species. Additionally, the results of a screen for indirect effects to listed species, using direct effect acute and chronic LOCs for each taxonomic group, are presented and evaluated.

6.3.5.3 Listed Species Risk Quotients

A description of the potential direct effects associated with exposure to acrolein is discussed for each of the taxonomic groups below. **Table 33** provides a summary of the direct effects for Federally-listed threatened/endangered species, including the range of RQ values and the acute dose-response slopes used in evaluating the probability of individual effects on listed species.

Table 33. Summary of direct effects for Federally listed species from herbicidal uses.			
Listed Species Taxonomic Group of Concern	**Direct Effects**	**Slope[a]**	**RQ**
Freshwater Fish	Acute: mortality	6.4	1,071
Aquatic-phase Amphibians	Acute: mortality	4.5	2,143
Freshwater Invertebrates	Acute: mortality/immobilization	4.5	>484
Saltwater Fish	Acute: mortality	4.5	35
Saltwater Mollusc	Acute mortality	4.5	273
Aquatic Plants: Vascular Non-vascular	Acute: cell density	4.5	600 1,250
Birds	Acute: mortality	4.5	0.47
Mammals	Acute: mortality	4.5	0.26
Terrestrial Plants: Monocots Dicots	Acute: no data Acute: no data	-- --	-- --

[a]Raw data were not provided so the default value of 4.5 is used.
*Dose-based value.

6.3.5.3.1 Freshwater Fish and Amphibians

Listed species acute risk LOCs for direct effects on freshwater fish (RQ = 1,071) and amphibians (RQ = 2,143) are exceeded for acrolein when used at the maximum label rate for herbicidal use in water.

6.3.5.3.2 Freshwater Invertebrates

Listed species acute risk LOCs for direct effects on freshwater invertebrates are exceeded (RQ>484) for acrolein when used at the maximum treatment rate for herbicidal use in flowing and static waters.

6.3.5.3.3 Estuarine/Marine Fish and Invertebrates

Listed species acute risk LOCs for direct effects on estuarine/marine fish and invertebrates are exceeded with RQ values of 35 and 273, respectively. No chronic estuarine/marine fish or invertebrate toxicity data were submitted and no useable data were located in the open literature for acrolein; therefore, chronic effects associated with estuarine/marine fish and invertebrate exposure to acrolein are unknown.

6.3.5.3.4 Aquatic Plants

As would be expected from an herbicide, listed species LOCs for direct effects on aquatic vascular and nonvascular plants are exceeded with RQ values of 600 and 1,250, respectively

6.3.5.3.5 Birds

The listed species acute risk LOC for direct effects on birds is exceeded with RQ values of 0.47 for species such as the spotted sandpiper that may rely on acrolein-treated canals for drinking water. No chronic toxicity data are available with which to evaluate potential chronic risks to birds from the use of acrolein.

6.3.5.3.6 Mammals

The listed species acute risk LOC for direct effects on mammals is exceeded with RQ values of 0.26 for species such as the river otter that may rely on acrolein-treated canals for drinking water. No chronic risk LOCs are exceeded for mammals

6.3.5.4 Probit Dose Response Relationship

6.3.5.4.1 Aquatic Listed Species Probability of Effects on Individuals

The probability of individual effects at estimated acute RQs above the listed species acute risk LOC was calculated. The probit slopes used in this analysis were obtained from dose-response relationships used in calculating RQs. For freshwater fish, the probit dose-response slope is 6.4. Should exposure to listed freshwater fish occur at the maximum treatment rate of 15 mg/L, the probability of one individual being affected is 1 in 1.00 (*i.e.*, 100%) (**Appendix E**).

The probability of individual effects to listed freshwater invertebrates should exposure occur at the maximum treatment rate is again 100%. The probit dose-response slope used for freshwater invertebrates was 4.5 (the default value used in OPP assessments).

6.3.5.5 Summary of Potential effects on Federally-listed species.

. **Table 30** provides a summary of potential direct effects to listed taxa. Across all taxa evaluated, there is a potential risk to listed species and to critical habitat for listed species.

Table 30. Potential listed species risks associated with direct or indirect effects due to treatment of irrigation canals with acrolein.

Listed Taxon	RQ	Direct Effects from Acute Exposures	Indirect Effects
		Aquatic	
Aquatic vascular plants	1,250	Yes	Yes[6]
Freshwater invertebrates	>484	Yes	Yes[4,5]
Marine/estuarine crustaceans			
Mollusks	273	Yes	Yes[4,5]
Freshwater fish	1,071	Yes	Yes[4,5]
Marine/estuarine fish	35	Yes	Yes[4,5]
Aquatic phase amphibians	2,143	Yes	Yes[4,5]
		Terrestrial	
Semi-aquatic plants	presumed[1]	presumed[1]	presumed[2]
Terrestrial plants	presumed[1]	presumed[1]	presumed[2]
Insects	presumed[1]	presumed[1]	presumed[2]
Birds	0.47	Yes	Yes[3,4]
Terrestrial phase amphibians	0.47	Yes	Yes[3]
Reptiles	0.47	Yes	Yes[3,4]
Mammals	0.26	Yes	Yes[3,4]

[1] No toxicity data are available to define RQ values for this exposure.
[2] Since the risks of direct effects to semi-aquatic and terrestrial plants are unknown, risks of indirect effects to organisms relying upon these plants are unknown.
[3] Direct effects to small mammals, amphibians, reptiles and birds could result in indirect effects to animals that rely upon them as food.
[4] Direct effects to aquatic animals could result in indirect effects to animals that rely upon them as food.
[5] Direct effects to aquatic plants (including unicellular and vascular) could result in indirect effects to animals that rely upon them as food.
[6] Direct effects to aquatic plants (including unicellular and vascular) could result in alterations in the plant community structure through changes in species interactions.

7 References

References from the Open Literature

Butler, P. A. 1965. *Effects of Herbicides on Estuarine Fauna*. 18: 576-580.

Caldironi, Hugo A., Diego J. Bentivegna, and Miles R. Rhea. 2004. Irrigation of pepper plant (*Capsicum* sp.) with water containing acrolein. *Agricultural Water Management* **67**(2004):235-240.

Environment Australia. 2002. Environmental Assessment Report Magnicide H Herbicide containing acrolein (950 g/L). Environmental Quality Division, Risk Assessment and Policy Section.

Geiger, D. L., L. T. Brooke, and D. J. Call. 1990. Acute Toxicities of Organic Chemicals to Fathead Minnows (Pimephales promelas). 5(): 332 p.-.

Geiger, D. L., D. J. Call, and L. T. Brooke. 1988. Acute Toxicities of Organic Chemicals to Fathead Minnows (Pimephales promelas). (): 355-.

Ghilarducci, D. P. and Tjeerdema, R. S. 1995. Fate and Effects of Acrolein. *Reviews of Environmental Contamination and Toxicology* **144:**95-146.

Holcombe, G. W., G. L Phipps, A. H. Sulaiman, and A.D. Hoffman. 1987. Simultaneous multiple species testing: Acute toxicity of 13 chemicals to 12 diverse freshwater amphibian, fish, and invertebrate families. *Archives of Environmental Contamination and Toxicology* **16**:697-710.

Hudson, R. H., R. K. Tucker, and M. A. Haegele. 1984. *Handbook of Toxicity of Pesticides to Wildlife*. Second Edition. U.S. Fish and Wildlife Service. Patuxent Wildlife Research Center. TRID 470214075.

Sabourin, T. D. 1986. *A Summary of the Results of Toxicity Tests Performed by Battelle Between March and August in 1986*. Letter to L. Brooke, University of Wisconsin-Superior, Center for Lake Superior Environmental Studies. September 3, 1986. 2 p.

Salma, Tauseef. 2001. *Henry's Law Constant for Acrolein.* Baker Petrolite Internal Memorandum to Miles Rhea, dated January 4, 2001.

Smith, Curtis W. 1962. *Acrolein.* John Wiley and Sons, London.

Spehar R. L. 1989. Aquatic Toxicity Test Information on Acrolein with Fathead Minnows (*Pimephales promelas*) and Flagfish (*Jordanella floridae*). (): 5 p.

State of Washington, Department of Ecology. 2002. *Irrigation System Aquatic Weed Control National Pollution Discharge Elimination System Waste Discharge General Permit,* Permit No. WAG-91000.

Sunzenauer, Ingrid, Edward Fite, Timothy Barry, Henry Nelson, Edward Odenkirchen, and Dirk Young. 2004. *A Discussion with the FIFRA Scientific Advisory Panel Regarding the Terrestrial and Aquatic Level II Refined Risk Assessment Models (Version 2.0).* Presentation to the FIFRA Science Advsiry Panel, March 4, 2004. Environmental Fate and Effects Division, Office of Pesticide Programs, United States Environmental Protection Agency. http://www.epa.gov/oppefed1/ecorisk/fifrasap/rra_title_cont.htm

USEPA. 1993. *Wildlife Exposure Factors Handbook.* United States Environmental Protection Agency. Office of Research and Development. EPA/600/R-93/187.

USEPA. 2006. *User's Guide: T-REX Version 1.3.1 (Terrestrial Residue Exposure model).* United States Environmental Protection Agency. Environmental Fate and Effects Division.

References Submitted by Registrants (MRIDs)

00117668. Tucker, R.; Hudson, R. 1970. *Acrolein: Acute Oral LD50 for Mallard Drakes.* (Unpublished study received Mar 20, 1975 under 10707-9; prepared by U.S. Fish and Wildlife Service, Denver Wildlife Research Center, Unit of Physiological and Pharmacological Studies, submitted by Magna Corp., Santa Fe Springs, CA; CDL:165015-A.

05008271. Macek, K. J., M. A. Lindberg, S. Sauter, K. S. Buxton, and P. A. Costa. 1976. *Toxicity of Four Pesticides to Water Fleas and Fathead Minnows.* Duluth, Minn.: U.S. Environmental Protection Agency, Environmental Research Laboratory. (EPA report no. EPA-600/3-76-099; available from: NTIS, Springfield, VA; PB-262 912).

40228401. Mayer, F. 1986. *Acute toxicity handbook of chemicals to estuarine organisms: EPA/600/X-86/231.* Prepared by USEPA Environmental Research Laboratory, Gulf Breeze, FL. 275 p.

40840602. Robillard, Kenneth A. *Water Solubility of Acrolein.* Performed by Health and Environmental Laboratories, Eastman Kodak Co. Rochester, NY. Study No. EN 040-UKA001-1. Submitted by Baker Performance Chemicals.. Houston, TX.

40945401. Haag, Werner. R., David Yao, Thomas Pettit, and Theodore Mill. 1988. *Estimation of Hydrolysis Rate Constants for Acrolein (Magnacide H Herbicide and Magnacide B Microbiocide) in the Environment.* Unpublished study performed by SRI, International, Menlo Park, CA. SRI Project 3562-3. Study submitted by Baker Performance Chemicals, Houston TX.

41257001. David, R. (1989) *Acute Oral Toxicity Study of Acrolein, Inhibited in Rats: Final Report: Study G-7230.220.* Unpublished study pre- pared by Microbiological Associates, Inc. 87 p.

41513201. Bowman, J. 1990. *Acute Flow-through Toxicity of Acrolein to Bluegill (Lepomis macrochirus): Lab Project Number: 37669.* Unpublished study prepared by Analytical Bio-chemistry Laboratories, Inc. 35 p.

41513202. Blakemore, G. 1990. *Acute Flow-through Toxicity of Acrolein to Daphnia magna: Lab Project Number: 37671.* Unpublished study prepared by Analytical Bio-chemistry Laboratories, Inc. 269 p.

41513203. Bowman, J. 1990. *Acute Flow-through Toxicity of Acrolein to Rainbow Trout (Oncorhynchus mykiss): Lab Project Number: 37670.* Un- published study prepared by Analytical Bio-chemistry Laboratories, Inc. 285 p.

42183301. Pedersen, C., and B. Helsten. 1991. *Acrolein: 21-Day Acute Oral LD50 Study in Mallard Ducks: Lab Project Number: 118-001-04.* Unpublished study prepared by Bio-Life Associates, Ltd. 54 p.

41869101. Hoberman, A. 1991. *Reproductive Effects of Acrolein Administered Orally via Gavage to Crl:CD (SD)BR Rats for Two Generations, with one Litter per Generation: Lab Project Number: 603/003: RD/ 0155/191.* Unpublished study prepared by Argus Research Laboratories, Inc. 1298 p.

42620901. Hughes, J., and M. Alexander. 1992. *The Toxicity of Acrolein to Anabaena flos-aquae: Lab Project Number: B962-01-2.* Unpublished study prepared by Malcolm Pirnie, Inc. 36 p.

42620902. Hughes, J., and M. Alexander. 1992. *The Toxicity of Acrolein to Navicula pelliculosa: Lab Project Number: B962-01-3.* Unpublished study prepared by Malcolm Pirnie, Inc. 36 p.

42620903. Hughes, J., and M. Alexander. 1992. *The Toxicity of Acrolein to Skeletonema costatum: Lab Project Number: B962-01-4.* Unpublished study prepared by Malcolm Pirnie, Inc. 36 p.

42620904. Hughes, J., and M. Alexander. 1992. *The Toxicity of Acrolein to Lemna gibba G3: Lab Project Number: B962-01-5.* Unpublished study prepared by Malcolm Pirnie, Inc. 34 p.

42620905. Hughes, J. and M. Alexander. 1992. *The Toxicity of Acrolein to Selenastrum capricornutum: Lab Project Number: B962-01-1.* Unpublished study prepared by Malcolm Pirnie, Inc. 36 p.

42837601. Smith, A. M. 1993. *(^{14}C-Acrolein) – Determination of the aerobic aquatic metabolism.* Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA; sponsored and submitted by Baker Performance Chemicals, Inc., Houston, TX. SLI Report: #91-3-3747; SLI Study #12167-0789-6100-750. Experiment initiated December 4, 1992, and completed February 1, 1993 (p. 11). Final report issued June 3, 1993.

42949201. Smith, A. M. 1993. *(^{14}C-Acrolein) – Determination of the anaerobic aquatic metabolism.* Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA; sponsored and submitted by Baker Performance Chemicals, Inc., Houston, TX. SLI Report # 91-3-3680, SLI Study # 12167-1089-6101-755. The experiment was initiated on November 9 and terminated on May 21, 1993 (p. 11). Final report issued September 22, 1993.

43164301. Bettencourt, M. 1994. *Acrolein--Acute Toxicity to Mysid Shrimp (Mysidopsis bahia) Under Flow-Through Conditions: Final Report: Lab Project Number: 94-1-5148: 12167.0292.6106.515.* Unpublished study prepared by Springborn Labs, Inc. 88 p.

43164302. Bettencourt, M. 1994. *Acrolein--Acute Toxicity to Eastern Oyster (Crassostrea virginica) Under Flow-Through Conditions: Final Report: Lab Project Number: 94-2-5151: 12167.0292.6107.504.* Unpublished study prepared by Springborn Labs, Inc. 88 p.

43225202. Bettencourt, M. (1994) *Acrolein--Acute Toxicity to Sheepshead Minnow (Cyprinodon variegatus) Under Flow-Through Conditions: Final Report: Lab Project Number: 94-1-5150: 12167.0292.6105. 505.* Unpublished study prepared by Springborn Labs., Inc. 91 p.

43037301. Chou, T. W., and R. J. Spanggord. 1990. Estimation of the aerobic biotransformation rates for acrolein (Magnacide H Herbicide, Magnacide B Biocide) in soil. SRI Project No. 3562-4. Unpublished study performed by SRI International, Menlo Park, CA; and submitted by Baker Performance Chemicals, Inc., Houston, TX.

45205107. Lorz, H., S. Glenn, R. Williams, *et al.* 1979. *Effects of Selected Herbicides on Smolting of Coho Salmon: Lab Project Number: R-804283:* EPA-600/3-79-071. Unpublished study prepared by Corvallis Environmental Research Laboratory. 103 p.

46976905. Preus, Martin W., and Charles L. Kissel. 1982. *Controlling Plant Growth in Irrigation Systems: 1982 Nebraska Summer Research with Magnacide H. 1982 Nebraska Irrigation Expo & Water Conference.* Performed by Magna Corporation, Santa Fe Springs, NM, and submitted by Baker Petrolite, Bakersfield CA.

46976913. Baker Petrolite Corporation.2006. *Magnacide H herbicide Application by State.* Submitted by Baker Petrolite Corporation.

46976916. Cardwell, Rick, Karen Garnes, and Brandon Ball. 2004. *Engineering Report to Support General Permit for Aquatic Weed Control in Irrigation Systems.* Prepared by Parametrix, Sumner, WA for the Washington State Water Resources Association. Submitted by Baker Petrolite Corporation, November 6, 2006.

47008401. Irwin, Katherine. 1988. *Henry's Law Constant for Acrolein (Magnacide H Herbicide and Magnacide B Microbiocide).* Performed by SRI International, 333 Ravenswood Avenue, Menlo Park, CA. Submitted by Baker Performance Chemicals, 3920 Essex Lane Houston, TX. SRI Project PYU 3562.

47008403. Bonnivier, Bonnie, and Joseph Penkala. 2000. *Magnacide H Herbicide Irrigation Dissipation in Kern County Water Storage Districts.* Study conducted and submitted by Baker Petrolite, Bakersfield, CA.

47008404. Baker Performance Chemicals. *1986 Washington Magnacide H Monitoring Report.* Submitted by Baker Petrolite, Bakersfield, CA.

47008407. Penkala, Joe. 2005. *Acrolein Residual Analysis During Magnacide H Herbicide Application in Support of Air Quality Monitoring in Kern Delta Irrigation District, Bakersfield, CA.* Submitted by Baker Petrolite Corporation, November 8, 2006.

92001003. Conn, R. 1990. *Baker Performance Chemicals Inc. Phase 3 Summary of MRID 00117672. Determination of* LD_{50} *Acrolein - Bobwhite Quail: Project K-1524.* Prepared by MBA Laboratories, Inc. 10 p.

Internal Office of Pesticide Program Documents

D179940. Spatz, Dana S. 1992. *Acrolein, Response dated August 6, 1991 to Phase IV Data Call-In.* Internal EPA Memorandum to Linda Deluise dated October 5, 1992

D320989. Jones, R. David, And Greg Orrick. 2007. Data Evaluation Records for Certain Aerobic Aquatic and Anaerobic Aquatic Metabolism Studies for Acrolein. Internal EPA Memorandum to Amaris Johnson, dated January 11, 2007.

8 APPENDIX A. Use Closure Memo

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

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

Memorandum

SUBJECT: Revised: Use Closure Memorandum for Acrolein (000701)

FROM: Amaris Johnson, Chemical Review Manager
RB1
Special Review and Reregistration Division

TO: Acrolein Team

DATE: December 12, 2005

The purpose of this memo is to provide use information that will be incorporated into the preliminary risk assessments for acrolein. This memorandum and its attachment act as a guide as the Agency prepares for the reregistration of acrolein. This information was compiled as a result of review of product labels, the August 30, 2005 SMART Meeting, and subsequent discussions with the registrant. Should additional use information become available during the development of the Preliminary Risk Assessments, the Chemical Review Manager will inform the entire team.

Acrolein is a restricted use pesticide with two major uses. The MAGNACIDE H product is used as an aquatic herbicide for the control of algae, and floating and submersed weeds in irrigation ditches and canals. The MAGNACIDE B product is used as a microbiocide in oilfields to control bacterial growth. In addition, there are several Special Local Need (SLN) registrations, for use in reservoirs. For both MAGNACIDE H and MAGNACIDE B, the technical grade active ingredient (TGAI) is 95% pure, and there are no residential uses.

The risk assessments for acrolein will be based on the use sites listed in the attached acrolein Use Patterns Table. Additional information can be found in the use and usage data contained in the product labels (registration #: 10707-9 and 10707-10), and in the materials distributed by Baker Petrolite at the aforementioned SMART Meeting.

Water treated with acrolein must be released into irrigated fields, either crop bearing, fallow or pasture where the water remains there. Otherwise, treated water must be held for 6 days before being released into fish bearing water bodies, or those that run into them. The maximum application concentration of MAGNACIDE H Herbicide in irrigation canals is 15 ppm. The professional applicators do routine checks of the irrigation canal to ensure that this 15ppm concentration is not exceeded during the course of an application (refer to Attachment A).

The attachments A, B and C for this document provide details on the labeled application rates of acrolein based on different factors such as weed conditions, total application time, and flow of water. The attachments also contain information on the state-specific decreased holding times and application rates. The information detailed in the attachments is from the MAGNACIDE H Herbicide Application and Safety Manual, which was revised in March 2005. Additional attachment information was obtained from the SLN labels. On both the labels and the MAGNACIDE H Herbicide Application and Safety Manual there is no reapplication interval, nor maximum number of reapplications specified. In addition, there is no description of how holding times are calculated.

<u>Supported Uses</u>

Baker Petrolite intends to support the use of MAGNACIDE H in irrigation canals, ditches, along with use in reservoirs (refer to Attachment A). In addition, the registrant will support the use of MAGNACIDE B in oil fields.

<u>Supported Registrations</u>:

There are 13 active acrolein registrations: 5 Section 3s and 8 SLNs (24(c)s). Baker Petrolite produces the TGAI, and as the sole technical registrant, intends to support two of the five section 3 registrations which are MAGNACIDE H (10707-9) and MAGNACIDE B (10707-10). The remaining 3, Section 3 registrations will be voluntarily cancelled: 10707-15, 10707-16, and 10707-17. There are 8 SLN (24(c)) registrations, yet Baker Petrolite has indicated that they are interested in supporting six of these SLNs. Three of these SLNs (WA0400017, ID900005, and NE030003) reduce the holding time specified on the Section 3 label for treated water (refer to Attachment B and C). The other three SLNs (UT030001, OR910018 and CA780039) are for reservoir use (refer to Attachment C). The two SLNs that will *not* be supported are OR950002 and CA930006 which are for use in rodent burrows and burrow entrances.

This memo includes three attachments: Attachment A is the Acrolein Use Patterns Table, Attachment B is the SLN for decreased holding time in Washington State, and Attachment C has the SLNs for decreased holding time in Idaho and Nebraska, as well as the SLNs for reservoir treatment in Utah, California, and Oregon. The preliminary risk assessments for acrolein are scheduled for completion in April 2006 with a projected RED signature date of January 2007.

Attachment A:

Table of Acrolein Use Patterns

MAGNACIDE H

Condition Code:	*Application Rate (gallons/cubic feet/second):*	*Application Rate (lb ai/cubic feet/second):*	*Application Rate (ppm):*
A: Little algae and pondweed less than 6 inches long	0.17	1.14	1.3[1]
B: Algae (non-floating) and pondweed <12 inches long	0.25	1.68	2.0[1]
			1.3[2]
			1.0[3]
C: Algae (some floating) and pondweed 12 - 24 inches long	0.50	3.35	3.9[1]
			2.6[2]
			1.9[3]
D: Algae (some floating) and mature pondweed	1.0	6.7	7.9[1]
			5.2[2]
			3.9[3]
E: Choked conditions	1.5	10.1	11.8[1]
			7.9[2]
			5.9[3]

[1] Based on a 4 hour application time
[2] Based on a 6 hour application time
[3] Based on an 8 hour application time

Reapplication Intervals: Depend on regrowth of aquatic weeds, water temperature, water quality, amount of sunlight, and rate of canal flow.

MAGNACIDE B		
Treatment Type:	*Application Rate (ppm)*:	
Continuous	5 - 50	Typical: 10 – 25
Batch/Slug	25 - 2000	Typical: 100 – 500
Down Hole Squeeze	0.5 - 1.2 % mixture, injected into well and surrounding formation, diluted by fluids present in the well bore and formation	

Attachment B

MAGNACIDE H Herbicide (10707-9) Reduced Holding Time for Washington State Special Local Need Registration
EPA SLN WA-040017

An NPDES permit is needed in the state of Washington for MAGNACIDE H Herbicide applications.

In order to determine the requisite, minimum holding time from the point of acrolein application to the confluence of the acrolein-treated Irrigation District water and any natural waterbody, consult the table below. Any application can be held longer than the minimum holding times outlined in the table below. First determine the appropriate Correction Factor that applies to the field situation at hand.

App. Rate (ppm)	**Correction Factor (cubic feet per second (cfs) of the natural waterbody divided by cfs of Irrigation District water)**										
	1	5	10	50	75	100	250	500	750	1000	1043
	Minimum Holding Time (Hours)										
8.0	115	91	81	57	51	47	34	23	17	13	12
7.0	113	89	79	55	49	45	32	21	15	12	12
6.0	111	87	77	53	47	43	29	19	13	12	12
5.0	108	84	74	50	44	40	27	16	12	12	12
4.0	105	81	71	47	41	37	23	13	12	12	12
3.0	100	77	67	43	37	33	19	12	12	12	12
2.0	95	71	61	37	31	27	13	12	12	12	12
1.0	84	61	50	27	21	16	12	12	12	12	12

Refer to the Special Local Need Registration EPA SLN WA-040017 for additional details.

Attachment C

MAGNACIDE H Herbicide (10707-9) Reduced Holding Times for Idaho Special Local Need Registration
EPA SLN No. ID-900005

PPM Acrolein	Holding Time in Hours*
8.1 - 15.0	60
4.1 - 8.0	50
2.1 - 4.0	40
1.1 - 2.0	30

* Do not release undiverted treated water into any fish bearing waters or where it will drain into them as mandated by the following treatment regime.

Refer to Special Local Need Registration EPA SLN ID-900005 for additional detail.

MAGNACIDE H Herbicide (10707-9) Reduced Holding Times for
Nebraska Special Local Need Registration
EPA SLN No. NE 03-0003

The SLN for Nebraska specifies that treated water should not be released for 36 hours into any fish bearing waters or where it will drain into them. All other applicable direction, restrictions and precautions on the EPA registered labeling are to be followed.

Refer to Special Local Need Registration EPA SLN NE03-0003 for additional detail.

MAGNACIDE H Herbicide (10707-9) Reservoir Treatment
Special Local Need Registrations:
UT-03-0001, CA-780039, OR-910018

These labels specify that the concentration of MAGNACIDE H should not exceed 15 ppm in water.
Water treated with MAGNACIDE H Herbicide must be used for irrigation of fields , either crop bearing, fallow or pasture, where the treated water remains on the field or held for 6 days before being released into fish bearing waters or where it will drain into them.

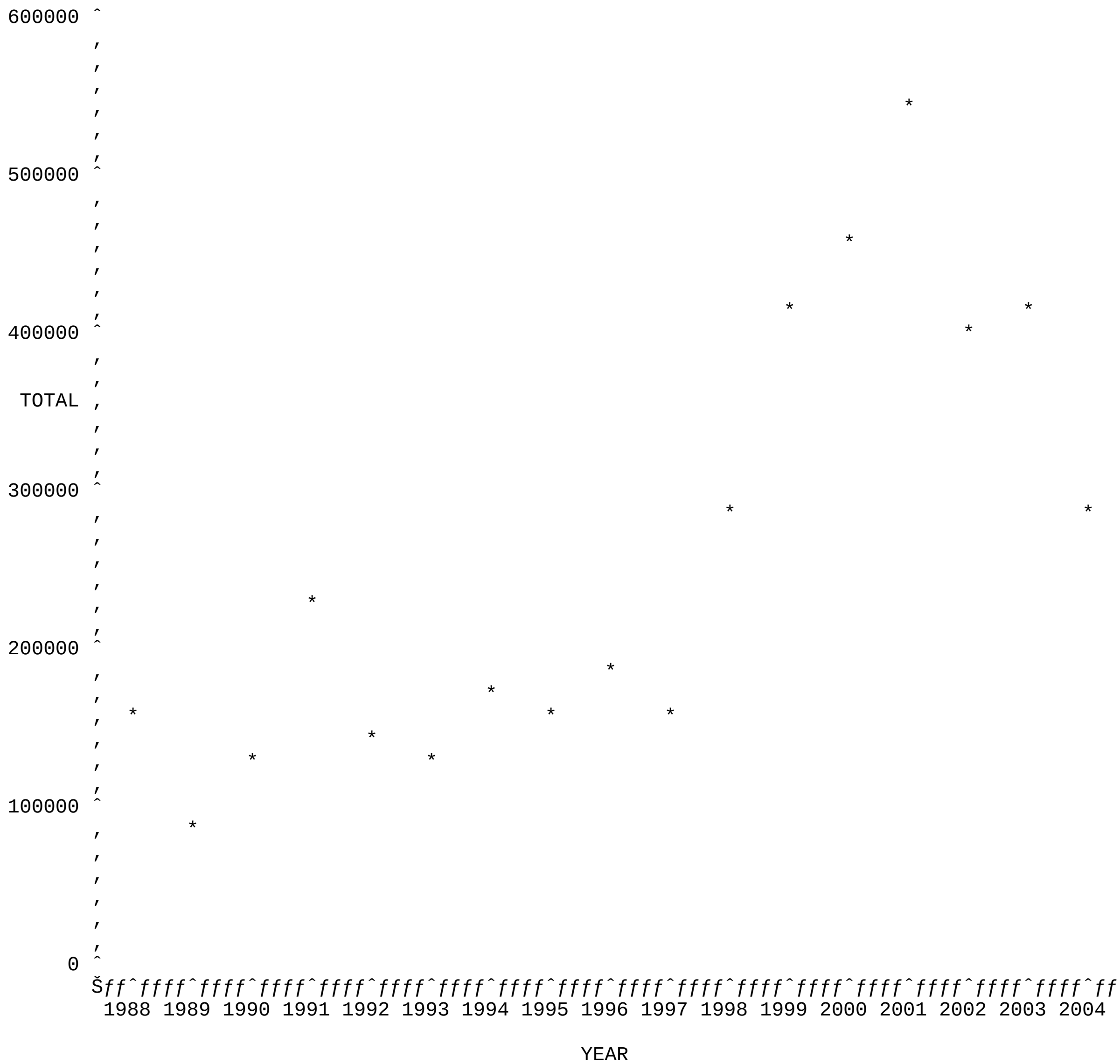
9 APPENDIX B. SAS Output for Toxic Release Inventory Data.

TOTAL ACROLEIN RELEASE BY YEAR (Pounds)

Obs	YEAR	TOTAL
1	1988	153593.00
2	1989	88042.00
3	1990	125103.00
4	1991	234408.00
5	1992	139285.00
6	1993	126104.00
7	1994	173184.00
8	1995	154771.00
9	1996	183186.00
10	1997	153593.00
11	1998	282320.00
12	1999	411914.00
13	2000	451233.00
14	2001	545452.00
15	2002	406679.60
16	2003	417145.78
17	2004	284480.39

TOTAL ACROLEIN RELEASE BY YEAR

Plot of TOTAL*YEAR. Symbol used is '*'.



SUMMARY STATISTICS FOR ACROLEIN RELEASES FROM 1995 THROUGH 2004

The UNIVARIATE Procedure
Variable: TOTAL

Moments

N	17	Sum Weights	17
Mean	254734.928	Sum Observations	4330493.77
Std Deviation	140544.497	Variance	1.97528E10
Skewness	0.75058248	Kurtosis	-0.7721418
Uncorrected SS	1.41917E12	Corrected SS	3.16044E11
Coeff Variation	55.1728411	Std Error Mean	34087.0474

Basic Statistical Measures

Location		Variability	
Mean	254734.9	Std Deviation	140544
Median	183186.0	Variance	1.97528E10
Mode	153593.0	Range	457410
		Interquartile Range	253087

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	7.473071	Pr > |t|	<.0001
Sign	M	8.5	Pr >= |M|	<.0001
Signed Rank	S	76.5	Pr >= |S|	<.0001

Quantiles (Definition 5)

Quantile	Estimate
100% Max	545452
99%	545452
95%	545452
90%	451233
75% Q3	406680
50% Median	183186
25% Q1	153593
10%	125103
5%	88042
1%	88042
0% Min	88042

SUMMARY STATISTICS FOR ACROLEIN RELEASES FROM 1995 THROUGH 2004

The UNIVARIATE Procedure
Variable: TOTAL

Extreme Observations

-----Lowest-----		-----Highest----	
Value	Obs	Value	Obs
88042	2	406680	15
125103	3	411914	12
126104	6	417146	16
139285	5	451233	13
153593	10	545452	14

CONTRIBUTION OF EACH STATE TO TOTAL ACROLEIN RELEASES DURING 1988 - 2004

The FREQ Procedure

STATE	Frequency	Percent	Cumulative Frequency	Cumulative Percent
Al	101780	2.35	101780	2.35
Ar	5	0.00	101785	2.35
Ca	509	0.01	102294	2.36
Ga	194026	4.48	296320	6.84
Ia	3731.91	0.09	300051.9	6.93
Il	168815	3.90	468866.9	10.83
In	58	0.00	468924.9	10.83
Ks	19559.99	0.45	488484.9	11.28
La	169160	3.91	657644.9	15.19
Me	16941	0.39	674585.9	15.58
Mi	38227	0.88	712812.9	16.46
Mn	180093	4.16	892905.9	20.62
Ms	459709	10.62	1352615	31.23
NC	247397.6	5.71	1600013	36.95
NY	6	0.00	1600019	36.95
Ne	8746	0.20	1608765	37.15
Oh	32875	0.76	1641640	37.91
Or	2614	0.06	1644254	37.97
Tn	6	0.00	1644260	37.97
Tx	2512765	58.02	4157025	95.99
Va	67780	1.57	4224805	97.56
WV	26251	0.61	4251056	98.17
Wi	79438.17	1.83	4330494	100.00

Obs	STATE	YEAR	_TYPE_	_FREQ_	SUM
1	Ca	1991	0	1	2.00
2	Ca	1992	0	1	2.00
3	Ca	2002	0	1	114.00
4	Ca	2003	0	1	253.00
5	Ca	2004	0	1	138.00
6	Ks	2002	0	1	7430.20
7	Ks	2003	0	1	5520.88
8	Ks	2004	0	1	6608.91
9	Ne	2002	0	1	2017.40
10	Ne	2003	0	1	4252.40
11	Ne	2004	0	1	2476.20
12	Or	1998	0	1	2614.00

10 APPENDIX C. Washington State Irrigation Canal Monitoring Data and Associated RQ Values.

Table X. Acute RQ values for acrolein from measured values at NPDES POC locations at WA irrigation districts.

Description of Location	Value (ppb)	Sample Info	FW Fish RQ[1]	FW Amphibian RQ[1]	FW Invertebrate RQ[1,2]	E/M Fish RQ[2]	E/M Invertebrate RQ[2]
Quincy (3 Gates)	1	*	0.07	0.14	~~0.03~~	~~0.00~~	~~0.02~~
South (Esquatzel Wasteway)	1		0.07	0.14	~~0.03~~	~~0.00~~	~~0.02~~
South (Wahluke Branch 5 Wasteway 1)	1.1		0.08	0.16	~~0.04~~	~~0.00~~	~~0.02~~
Quincy (5th Section Canal)	1.5	*	0.11	0.21	~~0.05~~	~~0.00~~	~~0.03~~
South (Esquatzel Wasteway)	2.2		0.16	0.31	0.07	~~0.01~~	~~0.04~~
Quincy (78-8)	2.4	*	0.17	0.34	0.08	~~0.01~~	~~0.04~~
Quincy (3 Gates)	2.9	*	0.21	0.41	0.09	~~0.01~~	0.05
South (Potholes East 16.4 Wasteway)	3.1		0.22	0.44	0.10	~~0.01~~	0.06
South (Esquatzel Wasteway)	5.6		0.40	0.80	0.18	~~0.01~~	0.10
Quincy (78-8)	8.3	*	0.59	1.19	0.27	~~0.02~~	0.15
South (Potholes East 16.4 Wasteway)	9.3		0.66	1.33	0.30	~~0.02~~	0.17
South (Wahluke Branch 5 Wasteway 1)	12.1		0.86	1.73	0.39	~~0.03~~	0.22
South (Esquatzel Wasteway)	14.6		1.04	2.09	0.47	~~0.03~~	0.27
South (Esquatzel Wasteway)	15		1.07	2.14	0.48	~~0.04~~	0.27
Quincy (5th Section Canal)	21.7		1.55	3.10	0.70	0.05	0.39
Quincy (5th Section Canal)	23.2	*	1.66	3.31	0.75	0.05	0.42
Quincy (W61L lateral)	23.5	*	1.68	3.36	0.76	0.05	0.43
Quincy (Farm Unit 88)	29.2		2.09	4.17	0.94	0.07	0.53
South (Potholes East 16.4 Wasteway)	36.1		2.58	5.16	1.16	0.08	0.66
South (Wahluke Branch 5 Wasteway 1)	62.5		4.46	8.93	2.02	0.15	1.14
Quincy (5th Section Canal)	67.2	*	4.80	9.60	2.17	0.16	1.22
Quincy (3 Gates)	117		8.36	16.71	3.77	0.27	2.13
South (Wahluke Branch 5 Wasteway 1)	225		16.07	32.14	7.26	0.53	4.09
South (Wahluke Branch 5 Wasteway 1)	254		18.14	36.29	8.19	0.59	4.62
Application rate	15000		1071.43	2142.86	483.87	35.05	272.73

* This sample was collected > 48 hours after application.

[1]Toxicity values are as follows: FW fish, 14 ppb; FW amphibian 7 ppb; FW invertebrate, <31 ppb; E/M Fish 428 ppb; E/M invertebrate 55 ppb.
[2]RQ values for FW invertebrates are > value in table.

11 APPENDIX D. Method for Calculating Equivalent Field Application Rate

Method for calculating application rate in lbs a.i./A from aqueous concentration (in mg/L):

1) CINTCP is a parameter used in PRZM that defines the maximum interception storage of the crop. This parameter estimates the amount of rainfall (in cm) that is intercepted by a fully developed plant canopy and retained on the plant surface. Therefore, this is assumed to be equivalent to the amount of irrigation water required for a crop. CINTCP values for crops with light, moderate and maximum canopy densities are listed in table 5-4 of the PRZM manual. The CINTCP for orchard is estimated as a conservative value of 0.40 cm. Example calculations for orchard are shown here.

2) To calculate the volume (cm^3) of irrigation water required for a 1 ha field (equivalent to $1E^8$ cm^2), the CINTCP value (cm) is multiplied by the area of the field. The result is then converted into units of L.

1×10^8 $cm^2 \times 0.4$ cm = 4×10^7 cm^3

4×10^7 cm^3 /ha x (1 L/1000 cm^3) = 4×10^4 L/ha

3) The volume of irrigation water required for a 1 ha field is multiplied by the concentration of acrolein in the irrigation water (mg/L).This results in an estimate of the mass of acrolein (mg) applied to a 1 ha field.

4×10^4 L/ha x 15 mg/L = 6×10^5 mg/ha

4) The units of mg/ha are converted to lbs/A.

6×10^5 mg/ha x ha/2.47 A = 2.43 $\times 10^5$ mg/A

2.43 $\times 10^5$ mg/A x (1g/1000 mg) x (1kg/1000g) x (2.2 lb/ 1kg) = **0.534 lb/A**

Crop	CINTCP (cm)	Volume irrigation water (L) for 1 ha field	Max amount (mg) of acrolein applied to 1 ha	Application rate in mg/A	Application rate in lbs a.i./A
Orchard	0.4	4.00E+04	6.00E+05	2.43E+05	0.534
maximum canopy density (e.g. corn)	0.3	3.00E+04	4.50E+05	1.82E+05	0.401
Moderate canopy density (e.g.soybeans, cotton, tobacco)	0.25	2.50E+04	3.75E+05	1.52E+05	0.334
Light canopy density (e.g. potatoes, peanuts, barley)	0.15	1.50E+04	2.25E+05	9.11E+04	0.200

12 APPENDIX E. Probit Dose-Response Probability of Individual Effect

IEC V1 - Individual Effect Chance Model Version 1

Predictor of chance of individual effect using probit dose-response curve slope and median lethal estimate

Enter LC_{50} or LD_{50}	14	Note: This is not used in calculation, just serves as a reminder to user
Enter desired threshold	1071	Note: This is either the RQ fraction of the toxicity endpoint, the EEC or dose fraction of the dose/concentration at tox endpoint, or the LOC
Enter slope of dose-response	6.4	Note: This is the slope of the dose response relationship from the study providing the above endpoint
z score result	19.3906526	z is the standard normal deviate
Probability associated with z	1	Uses Excel NORMDIST function to estimate P
Chance of individual effect, ~1 in . .	1.00E+00	Calculated as 1/P rounded to 0 decimals

This is based on the formula $\log LC_k = \log LC_{50} + (z/b)$

where: z is the standard normal deviate and b equals slope

Works for dose-response models based on a probit assumption (i.e. log normal distribution of individual sensitivity)

Note: Probability associated with z value may be reported as "0". This is due to the inability of Excel to handle extremes in z scores beyond -8.2
In such cases the chance of individual effect is defaulted to 1 in 10^{16}, which is the limit of Excel reporting.

Ed Odenkirchen, May 28, 2003 EFED/OPP/USEPA