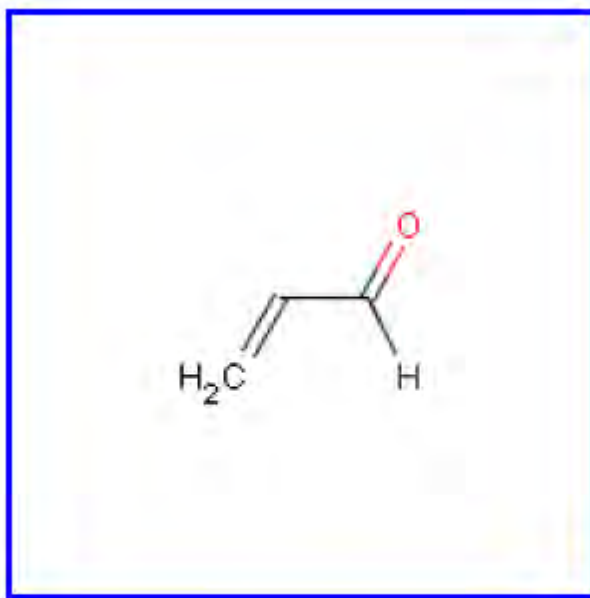


**Risks of Acrolein Use to Federally Threatened  
Alameda Whipsnake**  
(*Masticophis lateralis euryxanthus*)



**MAGNACIDE<sup>®</sup> H**  
CAS 107-02-8 PC Code 000701

**Pesticide Effects Determinations**

**Environmental Fate and Effects Division  
Office of Pesticide Programs  
Washington, D.C. 20460**

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## 1. Executive Summary

The purpose of this assessment is to evaluate potential direct and indirect effects on the Alameda whipsnake (*Masticophis lateralis euryxanthus*) (hereafter referred to as “whipsnake”) arising from FIFRA regulatory actions regarding use of acrolein on agricultural and non-agricultural sites. In addition, this assessment evaluates whether these actions can be expected to result in modification of designated critical habitat for the whipsnake. This assessment was completed in accordance with the U.S. Fish and Wildlife Service (USFWS) and National Marine Fisheries Service (NMFS) *Endangered Species Consultation Handbook* (USFWS/NMFS, 1998) and procedures outlined in the Agency’s Overview Document (U.S. EPA, 2004).

The whipsnake was listed as a threatened species by USFWS in 1997. The species is endemic to Alameda County and is likely to inhabit suitable chaparral and scrub habitats within Alameda, Contra Costa, and possibly western San Joaquin and northern Santa Clara Counties in California and Baja California (Mexico) and both coastal and interior mountain ranges.

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.<sup>1</sup> The chemical's use as an herbicide in irrigation canals and irrigation reservoirs is considered as part of the federal action evaluated in this assessment.

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). While the primary routes of dissipation and degradation are not known, they may include volatilization, microbial metabolism, and/or binding into plants by cross-linking of proteins. While volatilization is definitely a route of dissipation, the relative importance of volatilization to other degradation routes cannot be quantified at this time. Degradation via cross-linking of proteins is related to the pesticidal mode of action, but there are no direct data supporting this mechanism of degradation, and the extent of occurrence is uncertain.

Acrolein forms several degradates in the environment. One of these, 3-hydroxypropanal, forms abiotically, and is in equilibrium with acrolein, and thus reforms to acrolein as it dissipates by other routes. Other prominent degradates include acrylic acid, allyl alcohol, propanol, propionic acid, oxalic acid, and ultimately carbon dioxide. Available toxicity information for acrolein degradates indicates they are considerably less toxic than acrolein, with the exception of 3-hydroxypropanol, which equilibrates with acrolein in water. As is discussed below, the exposure section of the risk assessment is primarily based on the maximum treatment rate of 15 mg/L, with extensive consideration given to the wealth of monitoring data. Because these monitoring studies only report the parent,

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<sup>1</sup>Baker Petrolite. 2000. MAGNACIDE® H Herbicide Product Data.

data are available to consider the risks due to the only parent acrolein at this time. This is expected to only slightly underestimate the risk since the toxicity is dominantly associated with the parent compound. Additionally, the use of monitoring data inherently captures the reformation of acrolein from 3-hydroxypropanol.

The effects determinations for the whipsnake are based on a weight-of-evidence method which relies heavily on an evaluation of risks to each taxon relevant to assess both direct and indirect effects to the listed species and the potential for modification of their designated critical habitat (*i.e.*, a taxon-level approach). Exposure of the whipsnake, its prey, and its habitat to acrolein are assessed separately.

The peak estimated environmental concentration (EEC) resulting from acrolein use is based on the maximum treatment rate as specified in the MAGNACIDE H Application and Safety Manual<sup>2</sup>, *i.e.*, 15 mg/L (ppm). These estimates are supplemented with analysis of available California surface water monitoring data from the US Geological Survey's (USGS) National Water Quality Assessment (NAWQA) program and the California Department of Pesticide Regulation. The maximum concentration of acrolein reported by the National Pollution Discharge Elimination System (NPDES) compliance monitoring for California surface waters with agricultural watersheds is 54 mg/L. This value is approximately 3.6 times greater than the maximum label treatment rate. However, as discussed later in the document, there is uncertainty surrounding these measurements with regards to incomplete mixing, multiple applications to an irrigation ditch, etc., and since the number of measurements exceeding the maximum treatment rate of 15 mg/L is small compared to the total number of measurements, the maximum treatment rate was used in this assessment.

Acrolein is applied directly below the water surface; therefore, terrestrial exposure pathways and receptors typically considered in EPA's ecological risk assessments are not considered likely, *i.e.*, direct exposure of terrestrial animal food sources and plants via direct application or spray drift. However, mortality as a result of direct exposure at or near the application rate is expected for any whipsnake that may use a treated canal as a conveyance. Likewise, mortality of amphibians which rely on the irrigation ditches for conveyance due to direct exposure to the treated water is also expected, thus reducing available prey for the whipsnake. Although acrolein is intended to kill aquatic plants in irrigation systems, treated water may be used to irrigate agricultural fields in an effort to dissipate the chemical. 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. Since definitive terrestrial plant toxicity data are not currently available for acrolein, the application of acrolein-treated water to agricultural fields and the subsequent effect on terrestrial plants could not be fully evaluated.

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<sup>2</sup> Baker Petrolite. 2005. MAGNACIDE® H Herbicide Application and Safety Manual. Manual Revision Date: March 2005.



To assess exposure of terrestrial animals via ingestion of contaminated water, the maximum allowable concentration in irrigation canals is used.

The effects determination assessment endpoints for the whipsnake include direct toxic effects on the survival, reproduction, and growth of the whipsnake, as well as indirect effects, such as reduction of the prey base or modification of its habitat. If appropriate data are not available, toxicity data for birds are generally used as a surrogate for reptiles and terrestrial-phase amphibians and toxicity data from fish are used as a surrogate for aquatic-phase amphibians.

Risk quotients (RQs) are derived as quantitative estimates of potential high-end risk. Acute and chronic RQs are compared to the Agency's levels of concern (LOCs) to identify instances where acrolein use within the action area has the potential to adversely affect the whipsnake and designated critical habitat via direct toxicity or indirectly based on direct effects to its food supply or habitat. When RQs for each particular type of effect are below LOCs, the pesticide is determined to have "no effect" on the whipsnake. Where RQs exceed LOCs, a potential to cause adverse effects is identified, leading to a conclusion of "may affect." If a determination is made that use of acrolein "may affect" the whipsnake and/or its designated critical habitat, additional information is considered to refine the potential for exposure and effects. Best available information is used to distinguish those actions that "may affect, but are not likely to adversely affect" (NLAA) from those actions that are "likely to adversely affect" (LAA) for the whipsnake. For designated critical habitat, distinctions are made for actions that are expected to have "no effect" on a designated critical habitat from those actions that have a potential to result in "habitat modification."

Based on the best available information, the Agency makes a May Affect, and Likely to Adversely Affect determination for the California whipsnake from the use of acrolein. Additionally, the Agency has determined that there is the potential for modification of designated critical habitat for the Alameda whipsnake from the use of the chemical. Although it is not considered likely that the whipsnake will be directly exposed to acrolein in irrigation canals where the compound is applied directly to water to control nuisance plants, the whipsnake and its forage base could be exposed to acrolein-treated water when the treated water is used to irrigate agricultural fields. Acute risk LOCs are exceeded for birds which serve as surrogates for reptiles. Additionally, both acute and chronic risk LOCs are exceeded for small mammals that serve as prey for the whipsnake. Since there are no toxicity data to evaluate the potential chronic risk of acrolein to birds and by extension to reptiles, risk from repeated exposures is presumed, given the potential for repeated applications of acrolein (8 times per year with a minimum retreatment interval of 14 days). However, given acrolein's volatility and the potential for dissipation of acrolein during irrigation, the potential for continuous chronic exposure and risk is greatly reduced. There are also no data to evaluate the potential risks to terrestrial invertebrates that serve as prey for whipsnakes; therefore, risk is presumed. There are no data to evaluate the potential risk of acrolein to terrestrial plants; therefore, risk is presumed. However, given the wide use on agricultural fields to dissipate acrolein, the fact that only a single plant incident has been reported in the EGIS database, and that

preliminary results from the Tier II terrestrial plant studies show that exposure to acrolein at concentrations as high as 30 mg a.i./L resulted in EC<sub>25</sub> values that exceed rates roughly equivalent to those applied to agricultural fields, the likelihood of adverse effects on terrestrial plants appears to be low. A summary of the risk conclusions and effects determinations for the whipsnake and its designated critical habitat is presented in **Tables 1.1 and 1.2**. Further information on the results of the effects determination is included as part of the Risk Description in Section 5.2. Given the LAA determination for the Alameda whipsnake and potential modification of its designated critical habitat, a description of the baseline status and cumulative effects for the whipsnake is provided in **Attachment II**.

<b>Table 1.1. Effects Determination Summary for Effects of Acrolein on the Alameda Whipsnake</b>		
<b>Species</b>	<b>Effects Determination <sup>1</sup></b>	<b>Basis for Determination</b>
Alameda Whipsnake ( <i>Masticophis lateralis euryxanthus</i> )	LAA <sup>1</sup>	<b>Potential for Direct Effects</b>
		Acute risk LOCs exceeded for reptiles. Chronic toxicity data are not available for birds and reptiles; chronic risk is presumed, given the potential for repeated applications of acrolein (8 times per year with a minimum retreatment interval of 14 days). However, given acrolein's volatility and the potential for dissipation of acrolein during irrigation, the potential for continuous chronic exposure and risk is greatly reduced.
		<b>Potential for Indirect Effects</b>
		<b>Terrestrial prey items, riparian habitat</b>  Acute risk LOCs exceeded for birds, reptiles and terrestrial-phase amphibians that serve as prey for the whipsnake. Terrestrial-phase amphibians which may serve as prey for the whipsnake are affected by acute risk to aquatic-phase amphibians in treated canals/reservoirs. Chronic toxicity data are not available for birds and reptiles; chronic risk is presumed for these prey items, given the potential for repeated applications of acrolein (8 times per year with a minimum retreatment interval of 14 days). However, given acrolein's volatility and the potential for dissipation of acrolein during irrigation, the potential for continuous chronic exposure and risk is greatly reduced. No toxicity data are available for terrestrial invertebrates that serve as prey for juvenile whipsnakes and as such, risk is presumed.

<sup>1</sup> No effect (NE); May affect, but not likely to adversely affect (NLAA); May affect, likely to adversely affect (LAA)

<b>Table 1.2. Effects Determination Summary for the Critical Habitat Impact Analysis</b>		
<b>Designated Critical Habitat for:</b>	<b>Effects Determination <sup>1</sup></b>	<b>Basis for Determination</b>
Alameda Whipsnake	Habitat Modification	Acute risk LOCs exceeded for birds and reptiles that serve as prey for the whipsnake. Chronic toxicity data are not available for birds, reptiles and terrestrial-phase amphibians; chronic risk is presumed for these prey items, given the potential for repeated applications of acrolein (8 times per year with a minimum retreatment interval of 14 days). However, given acrolein's volatility and the potential for dissipation of acrolein during irrigation, the potential for continuous chronic exposure and risk is greatly reduced. No toxicity data are available for terrestrial invertebrates that serve as prey for juvenile whipsnakes and as such, risk is presumed. No toxicity data are available on the effects of acrolein on terrestrial plants and risk is presumed for plants that make up the

		habitat of the whipsnake. However, given the compound's wide use on agricultural fields, the fact that only a single plant incident has been reported in the EHS database, and that preliminary results from Tier II terrestrial plant studies show that exposure to acrolein at concentrations as high as 30 mg a.i./L resulted in EC <sub>25</sub> values that exceed rates equivalent to those applied to agricultural fields, the likelihood of adverse effects on terrestrial plants appears to be low.
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<sup>1</sup> Habitat Modification or No effect (NE)

Based on the conclusions of this assessment, a formal consultation with the U.S. Fish and Wildlife Service (USFWS) under Section 7 of the Endangered Species Act (ESA) should be initiated to seek concurrence with the LAA determinations for the Alameda whipsnake and to determine whether there are reasonable and prudent alternatives and/or measures to reduce and/or eliminate potential incidental take.

When evaluating the significance of this risk assessment's direct/indirect and adverse habitat modification effects determinations, it is important to note that pesticide exposures and predicted risks to the whipsnake and its resources (*i.e.*, food and habitat) are not expected to be uniform across the action area. In fact, given the assumptions of drift and downstream transport (*i.e.*, attenuation with distance), pesticide exposure and associated risks to the whipsnake and its resources are expected to decrease with increasing distance away from the treated field or site of application. Evaluation of the implication of this non-uniform distribution of risk to the whipsnake would require information and assessment techniques that are not currently available. Examples of such information and methodology required for this type of analysis would include the following:

- Enhanced information on the density and distribution of the Alameda whipsnake life stages within the action area and/or applicable designated critical habitat. This information would allow for quantitative extrapolation of the present risk assessment's predictions of individual effects to the proportion of the population extent within geographical areas where those effects are predicted. Furthermore, such population information would allow for a more comprehensive evaluation of the significance of potential resource impairment to individuals of the whipsnake.
- Quantitative information on prey base requirements for the whipsnake. While existing information provides a preliminary picture of the types of food sources utilized by the whipsnake, it does not establish minimal requirements to sustain healthy individuals at varying life stages. Such information could be used to establish biologically relevant thresholds of effects on the prey base, and ultimately establish geographical limits to those effects. This information could be used together with the density data discussed above to characterize the likelihood of adverse effects to individuals.
- Information on population responses of prey base organisms to the pesticide. Currently, methodologies are limited to predicting exposures and likely levels of direct mortality, growth or reproductive impairment

immediately following exposure to the pesticide. The degree to which repeated exposure events and the inherent demographic characteristics of the prey population play into the extent to which prey resources may recover is not predictable. An enhanced understanding of long-term prey responses to pesticide exposure would allow for a more refined determination of the magnitude and duration of resource impairment, and together with the information described above, a more complete prediction of effects to individual species and potential modification to critical habitat.

## **2. Problem Formulation**

Problem formulation provides a strategic framework for the risk assessment. By identifying the important components of the problem, it focuses the assessment on the most relevant life history stages, habitat components, chemical properties, exposure routes, and endpoints. The structure of this risk assessment is based on guidance contained in U.S. EPA's *Guidance for Ecological Risk Assessment* (U.S. EPA, 1998), the Services' *Endangered Species Consultation Handbook* (USFWS/NMFS, 1998) and is consistent with procedures and methodology outlined in the Overview Document (U.S. EPA, 2004) and reviewed by the U.S. Fish and Wildlife Service and National Marine Fisheries Service (USFWS/NMFS, 2004).

### **2.1 Purpose**

The purpose of this endangered species assessment is to evaluate potential direct and indirect effects on individuals of the federally threatened Alameda whipsnake (*Masticophis lateralis euryxanthus*) (whipsnake) arising from FIFRA regulatory actions regarding use of acrolein as a herbicide in irrigation canals and irrigation reservoirs. In addition, this assessment evaluates whether use in these use sites is expected to result in modification of designated critical habitat for the whipsnake. This ecological risk assessment has been prepared consistent with the settlement agreements in the court case referring to the whipsnake: *Center for Biological Diversity (CBD) vs. EPA et al.* (Case No. 07-2794-JCS).

In this assessment, direct and indirect effects to the whipsnake and potential modification to designated critical habitat for the whipsnake are evaluated in accordance with the methods described in the Agency's Overview Document (U.S. EPA 2004). The effects determinations for the whipsnake are based on a weight-of-evidence method that relies heavily on an evaluation of risks to each taxon relevant to assess both direct and indirect effects to the whipsnake and the potential for modification of their designated critical habitat (*i.e.*, a taxon-level approach). Screening-level methods include the use of the maximum treatment rate to estimate the aquatic exposure value and the use of standard models such as T-REX, described at length in the Overview Document. Use of such information is consistent with the methodology described in the Overview Document (U.S. EPA 2004), which specifies that "the assessment process may, on a case-by-case

basis, incorporate additional methods, models, and lines of evidence that EPA finds technically appropriate for risk management objectives” (Section V, page 31 of U.S. EPA 2004).

In accordance with the Overview Document, provisions of the ESA, and the Services’ *Endangered Species Consultation Handbook*, the assessment of effects associated with registrations of acrolein is based on an action area. The action area is the area directly or indirectly affected by the federal action, as indicated by the exceedence of the Agency’s LOCs. It is acknowledged that the action area for a national-level FIFRA regulatory decision associated with a use of acrolein may potentially involve numerous areas throughout the United States and its Territories. However, for the purposes of this assessment, attention will be focused on relevant sections of the action area including those geographic areas associated with locations of the whipsnake and its designated critical habitat within the state of California. As part of the “effects determination,” one of the following three conclusions will be reached for the whipsnake in the lawsuits regarding the potential use of acrolein in accordance with current labels:

- “No effect”;
- “May affect, but not likely to adversely affect”; or
- “May affect and likely to adversely affect”.

The whipsnake has designated critical habitats associated with it. Designated critical habitat identifies specific areas that have the physical and biological features, (known as primary constituent elements or PCEs) essential to the conservation of the whipsnake. Alameda whipsnakes inhabit local variations of chaparral—coastal sage scrub and northern coastal scrub. Although their home range centers on shrub communities, they venture as much as 500 feet into adjacent grasslands, oak savanna and oak-bay, open woodlands. As woodland canopies close and stands of vegetation grow tall and dense, a cool environment evolves that the Alameda whipsnake will then avoid. Rock outcrops and talus are characteristic of whipsnake habitat. They offer cover for whipsnakes and promote populations of their primary prey—lizards. Alameda whipsnakes also use small rodent burrows, rock and soil crevices, and brush and debris piles for retreat. They tend to be found on southwest, south, and southeast oriented slopes. In total, approximately 154,834 acres (62,659 hectares) of critical habitat are designated for the species. The critical habitat is located in Alameda, Contra Costa, Santa Clara, and San Joaquin Counties, California.

If the results of initial screening-level assessment methods show no direct or indirect effects (*i.e.*, no LOC exceedances) upon individuals or upon the PCEs of the whipsnake’s designated critical habitat, a “no effect” determination is made for use of acrolein as it relates to the whipsnake and its designated critical habitat. If, however, potential direct or indirect effects to individuals of the whipsnake are anticipated or effects may impact the PCEs of the designated critical habitat, a preliminary “may affect” determination is made for the FIFRA regulatory action regarding acrolein.

If a determination is made that use of acrolein “may affect” the whipsnake or its designated critical habitat, additional information is considered to refine the potential for exposure and for effects to the whipsnake and other taxonomic groups upon which the whipsnake depends (e.g., prey items). Additional information, including spatial analysis (to determine the geographical proximity of the whipsnake’s habitat and acrolein use sites) and further evaluation of the potential impact of acrolein on the PCEs is also used to determine whether modification of designated critical habitat may occur. Based on the refined information, the Agency uses the best available information to distinguish those actions that “may affect, but are not likely to adversely affect” from those actions that “may affect and are likely to adversely affect” the whipsnake and/or result in “no effect” or potential modification to the PCEs of its designated critical habitat. This information is presented as part of the Risk Characterization in Section 5 of this document.

The Agency believes that the analysis of direct and indirect effects to the whipsnake provides the basis for an analysis of potential effects on the designated critical habitat. Because acrolein is expected to directly impact living organisms within the action area (defined in Section 2.7), critical habitat analysis for acrolein is limited in a practical sense to those PCEs of critical habitat that are biological or that can be reasonably linked to biologically mediated processes (i.e., the biological resource requirements for the whipsnake associated with the critical habitat or important physical aspects of the habitat that may be reasonably influenced through biological processes). Activities that may modify critical habitat are those that alter the PCEs and appreciably diminish the value of the habitat. Evaluation of actions related to use of acrolein that may alter the PCEs of the whipsnake’s critical habitat form the basis of the critical habitat impact analysis. Actions that may affect the whipsnake’s designated critical habitat have been identified by the Services and are discussed further in Section 2.6.

## **2.2 Scope**

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. The current label indicates that an irrigation canal can be treated 8 times per year, with a minimum reapplication interval of 14 days. 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.*”

The end result of the EPA pesticide registration process (i.e., the FIFRA regulatory action) is an approved product label. The label is a legal document that stipulates how and where a given pesticide may be used. Product labels (also known as end-use labels) describe the formulation type (e.g., liquid or granular), acceptable methods of application, approved use sites, and any restrictions on how applications may be conducted. Thus, the use or potential use of acrolein in accordance with the approved product labels for California is “the action” relevant to this ecological risk assessment.

Although current registrations of acrolein allow for use in arid western states, this ecological risk assessment and effects determination addresses currently registered uses of acrolein in portions of the action area that are reasonably assumed to be biologically relevant to the whipsnake and its designated critical habitat. Further discussion of the action area for the whipsnake and its critical habitat is provided in Section 2.7.

A description of routine procedures for evaluating risk to the San Francisco Bay Species is provided in **Attachment I**.

### **2.2.1 Evaluation of Degradates**

Acrolein forms several degradates in the environment. One of these, 3-hydroxypropanal, forms abiotically, and is in equilibrium with acrolein, and thus reforms to 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 the risk assessment is primarily based on the maximum treatment rate of 15 mg/L, with extensive consideration given to the wealth of monitoring data, and these monitoring studies only report the parent, data are available to consider the risks due to parent acrolein only at this time. This is expected to only slightly underestimate the risk since the toxicity is dominantly associated with the parent compound. Additionally, use of acrolein monitoring data will inherently capture the reformation of acrolein from 3-hydroxypropanol.

### **2.2.2 Evaluation of Mixtures**

Acrolein does not have any registered products that contain multiple active ingredients.

## **2.3 Previous Assessments**

Acrolein was previously assessed in support of the Reregistration Eligibility Decision (RED) (USEPA 2007). Concurrent with the ecological risk assessment in support of the RED, the Office of Water developed an Aquatic Life Criteria for acrolein (USEPA, 2009). Based on the ecological risk assessment written in support of the RED, both direct and indirect risks to listed birds, reptiles, terrestrial-phase amphibians and mammals were considered likely. Because of the lack of toxicity data, direct and indirect risks to listed species of terrestrial plants and insects were presumed.

## **2.4 Stressor Source and Distribution**

### **2.4.1 Environmental Fate Properties**

The environmental fate of acrolein, or 2-propenal, is not well known based on current environmental fate data. Available data (**Table 2.1**) indicate potential for acrolein to reach natural surface water bodies which receive discharge water from irrigation canals. However, 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.*” 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 or 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 adsorption which is usually described in fate assessments for pesticides and is more akin to the denaturing effect of formaldehyde on tissue protetins. 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 and 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 150°C (Ghilarducci and Tjeerdema, 1985). Acrolein is a liquid at 25 °C 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  $1.9 \times 10^{-4}$  atm·m<sup>3</sup>/mol (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.

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

**Table 2.1** lists the environmental fate properties of acrolein, along with the major (*e.g.*, >10%) and minor degradates detected in the submitted environmental fate and transport studies.



<b>Table 2.1. Summary of Acrolein Environmental Fate Properties</b>				
<b>Study</b>	<b>Value (units)</b>	<b>Major Degradates <i>Minor Degradates</i></b>	<b>MRID #/Source</b>	<b>Study Status</b>
Molecular Mass	56.06 g/mol	NA	Baker Hughes 2005	
Vapor pressure	269 Torr (0.354 atm) at 25°C	NA	Smith, 1962	
Henry's Law Constant	$1.93 \times 10^{-4}$ atm-m <sup>3</sup> /mol	NA	47008401	
Solubility in water	237.6 g/L	NA	40840602	
Hydrolysis	3.83 days (pH 5.3) 1.55 days (pH 7.2) 0.79 days (pH 8.9)	3-hydroxypropanal	40945401	Acceptable
Direct Aqueous Photolysis	No data			Not Applicable
Soil Photolysis	No data			Not Applicable
Aerobic Soil Metabolism	No data			Not Applicable
Anaerobic Soil Metabolism	No data			Not Applicable
Anaerobic Aquatic Metabolism	Insufficient data	<b>acrylic acid, allyl alcohol, propionic acid, oxalic acid, bicarbonate, 3-hydroxypropanal, 3-hydroxypropionic acid, propanol</b>	42949201	Supplemental
Aerobic Aquatic Metabolism	Insufficient data	<b>acrylic acid, propionic acid, bicarbonate, propanol, allyl alcohol, oxalic acid, 3-hydroxypropionic acid, glyceric acid</b>	43227101	Supplemental
Log K <sub>ow</sub>	0.98-1.10		Hansch and Leo 1995; MRID 40840604	Acceptable
Soil partition coefficient (K <sub>OC</sub> )	1 - 4.9 L/kg (estimated)		EpiSuite 4.0	Not Applicable
Equilibrium Constant with 3-hydroxypropanal	10.4 ± 5.7 @ 25°C		40945401	Acceptable

### Hydrolysis / Photolysis

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. No acceptable data are currently available to characterize the rate of photolysis for acrolein in water.

### **Metabolism**

Submitted data provide evidence that acrolein does indeed degrade by both aerobic and anaerobic metabolism. Degradation rates could not be quantified due to deficiencies in available studies. However, DT<sub>50</sub> values of about one day in water in both an aerobic (MRID 43227101) and anaerobic (MRID 42949201) aquatic environs were observed. Both studies 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.

### **Mobility**

No acceptable data are available for estimating the sorption coefficient (K<sub>d</sub>) values for acrolein. However, in using the quantitative structural analysis tools in EPISuite (KOCWin), estimated K<sub>oc</sub> values ranged from 1 L/kg (Molecular Connectivity Index method) to 4.9 L/kg (log K<sub>ow</sub> method), indicating acrolein is highly mobile. Additionally, the very high solubility (237 g/L at 25°C) would indicate a very low tendency to absorb to sediment.

### **Field Studies**

No acceptable field dissipation studies have been submitted for acrolein. However, two non-guideline studies were conducted to assess applications of acrolein to water bodies. As detailed below, these studies show that while acrolein does indeed dissipate from the test site with half-lives of less than 1 day, it is sufficiently persistent to move long distances, up to 60 miles at concentrations which are of concern to aquatic wildlife. Degradation products were not assessed in these studies. Additional monitoring data providing measurements of acrolein in irrigation ditches and receiving water bodies during and after treatment in California are discussed in detail in **Section 3.2.4**.

*MAGNACIDE Monitoring Program for the State of Nebraska* (MRID 46976905) was conducted in eight 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 directly to water in irrigation canals, and the pesticide was monitored downstream to the discharge point from the irrigation canal.

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.

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<sub>50</sub> 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 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.

In the second study, *Washington State Monitoring Program* (MRID 47008404), the primary purpose 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) employing a protocol similar to the one that was used for the Nebraska study (MRID 46976905). Of the seven applications, four could be resolved into separate plumes traveling downstream. The other three plumes overlapped; a second application was made to the same segment of water before the pesticide from the first application had

completely dissipated. It was not possible to estimate degradation rates for the overlapping applications. 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. In all cases measurable concentrations of acrolein were found in the discharge from the canals.

Acrolein was found in the Scootenev 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 detectable levels (limit of detection not specified) 3.5 mi further downstream before discharging into the Scootenev 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 a different 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.”

An air monitoring study (see **Section 3.2.4.4** for a more detailed discussion) was conducted by the registrant associated with an application to the Kern Island Canal in the Kern Delta Water District in California in August 2005. Using an application concentration of 3.99 ppm, upwind samples ranged from 28 to 36 µg/m<sup>3</sup> (values increasing with distance downstream from the application point) and downwind samples were 92 (sampler parallel to the application point) and 120 µg/m<sup>3</sup> (sampler 52 feet downstream). Because concentrations were still rising with distance downstream, it is conceivable that higher air concentrations could have been seen further downstream.

### 2.4.2 Environmental Transport Mechanisms

Acrolein is applied directly to receiving waters. Acrolein is applied at the treatment concentration for periods ranging from 30 minutes to 8 hours creating a ‘wave of acrolein’ that reacts with weeds as it moves down the canal. Both the recommended concentration and the treatment time may vary depending on the weed growth condition, water flow rate, temperature, and application time desired. The current label indicates that an irrigation canal can be treated 8 times per year, with a minimum reapplication interval of 14 days. 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*”. Potential transport mechanisms include secondary drift of volatilized acrolein leading to deposition onto nearby or more distant ecosystems. Contact with treated irrigation water remaining on fields and spray drift from the use of treated irrigation water are also potential routes of exposure from acrolein, although exposure from spray drift is expected to be low. In general, irrigation of fields is normally done using ground spray equipment with very coarse droplets and at relatively low release heights (e.g., low ground boom), so the amount of drift from such applications is expected to be low.

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 terrestrial animals through inhalation. Based on experimental data and estimates derived using EPISuite’s AOPWin for atmospheric oxidation by hydroxyl radicals, the half-life for acrolein in the atmosphere is 4.97 to 6.45 hours, indicating a rapid breakdown of acrolein in the air. This is supported by the findings in the Concise International Chemical Assessment Document 43 (<http://www.inchem.org/documents/cicads/cicads/cicad43.htm#5.1>), which determined

*Acrolein emitted to air reacts primarily with photochemically generated hydroxyl radicals in the troposphere. Minor processes include direct photolysis, reaction with nitrate radicals, and reaction with ozone. Acrolein has been detected in rainwater, indicating that it may be removed by wet deposition. The calculated atmospheric half-life of acrolein, based on rate constants for hydroxyl radical reaction, is between 3.4 and 33.7 h. The overall reactivity-based half-life of acrolein in air, as estimated by Mackay et al. (1995), is less than 10 h. Based on these short estimated half-lives, acrolein is not a candidate for long-range atmospheric transport.*

As a result, long range transport is not considered in this assessment.

### 2.4.3 Mechanism of Action

Acrolein, a reactive aldehyde, is a contact herbicide that is phytotoxic to most submersed aquatic vegetation. 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.*<sup>3</sup> 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 gradually disintegrate into small fragments and float downstream.

#### 2.4.4 Use Characterization

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. Acrolein is applied to achieve and sustain a specific treatment concentration in both static and flowing water for periods ranging from 30 minutes to 8 hours creating a 'wave of acrolein' that reacts with weeds as it moves down the canal. Both the recommended concentration and the treatment time may vary depending on the weed growth condition, water flow rate, temperature, and application time desired. The current label indicates that an irrigation canal can be treated 8 times per year, with a minimum reapplication interval of 14 days. 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"*.

Analysis of labeled use information is the critical first step in evaluating the federal action. The current label for acrolein represents the FIFRA regulatory action; therefore, labeled use and application rates specified on the label form the basis of this assessment. The assessment of use information is critical to the development of the action area and selection of appropriate modeling scenarios and inputs.

**Table 2.2** presents the use and corresponding application rate and method of application considered in this assessment.

<b>Table 2.2. Acrolein Uses Assessed for California</b>		
<b>Use (Application Method)</b>	<b>Max. Treatment Rate (mg/L)</b>	<b>Max. Number of Application per Year</b>
Herbicide (Direct application to water)	15 mg/L	Not specified

National usage maps showing the estimated poundage of acrolein used across the United States are not available. Use of acrolein is typically limited to arid western states where crops are irrigated. Using the 2007 USDA Census of Agriculture, the types of crops

<sup>3</sup> 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.

grown in Alameda, Contra Costa, San Joaquin, and Santa Clara Counties, that might be irrigated with acrolein treated water were assessed. In 2002 and/or 2007, the following crops were grown in these counties: barley, corn, lima beans, oats, safflower, wheat, forage, alfalfa hay, peppers, potatoes, squash, tomatoes, grapes, stone fruit, pome fruit, citrus, nuts, lettuce, olives, and strawberries.

The Agency's Biological and Economic Analysis Division (BEAD) provides an analysis of both national- and county-level usage information (*County-Level Usage for Acephate; Acrolein; Bromadiolone; Cholecalciferol; Difethialone; Methyl Bromide; Methoprene; S-Methoprene; Warfarin; and Warfarin, Sodium Salt in California in Support of a San Francisco Bay Endangered Species Assessment*, dated 7/27/2011) using state-level usage data obtained from USDA-NASS<sup>4</sup>, Doane ([www.doane.com](http://www.doane.com); the full dataset is not provided due to its proprietary nature) and California's Department of Pesticide Regulation Pesticide Use Reporting (CDPR PUR) database<sup>5</sup>. CDPR PUR is considered a more comprehensive source of usage data than USDA-NASS or EPA proprietary databases, and thus the usage data reported for acrolein by county in this California-specific assessment were generated using CDPR PUR data. Eight years (1999-2006) of usage data were included in this analysis. Data from CDPR PUR were obtained for every agricultural pesticide application made on every use site at the section level (approximately one square mile) of the public land survey system.<sup>6</sup> BEAD summarized these data to the county-level by site, pesticide, and unit treated. Calculating county-level usage involved summarizing across all applications made within a section and then across all sections within a county for each use site and for each pesticide. The county-level usage data that were calculated include: average annual pounds applied, average annual area treated, and average and maximum application rate across all eight years. The units of area treated are also provided where available.

According to aquatic resource managers (personal communication, 2007, 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

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<sup>4</sup> United States Department of Agriculture (USDA), National Agricultural Statistics Service (NASS) Chemical Use Reports provide summary pesticide usage statistics for select agricultural use sites by chemical, crop and state. See <http://www.usda.gov/nass/pubs/estindx1.htm#agchem>.

<sup>5</sup> The California Department of Pesticide Regulation's Pesticide Use Reporting database provides a census of pesticide applications in the state. See <http://www.cdpr.ca.gov/docs/pur/purmain.htm>.

<sup>6</sup> Most pesticide applications to parks, golf courses, cemeteries, rangeland, pastures, and along roadside and railroad rights of way, and postharvest treatments of agricultural commodities. The primary exceptions to the reporting requirement are home-and-garden use and most industrial and institutional uses (<http://www.cdpr.ca.gov/docs/pur/purmain.htm>).

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. Annual acrolein use in California<sup>7</sup> from 2000 through 2009 is depicted **Figure 2.1** and shows that usage has declined by roughly 44% in 2009 compared to usage in 2000. **Figure 2.2** depicts the total number of surface acres of water treated with acrolein from 2000 to 2009 and shows a precipitous decline in acres treated from 2002 when 2,206 acres were treated to 2006 when only 18 acres were reported to have been treated. By 2009 though, the number of acres treated had increased to 1,497.

Based on the critical habitat and occurrence of the whipsnake, analysis of acrolein usage was limited to Alameda, Contra Costa, San Joaquin, and Santa Clara Counties in California. A summary of acrolein usage for these counties is provided below in **Table 2.3**. Based on the PUR data, acrolein has only been used in two of the four counties, Contra Costa and San Joaquin.

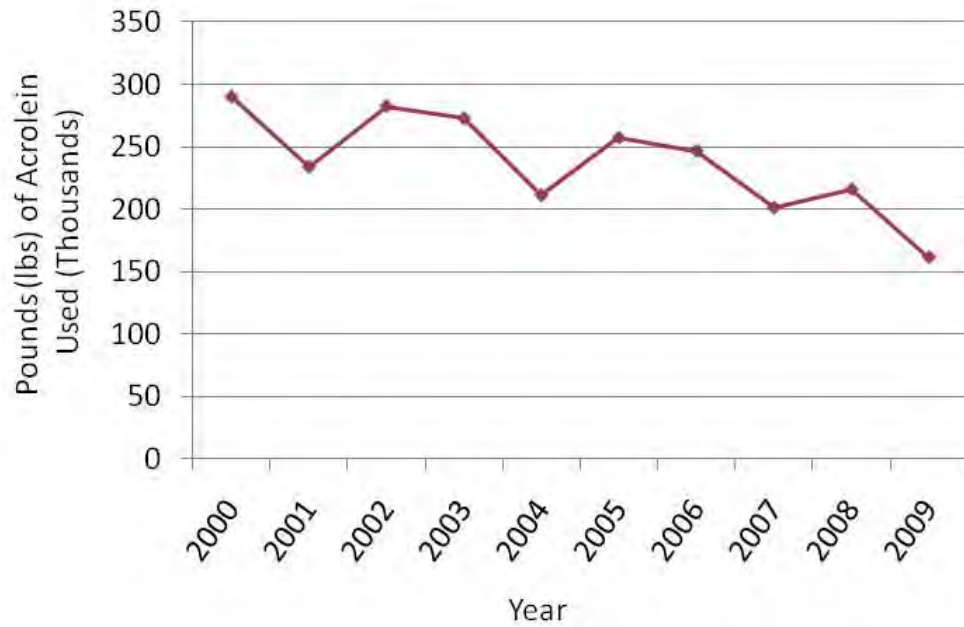
**Table 2.3. Summary of CDPR PUR Data from 1999 to 2006 for Currently Registered Acrolein Uses<sup>1</sup>**

Site Name	Average Annual Pounds Applied (lbs a.i.)	Average Amount Applied per Use (lbs a.i.)	Maximum Amount Applied per Use (lbs a.i.)
Contra Costa	6,888	197	1,287
San Joaquin	7,235	713	2,326

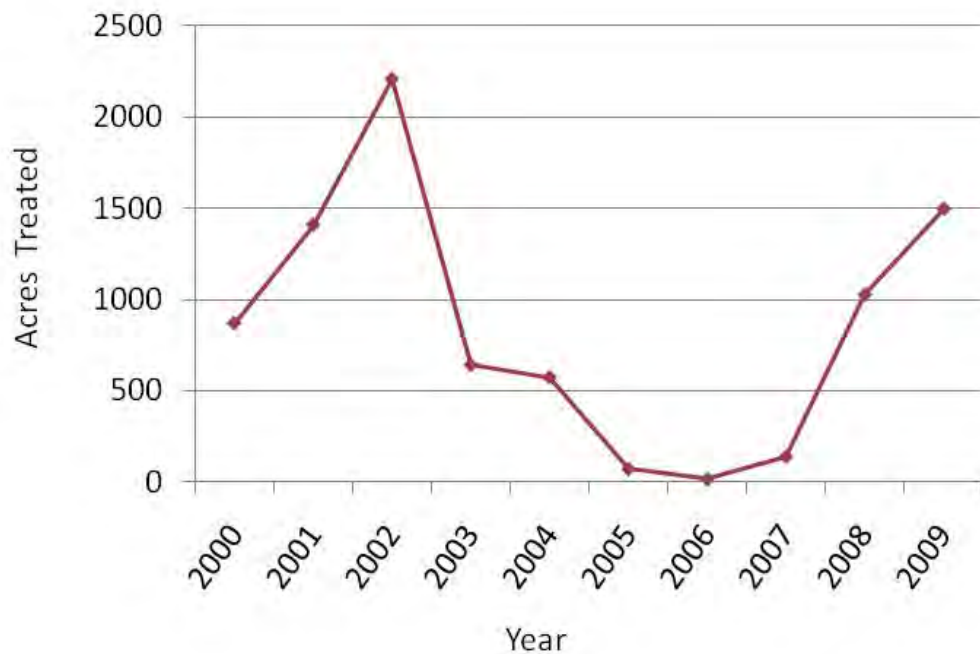
1. Based on data supplied by BEAD (County-Level Usage for Acephate; Acrolein; Bromadiolone; Cholecalciferol; Difethialone; Methyl Bromide; Methoprene; S-Methoprene; Warfarin; and Warfarin, Sodium Salt in California in Support of a San Francisco Bay Endangered Species Assessment, dated 7/27/2011).

<sup>7</sup> California Department of Pesticide Regulation 2009. Summary of Pesticide Use Report Data 2009 Indexed by Chemical





**Figure 2.1. Acrolein Use (lbs x 1000) in California by Year. (Source: California Dept. of Pesticide Regulation Pesticide Use Report 2009)**



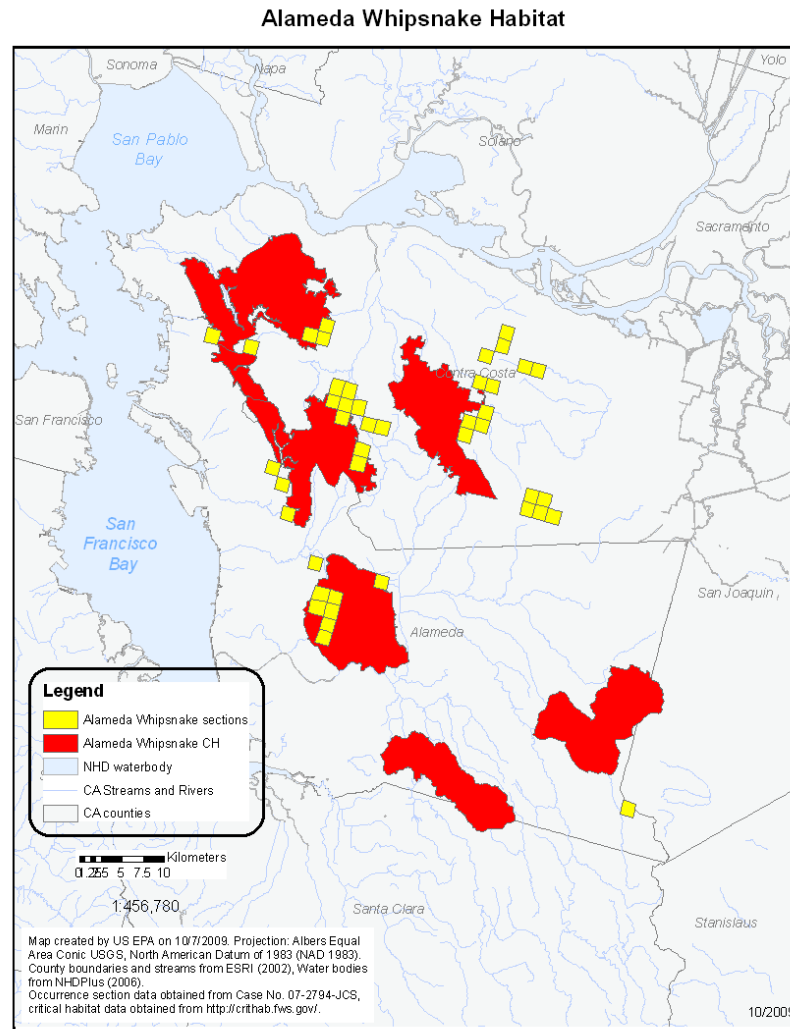
**Figure 2.2. Total Surface Acres of Water Treated with Acrolein Use in California by Year. (Source: California Dept. of Pesticide Regulation Pesticide Use Report 2009)**

## 2.5 The Alameda Whipsnake

**Table 2.4** provides a summary of the current distribution, habitat requirements, and life history parameters for the Alameda whipsnake. More detailed life-history and distribution information can be found in **Attachment III**. See **Figure 2.3** for a map of the current range and designated critical habitat of the whipsnake.

Assessed Species	Size	Current Range	Habitat Type	Designated Critical Habitat?	Reproductive Cycle	Diet
CA Alameda whipsnake ( <i>Masticophis lateralis euryxanthus</i> )	3 – 5 ft	Contra Costa and Alameda Counties in California (additional occurrences in San Joaquin and Santa Clara Counties)	Primarily, scrub and chaparral communities. Also found in grassland, oak savanna, oak-bay woodland, and riparian areas. Lands containing rock outcrops, talus, and small mammal burrows.	Yes	Emerge from hibernation and begin mating from late March through mid-June. Females lay eggs in May through July. Eggs hatch from August through November. Hibernate during the winter months.	Lizards, frogs, small mammals, nesting birds, small insects and other snakes including rattlesnakes

<sup>1</sup> For more detailed information on the distribution, habitat requirements, and life history information of the whipsnake, see Attachment III



**Figure 2.3. Critical habitat and occurrence sections of the Alameda whipsnake, as identified in Case No. 07-2794-JCS.**

## 2.6 Designated Critical Habitat

Critical habitat has been designated for the Alameda whipsnake. ‘Critical habitat’ is defined in the ESA as the geographic area occupied by the species at the time of the listing where the physical and biological features necessary for the conservation of the species exist, and there is a need for special management to protect the listed species. It may also include areas outside the occupied area at the time of listing if such areas are ‘essential to the conservation of the species.’ Critical habitat receives protection under Section 7 of the ESA through prohibition against destruction or adverse modification with regard to actions carried out, funded, or authorized by a federal Agency. Section 7 requires consultation on federal actions that are likely to result in the destruction or adverse modification of critical habitat.

To be included in a critical habitat designation, the habitat must be ‘essential to the conservation of the species.’ Critical habitat designations identify, to the extent known using the best scientific and commercial data available, habitat areas that provide essential life cycle needs of the species or areas that contain certain primary constituent elements (PCEs) (as defined in 50 CFR 414.12(b)). PCEs include, but are not limited to, space for individual and population growth and for normal behavior; food, water, air, light, minerals, or other nutritional or physiological requirements; cover or shelter; sites for breeding, reproduction, rearing (or development) of offspring; and habitats that are protected from disturbance or are representative of the historic geographical and ecological distributions of a species. **Table 2.5** describes the PCEs for the critical habitats designated for the Alameda whipsnake.

<b>Table 2.5. Designated Critical Habitat PCEs for the Alameda Whipsnake<sup>1</sup></b>		
<b>Species</b>	<b>PCEs</b>	<b>Reference</b>
Alameda whipsnake	PCE 1: Scrub/shrub communities with a mosaic of open and closed canopy	71 FR 58175 58231, 2006
	PCE 2: Woodland or annual grassland plant communities contiguous to lands containing PCE 1	
	PCE 3: Lands containing rock outcrops, talus, and small mammal burrows within or adjacent to PCE 1 and or PCE 2	

<sup>1</sup> These PCEs are in addition to more general requirements for habitat areas that provide essential life cycle needs of the whipsnake such as, space for individual and population growth and for normal behavior; food, water, air, light, minerals, or other nutritional or physiological requirements; cover or shelter; sites for breeding, reproduction, rearing (or development) of offspring; and habitats that are protected from disturbance or are representative of the historic geographical and ecological distributions of the whipsnake.

More detail on the designated critical habitat applicable to this assessment can be found in **Attachment III** for the Alameda whipsnake. Activities that may destroy or adversely modify critical habitat are those that alter the PCEs and jeopardize the continued existence of the whipsnake. Evaluation of actions related to use of acrolein that may alter the PCEs of the designated critical habitat for the Alameda whipsnake form the basis of the critical habitat impact analysis.

As previously noted in Section 2.1, the Agency believes that the analysis of direct and indirect effects to the whipsnake provides the basis for an analysis of potential effects on

the designated critical habitat. Because acrolein is expected to directly impact living organisms within the action area, critical habitat analysis for acrolein is limited in a practical sense to those PCEs of critical habitat that are biological or that can be reasonably linked to biologically mediated processes.

## **2.7 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 (50 CFR 402.02). It is recognized that the overall action area for the national registration of acrolein is likely to encompass considerable portions of the western United States based on the large array of uses in irrigation systems. However, the scope of this assessment limits consideration of the overall action area to those portions that may be applicable to the protection of the Alameda whipsnake and its designated critical habitat within the state of California. Although the watershed for the San Francisco Bay extends northward into the very southwestern portion of Lake County, Oregon, and westward into the western edge of Washoe County, Nevada, the non-California portions of the watershed are small and very rural. Therefore, no use of acrolein is expected in these areas, and they are not considered as part of the action area applicable to this assessment.

Following a determination of the assessed uses, an evaluation of the potential “footprint” of acrolein use patterns (*i.e.*, the area where herbicide application occurs) is determined. This “footprint” represents the initial area of concern, based on an analysis of available land cover data for the state of California. The initial area of concern is defined as all land cover types and the stream reaches within the land cover areas that represent the labeled uses described above. As acrolein can be used in irrigation canals and certain reservoirs and ponds that are associated with irrigation water for weed control, the initial area of concern is considered the entire state of California.

## **2.6 Assessment Endpoints and Measures of Ecological Effect**

Assessment endpoints are defined as “explicit expressions of the actual environmental value that is to be protected.”<sup>8</sup> Selection of the assessment endpoints is based on valued entities (*e.g.*, the Alameda whipsnake, organisms important in the life cycle of the whipsnake, and the PCEs of its designated critical habitat), the ecosystems potentially at risk (*e.g.*, waterbodies, riparian vegetation, and upland and dispersal habitats), the migration pathways of acrolein (*e.g.*, volatilization, spray drift, *etc.*), and the routes by which ecological receptors are exposed to acrolein (*e.g.*, direct contact, *etc.*).

### **2.6.1 Assessment Endpoints**

Assessment endpoints for the Alameda whipsnake include direct toxic effects on the survival, reproduction, and growth of individuals, as well as indirect effects, such as reduction of the prey base or modification of its habitat. In addition, potential

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<sup>8</sup> From U.S. EPA (1992). *Framework for Ecological Risk Assessment*. EPA/630/R-92/001.

modification of critical habitat is assessed by evaluating potential effects to PCEs, which are components of the habitat areas that provide essential life cycle needs of the whipsnake. Each assessment endpoint requires one or more “measures of ecological effect,” defined as changes in the attributes of an assessment endpoint or changes in a surrogate entity or attribute in response to exposure to a pesticide. Specific measures of ecological effect are generally evaluated based on acute and chronic toxicity information from registrant-submitted guideline tests that are performed on a limited number of organisms. Additional ecological effects data from the open literature are also considered. It should be noted that assessment endpoints are limited to direct and indirect effects associated with survival, growth, and fecundity, and do not include the full suite of sublethal effects used to define the action area. According the Overview Document (USEPA 2004), the Agency relies on acute and chronic effects endpoints that are either direct measures of impairment of survival, growth, or fecundity or endpoints for which there is a scientifically robust, peer reviewed relationship that can quantify the impact of the measured effect endpoint on the assessment endpoints of survival, growth, and fecundity.

A complete discussion of all the toxicity data available for this risk assessment, including resulting measures of ecological effect selected for each taxonomic group of concern, is included in Section 4 of this document. A summary of the assessment endpoints and measures of ecological effect selected to characterize potential assessed direct and indirect risks for the whipsnake associated with exposure to acrolein is provided in Section 2.5 and **Table 2.6**.

As described in the Agency’s Overview Document (U.S. EPA, 2004), the most sensitive endpoint for each taxon is used for risk estimation. For this assessment, evaluated taxa include birds (surrogate for terrestrial-phase amphibians and reptiles), mammals, terrestrial invertebrates, and terrestrial plants. Acute (short-term) and chronic (long-term) toxicity information is characterized based on registrant-submitted studies and a comprehensive review of the open literature on acrolein.

**Table 2.6** identifies the taxa used to assess the potential for direct and indirect effects from the uses of acrolein for the Alameda whipsnake assessed here. The specific assessment endpoints used to assess the potential for direct and indirect effects to the whipsnake are provided in **Table 2.7**.

<b>Table 2.6. Taxa Used in the Analyses of Direct and Indirect Effects for the Assessed Listed Species</b>				
<b>Listed Species</b>	<b>Birds</b>	<b>Mammals</b>	<b>Terrestrial Plants</b>	<b>Terrestrial Invertebrates</b>
Alameda whipsnake	Direct  Indirect (prey)	Indirect (prey/habitat)	Indirect (habitat)	Indirect (prey)

**Table 2.7. Taxa and Assessment Endpoints Used to Evaluate the Potential for the Use of Acrolein to Result in Direct and Indirect Effects to the Alameda Whipsnake**

Taxa Used to Assess Direct and/or Indirect Effects to Assessed Species	Assessed Listed Species	Assessment Endpoints	Measures of Ecological Effects
1. Birds	<u>Direct Effect</u>	Survival, growth, and reproduction of individuals via direct effects	6a. Most sensitive bird <sup>b</sup> , reptile, or terrestrial-phase amphibian acute LC <sub>50</sub> or LD <sub>50</sub> (guideline or ECOTOX) 6b. Most sensitive bird <sup>b</sup> , reptile, or terrestrial-phase amphibian chronic NOAEC (guideline or ECOTOX)
	<u>Indirect Effect (prey)</u>	Survival, growth, and reproduction of individuals via indirect effects on terrestrial prey (birds, reptiles, and amphibians in the terrestrial environment)	
2. Mammals	<u>Indirect Effect (prey/habitat from burrows)</u>	Survival, growth, and reproduction of individuals via indirect effects on terrestrial prey (mammals)	7a. Most sensitive laboratory rat acute LC <sub>50</sub> or LD <sub>50</sub> (guideline or ECOTOX) 7b. Most sensitive laboratory rat chronic NOAEC (guideline or ECOTOX)
3. Terrestrial Invertebrates	<u>Indirect Effect (prey)</u>	Survival, growth, and reproduction of individuals via indirect effects on terrestrial prey (terrestrial invertebrates)	8a. Most sensitive terrestrial invertebrate acute EC <sub>50</sub> or LC <sub>50</sub> (guideline or ECOTOX) <sup>c</sup> 8b. Most sensitive terrestrial invertebrate chronic NOAEC (guideline or ECOTOX)
4. Terrestrial Plants	<u>Indirect Effect (habitat) (non-obligate relationship)</u>	Survival, growth, and reproduction of individuals via indirect effects on food and habitat ( <i>i.e.</i> , riparian and upland vegetation)	9a. Distribution of EC <sub>25</sub> for monocots (seedling emergence, vegetative vigor, or ECOTOX)

### 2.6.2 Assessment Endpoints for Designated Critical Habitat

As previously discussed, designated critical habitat is assessed to evaluate actions related to the use of acrolein that may alter the PCEs of the whipsnake's designated critical habitat. PCEs for the whipsnake were previously described in Section 2.6. Actions that may modify critical habitat are those that alter the PCEs and jeopardize the continued existence of the whipsnake. Therefore, these actions are identified as assessment endpoints. It should be noted that evaluation of PCEs as assessment endpoints is limited to those of a biological nature (*i.e.*, the biological resource requirements for the whipsnake associated with the critical habitat) and those for which acrolein effects data are available.

Assessment endpoints used to evaluate potential effects to designated critical habitat are equivalent to the assessment endpoints used to evaluate potential for direct and indirect effects. For the whipsnake, the relevant assessment endpoints for critical habitat are those that measure effects of acrolein on the survival and reproduction of terrestrial plants and small mammals. Effects on small mammals are important because the presence of small mammal burrows is a component of PCE 3 of whipsnake's critical habitat. If a potential

for direct or indirect effects to terrestrial plants and small mammals is found, then there is also a potential for effects to critical habitat. Some components of these PCEs are associated with physical abiotic features (*e.g.*, presence of rock outcroppings), which are not expected to be measurably altered by use of pesticides.

## **2.7 Conceptual Model**

### **2.7.1 Risk Hypotheses**

Risk hypotheses are specific assumptions about potential adverse effects (*i.e.*, changes in assessment endpoints) and may be based on theory and logic, empirical data, mathematical models, or probability models (U.S. EPA, 1998). For this assessment, the risk is stressor-linked, where the stressor is the release of acrolein to the environment. The following risk hypotheses are presumed for the whipsnake in this assessment:

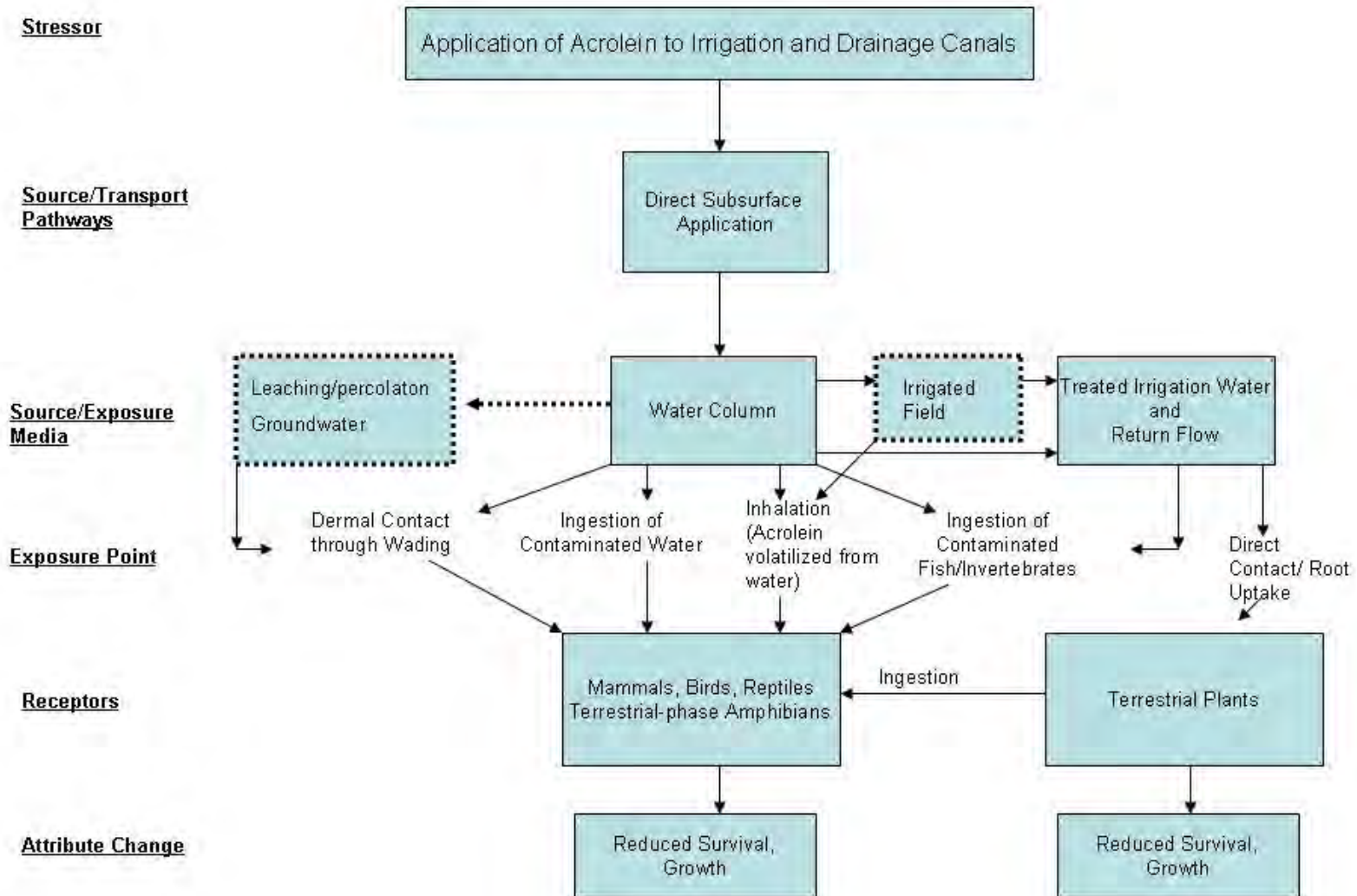
The labeled use of acrolein within the action area may:

- directly affect the Alameda whipsnake by causing mortality or by adversely affecting growth or fecundity;
- indirectly affect the Alameda whipsnake and/or modify its designated critical habitat by reducing or changing the composition of food supply;
- indirectly affect the Alameda whipsnake and/or modify its designated critical habitat by reducing or changing the composition of the terrestrial plant community in the whipsnake's current range.

### **2.7.2 Diagram**

The conceptual model is a graphic representation of the structure of the risk assessment. It specifies the acrolein release mechanisms, biological receptor types, and effects endpoints of potential concern. The conceptual model for the Alameda whipsnake and its PCE components of critical habitat are shown in **Figure 2.4**. Although the conceptual model for direct/indirect effects and modification of designated critical habitat PCEs are shown on the same diagram, the potential for direct/indirect effects and modification of PCEs are evaluated separately in this assessment. Exposure routes shown in dashed lines are not quantitatively considered because the contribution of those potential exposure routes to potential risks to the Alameda whipsnake and modification to designated critical habitat is expected to be negligible.





Note: Exposure routes shown in dashed lines are not quantitatively considered because the contribution of those potential exposure routes to potential risks to the Alameda whipsnake and modification to designated critical habitat is expected to be negligible.

**Figure 2.4. Conceptual model depicting stressor, exposure pathways, and potential effects to terrestrial organisms from the use of acrolein**

## **2.8 Analysis Plan**

In order to address the risk hypothesis, the potential for direct and indirect effects to the Alameda whipsnake, prey items, and habitat is estimated based on a taxon-level approach. In the following sections, the use, environmental fate, and ecological effects of acrolein are characterized and integrated to assess the risks. This is accomplished using a risk quotient (ratio of exposure concentration to effects concentration) approach. Although risk is often defined as the likelihood and magnitude of adverse ecological effects, the risk quotient-based approach does not provide a quantitative estimate of likelihood and/or magnitude of an adverse effect. However, as outlined in the Overview Document (U.S. EPA, 2004), the likelihood of effects to individual organisms from particular uses of acrolein is estimated using the probit dose-response slope and either the level of concern (discussed below) or actual calculated risk quotient value.

Descriptions of routine procedures for evaluating risk to the San Francisco Bay Species are provided in **Attachment I**.

### **2.8.1 Measures to Evaluate the Risk Hypothesis and Conceptual Model**

#### **2.8.1.1 Measures of Exposure**

The environmental fate properties of acrolein along with available monitoring data indicate that contact with treated irrigation water remaining on fields and spray drift from use of treated irrigation water are the principle potential transport mechanisms of acrolein to the aquatic and terrestrial habitats of the Alameda whipsnake. In general, irrigation of fields is normally done using ground spray equipment with very coarse droplets and at relatively low release heights (*e.g.*, low ground boom), so the amount of drift from such applications is expected to be low. Although acrolein is applied directly to water in irrigation canals/reservoirs, the greatest likelihood of terrestrial animal exposure from direct applications is through ingestion of treated water and inhalation of volatilized material from the treated water. In this assessment, transport of acrolein through contact with treated irrigation water remaining on fields and spray drift from use of treated irrigation water is considered in deriving quantitative estimates of acrolein exposure to the Alameda whipsnake, its prey and habitats. Based on the estimated atmospheric half-life for acrolein (4.97 to 6.45 hours) and the low potential for spray drift from fields irrigated with treated water, the potential for long-range atmospheric transport is considered unlikely. However, there is the potential from exposure to acrolein vapors near treated water bodies, as well as inhalation exposure on irrigated fields and exposure from acrolein deposition vapors via rainfall.

Measures of exposure are based on terrestrial models that predict estimated environmental concentrations (EECs) of acrolein using maximum treatment rates and estimate equivalent field application rates where acrolein-treated water is used to irrigate agricultural fields. For aquatic EECs, the maximum treatment rate (15 mg/L) is used. The model used to predict screening-level terrestrial EECs on food items is T-REX. This model is parameterized using relevant environmental fate data provided in reviewed,

registrant-submitted studies, or, when missing, developed using structure activity relationship models.

Exposure estimates for the terrestrial animals assumed to be in the target area or in an area exposed to application of irrigation water are derived using the T-REX model (version 1.4.1, 12/07/2006). This model incorporates the Kenega nomograph, as modified by Fletcher *et al.* (1994), which is based on a large set of actual field residue data. The upper limit values from the nomograph represented the 95th percentile of residue values from actual field measurements (Hoerger and Kenega, 1972).

Previous assessments (USEPA, 2011) for the Alameda whipsnake have estimated the bodyweight of the whipsnake to range from 2.5 to 897 g, using the equations available in USEPA (1993). As such, for modeling purposes, direct exposures of the Alameda whipsnake to acrolein through contaminated food are estimated using the EECs for the large (1000g), medium (100 g), and small (20 g) bird. Dietary-based and dose-based exposures of potential prey (mammals) are assessed using the large (1000 g), medium (35 g), and small (15 g) mammal which consume short grass. These categories are used because they represent the largest RQs of the size and dietary categories in T-REX that are appropriate surrogates for the Alameda whipsnake and its prey items. Estimated exposures of terrestrial insects to acrolein are bound by using the dietary based EECs for small insects and large insects.

Birds are currently used as surrogates for terrestrial-phase amphibians and reptiles. However, amphibians and reptiles are poikilotherms (body temperature varies with environmental temperature) whereas birds are homeotherms (temperature is regulated, constant, and largely independent of environmental temperatures). Therefore, amphibians and reptiles tend to have much lower metabolic rates and lower caloric intake requirements than birds or mammals. As a consequence, birds are likely to consume more food than amphibians and reptiles on a daily dietary intake basis, assuming similar caloric content of the food items. Therefore, the use of the avian food intake allometric equation as a surrogate for amphibian and reptile food intake is likely to result in an over-estimation of exposure and risk for reptiles and terrestrial-phase amphibians. Therefore, T-REX (version 1.4.1) has been refined to the T-HERPS model (v. 1.0), which allows for a refined estimation of food intake for poikilotherms using the same basic procedure as T-REX to estimate avian food intake. When LOCs are exceeded based on model results from T-REX, T-HERPS is used to refine the estimates.

More information on these models is available in **Attachment I**.

#### **2.8.1.2 Measures of Effect**

Data identified in Section 2.8 are used as measures of effect for direct and indirect effects to the Alameda whipsnake. Data were obtained from registrant submitted studies or from literature studies identified by ECOTOX. The ECOTOXicology database (ECOTOX) was searched in order to provide more ecological effects data and in an attempt to bridge existing data gaps. 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 USEPA, Office of Research and Development, and the National Health and Environmental Effects Research Laboratory's Mid-Continent Ecology Division. More information on the ECOTOXicology (ECOTOX) database and how toxicological data is used in assessments is available in **Attachment I**.

The assessment of risk for direct effects to the Alameda whipsnake makes the assumption that toxicity of acrolein to birds is similar to or more than the toxicity of acrolein to terrestrial-phase amphibians and reptiles (this also applies to potential prey items). Since potential forage items and habitat for the Alameda whipsnake only involve terrestrial animals (*i.e.*, mammals, other reptiles, terrestrial insects and terrestrial plants), the effects assessment will only consider these taxa.

The acute measures of effect used for animals in this screening level assessment are the LD<sub>50</sub>, LC<sub>50</sub> and EC<sub>50</sub>. LD stands for "Lethal Dose," and LD<sub>50</sub> is the amount of a material, given all at once, that is estimated to cause the death of 50% of the test organisms. LC stands for "Lethal Concentration," and LC<sub>50</sub> is the concentration of a chemical that is estimated to kill 50% of the test organisms. EC stands for "Effective Concentration," and the EC<sub>50</sub> is the concentration of a chemical that is estimated to produce a specific effect in 50% of the test organisms. Endpoints for chronic measures of exposure for listed and non-listed animals are the NOAEL/NOAEC and NOEC. NOAEL stands for "No Observed-Adverse-Effect-Level" and refers to the highest tested dose of a substance that has been reported to have no harmful (adverse) effects on test organisms. The NOAEC (*i.e.*, "No-Observed-Adverse-Effect-Concentration") is the highest test concentration at which none of the observed effects were statistically different from the control. The NOEC is the No-Observed-Effects-Concentration. For non-listed plants, only acute exposures are assessed (*i.e.*, EC<sub>25</sub> for terrestrial plants and EC<sub>50</sub> for aquatic plants).

It is important to note that the measures of effect for direct and indirect effects to the whipsnake and its designated critical habitat are associated with impacts to survival, growth, and fecundity, and do not include the full suite of sublethal effects used to define the action area. According to the Overview Document (USEPA 2004), the Agency relies on effects endpoints that are either direct measures of impairment of survival, growth, or fecundity or endpoints for which there is a scientifically robust, peer reviewed relationship that can quantify the impact of the measured effect endpoint on the assessment endpoints of survival, growth, and fecundity.

### **2.8.1.3 Integration of Exposure and Effects**

Risk characterization is the integration of exposure and ecological effects characterization to determine the potential ecological risk from agricultural and non-agricultural uses of acrolein, and the likelihood of direct and indirect effects to the Alameda whipsnake in aquatic and terrestrial habitats. The exposure and toxicity effects data are integrated in order to evaluate the risks of adverse ecological effects on non-target species. For the assessment of acrolein risks, the risk quotient (RQ) method is used to compare exposure and measured toxicity values. EECs are divided by acute and chronic toxicity values.

The resulting RQs are then compared to the Agency's levels of concern (LOCs) (USEPA, 2004) (see **Appendix A**).

For this endangered species assessment, listed species LOCs are used for comparing RQ values for acute and chronic exposures of acrolein directly to the Alameda whipsnake. If estimated direct exposures of the whipsnake to acrolein resulting from a particular use are sufficient to exceed the listed species LOC, then the effects determination for that use is "may affect." When considering indirect effects to the whipsnake due to effects to prey, the listed species LOCs are also used. If estimated exposures of the prey of the whipsnake to acrolein resulting from a particular use are sufficient to exceed the listed species LOC, then the effects determination for that use is a "may affect." If the RQ being considered also exceeds the non-listed species acute risk LOC, then the effects determination is a LAA. If the acute RQ is between the listed species LOC and the non-listed acute risk species LOC, then further lines of evidence (*i.e.*, probability of individual effects, species sensitivity distributions) are considered in distinguishing between a determination of NLAA and a LAA. If the RQ being considered for a particular use exceeds the non-listed species LOC for plants, the effects determination is "may affect". Further information on LOCs is provided in **Appendix A**. More information on standard assessment procedures is available in **Attachment I**.

### **2.8.2 Data Gaps**

Limited fate data are available for acrolein. Effects of photodegradation in water and soil, aerobic aquatic metabolism, and soil leaching have not been evaluated. No avian subacute dietary or chronic avian toxicity data are available. No terrestrial invertebrate toxicity data are available and no terrestrial plant toxicity data are available. No toxicity data on acrolein are available for reptiles and therefore birds would serve as surrogates for reptiles; however, avian toxicity data are not available for estimating effects from subacute dietary exposures and chronic exposures. These data gaps will limit the extent to which direct effects on the Alameda whipsnake and indirect effects on its forage base and habitat can be characterized.

## **3. Exposure Assessment**

Acrolein is formulated as a liquid and is applied from pressurized containers using a stream of industrial grade nitrogen, supplied from a separate cylinder, 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 pressurized nitrogen with settings ranging from 6 to 60 psig. In order to dissipate acrolein, treated canal water may be used to irrigate agricultural fields.

### 3.1 Label Application Rates and Intervals

MAGNACIDE H Herbicide is a restricted use pesticide used for the control of submersed and floating weeds and algae in irrigation systems. USEPA 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<sup>9</sup>, which is referenced on the pesticide label, 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. 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.

Currently registered uses of acrolein within California include using the pesticide for control of submerged and floating aquatic weeds and algae in irrigation canals and irrigation reservoirs. The uses being assessed are summarized in **Table 3.1**.

In California, the state with the most irrigation systems that reported use of acrolein nationally, the most common number of applications is two (MRID 46976913). Reported treatment durations ranged from 1 to 12 hours with 4 hours being the common application duration.

Scenario	Condition Code:	Application Rate (gallons/cubic feet/second)	Application Rate (lb ai/cubic feet/second)	Treatment Rate (ppm)
Herbicide	A: Little algae and pondweed less than 6 inches long	0.17	1.14	1.3 <sup>1</sup>
	B: Algae (non-floating) and pondweed <12 inches long	0.25	1.68	2.0 <sup>1</sup>
				1.3 <sup>2</sup>
				1.0 <sup>3</sup>
	C: Algae (some floating) and pondweed 12 - 24 inches long	0.50	3.35	3.9 <sup>1</sup>
				2.6 <sup>2</sup>
				1.9 <sup>3</sup>
	D: Algae (some floating) and mature pondweed	1.0	6.7	7.9 <sup>1</sup>
				5.2 <sup>2</sup>
				3.9 <sup>3</sup>
	E: Choked conditions	1.5	10.1	15.0 <sup>4</sup>
				11.8 <sup>1</sup>
				7.9 <sup>2</sup>
				5.9 <sup>3</sup>

<sup>9</sup> Baker Petrolite. 2005. MAGNACIDE H Herbicide Application and Safety Manual. Manual Revision Date: March 2005.

<sup>a</sup> Uses assessed based on MAGNACIDE H Application and Safety Manual

<sup>1</sup> Based on 4 hour application time

<sup>2</sup> Based on 6 hour application time

<sup>3</sup> Based on 8 hour application time

<sup>4</sup> Based on 3 hour application time

## **3.2 Aquatic Exposure Assessment**

### **3.2.1 Aquatic Exposure Concentrations**

According to the MAGNACIDE H Application and Safety Manual<sup>10</sup>, 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 durations) ranging from 30 minutes to 8 hours. Since acrolein is applied directly to water, estimated aquatic environmental concentrations are assumed to be the maximum labeled treatment rate, *i.e.*, 15 mg/L.

### **3.2.4 Existing Monitoring Data**

A critical step in the process of characterizing EECs is comparing the maximum treatment concentration with available surface water monitoring data. The following section summarizes results of monitoring studies EPA was able to identify including data made available by the registrant, and data provided by State agencies. These include LaGrangian field studies, monitoring studies supporting NPDES permit compliance, dissipation studies in agricultural fields, and air monitoring studies.

Studies conducted in Washington and Nebraska (see Section 2.4.1) show that, while acrolein does indeed dissipate with half-lives of less than 1 day, it is sufficiently persistent to move long distances, up to 60 miles at concentrations up to 50 µg/L. These studies, however, were conducted in the 1980s and were used to adjust label language to include required holding time for treated water or to use as irrigation water. As presented below, more recent data from California do not indicate such a persistence trend at downstream sites.

#### **3.2.4.1 California NPDES Surface Water Data**

The State of California began requiring monitoring for acrolein by irrigation districts as part of its NPDES permitting program in 2002, and data from 14 irrigation districts in the state that use acrolein were made available for review, and are described below. The monitoring plans and the reporting varied substantially as each district had leeway to tailor the monitoring program to their own particular needs and situation.

For most cases, the data have been summarized to reflect the detection found at the longest time after application. Application durations are the time from the beginning to the end of the application. If there were multiple applications in the canal being

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<sup>10</sup> Baker Petrolite. 2005. MAGNACIDE® H Herbicide Application and Safety Manual. Manual Revision Date: March 2005.

monitored, the sum of the application durations was reported. The time of last detection was determined from the beginning of the application. Districts generally did not report distances downstream and did not provide scales on district maps so it was not possible to estimate travel distance for acrolein. Instead, the site farthest away from the application site where detection occurred was listed.

In this set of monitoring studies, there were only a few detections at any great distance from the application site, *i.e.*, a majority of detections were near the application site and relatively close to the application time. Consequently, there are a great number of detections over 1000 µg/L. In a few cases, measurements of acrolein were greater than the application rate, which may be due to incomplete mixing, misapplication, or problems with the chemical analysis. The limited number of detections at longer times was attributed to a variety of reasons, including the following: post-application samples were not taken where the chemical pulse was in the canal, post-application samples were taken 4 or 5 days after application and acrolein had dissipated, and treated water was restricted from reaching the lower sampling points. Because of the uneven quality of these data and since they mainly reflect measurements at application and not near points of discharge from the irrigation system, they are not used in the risk assessment but are included here for qualitative characterization only.

Summaries for each irrigation district follow:

#### *South San Joaquin Irrigation District*

The South San Joaquin Irrigation District serves farmers near Escalon, Ripon, and Manteca in the Central Valley of California. The Main Distribution Canal for the system starts at the discharge of Woodward Reservoir and is approximately 26 miles long. There are about 180 miles of lateral canals, 360 miles of pipes, and 70 miles of drainage ditches in the system. The system has approximately 25 drain locations that enter either the Lone Tree Creek/Little John Creek system or the French Camp outlet canal, both of which drain to the San Joaquin River. There are five additional drainage points into the Stanislaus River. Most applications are made at the outlet of Woodward Reservoir into the Main Drainage Canal; however, applications made during low-flow conditions may be made further down the canal. The Irrigation District noted in their 2004 report that the entry to the irrigation system at Woodward Reservoir is screened to prevent fish entry, and all outlets are discharged above the surface of the receiving water so fish cannot swim up into the system.

Although there were seven acrolein applications in 2002 at the outlet of Woodward Reservoir into the Main Drainage Canal, acrolein monitoring data were only reported for two of the applications, June 26 and August 7. On June 26, five measurements were made at different points down the treated canal. Of these measurements, there was one sample (20 µg/L) above the level of detection; however, the limit of detection (LOD) was not reported (**Table 3.2**). The analytical method for these measurements was not stated although it appeared to be a field detection method. Three samples were taken on August 7 where two of the samples were below the LOD using a field detection method. The



third sample was subjected to laboratory analysis by GC/MS method, (otherwise not described in the report), and it too had no detectable acrolein. Quality assurance/control (QA/QC) procedures (method blank, matrix spike) were followed for this sample; however, acrolein was apparently not included in the compounds used for the matrix spike.

Two application events were monitored in 2004, July 7 and September 9 (**Table 3.2**). These two dates were selected to reflect different flow regimes in the canal: July 7 was high flow and September 9 was low flow. Pre-application sampling showed no acrolein in the canal on either date. Monitoring data indicated acrolein residues of 110 µg/L at the end of the treatment area 25 hours after the initiation of treatment on September 9.

**Table 3.2. Acrolein NPDES Compliance Monitoring Data for the South San Joaquin Irrigation District in California in 2004-2005**

Location	Date	App Rate	Duration	Concentration	Time of last detection	Site of Farthest Detection
Main Irrigation Canal	7/7/2004	5.5 mg/L	2.9 h	110 µg/L	25 h	NR (Ripon Drain)
Main Irrigation Canal	9/9/2004	6.3 mg/L	2.5 h	84 µg/L	21.3 h	NR (Ripon Drain)
Main Irrigation Canal	7/20/2005	4.3 mg/L	3.7 h	3,300 µg/L	5.3 h	NR (Drop 1)
Main Irrigation Canal	9/1/2005	4.4 mg/L	3.6 h	5,600 µg/L	5.5 h	NR (Drop 1)
Main Irrigation Canal	6/27/2006	6.3 mg/L	3.6 h	220 µg/L	25.4 h	NR (Ripon Drain)
Main Irrigation Canal	8/29/2006*	5.7 mg/L	1.2 h	390 µg/L	29.5 h**	NR (Ripon Drain)

\* While the intended application rate was 5.7 mg/L, 11 mg/L was detected in the canal at the application point. The irrigation district attributed this to poor mixing at the application site.

\*\* 3000 µg/L was detected at Ripon drain 23.8 h after the application

It is worth noting that fish were killed in a private pond (discussed later in this assessment) that received water from the irrigation system during the first treatment event (May 26) of the 2004 season. Subsequently, the district added private pond owners to the list of those receiving notification 24 hours prior to acrolein applications.

### *Nevada Irrigation District*

The Nevada Irrigation District serves farmers in Nevada, Placer and Yuba Counties in the Sacramento Valley in California. The irrigation district supplies both drinking water and irrigation water, and generates hydroelectric power. The irrigation districts website (<http://www.nid.dst.ca.us/irrigation-water.cfm>) notes that besides being used for growing crops, irrigation water in its system is used to fill ponds and reservoirs for stock watering,

for fire suppression, and recreation. The system has 10 reservoirs that hold over 280,000 acre-feet of water.

Monitoring data were available for acrolein applications in the Nevada Irrigation District for 2005 through 2006 (**Table 3.3**). Four different laboratories were involved in the analyses and method detection limits (MDL) ranged from 5 µg/L to 50 µg/L. In most cases, samples were collected both above and below the discharge point from the canal, although it was not clear whether the discharge point was into a natural body of water. Acrolein has not been detected in any sample taken from the Nevada Irrigation District.

<b>Table 3.3. Acrolein NPDES Compliance Monitoring Data for the Nevada Irrigation District in California</b>			
<b>Year</b>	<b>Location</b>	<b>Number of Samples (above/below outlet)</b>	<b>Number of Detections (above/below outlet)</b>
2002	Sailors Ravine	4/4	0/0
2002	Doty Ravine	2/2	0/0
2004	Sailors Ravine	3/3	0/0
2005	Sailors Ravine	8/8	0/0
2006	Sailors Ravine	14/2	0/0

#### *Modesto Irrigation District*

The Modesto Irrigation District serves an area in the San Joaquin River Basin on the east side of the Central Valley between the Stanislaus and Tuolumne Rivers. The district has 142 miles of open channel canals, 85% of which are concrete-lined.

The Modesto Irrigation District used EPA method 8260 to measure acrolein. The reporting limit for this method was 20 µg/L. The irrigation district report included quality assurance methods, method blanks, matrix spikes, laboratory control samples, travel blanks and field duplicates. The district listed four water bodies which could be potentially impacted by discharge: Dry Creek, Tuolumne River, Stanislaus River and the San Joaquin River.

Although samples were collected for four different application events in 2002, acrolein was not detected. Information on how and where samples were collected was not provided for 2002 applications. In 2003, 14 samples were collected at 5 different locations throughout the district. During the treatment year, acrolein was detected only once at 35 µg/L. This detection was made over a day after application. In 2004 and 2005, samples were collected from multiple locations along two lateral canals following multiple acrolein applications so the acrolein measurement may reflect the contributions from more than a single application. Monitoring results for the Modesto Irrigation District are summarized in **Table 3.4**.

**Table 3.4. Acrolein NPDES Compliance Monitoring Data for the Modesto Irrigation District in California, 2002-2005**

Location	Date	App. Rate (mg/L)	Duration of App.	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detection
NR	7/24/02	NR	NR	ND	NA	NNA
NR	7/30/02	NR	NR	ND	NA	NA
NR	9/19/02	NR	NR	ND	NA	NA
NR	9/24/02			ND	NA	NA
Head Lateral 3 or Main canal @ L3 head*	7/22/03	0.53-0.55	3 h	ND	NA	NA
L-4 Lateral	7/28/03	12.9**	7** h	ND	NA	NA
Head Lateral 3 or Main canal @ L3 head*	9/16/03	0.88 mg/L	3 h	35	25.4 h	
Lateral 6	5/26/04	1.15	1.5 h	400	6 h	@ Pelandale Ave
	6/9/04	1.5	2 h	420	50.3 h	@ Pelandale Ave
	6/23/04	1.1	2 h	990	11.5 h	Lat. 7 @ Prescott
	7/8/04	0.95	1.5 h	830	9.3 h	@ Pelandale Ave
	7/21/04	0.94	1.5 h	820	10.1 h	Lat. 7 @ Prescott
	8/4/04	0.71	1.5 h	740	11.8 h	Lat. 7 @ Prescott
	8/18/04	1.6	1.5h	700	20.1 h	Lat. 7 @ Prescott
	9/15/04	0.96	2 h	330	30.9 h	Lat. 7 @ Prescott
	9/29/04	1.8*	2.5 h	1,200	24.6 h	@ Pelandale Ave
Lateral 3	5/22/04	2.7-5.8*	7 h*	2,600	9.6 h	Butler Ditch @ Woodland Ave
	6/2/04	4.8-5.8*	6.5 h*	930	28.2 h	Lateral 3 Spill
	6/15/04	5.4*	6.5 h*	190	26.1 h	Lateral 3 Spill
	6/29/04	2.3-5.4*	6 h*	ND	NA	NA
	7/13/04	2.3-6.6*	7 h*	2,700	10.6 h	Lateral 3 Spill
	7/27/04	5.8-7.7*	6 h*	56	34.5 h	Lateral 3 Spill
	8/10/04	5.8*	6.5 h*	1,300	30.8 h	Lateral 3 Spill
	8/24/04	3.1-7.7*	6 h*	4,200	8.4 h	Lateral 3 Spill
	9/8/04	5.8*	6.5 h*	ND	NA	NA
	9/21/04	4.1-7.7*	6.5 h*	ND	NA	NA
	10/5/04	5.4*	6.5 h	3,000	25.9 h	Lateral 3 Spill
Lateral 6	5/25/05	1.4	1.5 h	630	15.5 h	@ Pelandale Ave
	6/8/05	1.5	2 h	2,400	15.2 h	@ Pelandale Ave
	6/22/05	1.5	2 h	475***	15.4 h	@ Pelandale Ave
	7/6/05	1.3	2 h	270	13.8 h	Lat. 7 @ Prescott
	7/20/05	1.1	2 h	600	8.8 h	Lat. 7 @ Prescott
	8/3/05	1.2	2 h	420	13.1 h	Lat. 7 @ Prescott
	8/17/05	1.5	2 h	690	15.8 h	Lat. 7 @ Prescott
	8/31/05	1.2	2 h	740	10.5 h	Lat. 7 @ Prescott
	9/14/05	2.1	2 h	870	6.7 h	@ Pelandale Ave
	9/28/05	2.5	2 h	ND	NA	NA
	5/17/05	5.4**	6.5 h**	ND	NA	NA
Lateral 3	6/1/05	5.8-6.4**	4.5 h**	26,000 <sup>†</sup>	7.2 h	Lateral 3 Spill
	6/14/05	4.8-5.8**	6.2 h**	26,000 <sup>†</sup>	23 h	Lateral 3 Spill
	6/28/05	2.8-5.8**	6.5 h**	2400	3.7 h	Butler Ditch

**Table 3.4. Acrolein NPDES Compliance Monitoring Data for the Modesto Irrigation District in California, 2002-2005**

Location	Date	App. Rate (mg/L)	Duration of App.	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detection
	7/12/05	3.8**	5.5 h**	380	12.9 h	Lateral 3 Spill
	7/26/05	2.0-3.7**	6 h**	1,300	11.4 h	Lateral 3 Spill
	8/9/05	2.3-5.8**	6 h**	900	13.5 h	Lateral 3 Spill
	8/23/05	2.7**	6.5 h**	4,500	10 h	Butler Ditch
	9/7/05	3.8-6.8**	6.5 h**	67	28.4 h	Butler @ Hart Rd
	9/20/05	5.8**	6.5 h**	2,700	15.2 h	Lateral 3 Spill
	10/4/05	2.1-4.4**	6.5 h**	710	24 h	Butler Ditch

NA – not applicable; NR – not reported; ND – not detected

\*It could not be determined which application was associated with the sampling sites.

\*\* Multiple applications to the same canal were made at different locations along the canal during the day. The application concentrations shown are for the range over the multiple locations if they were not the same at all application sites. The duration is the sum of the duration for the applications made to lateral 3 on the application day.

\*\*\* Average of measurements of a split samples measured by two different laboratories.

† Report authors indicate that “data questionable additional sampling indicated the results were high by a factor of 4 or 5.”

There were some analytical complications associated with the measurements made in 2005. Three samples had concentrations well above the nominal application rate, at 26, 26, and 9.1 mg/L. The tank from which the application was made was weighed and the amount of acrolein actually applied was in reasonable agreement with the intended amount. The reason for the discrepancy could not be determined. A number of measurements that were non-detects made on samples collected from Lateral 3 on June 28 had poor recoveries based on field spikes and thus might be lower than actual levels. However, the value reported in **Table 3.4** was measured by a different analytical service and does not suffer from quality control concerns.

#### *Solano County Water Agency*

The Solano County Water Agency reported NPDES compliance monitoring data for acrolein for 2002. Samples were collected at 12 sites in the county on July 1 and September 30. With a detection limit of 20 µg/L, there were no detects of acrolein in any of the samples. The locations of the sampling sites were provided in the report, but no information was supplied on the nature or location of the associated applications of acrolein.

#### *Woodbridge Irrigation District*

The Woodbridge Irrigation District is in the Mokelumne River Basin, near Lodi, California. The Irrigation District reported acrolein monitoring results for 2004 and 2005; however, results from 2004 are not interpretable. In July 2005, samples were collected at the “headworks” for the irrigation system and acrolein was not detected in pre-treatment, treatment, or post-treatment samples. The intended application rate was 5.5 mg/L and was applied for 2 h.

*Provident & Princeton-Codora-Glenn Irrigation District*

The Provident and Princeton-Codora-Glenn Irrigation District channels water from the Sacramento River to over 16,000 acres in Glenn and Colusa counties. Acrolein was applied 3 times in 2005 for the Provident Irrigation District and twice for Princeton-Codora-Glenn. Both facilities share the same entryway and applications for both districts were made at the Sidds Pumping Plant. A nominal application rate of 5 mg/L was used for all applications. Both sites had detects with all applications and all had non-detects for the last sample collected (**Table 3.5**). The longest post-application detection interval was 14 h for the July 5 treatment in the Provident District. The detection limit was reported as 100 µg/L. It is not clear from the reports how sampling sites relate to actual discharge sites from the irrigation systems.

**Table 3.5. Acrolein NPDES Compliance Monitoring Data for the Provident Irrigation District and Princeton-Codora-Glenn Irrigation District in California, 2005**

Location	Date	App Rate (mg/L )	Duration	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detection
Sidds Pumping Plant (Prov.)	5/24/05	5*	NR	7,700	3.5 h	Sidds Landing
Sidds Pumping Plant (Prov.)	7/5/05	5 *	NR	1,900	14 h	County Rd 46
Sidds Pumping Plant (Prov.)	8/2/2005	5 *	NR	3,600	5.5 h	Hwy 162
Sidds Pumping Plant (PCG)	6/14/05	5	3 h	1,900	0.75 h	App. Site
Sidds Pumping Plant (PCG)	7/12/05	5	3 h	580	3.5 h	Count Rd 56

NR – not reported

\* nominal application; actual application rate was not reported

*Natomas Central Mutual Water Company.*

Natomas provides irrigation water mostly for rice irrigation in the Sacramento River basin in north-central California. Natomas operates a ‘closed’ system and recirculates irrigation water during the growing season of April to September. This allows pesticides and other agricultural chemicals to dissipate or dilute before the water is released to the river system. The 2003 monitoring discharge report indicated that they were “*working diligently to eliminate the need for Magnicide on annual basis and for the 2003 irrigation season.*”

*Byron-Bethany Irrigation District*

Byron-Bethany District serves San Joaquin, Alameda, and Contra Costa counties. Byron-Bethany District made 3 applications of acrolein in 2004. Samples were collected in

association with all three treatments; however, samples from August 3 were compromised during handling and results were not reported. Applications were made on the same date to two canals systems, the Byron Division and the Bethany Division. Results of monitoring for the two systems are presented separately in **Table 3.6**. Detection limits and other details on analytical methodology were not reported.

Ten total applications were made in 2005. In addition to acrolein, 3-hydroxypropanal was measured and was found in 4 samples. One of these samples had no detectable acrolein. Results for 3-hydroxypropanal analyses are reported in parentheses in **Table 3.6**. When acrolein was found it was generally above 1000 µg/L. Detections occurred approximately 1 day after application at the discharge points in both the Byron and Bethany Divisions. It is important to note that the gates to both creeks were closed and the freeboard maintained so that no system discharge occurred during application events.

<b>Table 3.6. Acrolein NPDES Compliance Monitoring Data for the Bethany-Byron Irrigation District in California in 2004-2005</b>						
<b>Location</b>	<b>Date</b>	<b>App Rate (mg/L )</b>	<b>Duration</b>	<b>Concentration (µg/L)*</b>	<b>Time of Last Detection</b>	<b>Site of Farthest Detection</b>
1-N (Byron)	8/17/04	11.8	4 h	ND	NA	
1-S (Bethany)	8/17/04	11.8	4 h	ND	NA	
1-N (Byron)	8/31/04	11.8	4 h	ND	NA	
1-S (Bethany)	8/31/04	11.8	4 h	ND	NA	
1-N (Byron)	5/3/05	5.2	6 h	1,200 (89)	10 8 h	Radial gate @ Kellogg Creek
1-N (Byron)	5/24/05	7.9	4 h	ND	NA	NA
1-S (Bethany)	5/24/05	7.9	4 h	2,100 (370)	25.5 h	120 Spillway
1-N (Byron)	6/7/05	7.9	4 h	ND	NA	NA
1-S (Bethany)	6/21/05	7.9	4 h	ND	NA	NA
1-N (Byron)	7/6/05	7.9	4 h	ND (22)	9.8 h	Radial gate @ Kellogg Creek
1-S (Bethany)	7/19/05	7.9	4 h	ND	NA	NA
1-N (Byron)	8/2/05	7.9	4 h	3,400 (520)	24 h	Radial gate @ Kellogg Creek
1-S (Bethany)	8/16/05	7.9	4 h	ND	NA	NA
1-N (Byron)	8/30/05	7.9	4 h	ND	NA	NA
1-S (Bethany)	9/12/05	7.9	4 h	ND	NA	NA

NR – not reported; NA – not applicable

\* 3-hydroxypropanal concentrations are reported in parentheses. If none are reported 3-hydroxypropanal was not detected.

### *South Sutter Water District*

The South Sutter Irrigation District serves farmers in Placer, Sutter, and Yuba counties in the Sacramento River Basin. Samples were collected for three treatment events in 2005 with a sample collected above the application site, one at or near the application site and a third taken approximately one week later. Detections of acrolein were found in the samples which were taken near the application time (**Table 3.7**). The detection limit was 5 µg/L. Insufficient information was provided to determine the application concentration or the duration of application. No information on sample handling or analytical QA/QC was provided.

**Table 3.7. Acrolein NPDES Compliance Monitoring Data for the South Sutter Water District in California for 2005**

Location	Date	App Rate (mg/L )	Duration	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detection
Line 1 Headgate	5/24/05	NR	NR	6,200	NR	Slide Gates
Bear River Drive Canal	8/11/05	NR	NR	2,200	NR	App site
Line 1 Headgate	9/9/05	NR	NR	69	NR	Slide Gates

NR – not reported;

#### *Maine Prairie Water District*

The Maine Prairie Water District is in Solano County, California, and reported monitoring results for the NPDES compliance program for 2005. There were six applications of acrolein in 2005 and monitoring was conducted in association with four of them (**Table 3.8**). The detection limit was 5 µg/L. Insufficient information was provided to determine the application concentration or the duration of application. No information on sample handling or analytical QA/QC was provided. Reported acrolein residues exceeded the maximum application rate, but the sample was taken near the application site and may reflect incomplete mixing.

**Table 3.8. Acrolein NPDES Compliance Monitoring Data for the Maine Prairie Water District in California for 2005**

Location	Date	App Rate (mg/L )	Duration	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detect
Line 1	8/3/05	NR	NR	15,000	NR	Pit Rd School
Line 1	8/10/05	NR	NR	ND	NA	NA
Line 1	8/18/05	NR	NR	24,000	NR	Line 1
Line 1 @ Dam 1	8/24/05	NR	NR	ND	NA	NA

NA – not applicable; NR – not reported

#### *Reclamation District No. 1004*

This district is located in Glenn, Colusa, and Sutter counties and comprises 35.94 square miles. Water from the district primarily comes from the Sacramento River with supplemental water from Butte Creek. This district uses recirculation pumps throughout the drainage system to minimize water loss. One application of 4 h duration at 7.3 mg/L of acrolein was made to the district in 2005. Acrolein was detected at the application site at 1000 µg/L but was not found in samples taken 6 miles downstream 8 h later, or 10 miles downstream 16 h after the start of application. The detection limit was 100 µg/L. No information was provided on the analytical method or QA/QC procedures.

### *Glenn-Colusa Irrigation District*

This district supplies water to 141,000 acres of farmland and 20,000 acres of National Wildlife Refuge in Glenn and Colusa counties in California. Water for the district comes from the Sacramento River and is discharged to the Colusa Drain and other irrigation districts through a 65-mi long main canal and a 900-mile long network of smaller canals, laterals, and drains. Monitoring was conducted for acrolein in association with an application made July 16, 2005, to the unlined lateral canal. Three samples were collected, one upstream of application, and two downstream at 2 and 25.5 h after application. All samples were analyzed by both EPA method 624 and a Hach colorimeter at 450 nm. There were no detections of acrolein made using EPA method, but the colorimeter method indicated that 2 mg/L was present in the downstream sample taken 2 h after application. The report authors thought that the EPA measurement was in error due to sample degradation during transport and handling. The colorimeter measurement was made 10 min after sampling and thus had little time to degrade or volatilize. Detection limits for the EPA methods and the colorimeter method were 10 µg/L and 100 µg/L, respectively. QA/QC for the samples was not reported.

### *Oakdale Irrigation District*

The Oakdale Irrigation District supplies water to over 55,000 acres through 105 miles of lined canals, 125 miles of unlined canals, and 100 mi of buried pipeline. Water is diverted into the district from the Stanislaus River in the Central Valley at Goodwin Dam and returns water through approximately 110 miles of canals to the Stanislaus River, Dry Creek, Lone Tree Creek, and to the Main Canals of the Modesto and South San Joaquin Irrigation Districts. In addition to water supplied from the Stanislaus River, the District pumps 6,700 acre-feet of water annually from 24 deep agricultural wells.

Data were available for acrolein measurements made in association with acrolein applications made in the district from 2004-2006. Measurements of acrolein were made using EPA method 8260; the detection limit for most samples was 5 µg/L. Samples collected on May 26 and July 6 of 2004 had a detection limit of 3.6 µg/L and a practical quantitation limit of 50 µg/L. The sampling locations for the downstream samples were not reported (**Table 3.9**). The majority of samples were below the level of quantitation; however, detections as high as 3700 µg/L are reported up to 7.2 hours after initiation of treatment.

<b>Table 3.9. Acrolein NPDES Compliance Monitoring Data for the Oakdale Irrigation District in California for 2004-2006</b>						
<b>Location</b>	<b>Date</b>	<b>App Rate (mg/L )</b>	<b>Duration</b>	<b>Concentration (µg/L)</b>	<b>Time of Last Detection</b>	<b>Site of Farthest Detect</b>
South Main Canal	5/26/04	3.9	2 h	<PQL	NA	NA
Claribel Lateral	7/6/04	7.8	2 h	<PQL	NA	NA
South Main Canal	7/21/04	7.8	3 h	3,700	7.2 h	NR
Kuhn Drain	8/31/04	7.8	2 h	860*	7.0 h	NR
Claribel Lateral	5/24/05	5.2	3 h	ND	NA	NA



**Table 3.9. Acrolein NPDES Compliance Monitoring Data for the Oakdale Irrigation District in California for 2004-2006**

Location	Date	App Rate (mg/L)	Duration	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detect
South Main Canal	6/7/05	3.9	2 h	ND	NA	NA
South Main Canal	8/4/05	2.6	3 h	ND	NA	NA
Sweet Lateral	8/18/05	7.8	2 h	ND	NA	NA
South Main Canal	6/8/06	7.8	2 h	1,900	7.7 h	NR
South Main Canal	9/13/06	5.2	1 h	ND	NA	NA

NA – not applicable; NR – not reported; PQL – practical quantitation limit

\* Detection was made in a Modesto Irrigation District Canal that received water from the Kuhn Drain. Detection may have been due to application in the Modesto Irrigation District on the same day.

### *Turlock Irrigation District*

In this irrigation district, water is collected from the Tuolumne River at LaGrange Dam and is conveyed to Turlock Lake which acts as the regulating reservoir for the Irrigation District. Water is released from Turlock Lake into the Main Irrigation Canal for distribution to growers through 250 miles of canals and laterals. There are 15 spill locations from the irrigation system which are consolidated into 9 points of discharge to the San Joaquin, Tuolumne and Merced Rivers. The district also supplies water to the community of La Grange by diverting water from the Upper Main Canal into a small retention reservoir used for this purpose. Acrolein applications are apparently not made in the main canal above where diversion to the retention reservoir occurs.

In 2004, samples were collected pre-event, event and post event. Pre-event samples were collected immediately before application. Event samples were collected during application and a day or so after. Post-event samples were collected 4- or 5-days after application event. Since acrolein is not expected to persist near the application site at detectable levels for 4 or 5 days, it is not surprising that there were no detections in this lateral canal in 2004. In 2005, post-event samples were again being collected on the same day as the application, but at sampling locations further down the canal, as was done in 2002 and 2003. No acrolein was detected in 2005 (**Table 3.10**).

**Table 3.10. Acrolein NPDES Compliance Monitoring Data for the Turlock Irrigation District in California for 2002-2005**

Location	Date	App Rate	Duration	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detect
Lower lateral 2½: Drop 2	7/2/02	0.3 gal/cfs	NR	ND	NA	NA
Ceres Main: Drop 2	8/12/02	0.25 gal/cfs	NR	*	7.2 h	Hodges
Highline Canal -Drop 2	8/12/02	0.25 gal/cfs	NR	ND	NA	NA
Lower lateral 2½: Drop 9	9/23/02	0.30 gal/cfs	NR	ND	NA	NA

<b>Table 3.10. Acrolein NPDES Compliance Monitoring Data for the Turlock Irrigation District in California for 2002-2005</b>						
<b>Location</b>	<b>Date</b>	<b>App Rate</b>	<b>Duration</b>	<b>Concentration (µg/L)</b>	<b>Time of Last Detection</b>	<b>Site of Farthest Detect</b>
Highline Canal: Drops 2, 1, 4, 10	9/23/02	0.30-0.35 gal/cfs**	NR	78	4.2 h	Highline Spill
Lower lateral 2½: Drop 9	5/8/03	0.2 gal/cfs	NR	ND	NA	NA
Highline Canal: above Drop 4, 14	6/2/03	0.25 gal/cfs**	NR	ND	NA	NA
Ceres Main Canal: Drop 1, C Ditch	6/10/03	0.25 gal/cfs**	NR	ND	NA	NA
Highline Canal: Drop 2	7/14/03	0.25 gal/cfs**	NR	ND	NA	NA
Lower lateral 2½: Drops 20, 14	7/17/03	0.25 gal/cfs**	NR	ND	NA	NA
Lower lateral 2½: Drop 9	6/3/04	7.7 mg/L	2 h	ND	NA	NA
Ceres Main: Drop 1	6/9/04	3.0 mg/L	4 h	4,900	22.2 h	Drop 5
Lower lateral 2½: Drop 9	6/16/04	4.7 mg/L	2 h	ND	NA	NA
Lower lateral 2½: Drop 9	7/1/04	4.7 mg/L	2 h	ND	NA	NA
Lower lateral 2½: Drop 9	7/28/04	5.3 mg/L	2 h	ND	NA	NA
Ceres Main: Drop 1	8/10/04	2.4 mg/L	5 h	2,400	22.2 h	Drop 5
Lower lateral 2½: Drop 9	8/12/04	6.2 mg/L	2 h	ND	NA	NA
Lower lateral 2½: Drop 1	9/9/04	5.5 mg/L	2 h	ND	NA	NA
Lower lateral 2½: Drop 9	5/23/05	4.7 mg/L	2 h	ND	NA	NA
Lower lateral 2½: Drop 9	6/6/05	4.7 mg/L	2 h	ND	NA	NA
Ceres Main: Drop 1	6/14/05	1.9 mg/L	5 h	ND	NA	NA
Lower lateral 2½: Drop 9	7/5/05	5.5 mg/L	2 h	ND	NA	NA
Ceres Main: Drop 1	7/12/05	2.7 mg/L	4 h	ND	NA	NA
Lower lateral 2½: Drop 9	7/18/05	5.5 mg/L	2 h	ND	NA	NA
Lower lateral 2½: Drop 9	8/1/05	5.5 mg/L	2 h	ND	NA	NA
Lower lateral 2½: Drop 9	8/15/05	3.7 mg/L	3 h	ND	NA	NA

**Table 3.10. Acrolein NPDES Compliance Monitoring Data for the Turlock Irrigation District in California for 2002-2005**

Location	Date	App Rate	Duration	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detect
Lower lateral 2½: Drop 9	9/14/05	5.5 mg/L	2 h	ND	NA	NA

NA – not applicable; NR – not reported;

\* While a significant detection occurred in a sample from this application in the Highline Canal and the Hodges sampling station at least a day after application, the concentration and the time after application were not included in the report.

\*\* Multiple applications to the same canal were made at different locations along the canal during the day. The application concentrations shown are for the range over the multiple locations if they were not the same at all application sites.

### *Merced Irrigation District*

Water from the Merced Irrigation District irrigates 110,000 acres of land with the use of 750 miles of canals. The district's source is the Merced River and its storage site is the McClure Reservoir, which is located on the Merced River in Yosemite National Park.

Data were available for acrolein measurements made in association with acrolein applications made in the district from 2002-2005. Samples were analyzed for acrolein using EPA Method 8260; the detection limit was 5 µg/L. Quality control sampling included travel blanks, method blanks, laboratory spikes, and matrix spikes. The only samples that had acrolein detections were those taken during the event. Some of these were above the application rate which may have been caused by incomplete mixing through the canal at the sampling point. The post-event samples were not expected to have detects as the report indicated that water containing acrolein was not allowed to reach these sampling points (**Table 3.11**).

**Table 3.11. Acrolein NPDES Compliance Monitoring Data for the Merced Irrigation District in California for 2002-2005**

Location	Date	App Rate (mg/L) *	Duration	Concentration (µg/L)	Time of Last Detection	Site of Farthest Detect
Livingston Canal	7/16/02	7.2-10.5 **	1.4 h	ND	NA	NA
Livingston Canal	8/13/02	.44-.5 gal/cfs *	NR	ND	NA	NA
Le Grand Canal	7/23/02	0.5 gal/cfs	NR	ND	NA	NA
Le Grand Canal	9/3/02	3.6	4.4 h	ND	NA	NA
Livingston Canal	7/14/03	7.2*	2.2 h	ND	NA	NA
Livingston Canal	9/8/03	10.5*	1.5 h	ND	NA	NA
Le Grand Canal	7/21/03	4.1	3.9 h	ND	NA	NA
Le Grand Canal	9/3/03	0.5 gal/cfs *	NR	ND	NA	NA
Livingston Canal	7/26/04	7.8**	3 h**	54,000	NR***	Almond Ave.
Le Grand Canal	8/13/04	5.2-7.8**	6.8 h**	6,500	NR***	App. site
Le Grand Canal	5/23/05	3.9	4 h	30,000	NR***	below Black Rascal Creek
Le Grand Canal	7/19/05	5.2**	6 h**	5,400	NR***	App. site

NA – not applicable; NR – not reported; PQL – practical quantitation limit

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\* Some applications could not be converted to mg/L because of incomplete application information so are reported in gal/cfs.

\*\* Multiple applications to the same canal were made at different locations along the canal during the day. The application concentrations shown are for the range over the multiple locations if they were not the same at all application sites. Duration is the sum of the durations for all applications made to the canal.

\*\*\* Time for detect was not provided, but the sampling was described as during the application event.

*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' concluded that "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."

#### **3.2.4.2 USGS NAWQA Surface and Groundwater Data**

The USGS collected 34 samples of surface water in Sacramento County between 1996 and 1998 and measured for acrolein. All of the samples were reported below the detection limit, which ranged from 2.864 to 500 µg/L. Since 1998, no other samples were reported in NAWQA. The USGS sampled for acrolein in groundwater in 1996 in Butte, Placer, Sacramento, Sutter, and Yuba counties in California. All samples were below the detection limit of 2 µg/L. No other samples were reported in NAWQA.

#### **3.2.4.3 California Department of Pesticide Regulation (CDPR) Data**

Acrolein is not included as one of the analytes monitored in surface water or sediment samples collected by California Department of Pesticide Regulation (CDPR) (<http://cdpr.ca.gov/docs/emon/surfwtr/surfcont.htm>).

#### **3.2.4.4 Atmospheric Monitoring Data**

*Air Monitoring, Kern Delta Irrigation District (MRID 47008407).* An air monitoring study by the registrant was conducted in 2005 associated with an application to the Kern Island Canal in the Kern Delta Water District in California in August, 2005. These 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 two 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 are not available. The upwind samples on the upwind bank ranged from 28 to 36  $\mu\text{g}/\text{m}^3$  with the values increasing with distance downstream from the application point. The downwind samples were 92 and 120  $\mu\text{g}/\text{m}^3$  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 could 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 farthest downstream measurements were made in water. This apparent increase is likely due to incomplete mixing of acrolein in the canal.

### **3.3 Terrestrial Animal Exposure Assessment**

T-REX (Version 1.4.1) is used to calculate dietary and dose-based EECs of acrolein for birds, mammals, and terrestrial invertebrates. T-REX simulates a 1-year time period. For this assessment, ground spray applications of acrolein-treated irrigation water are considered, as discussed in below.

#### ***Dietary Exposure***

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 (L/acre) that is applied and sticks to the crop is required. The maximum interception storage for a crop (CINTCP) is a parameter used in the Pesticide Root Zone Model (PRZM) that 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 heavy canopy densities are listed in Table 5-4 of the PRZM manual (0.0-0.30 cm). Orchards are not identified in the PRZM manual, so the CINTCP for orchard is estimated as a conservative value of 0.40 cm. To calculate the volume ( $\text{cm}^3$ ) of irrigation water sticking to the foliage, the area of a unit field, 1 ha (or  $1 \times 10^9 \text{ cm}^2$ ) 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 (15 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, *i.e.*, 0.534 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 B** for calculations).

Terrestrial EECs for foliar applications of acrolein were derived for the uses summarized in **Table 3.12**. 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 based on the work of Willis and McDowell (1987). However, given acrolein's fate properties, the default value of 35 days is not reasonable. Acrolein rapidly volatilizes if not kept in a close container (Ghilarducci and Tjeerdema, 1985). Observed DT<sub>50</sub> values in water in both aerobic (MRID 43227101) and anaerobic (MRID 42949201) aquatic environs, as well as terrestrial field studies in Nebraska (MRID 46976905) and Washington (MRID 47008404) were less than 1 day. As such, a 1-day foliar dissipation half-life appears more appropriate. It is expected that this value will be conservative relative to the usual rate of foliar dissipation of acrolein in the environment. An example output from T-REX is available in **Appendix C**.

<b>Table 3.12. Input Parameters for Foliar Applications Used to Derive Terrestrial EECs for Acrolein with T-REX</b>				
<b>Use (Application method)</b>	<b>Treatment Rate lbs ai/A</b>	<b>Number of Applications</b>	<b>Application Interval</b>	<b>Foliar Dissipation Half-Life</b>
Irrigation of Agricultural Fields	0.534	8	14 days	1 day

N/A = Non-applicable

Upper-bound Kenega nomogram values reported by T-REX are used for derivation of dietary EECs for the Alameda whipsnake and its potential prey (**Table 3.13**). Potential direct acute and chronic effects of acrolein to the Alameda whipsnake are derived by considering dietary-based exposures modeled in T-REX for a large bird (1000 g), a mid-sized bird (100 g), and a small bird (20 g) consuming small invertebrates. Potential indirect acute and chronic effects of acrolein to the Alameda whipsnake are derived by considering dietary-based exposures modeled in T-REX for potential prey, a large mammal (1000 g), a mid-sized mammal (35 g), small mammal (15 g) consuming short grass. Upper-bound Kenega nomogram values reported by T-HERPS are used for derivation of dietary EECs for the Alameda whipsnake (**Table 3.14**). Potential direct acute and chronic effects of acrolein to the Alameda whipsnake are derived by considering dietary-based exposures modeled in T-HERPS for a mid-size herpetofauna (34g) consuming small invertebrates.

Dietary-based EECs for small and large insects reported by T-REX as well as the resulting adjusted EECs are available in **Table 3.13**. An example output from T-REX v. 1.4.1 is available in **Appendix C**. Dose-based and dietary-based EECs for snakes consuming herbivorous mammals reported by T-HERPS as well as the resulting adjusted EECs are available in **Table 3.14**. An example output from T-HERPS is available in **Appendix D**.

**Table 3.13. Upper-bound Kenega Nomogram EECs for Dietary- and Dose-based Exposures of Direct Effects (Small Birds) and Indirect Effects (Small Mammals as Prey) to Acrolein**

Dietary Category	Dose-based EECs (mg/kg-bw)						Dietary-based EECs (mg/kg-diet)
	Avian Classes and Body Weight			Mammalian Classes and Body Weight			
	20 g	100 g	1000 g	15 g	35 g	1000 g	
Short Grass	146	83	37	122	84	20	128
Tall Grass	67	38	17	56	39	9.0	59
Broadleaf plants/sm Insects	82	47	21	69	48	11	72
Fruits/pods/seeds/lg insects	9.1	5.2	2.3	7.6	5.3	1.2	8.0

**Table 3.14. Upper-bound Kenega Nomogram EECs for Dietary- and Dose-based Exposures of Alameda Whipsnake to Acrolein**

Use(s)	App. Rate (lbs a.i./A), # Apps., Interval (days)			Whipsnake (consuming herbivorous mammals)			
				Dietary-Based (mg/kg-diet)	Dose-Based (mg/kg-bw)		
					2.5 g	100 g	1000 g
Irrigation water	0.534	8	14	84.5	NA	30	3.0

### *Drinking Water Exposure*

For drinking water intake, drinking water intake equations for birds and mammals were taken from USEPA's Wildlife Exposure Factors Handbook (USEPA, 1993). For birds, the drinking water intake is given by the following equation

$$\text{Water intake (L/day)} = 0.059 \times (\text{weight (kg)})^{0.67}$$

For mammals, the drinking water intake is given by the following equation

$$\text{Water intake (L/day)} = 0.099 \times (\text{weight (kg)})^{0.9}$$

The water intake values are divided by the weight of the bird or mammal, in kilograms, to derive a dose in L-water/kg-day. Drinking water intake rates were developed for six organisms: a large mammal, a medium-sized mammal, a mouse, a mallard, a gull, and a songbird. These species were selected to evaluate direct exposure (mallard, gull, and songbird) and indirect exposure (songbird, large mammal, medium-sized mammal, and mouse as prey) to the Alameda whipsnake. The drinking water intakes for a 1.58 kg bird (mallard), a 0.35 kg bird (gull), and a 0.02 kg bird (songbird) are 0.05 L/kg-day, 0.08 L/kg-day, and 0.21 L/kg-day, respectively. Multiplying by the conservative, worst-case concentration of acrolein in treated irrigation water (15 mg/L), drinking water exposure estimates are 0.75 mg/kg-d, 1.2 mg/kg-d, and 3.2 mg/kg-d for mallards, gulls, and songbirds, respectively. The drinking water intakes for a 1.0 kg (large mammal), a 0.035

kg (medium-sized mammal), and a 0.015 kg mammal (mouse) are 0.099 L/kg-day, 0.14 L/kg-day, and 0.15 L/kg-day, respectively. Multiplying by the conservative, worst-case concentration of acrolein in treated irrigation water (15 mg/L), drinking water exposure estimates are 1.5 mg/kg-d, 2.1 mg/kg-d, and 2.3 mg/kg-d for large mammals, medium-sized mammals, and mice, respectively. It should be noted that these estimates may underestimate whipsnake water exposure, as the water balance for reptiles is complex, given that reptiles can absorb water through their skin, as well as drink water and extract water from food.

### *Inhalation Exposure*

Because acrolein is volatile and because inhalation toxicity data are available for mammals, direct and indirect exposure 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  $\mu\text{g}/\text{m}^3$  which is equal to  $1.2 \times 10^{-4}$  mg/L. 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 ( $1.95 \times 10^{-4}$  atm·m<sup>3</sup>/mol) 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 which is equivalent to  $1.18 \times 10^{-1}$  mg/L. The results of the second method are approximately a factor of 1000 greater than that measured in the air during the field study; however, the field study results are based on a treatment rate that is 73% lower than the maximum label rate of 15 mg/L.

Again, these concentrations were used to calculate vapor inhalation doses (VID) for six organisms: a large mammal, a medium-sized mammal, a mouse, a mallard, a gull, and a songbird (**Table 3.15**) according to the method outlined in Sunzenauer *et al.* (2004). These species were selected to evaluate direct exposure (mallard, gull, and songbird) and indirect exposure (songbird, large mammal, medium-sized mammal, and mouse as prey) to the Alameda whipsnake. The VID was calculated for each species as follows. First, a respiration rate in liters per minute (L/min) was estimated using allometric equations relating the respiration rate to body weights for mammals and birds (USEPA, 1993, equations are footnoted in **Table 3.15**). These rates are multiplied by three to conservatively convert the resting respiration rate to the field active respiration rate. The respiration rates are then multiplied by the exposure duration of 4 hours (240 min) to estimate the  $V_{\text{inh}}$ , *i.e.*, 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 ( $C_{\text{air}}$ ) in mg/L, was then multiplied by the inhaled volume ( $V_{\text{inh}}$ ) in liters, and divided by the body weight in kg to calculate VID in mg/kg.



<b>Table 3.15. Calculated Vapor Inhalation Doses (VID) for a mammal and two birds</b>					
<b>Species</b>	<b>Body Weight (kg)</b>	<b>Respiration Rate<sup>1</sup>(L/min)</b>	<b>Inhaled Volume<sup>2</sup> (L)</b>	<b>Lower Bound VID<sup>3</sup> (mg/kg)</b>	<b>Upper Bound VID (mg/kg)</b>
Mallard	1.58	1.21	291	$2.2 \times 10^{-2}$	$2.2 \times 10^1$
Gull	0.35	0.38	91.1	$3.1 \times 10^{-2}$	$3.1 \times 10^1$
Songbird	0.020	0.0419	10.1	$6.0 \times 10^{-2}$	$5.9 \times 10^1$
Large mammal	1.0	1.14	273	$3.3 \times 10^{-2}$	$3.2 \times 10^1$
Medium mammal	0.035	0.078	18.7	$6.4 \times 10^{-2}$	$6.3 \times 10^1$
Mouse	0.015	0.0395	9.48	$7.6 \times 10^{-2}$	$7.5 \times 10^1$

1)  $R_{\text{rate}} = 284(\text{BW})^{0.77} \times 3/1000$  (birds);  $R_{\text{rate}} = 379(\text{BW})^{0.80} \times 3/1000$  (mammals)

2)  $V_{\text{inh}} = R_{\text{rate}} \times \text{ED}$ ; ED = exposure duration of 240 m (4 h)

3)  $\text{VID} = C_{\text{air}} \times V_{\text{inh}}/\text{BW}$ ; lower bound  $C_{\text{air}} = 1.2 \times 10^{-4}$  mg/L; upper bound  $C_{\text{air}} = 1.18 \times 10^{-1}$  mg/L;

### 3.4 Terrestrial Plant Exposure Assessment

EECs for non-target plant species inhabiting dry and semi-aquatic areas were not estimated, as terrestrial plant toxicity data are not available. Although acrolein-treated water is routinely applied to agricultural fields to dissipate the compound, without appropriate toxicity data, it is not possible at this time to assess the potential risks associated this use.

### 3.5 Terrestrial Invertebrate Exposure Assessment

EECs for non-target terrestrial invertebrate species inhabiting dry and semi-aquatic areas were not estimated, as terrestrial invertebrate toxicity data are not available.

## 4. Effects Assessment

This assessment evaluates the potential for acrolein to directly or indirectly affect the Alameda whipsnake or modify its designated critical habitat. As previously discussed in Section 2.7, assessment endpoints for the effects determination for the whipsnake include direct toxic effects on the survival, reproduction, and growth, as well as indirect effects, such as reduction of the prey base or modification of its habitat. In addition, potential modification of critical habitat is assessed by evaluating effects to the PCEs, which are components of the critical habitat areas that provide essential life cycle needs of the whipsnake. Effects to terrestrial-phase amphibian effects and reptiles are based on avian toxicity data, given that birds are generally used as a surrogate for terrestrial-phase amphibians and reptiles.

As described in the Agency's Overview Document (U.S. EPA, 2004), the most sensitive endpoint for each taxon is used for risk estimation. For this assessment, evaluated taxa include birds (used as a surrogate for reptiles and amphibians in the terrestrial environment), mammals, terrestrial invertebrates, and terrestrial plants. Acute (short-term) and chronic (long-term) toxicity information is characterized based on registrant-submitted studies and a comprehensive review of the open literature on acrolein.

Toxicity endpoints are established based on data generated from guideline studies submitted by the registrant, and from open literature studies that meet the criteria for

inclusion into the ECOTOX database maintained by EPA/Office of Research and Development (ORD) (U.S. EPA, 2004). Open literature data presented in this assessment were obtained from ecological risk assessment written in support of the Reregistration eligibility decision (RED) as well as ECOTOX information obtained on April 15, 2011. In order to be included in the ECOTOX database, papers must meet the following minimum criteria:

- (1) the toxic effects are related to single chemical exposure;
- (2) the toxic effects are on an aquatic or terrestrial plant or animal species;
- (3) there is a biological effect on live, whole organisms;
- (4) a concurrent environmental chemical concentration/dose or application rate is reported; and
- (5) there is an explicit duration of exposure.

Data that pass the ECOTOX screen are evaluated along with the registrant-submitted data, and may be incorporated qualitatively or quantitatively into this endangered species assessment. In general, effects data in the open literature that are more conservative than the registrant-submitted data are considered. The degree to which open literature data are quantitatively or qualitatively characterized for the effects determination is dependent on whether the information is relevant to the assessment endpoints (*i.e.*, survival, reproduction, and growth) identified in Section 2.8. For example, endpoints such as behavior modifications are likely to be qualitatively evaluated, because quantitative relationships between modifications and reduction in species survival, reproduction, and/or growth are not available. Although the effects determination relies on endpoints that are relevant to the assessment endpoints of survival, growth, or reproduction, it is important to note that the full suite of sublethal endpoints potentially available in the effects literature (regardless of their significance to the assessment endpoints) are considered to define the action area for acrolein.

Citations of all open literature not considered as part of this assessment because they were either rejected by the ECOTOX screen or accepted by ECOTOX but not used (*e.g.*, the endpoint is less sensitive) are included in **Appendix E**. **Appendix E** also includes a rationale for rejection of those studies that did not pass the ECOTOX screen and those that were not evaluated as part of this endangered species risk assessment. Citations for the available, acceptable ECOTOX open literature data, including the full suite of lethal and sublethal endpoints, are also presented in **Appendix E**. **Appendix F** includes a summary of the human health effects data for acrolein.

In addition to registrant-submitted and open literature toxicity information, other sources of information, including use of the acute probit dose response relationship to establish the probability of an individual effect and reviews of the Ecological Incident Information System (EIIS), are conducted to further refine the characterization of potential ecological effects associated with exposure to acrolein. A summary of the available aquatic and terrestrial ecotoxicity information, use of the probit dose response relationship, and the incident information for acrolein are provided in Sections 4.1 through 4.4, respectively.

ECOTOX contained data for propanol, a degradate of acrolein, however, it was not considered reliable to evaluate its potential toxicity relative to the parent compound. Available toxicity information for other acrolein degradates indicated they were considerably less toxic than acrolein, with the exception of 3-hydroxypropanol, which equilibrates with acrolein in water. Exposure of 3-hydroxypropanol will be captured using monitoring data for acrolein, so toxicity data for this compound was not considered pertinent for this assessment.

#### 4.1 Toxicity of Acrolein to Terrestrial Organisms

**Table 4.1** summarizes the most sensitive terrestrial toxicity endpoints, based on an evaluation of both the submitted studies and the open literature. A brief summary of submitted and open literature data considered relevant to this ecological risk assessment is presented below.

<b>Table 4.1. Terrestrial Toxicity Profile for Acrolein</b>					
<b>Endpoint (1)</b>	<b>Acute/ Chronic</b>	<b>Species</b>	<b>Toxicity Value Used in Risk Assessment</b>	<b>Citation MRID# (Author &amp; Date)</b>	<b>Comment</b>
Birds (surrogate for terrestrial-phase amphibians and reptiles)	A	Mallard duck <i>Anas platyrhynchos</i>	LD <sub>50</sub> = 9.11 mg a.i./kg bw	00117668	Acceptable
	C		No data	N/A	N/A
Mammals	A	Laboratory rat <i>Rattus norvegicus</i>	LD <sub>50</sub> = Males: 10.3 Females: 11.8 mg/kg	41257001	Acceptable
	C	Laboratory rat <i>Rattus norvegicus</i>	NOAEL= 3 mg/kg/day LOAEL=6 mg/kg/day	41869101	Acceptable Decreased body weight
Terrestrial invertebrates	A	Honeybee <i>Apis mellifera</i>	No data	N/A	N/A
Terrestrial Plants	N/A	<u>Seedling Emergence</u> Monocots	No data	N/A	N/A
	N/A	<u>Seedling Emergence</u> Dicots	No data	N/A	N/A
	N/A	<u>Vegetative Vigor</u> Monocots	No data	N/A	N/A
	N/A	<u>Vegetative Vigor</u> Dicots	No data	N/A	N/A

N/A: not applicable

(1) Direct effects are assessed using toxicity data for birds; indirect effects are assessed using toxicity data for birds, mammals, and terrestrial invertebrates; habitat modification is assessed using toxicity data for mammals and terrestrial plants.

Acute toxicity to terrestrial animals is categorized using the classification system shown in **Table 4.2** (U.S. EPA, 2004). Toxicity categories for terrestrial plants have not been defined.

<b>Table 4.2. Categories of Acute Toxicity for Avian and Mammalian Studies</b>		
<b>Toxicity Category</b>	<b>Oral LD<sub>50</sub></b>	<b>Dietary LC<sub>50</sub></b>
Very highly toxic	< 10 mg/kg	< 50 ppm
Highly toxic	10 - 50 mg/kg	50 - 500 ppm
Moderately toxic	51 - 500 mg/kg	501 - 1000 ppm
Slightly toxic	501 - 2000 mg/kg	1001 - 5000 ppm
Practically non-toxic	> 2000 mg/kg	> 5000 ppm

#### **4.1.1 Toxicity to Birds, Reptiles, and Terrestrial-Phase Amphibians**

As specified in the Overview Document, the Agency uses birds as a surrogate for reptiles and terrestrial-phase amphibians when toxicity data for each specific taxon are not available (U.S. EPA, 2004). A summary of acute and chronic bird, reptile and terrestrial-phase amphibian data, including data published in the open literature, is provided below in Sections 4.1.1.1 through 4.1.1.4. Although not specifically evaluated in this assessment, terrestrial-phase amphibians could potentially serve as prey for the Alameda whipsnake. Amphibians attempting to breed in irrigation canals treated with acrolein would likely succumb to the chemical. The most sensitive endpoint for amphibians identified in the RED (USEPA 2007) is a 96-hr LC<sub>50</sub> of 7 µg/L (Holcombe *et al.*, 1987).

##### **4.1.1.1 Birds: Acute Exposure (Mortality) Studies**

Acrolein is very highly toxic (LD<sub>50</sub> <10 mg/kg) to birds on an acute oral exposure basis (**Table 4.1**). Male mallard ducks (*Anas platyrhynchos*) dosed with 92% acrolein resulted in an LD<sub>50</sub> of 9.1 mg a.i./kg-bw. 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 (MRID 00117668). The most sensitive endpoint used to assess the acute oral toxicity of acrolein is 9.1 mg a.i./kg-bw.

In order to evaluate exposure to drinking water, 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.*, mallard, gull, and songbird). Due to a lack of chronic toxicity data for birds, only acute, dose-based exposures to birds are considered. These adjustments are made according to the equation below (USEPA, 2006), where: AT = adjusted toxicity value; LD<sub>50</sub>; TW = body weight of tested animal (1580 g mallard duck); AW = body weight of assessed animals (1580 g for mallard, 350 g for gull, and 20 g for songbird); x = Mineau scaling factor (default value of 1.15 used). To assess acute risks to birds, the measured LD<sub>50</sub> for mallard is 9.11 mg/kg (MRID 00117668).

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

For mallards, gulls, and songbirds, the adjusted toxicity values are 9.11 mg/kg, 7.27 mg/kg, and 4.73 mg/kg, respectively.

In order to assess the risk to birds from inhalation, it is necessary to estimate the inhalation LD<sub>50</sub> 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<sub>50</sub> for a 350 g bird from the available avian oral LD<sub>50</sub> data, 2) estimate a factor (Q<sub>a</sub>/Q<sub>m</sub>) that accounts for differences in lung transfer efficiency for birds and mammals, 3) estimate the avian inhalation LD<sub>50</sub> for a representative bird using Q<sub>a</sub>/Q<sub>m</sub> using the avian oral LD<sub>50</sub> estimates and mammalian inhalation LD<sub>50</sub> and oral LD<sub>50</sub> data, and 4) estimate avian inhalation LD<sub>50</sub>s for other avian species of interest.

This overall calculation uses the assumption that the ratio of oral LD<sub>50</sub> to inhalation LD<sub>50</sub> 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 (USEPA, 1993), 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 300 to 700 g (Cornell University, 2011), making it a suitable 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<sub>50</sub>s for a ring-bill gull was estimated from the using the equation:

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

where LD<sub>50(oral, A)</sub> is the adjusted toxicity for the new species, LD<sub>50(oral, mallard)</sub> is the measured LD<sub>50</sub> for mallard ducks (9.1 mg/kg), BW<sub>A</sub> is the body weight of the new species (*e.g.*, ring-bill gull BW=0.35 kg), and BW<sub>mallard</sub> is the body weight for the mallard (1.58 kg). The resulting oral LD<sub>50</sub> for the ring-bill gull is 7.25 mg/kg.

The second step is to calculate a factor, Q<sub>a</sub>/Q<sub>m</sub>, which accounts for the differences in the rate that pesticides pass through lung tissue of avian species (Q<sub>a</sub>) compared to mammalian species (Q<sub>m</sub>). 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 is 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

$$SA = 60.6 \times BW^{0.883} \quad \text{and} \quad Th = 116.51 \times BW^{0.044}$$

For mammals the equations for lung surface area and thickness are

$$SA = 52.1 \times BW^{0.883} \quad \text{and} \quad Th = 237.66 \times BW^{0.090}$$

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<sub>a</sub>) and 9188/403 = 22.8 for a mammal (Q<sub>m</sub>) at the same weight. The ratio Q<sub>a</sub>/Q<sub>m</sub> is then 3.11 for 350 g species.

The third step is estimating the avian inhalation LD<sub>50</sub> from the oral LD<sub>50</sub> estimated in step 1. The formula for this is:

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

The oral LD<sub>50</sub> for the gull is divided by the ratio of the oral LD<sub>50</sub> to the inhalation LD<sub>50</sub> for the rat, which has been adjusted by multiplying by the ratio Q<sub>a</sub>/Q<sub>m</sub> which was estimated in step 2. As the rat acute oral LD<sub>50</sub> is 10.3 mg/kg and the rat inhalation LD<sub>50</sub> is 2.02 mg/kg, the resulting inhalation LD<sub>50</sub> for the gull is 7.25/(10.3\*3.11/2.02) = 0.45 mg/kg. This value is in **Table 4.3**.

The final step is to estimate inhalation LD<sub>50</sub>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<sub>50</sub>s for differences in body size, except in this case the reference species is the ring-billed gull rather than the mallard. A 20-g songbird was chosen as representative of small avian species which are more likely to be susceptible to toxic chemicals. 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 mallard was chosen for to represent large birds and it is also the source of the acute oral toxicity data for birds. The adjusted inhalation LD<sub>50</sub> for the mallard, ring-bill gull, and songbird are in **Table 4.3**.

<b>Table 4.3. LD<sub>50</sub> for representative birds estimated from the acute oral LD<sub>50</sub> for mallard duck and the adjusted rat inhalation LD<sub>50</sub>. Calculations are described in the text.</b>			
<b>Species</b>	<b>Body weight (g)</b>	<b>Oral LD<sub>50</sub> (mg/kg)</b>	<b>Inhalation LD<sub>50</sub> (mg/kg)</b>
mallard	1580	9.1	0.574 <sup>3</sup>
ring-bill gull	350	7.25 <sup>1</sup>	0.458 <sup>2</sup>
songbird	20	4.72 <sup>1</sup>	0.298 <sup>3</sup>

<sup>1</sup> oral LD<sub>50</sub>(oral, A) = LD<sub>50</sub>(oral, mallard)(BW<sub>A</sub>/BW<sub>mallard</sub>)<sup>(1.15-1)</sup>

<sup>2</sup> inhalation LD<sub>50</sub>(inh, gull) = LD<sub>50</sub>(or, gull) / (LD<sub>50</sub>(or, rat) \* Fre / LD<sub>50</sub>(inh, rat)), Fre calculation is in text)

<sup>3</sup> adjusted LD<sub>50</sub>(inh) for mallard and songbird: LD<sub>50</sub>(inh, A) = LD<sub>50</sub>(inh, gull)(BW<sub>A</sub>/BW<sub>gull</sub>)<sup>(1.15-1)</sup>

No data are available to evaluate the subacute dietary toxicity (LC<sub>50</sub>) of acrolein to birds either through registrant-submitted data or through a search of the open literature contained in ECOTOX.

#### 4.1.1.2 Birds: Chronic Exposure (Growth, Reproduction) Studies

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.

#### 4.1.2 Toxicity to Mammals

A summary of acute and chronic mammalian data, including data published in the open literature, is provided below in Sections 4.1.2.1 through 4.1.1.2

##### 4.1.2.1 Mammals: Acute Exposure (Mortality) Studies

Acrolein is highly toxic to mammals on an acute oral exposure basis. The acute oral LD<sub>50</sub> for male and female rats (*Rattus norvegicus*) is 10.3 and 11.8 mg/kg, respectively (**Table 4.1**). 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 via inhalation. The inhalation LC<sub>50</sub> for acrolein is 17 mg/m<sup>3</sup>/4 hours for rats. 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. The rate is multiplied by three to conservatively convert the resting respiration rate to the field active respiration rate. The same equation for respiration rate, as was used in Section 3.3, is used to estimate the acrolein inhalation exposure:

$$R_{\text{rate}} = 379(\text{BW})^{0.80} \times 3/1000$$

In this equation, BW is the body weight, which is 0.350 kg for the rat. The resulting respiration rate is 0.49 L/min. Since the toxicity test was conducted for 4 h (240 min), the volume of air inhaled during the test was 117.6 L. Multiplying this volume by the concentration of acrolein maintained during the test and dividing by the body weight gives the acrolein inhalation LD<sub>50</sub> of 5.71 mg/kg.

For drinking water, acute and chronic dose-based exposures to mammals are considered to assess indirect effects on prey. Available dose-based toxicity values are adjusted for the weights of the animal tested (*e.g.*, laboratory rat) and of the animal for which the risks are being assessed (*e.g.*, large mammal, medium-sized mammal, and mouse). These adjustments are made according to the following equation (USEPA, 2006), where: AT = adjusted toxicity value; LD<sub>50</sub> or NOAEL = endpoint reported by toxicity study; TW = body weight of tested animal (350 g rat); AW = body weight of assessed animal (1000 g for large mammal, 35 g for medium-sized mammal, and 15 g for a mouse). For mammals, the measured LD<sub>50</sub> for rats used to assess acute risks is 10.3 mg/kg (MRID

41257001); and the measured NOAEL for rats used to assess chronic risks is 3 mg/kg/day (MRID 41869101).

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

For large mammals, the acute and chronic adjusted toxicity values are 7.92 mg/kg and 2.31 mg/kg, respectively. For medium-sized mammals, the acute and chronic adjusted toxicity values are 18.3 mg/kg and 5.3 mg/kg, respectively. For mice, the acute and chronic adjusted toxicity values are 22.6 mg/kg and 6.6 mg/kg, respectively.

#### 4.1.2.2 Mammals: Chronic Exposure (Growth, Reproduction) Studies

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 a body weight decrease in the F<sub>1</sub> generation. The NOAEL for offspring toxicity is 3 mg/kg/day (**Table 4.1**).

#### 4.1.3 Toxicity to Terrestrial Invertebrates

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

#### 4.1.4 Toxicity to Terrestrial 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. As part of the ecological risk assessment written in support of the Reregistration Eligibility Decision on acrolein, EFED recommended both a Tier II vegetative vigor (OCSPP Guideline 850.4250<sup>11</sup>) and Tier II seedling emergence (OCSPP Guideline 850.4225<sup>12</sup>) studies. The studies were included in a generic data call-in on acrolein and in January 2011, EFED completed its review of registrant-submitted protocols entitled “*Acrolein: A Tier II Toxicity Test to Determine the Effects of the Test Substance on Vegetative Vigor of Ten Species of Plants*” and “*Acrolein: A Tier II Toxicity Test to Determine the Effects of the Test Substance on Seedling Emergence of Ten Species of Plants*.” The protocols propose to treat 10 agricultural crops consisting of

<sup>11</sup> USEPA 1996. Ecological Effects Test Guidelines OPPTS 850.4250 Vegetative Vigor, Tier II, EPA 712-C-96-364. [http://www.epa.gov/ocspp/pubs/frs/publications/OPPTS\\_Harmonized/850\\_Ecological\\_Effects\\_Test\\_Guidelines/Drafts/850-4250.pdf](http://www.epa.gov/ocspp/pubs/frs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-4250.pdf)

<sup>12</sup> USEPA 1996. Ecological Effects Test Guidelines OPPTS 850.4225 Seedling Emergence, Tier II. EPA 712-C-96-363. [http://www.epa.gov/ocspp/pubs/frs/publications/OPPTS\\_Harmonized/850\\_Ecological\\_Effects\\_Test\\_Guidelines/Drafts/850-4225.pdf](http://www.epa.gov/ocspp/pubs/frs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-4225.pdf)



four monocotyledenous (monocots) plants, *i.e.*, ryegrass (*Lolium perenne*), onion (*Allium cepa*), wheat (*Triticum aestivum*) and corn (*Zea mays*), and five dicotyledenous (dicots) plants, *i.e.*, soybean (*Glycine max*), bean (*Phaseolus vulgaris*), oilseed rape (*Brassica napus*), cabbage (*Brassica oleracea*), tomato (*Lycopersicon esculentum*) and lettuce (*Lactuca sativa*). Seeds and seedlings of similar size and condition will be exposed to a single application via a soil application in the seedling emergence study and via a foliar spray in the vegetative vigor study. At least five (5) concentrations of acrolein will be tested along with a negative control in each study. For the seedling emergence study, each treatment and control will consist of four (4) replicates with ten (10) seeds per replicate. For the vegetative vigor study, each treatment and control will consist of six (6) replicates with five (5) plants per replicate. According to the protocol, the actual test concentrations of acrolein used in each study will be amended on to their respective protocol.

The study will measure the effect rate for 25% and 50% of the plants tested, *i.e.*, the ER<sub>25</sub> and ER<sub>50</sub> values, respectively, and if possible the no-observed-effect rate (NOER) and the lowest-observed-effect rate (LOER). When possible, ER<sub>x</sub> estimates will be made for mean seedling emergence, mean shoot weight and height of seedlings at test termination, and seedling mortality when warranted. The studies will be conducted in a greenhouse with a photoperiod of at least 16 hours. The targeted spray volume in each study is equivalent to 200 L/ha (~21 gal/A) and was selected to simulate off-site drift from acute use conditions of the product. Plants will be observed weekly over the 21-day study period to record seedling emergence and growth of emerged seedlings in the seedling emergence study, and mortality and/or recovery in the vegetative vigor study. At the end of the in-life portion of the seedling emergence study, height measurements and the condition of the emerged seedlings will be recorded; emergence, survival, shoot height and dry weight of surviving plants will be determined. At the end of the in-life portion of the vegetative vigor study, surviving plants will be clipped at soil level and the above-ground portion(shoot) of the plants will be dried by replicate and weight; mean shoot dry weight will be calculated by dividing the total by the number of plants weighed. In both studies, a numerical rating will be assigned to evaluate changes in plant morphology including chlorosis, necrosis, general development and any other characteristic that may be deemed a response of the plant to the treatment.

At the time of this assessment, the Tier II terrestrial plant studies have yet to be submitted to EPA; however, discussion with John Porch (personal communication August 2, 2011: John Porch, Manager of Plant and Invertebrate Toxicology, Wildlife International, Ltd., Easton, Maryland) provided preliminary information on the outcome of those studies. Exposure concentrations used in the study ranged from 1.9 to 30 mg active ingredient/L and the material was applied at rates as high as 0.1 lb ai/A via overhead spray application. According to the project manager, the EC<sub>25</sub> values for both the seedling emergence and vegetative vigor studies exceeded the highest test concentration and application rate tested. However, since these are preliminary data and EPA has not had an opportunity to review these studies, it is not possible to use the data to characterize potential risks.

## **4.2 Use of Probit Slope Response Relationship to Provide Information on the Endangered Species Levels of Concern**

The Agency uses the probit dose response relationship as a tool for providing additional information on the potential for acute direct effects to individual listed species and aquatic animals that may indirectly affect the listed species of concern (U.S. EPA, 2004). As part of the risk characterization, an interpretation of acute RQs for listed species is discussed. This interpretation is presented in terms of the chance of an individual event (*i.e.*, mortality or immobilization) should exposure at the EEC actually occur for a species with sensitivity to acrolein on par with the acute toxicity endpoint selected for RQ calculation. To accomplish this interpretation, the Agency uses the slope of the dose response relationship available from the toxicity study used to establish the acute toxicity measures of effect for each taxonomic group that is relevant to this assessment. The individual effects probability associated with the acute RQ is based on the mean estimate of the slope and an assumption of a probit dose response relationship. In addition to a single effects probability estimate based on the mean, upper and lower estimates of the effects probability are also provided to account for variance in the slope, if available.

Individual effect probabilities are calculated based on an Excel spreadsheet tool IECV1.1 (Individual Effect Chance Model Version 1.1) developed by the U.S. EPA, OPP, Environmental Fate and Effects Division (June 22, 2004). The model allows for such calculations by entering the mean slope estimate (and the 95% confidence bounds of that estimate) as the slope parameter for the spreadsheet. In addition, the acute RQ is entered as the desired threshold.

## **4.3 Incident Database Review**

A review of the EHS database for ecological incidents involving acrolein was completed on August 16, 2011. The results of this review for terrestrial, plant, and aquatic incidents are discussed below. A complete list of the incidents involving acrolein including associated uncertainties is included as **Appendix G**. A total of 13 incidents have been reported to the Agency associated with the use of acrolein from 1971 to 2011. The majority (85%) has been associated with the deaths of fish and aquatic invertebrates; one incident was reported involving aquatic birds and one involved terrestrial plants. The largest loss (Incident #B0000-700-01) of aquatic animals, *i.e.*, 338,600 animals killed in 1977 in Josephine County, Oregon, resulted from an inadequate holding time. Although 13 incidents have been reported, this does not preclude the possibility that non-target mortality may be occurring but is unnoticed or not reported. It is also possible that the low number of reported incidents relative to some 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 currently no definitive terrestrial plant toxicity data with which to evaluate potential risk, there is an incident report of damage to an agricultural crop

(squash) from the application of acrolein-treated water (Incident # I000782-001). However, acrolein-treated water is routinely applied to agricultural fields in order to dissipate the compound and although there is a plant incident report, effects to terrestrial plants appear to be limited. It is possible that the waxy cuticle of terrestrial plants that protects them from desiccation may also serve to protect them from the toxic effects of acrolein. Terrestrial plant toxicity tests are not currently available to address uncertainties associated with terrestrial plant risks; the incident report suggests however, that terrestrial plants can nevertheless be affected by acrolein.

## **5. Risk Characterization**

Risk characterization is the integration of the exposure and effects characterizations. Risk characterization is used to determine the potential for direct and/or indirect effects to the Alameda whipsnake or for modification to their designated critical habitat from the use of acrolein in California. The risk characterization provides an estimation (Section 5.1) and a description (Section 5.2) of the likelihood of adverse effects; articulates risk assessment assumptions, limitations, and uncertainties; and synthesizes an overall conclusion regarding the likelihood of adverse effects to the whipsnake or its designated critical habitat (*i.e.*, “no effect,” “likely to adversely affect,” or “may affect, but not likely to adversely affect”).

### **5.1 Risk Estimation**

Risk is estimated by calculating the ratio of exposure to toxicity. This ratio is the risk quotient (RQ), which is then compared to pre-established acute and chronic levels of concern (LOCs) for each category evaluated (**Appendix A**). For acute exposures to terrestrial invertebrates, the LOC is 0.05. For acute exposures to the birds (and, thus, reptiles) and mammals, the LOC is 0.1. The LOC for chronic exposures to animals, as well as acute exposures to plants is 1.0.

Acute risks to terrestrial animals are estimated based on exposures resulting from applications of acrolein (**Tables 3.13 through 3.15**) and the appropriate toxicity endpoint from **Table 4.1**. Potential risks to non-target organisms from chronic exposure to acrolein are also evaluated based on exposures resulting from applications of acrolein (**Table 3.13**) and the appropriate toxicity endpoint from **Table 4.1**. It should be noted, though, that acrolein is applied to water at concentrations which are expected to result in a complete loss of organisms; therefore, there is a low likelihood that any biological receptors would remain in the treatment area. Additionally, untreated water would soon displace the acrolein-treated water as most irrigation canals would have sufficient flow to move the compound through the desired treatment area. Acrolein-treated water is then applied to agricultural fields to dissipate the compound. So while acrolein can be applied up to eight times per year, the application of treated water to agricultural fields is expected to effectively dissipate the compound and the likelihood of chronic exposure in treated fields is expected to be low.

Exposures were not derived for terrestrial plants or terrestrial invertebrates, as discussed in Section 3.3, as toxicity data for terrestrial plants and terrestrial invertebrates were not available.

## 5.1.1 Exposures in the Terrestrial Habitat

### 5.1.1.1 Birds (surrogate for Reptiles and Terrestrial-phase amphibians)

As previously discussed in Section 3.3, potential direct effects to terrestrial species are based on irrigation of acrolein-treated water to food items on fields. Potential risks to birds (and, thus, reptiles and terrestrial-phase amphibians) are derived using T-REX, acute toxicity data for the most sensitive bird species for which data are available, and a variety of body-size and dietary categories.

Potential direct acute effects to the Alameda whipsnake are derived by considering dose-based EECs modeled in T-REX for a large (1000 g), a medium-sized (100 g), and a small bird (20 g) (**Table 3.13**) and acute oral toxicity endpoints for avian species. Since no subacute dietary toxicity data are available for birds, dietary-based RQ cannot be calculated. Direct acute effects from the consumption of treated irrigation water as drinking water and inhalation exposure were also assessed.

As there are no avian chronic toxicity data available for acrolein, potential direct chronic effects of acrolein to the Alameda whipsnake could not be derived.

<b>Table 5.1. Acute RQs for Acrolein and Birds Via Dietary Exposure<sup>1</sup></b>		
<b>Dietary Category</b>	<b>Body Size</b>	<b>Acute Dose-based RQ<sup>2</sup></b>
<b>Short Grass</b>	<b>20 g</b>	<b>31</b>
	<b>100 g</b>	<b>14</b>
	<b>1000 g</b>	<b>4.4</b>
<b>Tall Grass</b>	<b>20 g</b>	<b>14</b>
	<b>100 g</b>	<b>6.3</b>
	<b>1000 g</b>	<b>2.0</b>
<b>Broadleaf Plants/Small Insects</b>	<b>20 g</b>	<b>17</b>
	<b>100 g</b>	<b>7.8</b>
	<b>1000 g</b>	<b>2.5</b>
<b>Fruits/Pods/Seeds/Large Insects</b>	<b>20 g</b>	<b>1.9</b>
	<b>100 g</b>	<b>0.86</b>
	<b>1000 g</b>	<b>0.27</b>
1. Application rate = 0.534 lbs ai/A, 8 apps, RTI = 14 days. LD50 = 9.11 mg/kg-bw (mallard)		
2. LOC exceedances (RQ $\geq$ 0.1) are bolded.		

Acute dose-based RQ values for birds consuming acrolein-contaminated diet through irrigation water exceed the acute risk to listed species LOC by factors ranging from 3 – 310x. Based on these RQ values, acrolein does have the potential to directly affect the Alameda whipsnake. Additionally, since the acute RQs are exceeded, there is a potential for indirect effects to the Alameda whipsnake based on effects on its prey (birds, reptiles and/or terrestrial-phase amphibians).

Direct effects on the Alameda whipsnake were evaluated in the same manner as above for birds except T-HERPS was used instead of T-REX. The model T-HERPS is a modified form of T-REX, which is designed to be more reflective of the food requirements of reptiles and amphibians (including consumption of small herbivorous and insectivorous mammals and small amphibians) and allow for an estimation of food intake for poikilotherms using the same basic procedure as T-REX. This involves adjusting daily food intake with an allometric model that accounts for the lower food intake of poikilothermic reptiles and amphibians. The net effect of this approach is a reduction in pesticide exposure due to reduced food consumption.

Potential direct acute effects to the Alameda whipsnake are derived by considering dose-based EECs modeled in T-HERPS for a medium sized snake (34 g) consuming small invertebrates (**Table 5.2**) and acute oral toxicity endpoints for avian species. Acute dose-based RQ values for 34-g whipsnakes exceed the acute risk to listed species LOC by a factor of 32x. Based on these RQ values, acrolein does have the potential to directly affect the Alameda whipsnake.

<b>Table 5.2. Acute RQ for Acrolein and Herpetofaunal Via Dietary Exposure<sup>1</sup></b>						
Use(s)	App. Rate (lbs a.i./A), # Apps., Interval (days)			Whipsnake (consuming herbivorous mammals)		
				Dose-Based <sup>2</sup> (mg/kg-bw)		
				2.5 g	100 g	1000 g
Irrigation water	0.534	8	14	NA	<b>3.2</b>	<b>0.32</b>

1. LD<sub>50</sub> = 9.11 mg/kg-bw (mallard)

2. LOC exceedances (RQ ≥ 0.1) are bolded

Potential direct acute effects to the Alameda whipsnake due to ingestion of drinking water were derived by evaluating drinking water exposure to large, medium, and small birds. **Table 5.3** lists acute RQ values for birds via exposure through drinking water. The drinking water LC<sub>50</sub>s for acrolein are 9.11 mg/kg, 7.27 mg/kg, and 4.73 mg/kg for the mallard, gull, and songbird, respectively. 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 medium-sized and small birds based on exposure to acrolein in the drinking water. The risk quotients for acute mortality based on drinking water exceed the acute risk LOC by a factor of 1.7-6.8X.

<b>Table 5.3. Acute RQs for Acrolein and Birds Via Drinking Water Exposure<sup>1,2</sup></b>		
Species	Body Size	Acute Dose-based RQ <sup>3</sup>
Mallard	1580 g	0.08
Gull	350 g	<b>0.17</b>
Songbird	20 g	<b>0.68</b>
1. Drinking water exposure estimates 0.75 mg/kg-d, 1.2 mg/kg-d, and 3.2 mg/kg-d for mallards, gulls, and songbirds, respectively. 2. LC <sub>50</sub> s are 9.11 mg/kg, 7.27 mg/kg, and 4.73 mg/kg for the mallard, gull, and songbird, respectively. 3. LOC exceedances (RQ ≥ 0.1) are bolded.		

Potential direct acute effects to the Alameda whipsnake due to inhalation of acrolein volatilizing from treated waters were derived by evaluating drinking water exposure to large, medium, and small birds. **Table 5.4** lists acute RQ values for birds via exposure through inhalation. The inhalation LC<sub>50</sub>s for acrolein are 0.574 mg/kg, 0.458 mg/kg, and 0.298 mg/kg for the mallard, gull, and songbird, respectively. A field study measured air concentrations during an actual treatment, but the treatment rate was 73% lower than the maximum label rate of 15 mg/L. As such, these measured concentrations are assumed to represent a lower bound on the exposure used to estimate risk, whereas the equilibrium-based EECs, based on the maximum label rate of 15 mg/L, are assumed to represent an upper-bound estimate. 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 birds 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 a factor of 380-2000X. 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, the rate of mixing in the atmosphere, and the treatment concentration (4 mg/L) in the field study, it is expected that concentrations in air would be closer to this value than the equilibrium-estimated value in the great majority of cases.

<b>Table 5.4. Acute Inhalation RQs for Acrolein and Birds</b>			
<b>Species</b>	<b>Body Size</b>	<b>Acute Dose-based RQ, Measured VID<sup>1,3,4</sup></b>	<b>Acute Dose-based RQ, Modeled (Upper Bound) VID<sup>2,3,4</sup></b>
<b>Mallard</b>	<b>1580 g</b>	0.04	<b>38</b>
<b>Gull</b>	<b>350 g</b>	0.07	<b>68</b>
<b>Songbird</b>	<b>20 g</b>	<b>0.20</b>	<b>198</b>

1. Lower bound inhalation exposure estimates are  $2.2 \times 10^{-2}$ ,  $3.1 \times 10^{-2}$ , and  $6.0 \times 10^{-2}$  mg/kg for the mallard, gull and songbird, respectively.
2. Upper bound inhalation exposure estimates are  $2.2 \times 10^1$ ,  $3.1 \times 10^1$ , and  $5.9 \times 10^1$  mg/kg for the mallard, gull and songbird, respectively.
3. LC<sub>50</sub>s for acrolein are 0.574 mg/kg, 0.458 mg/kg, and 0.298 mg/kg for the mallard, gull, and songbird, respectively
4. LOC exceedances (RQ  $\geq$  0.1) are bolded.

It should be noted that if the maximum concentration derived from existing monitoring data (54 mg/L) were used in lieu of the maximum labeled treatment rate (15 mg/L), drinking water and irrigation water RQs would still be exceeded.

### 5.1.1.2 Mammals

Potential indirect acute and chronic effects to the Alameda whipsnake are evaluated by modeling potential risks to mammals, which are considered prey for the whipsnake. RQs are derived using T-REX, acute and chronic rat toxicity data, and a variety of body-size and dietary categories.

<b>Table 5.5. Acute and Chronic RQs for Acrolein and Mammals Via Dietary Exposure</b>				
<b>Dietary Category</b>	<b>Body Size</b>	<b>Acute Dose-based RQ<sup>2</sup></b>	<b>Chronic Dose-based RQ<sup>3</sup></b>	<b>Chronic Dietary-based RQ<sup>3</sup></b>
<b>Short Grass</b>	<b>15 g</b>	<b>5.4</b>	<b>19</b>	<b>2.1</b>
	<b>35 g</b>	<b>4.6</b>	<b>16</b>	
	<b>1000 g</b>	<b>2.5</b>	<b>8.5</b>	
<b>Tall Grass</b>	<b>15 g</b>	<b>2.5</b>	<b>8.5</b>	0.98
	<b>35 g</b>	<b>2.1</b>	<b>7.3</b>	
	<b>1000 g</b>	<b>1.1</b>	<b>3.9</b>	
<b>Broadleaf Plants/Small Insects</b>	<b>15 g</b>	<b>3.0</b>	<b>10</b>	<b>1.2</b>
	<b>35 g</b>	<b>2.6</b>	<b>8.9</b>	
	<b>1000 g</b>	<b>1.4</b>	<b>4.8</b>	
<b>Fruits/Pods/Seeds/Large Insects</b>	<b>15 g</b>	<b>0.34</b>	<b>1.2</b>	0.13
	<b>35 g</b>	<b>0.29</b>	0.99	
	<b>1000 g</b>	<b>0.15</b>	0.53	
<b>Drinking water</b>	<b>15 g</b>	<b>0.10</b>	NA	NA
	<b>35 g</b>	<b>0.11</b>		
	<b>1000 g</b>	<b>0.19</b>		

1. LC<sub>50</sub> is 10.3 mg/kg-day. LOC exceedances (RQ ≥ 0.1) are bolded.

2. LC<sub>50</sub>s are 7.92 mg/kg-day, 18.3 mg/kg-day, and 22.6 mg/kg-day for the large, medium-sized, and small mammals, respectively. LOC exceedances (RQ ≥ 0.1) are bolded.

3. NOAEL is 3 mg/kg-day. LOC exceedances (RQ ≥ 1.0) are bolded.

Based on the maximum estimated application rate of 0.534 lbs ai/A and T-REX-generated exposure values, acute and chronic dose-based RQ values are exceeded for all sized mammals in each of the forage categories evaluated except for medium and large mammals consuming fruits, pods, seeds, and large insects. Additionally, for mammals feeding on short grasses and broadleaf plants/small insects, dietary-based RQ values exceed the chronic risk LOC. Based on the maximum treatment rate for acrolein (15 mg/L), the dose-based acute RQs exceed the acute risk LOC for large mammals, medium-sized mammals, and mice consuming acrolein-treated drinking water. Chronic risks to drinking water were not evaluated as the treated irrigation water is only expected to be present for a short period of time. Based on the upper-bound inhalation doses (Table 5.6), the dose-based acute RQ values exceed the acute risk LOC (0.1) for large mammals, medium-sized mammals, and mice inhaling acrolein volatilizing from water bodies. The lower-bound inhalation dose-based RQs are below the LOC. Based on these results for acrolein, there is a potential for indirect effects to the Alameda whipsnake since it relies on mammals during at least some portion of its life-cycle. It should be noted that if the maximum concentration derived from existing monitoring data (54 mg/L) were used in lieu of the maximum labeled treatment rate (15 mg/L), drinking water and irrigation water RQs would still be exceeded.

<b>Table 5.6. Acute Inhalation RQs for Acrolein and Mammals</b>			
<b>Species</b>	<b>Body Size</b>	<b>Acute Dose-based RQ, Measured VID<sup>1,3,4</sup></b>	<b>Acute Dose-based RQ, Modeled (Upper Bound) VID<sup>2,3,4</sup></b>
<b>Large</b>	<b>1000 g</b>	0.01	<b>5.6</b>
<b>Medium</b>	<b>35 g</b>	0.01	<b>8.9</b>
<b>Mice</b>	<b>15 g</b>	0.01	<b>13</b>

1. Lower bound inhalation exposure estimates are  $3.3 \times 10^{-2}$ ,  $5.2 \times 10^{-2}$ , and  $7.6 \times 10^{-2}$  mg/kg for the large mammal, medium-sized mammal, and mouse, respectively.

2. Upper bound inhalation exposure estimates are  $3.2 \times 10^1$ ,  $5.1 \times 10^1$ , and  $7.5 \times 10^1$  mg/kg for the large mammal, medium-sized mammal, and mouse, respectively.

3. LC<sub>50</sub>s for acrolein is 5.71 mg/kg (rat)

4. LOC exceedances (RQ  $\geq 0.1$ ) are bolded.

### 5.1.1.3 Terrestrial Invertebrates

In order to assess the risks of acrolein to terrestrial invertebrates, the honey bee or other terrestrial invertebrate, depending on which is more sensitive, is used as a surrogate for terrestrial invertebrates. However, no toxicity data are available for acrolein on terrestrial invertebrates; therefore, risk to terrestrial invertebrates cannot be quantified and risk is presumed.

### 5.1.1.4 Terrestrial Plants

No toxicity data are available for acrolein on terrestrial plants; therefore, risk to terrestrial invertebrates cannot be quantified and risk is presumed.

## 5.1.2 Primary Constituent Elements of Designated Critical Habitat

For acrolein use, the assessment endpoints for designated critical habitat PCEs involve the same endpoints as those being assessed relative to the potential for direct and indirect effects to the whipsnake. Therefore, the effects determinations for direct and indirect effects are used as the basis of the effects determination for potential modification to designated critical habitat.

## 5.2 Risk Description

The risk description synthesizes overall conclusions regarding the likelihood of adverse impacts leading to an effects determination (*i.e.*, “no effect,” “may affect, but not likely to adversely affect,” or “likely to adversely affect”) for the whipsnake and the potential for modification of its designated critical habitat.

If the RQs presented in the Risk Estimation (Section 5.1) show no direct or indirect effects for the whipsnake, and no modification to PCEs of the designated critical habitat, a “no effect” determination is made, based on acrolein’s use within the action area. However, if LOCs for direct or indirect effect are exceeded or effects may modify the PCEs of the critical habitat, the Agency concludes a preliminary “may affect”



determination for the FIFRA regulatory action regarding acrolein. For birds and reptiles, RQ values exceed acute risk LOCs; for mammals, both acute and chronic risk LOCs are exceeded. Since no data are available evaluating the chronic effects of acrolein on birds or for evaluating effects of the chemical on terrestrial invertebrates and plants, risk is presumed. As such, the use of acrolein in irrigation canals and the subsequent application of treated canal water may affect the Alameda whipsnake both directly and indirectly (effects on prey) and may affect critical habitat because of potential effects on terrestrial plants and forage base. A summary of the risk estimation results are provided in **Table 5.7** for direct and indirect effects to the whipsnake and in **Table 5.8** for the PCEs of its designated critical habitat.

Although not specifically evaluated in this assessment, terrestrial-phase amphibians could potentially serve as prey for the Alameda whipsnake. Amphibians attempting to breed in irrigation canals treated with acrolein would likely succumb to the chemical. The most sensitive endpoint for amphibians identified in the RED (USEPA 2007) is a 96-hr LC<sub>50</sub> of 7 µg/L (Holcombe *et al.*, 1987). At treatment rates up to 15,000 µg/L, the acute RQ is 2,143 and exceeds the acute risk to non-listed species LOC by a factor of 4,286X. Therefore, to the extent that amphibians rely on treated canals/reservoirs to breed, they would likely be adversely affected by acrolein.

<b>Table 5.7. Risk Estimation Summary for Acrolein - Direct and Indirect Effects</b>			
<b>Taxa</b>	<b>Preliminary Effects Determination</b>	<b>Description of Results of Risk Estimation</b>	<b>Assessed Species Potentially Affected</b>
Birds, Reptiles, and terrestrial-phase amphibians	Direct: May affect	Risk of acute effects to birds and reptiles; risk of chronic effects presumed due to the lack of toxicity data.	Alameda whipsnake.
	Indirect: May affect	Risk of secondary poisoning from snakes feeding on nesting birds, reptiles, and small insects.	Alameda whipsnake.
Mammals	Indirect: May affect	Risk of secondary poisoning from snakes feeding on small mammals.	Alameda whipsnake.
Terrestrial Invertebrates	Indirect: May affect	Risk effects presumed due to the lack of toxicity data	Alameda whipsnake.
Terrestrial Plants - Monocots	Indirect: May affect	Risk effects presumed due to the lack of toxicity data	Alameda whipsnake.
Terrestrial Plants - Dicots	Indirect: May affect	Risk effects presumed due to the lack of toxicity data	Alameda whipsnake.

<b>Table 5.8. Risk Estimation Summary for Acrolein – Effects to Designated Critical Habitat (PCEs)</b>			
<b>Taxa</b>	<b>Habitat Modification? (Y/N)</b>	<b>Description of Results of Risk Estimation</b>	<b>Assessed Species Potentially Affected</b>
<b>PCE1:</b> Scrub/shrub communities with a mosaic of open and closed canopy			
Effects on PCE1 through direct effects on terrestrial plants ( <i>e.g.</i> , habitat modification and primary productivity)	Y	Risk effects presumed due to the lack of toxicity data	Alameda whipsnake.
<b>PCE2:</b> Woodland or annual grassland plant communities contiguous to lands containing PCE 1			
Effects on PCE2 through direct effects on terrestrial plants ( <i>e.g.</i> , habitat modification and primary productivity)	Y	Risk effects presumed due to the lack of toxicity data	Alameda whipsnake.
<b>PCE3:</b> Lands containing rock outcrops, talus, and small mammal burrows within or adjacent to PCE 1 and or PCE 2			
Effects on PCE3 through direct effects on terrestrial plants( <i>e.g.</i> , habitat modification and primary productivity)	Y	Risk effects presumed due to the lack of toxicity data	Alameda whipsnake.

Following a “may affect” determination, additional information is considered to refine the potential for exposure at the predicted levels based on the life history characteristics (*i.e.*, habitat range, feeding preferences, *etc.*) of the whipsnake. Based on the best available information, the Agency uses the refined evaluation to distinguish those actions that “may affect, but are not likely to adversely affect” from those actions that are “likely to adversely affect” the whipsnake and its designated critical habitat.

The criteria used to make determinations that the effects of an action are “not likely to adversely affect” the whipsnake or modify its designated critical habitat include the following:

- **Significance of Effect:** Insignificant effects are those that cannot be meaningfully measured, detected, or evaluated in the context of a level of effect where “take” occurs for even a single individual. “Take” in this context means to harass or harm, defined as the following:
  - Harm includes significant habitat modification or degradation that results in death or injury to the whipsnake by significantly impairing behavioral patterns such as breeding, feeding, or sheltering.
  - Harass is defined as actions that create the likelihood of injury to the whipsnake to such an extent as to significantly disrupt normal behavior patterns which include, but are not limited to, breeding, feeding, or sheltering.
- **Likelihood of the Effect Occurring:** Discountable effects are those that are extremely unlikely to occur.

- Adverse Nature of Effect: Effects that are wholly beneficial without any adverse effects are not considered adverse.

A description of the risk and effects determination for each of the established assessment endpoints for the whipsnake and its designated critical habitat is provided in **Section 5.2.1**. The section will start with a discussion of the potential for direct effects, followed by a discussion of the potential for indirect effects. The section will end with a discussion on the potential for modification to the critical habitat from the use of acrolein.

### **5.2.1 Alameda Whipsnake**

#### **5.2.1.1 Direct Effects**

The results of this risk assessment indicate that the use of acrolein-treated water to irrigate agricultural fields poses a risk of acute toxicity to the Alameda whipsnake from direct exposure via diet, ingestion of drinking water, and inhalation. It should be noted that if maximum concentration derived from existing monitoring data (54 mg/L) were used in lieu of the maximum labeled treatment rate (15 mg/L), the risk conclusions would have been the same. Concentrations in the irrigation water would need to be below 30 µg/L before risks would be mitigated from dietary items contaminated with irrigation water. Since no chronic toxicity data are available for birds, which serve as a surrogate for reptiles, the potential for direct chronic risks to the whipsnake are presumed. Additionally, although acrolein dissipates rapidly, acrolein can be applied 8 times annually with a retreatment interval of 14 days, resulting in the potential for chronic exposure from repeated applications.

#### **5.2.1.2 Indirect Effects**

##### ***Potential Loss of Prey***

Acute dose-based RQ values exceed both listed and non-listed LOCs for small birds which serve as surrogates for reptiles and amphibians in the terrestrial environment, and chronic risk to birds, reptiles, and amphibians is presumed due to the lack of toxicity data for these taxa. Additionally, both acute and chronic risk LOCs are exceeded for small-sized mammals which serve as food for the Alameda whipsnake. Since there are no data to evaluate the toxicity of acrolein to terrestrial invertebrates which serve as food for whipsnakes, risk to this taxa is presumed. Given both the estimated and presumed risk to small birds, mammals and insects that serve as food for Alameda whipsnakes, the use of acrolein-treated water to irrigate irrigation fields is considered likely to result in the potential loss of prey. It should be noted that if maximum concentration derived from existing monitoring data (54 mg/L) were used in lieu of the maximum labeled treatment rate (15 mg/L), the risk conclusions would have been the same.

### ***Potential Modification of Habitat***

Acrolein is an herbicide intended to control aquatic plants in irrigation canals and reservoirs. While there are data demonstrating that acrolein affects both aquatic nonvascular (5-day EC<sub>50</sub> for *Skeletonema costatum* = 28 µg a.i./L) and vascular plants (14-day EC<sub>50</sub> for *Lemna gibba* = 72 µg a.i./L), there are no data available for the effects of acrolein on terrestrial plants. Although there is a terrestrial plant incident reported in the Ecological Incident Information System where the registered use of acrolein was associated with damage to 210 acres of squash plants (Incident Number: I000782-001), acrolein is regularly applied to agricultural fields as a means of dissipating the compound. It is also possible though that the waxy cuticle of terrestrial plants that protects them from desiccation may also limit the extent to which the reactive acrolein adversely affects plants. Given the compound's wide use on agricultural fields and the fact that only a single plant incident has been reported in the EIIIS database, the likelihood of adverse effects on terrestrial plants appears to be low. This is further collaborated by the preliminary results from the Tier II terrestrial plant studies which show that exposure to acrolein at concentrations as high as 30 mg a.i./L resulted in EC<sub>25</sub> values that exceed application rates equivalent to 0.1 lbs a.i./A. Since these data have not been substantiated and since the absence of incident reports cannot be construed as the absence of incidents, potential risks to terrestrial plants cannot be dismissed at this time. EFED recommends that the Service consider the results of the terrestrial plant toxicity studies in their biological opinion as those studies will likely have been summarized by that time. These data suggest that acrolein use as prescribed by the label, will not affect terrestrial plants.

Terrestrial plants serve several important habitat-related functions for the whipsnake. In addition to providing habitat and cover for invertebrate and vertebrate prey items of the whipsnake, terrestrial vegetation also provides shelter and cover from predators while foraging. Upland vegetation including grassland and woodlands provides cover during dispersal. Riparian vegetation helps to maintain the integrity of aquatic systems by providing bank and thermal stability, serving as a buffer to filter out sediment, nutrients, and contaminants before they reach the watershed, and serving as an energy source.

#### **5.2.1.3 Modification of Designated Critical Habitat**

As described previously, the assessment endpoints for the designated critical habitat prey base and PCEs involve the same endpoints as those being assessed relative to direct and indirect effects to the whipsnake from the evaluated uses of acrolein. As described in Table 2.5, the designated PCEs for the Alameda whipsnake are as follows:

*PCE1: Scrub/shrub communities with a mosaic of open and closed canopy*

*PCE2: Woodland or annual grassland plant communities contiguous to lands containing PCE 1*

*PCE3: Lands containing rock outcrops, talus, and small mammal burrows within or adjacent to PCE 1 and or PCE 2*

It should be noted that these PCEs are in addition to more general requirements for habitat areas that provide essential life cycle needs of the whipsnake such as space for individual and population growth and for normal behavior; food, water, air, light, minerals, or other nutritional or physiological requirements; cover or shelter; sites for breeding, reproduction, rearing (or development) of offspring; and habitats that are protected from disturbance or are representative of the historic geographical and ecological distributions of the whipsnake.

Assessment endpoints used to evaluate potential risk to the prey base associated with designated critical habitat include direct effects upon small mammals and birds (*i.e.*, terrestrial-phase amphibians). In the absence of phytotoxicity data for acrolein, risk to terrestrial plants is presumed. RQ values (based on acrolein toxicity data) for the other taxonomic groups exceed the Agency's LOCs.

Assessment endpoints used to evaluate risk to designated critical habitat PCEs for the whipsnake include direct effects on terrestrial plants (PCE1, PCE2, PCE3) and small mammals (PCE2, PCE3). Risk to plants is presumed, in the absence of acrolein toxicity data suitable for risk estimation. RQ values for small mammals exceed the LOC for uses of acrolein.

Based on the weight-of-evidence, an overall "habitat modification" determination is made for potential effects of acrolein to the whipsnake prey base and the specified, biologically mediated PCEs of designated critical habitat.

### **5.2.2 Spatial Extent of Potential Effects**

An LAA effects determination applies to those areas where it is expected that the pesticide's use will directly or indirectly affect the Alameda whipsnake or its designated critical habitat. To determine this area, the footprint of acrolein's use pattern is identified, using land cover data that correspond to acrolein's use pattern. For normal applications of pesticides, the spatial extent of the effects determination also includes areas beyond the initial area of concern that may be impacted by runoff and/or spray drift. In the case of acrolein, which is applied directly to water bodies, the only potential for runoff or spray drift occurs when the treated water is used for irrigation purposes. Irrigation of fields is normally done using techniques with very coarse droplets and at relatively low release heights (*e.g.*, irrigation sprayers, flood furrow, drip, subterranean, and by sprayers above and below the canopy). As such, the amount of spray drift from such applications is expected to be minimal and not impact the spatial extent beyond the initial area of concern. Concentrations resulting from runoff will be less than the amount applied to the waterbody, so expansion of the area of concern due to runoff is also considered negligible. The identified direct and indirect effects and modification to critical habitat are anticipated to occur only for those currently occupied core habitat areas, California Natural Diversity Database (CNDDDB) occurrence sections, and designated critical habitat for the Alameda whipsnake that overlap with the initial area of concern. It is assumed that non-flowing water bodies (or potential habitat) are included within this area.

### **5.2.3 Overlap between Alameda Whipsnake Habitat and Spatial Extent of Potential Effects**

An LAA effects determination is made to those areas where it is expected that the pesticide's use will directly or indirectly affect the Alameda whipsnake or its designated critical habitat, and the area overlaps with the core areas, critical habitat and available occurrence data for whipsnakes and critical habitat for the whipsnakes.

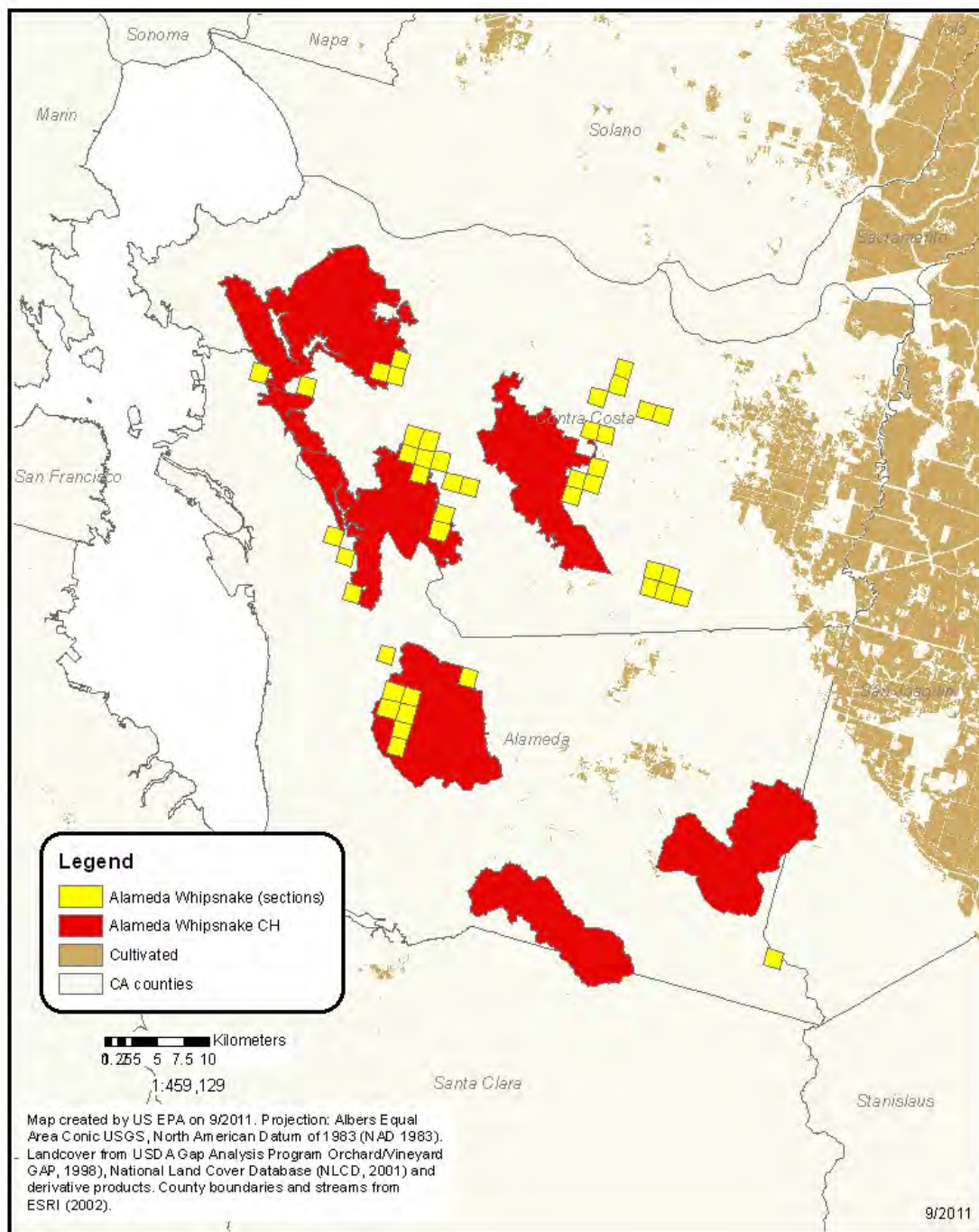
For acrolein, irrigation ditches are used in Alameda, Contra Costa, San Joaquin, and Santa Clara Counties to irrigate crops. CA PUR data (**Table 2.3**) indicate significant use of acrolein in the Contra Costa and San Joaquin Counties. An analysis was conducted comparing the land classified as agriculture (*i.e.*, cultivated crops) and pastureland/hay in the 2006 National Land Cover Data to the spatial habitat of the Alameda whipsnake (**Figure 5.1**). The bulk of the agriculture in these counties where acrolein might be used in irrigation ditches appears to occur 6 or more miles to the east of the whipsnake habitat. While agriculture does appear to be within 6 miles of whipsnake critical habitat in Alameda County, California's Department of Pesticide Regulation Pesticide Use Reporting (CDPR PUR) data has indicated that acrolein has not been used in Alameda County since 1996. Additionally, the chamise chaparral habitat of the Hayward Foothills located within this area, which constitutes the primary habitat of the whipsnake, is not conducive to the use of irrigation canals and/or agriculture. While data on specific locales for applications to irrigation ditches and the agricultural areas which use the water for irrigation are not of sufficient resolution to permit the dismissal of the impact to the whipsnake habitat, this qualitative assessment of the agricultural areas and their vicinity to the whipsnake habitat indicates that effects would not likely extend spatially into the critical habitat of the Alameda whipsnake.

## **6. Uncertainties**

### **6.1 Exposure Assessment Uncertainties**

#### **6.1.1 Maximum Use Scenario**

The screening-level risk assessment focuses on characterizing potential ecological risks resulting from a maximum use scenario, which is determined from labeled statements of maximum treatment rate. The frequency at which the concentrations in the water reach the maximum use scenario (15 mg/L) may be dependent on plant density, timing of applications, cultural practices, and market forces. This maximum use scenario also does not account for potential routes of dissipation, such that the concentration could over estimate exposure doses. However, given the maximum values recorded in monitoring studies (54 mg/L), it is unlikely that the use of this value will be overly conservative.



**Figure 5. 1. Alameda Whipsnake Habitat versus Land Used for Agriculture**

### 6.1.2 Usage Uncertainties

County-level usage data were obtained from California's Department of Pesticide Regulation Pesticide Use Reporting (CDPR PUR) database. Six years of data (1999 – 2006) were included in this analysis because statistical methodology for identifying outliers, in terms of area treated and pounds applied, was provided by CDPR for these years only. No methodology for removing outliers was provided by CDPR for 2001 and

earlier pesticide data; therefore, this information was not included in the analysis because it may misrepresent actual usage patterns. CDPR PUR documentation indicates that errors in the data may include the following: a misplaced decimal; incorrect measures, area treated, or units; and reports of diluted pesticide concentrations. In addition, it is possible that the data may contain reports for pesticide uses that have been cancelled. As with all pesticide usage data, there may be instances of misuse and misreporting. The Agency made use of the most current, verifiable information; in cases where there were discrepancies, the most conservative information was used.

### **6.1.3 Terrestrial Exposure Modeling of Acrolein**

The Agency relies on the work of Fletcher *et.al.* (1994) for setting the assumed pesticide residues in wildlife dietary items. These residue assumptions are believed to reflect a realistic upper-bound residue estimate, although the degree to which this assumption reflects a specific percentile estimate is difficult to quantify. It is important to note that the field measurement efforts used to develop the Fletcher estimates of exposure involve highly varied sampling techniques. It is entirely possible that much of these data reflect residues averaged over entire above ground plants in the case of grass and forage sampling.

It was assumed that ingestion of food items in the field occurs at rates commensurate with those in the laboratory. Although the screening assessment process adjusts dry-weight estimates of food intake to reflect the increased mass in fresh-weight wildlife food intake estimates, it does not allow for gross energy differences. Direct comparison of a laboratory dietary concentration-based effects threshold to a fresh-weight pesticide residue estimate would result in an underestimation of field exposure by food consumption by a factor of 1.25 – 2.5 for most food items.

Differences in assimilative efficiency between laboratory and wild diets suggest that current screening assessment methods do not account for a potentially important aspect of food requirements. Depending upon species and dietary matrix, bird assimilation of wild diet energy ranges from 23 – 80%, and mammal's assimilation ranges from 41 – 85% (U.S. Environmental Protection Agency, 1993). If it is assumed that laboratory chow is formulated to maximize assimilative efficiency (*e.g.*, a value of 85%), a potential for underestimation of exposure may exist by assuming that consumption of food in the wild is comparable with consumption during laboratory testing. In the screening process, exposure may be underestimated because metabolic rates are not related to food consumption.

For the terrestrial exposure analysis, application rates for irrigation water were derived using estimates for the maximum interception storage for a crop obtained from the PRZM manual. These values were derived for fully developed plant canopies, which may not be representative of crops where acrolein-treated water is applied. Crops without fully developed canopies would store less water, so the estimates derived in this assessment could overestimate exposure for these crops.



For the terrestrial exposure analysis of this risk assessment, a generic bird or mammal was assumed to occupy either the treated field or adjacent areas receiving a treatment rate on the field. Actual habitat requirements of any particular terrestrial species were not considered, and it was assumed that species occupy, exclusively and permanently, the modeled treatment area. Spray drift model predictions suggest that this assumption leads to an overestimation of exposure to species that do not occupy the treated field exclusively and permanently. Drinking water estimates were based on bird and mammal intake equations developed from USEPA's Wildlife Exposure Factors Handbook. However, water intake for reptiles, particularly the whipsnake, is complicated because reptiles can absorb water, as well as intake water through their skin. As a result, the drinking water intake values may underestimate exposure.

## **6.2 Effects Assessment Uncertainties**

### **6.2.1 Use of Surrogate Species Effects Data**

Guideline toxicity tests and open literature data on acrolein are not available for reptiles and as such, birds are used as surrogates for reptiles. Efforts are made to select the organisms most likely to be affected by the type of compound and usage pattern; however, there is an inherent uncertainty in extrapolating across phyla. In addition, the Agency's LOCs are intentionally set very low, and conservative estimates are made in the screening level risk assessment to account for these uncertainties.

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.

### **6.2.2 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.

### **6.2.3 Sublethal Effects**

When assessing acute risk, the screening risk assessment relies on the acute mortality endpoint as well as a suite of sublethal responses to the pesticide, as determined by the testing of a species' response to chronic exposure conditions and subsequent chronic risk assessment. Consideration of additional sublethal data in the effects determination is exercised on a case-by-case basis and only after careful consideration of the nature of the sublethal effect measured and the extent and quality of available data to support establishing a plausible relationship between the measure of effect (sublethal endpoint) and the assessment endpoints. However, the full suite of sublethal effects from valid open literature studies is considered for the purposes of defining the action area. To the extent to which sublethal effects are not considered in this assessment, the potential direct and indirect effects of acrolein on the whipsnake may be underestimated.

### **6.2.4 Age Class and Sensitivity of Effects Thresholds**

Test organism age may have a significant impact on the observed sensitivity to a toxicant. Acute dietary testing with birds is 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.

## 6.2.5 Location of Wildlife Species

For the terrestrial exposure analysis of this risk assessment, a generic bird or mammal was assumed to occupy either the treated field or adjacent areas receiving a treatment rate on the field. Actual habitat requirements of any particular terrestrial species were not considered, and it was assumed that species occupy, exclusively and permanently, the modeled treatment area. Spray drift model predictions suggest that this assumption leads to an overestimation of exposure to species that do not occupy the treated field exclusively and permanently.

## 7. Risk Conclusions

In fulfilling its obligations under Section 7(a)(2) of the Endangered Species Act, the information presented in this endangered species risk assessment represents the best data currently available to the Agency to assess the potential risks of acrolein to the Alameda whipsnake and its designated critical habitat.

Based on the best available information, the Agency makes a Likely to Adversely Affect determination for the Alameda whipsnake from the use of acrolein. Additionally, the Agency has determined that there is the potential for modification of the designated critical habitat for the Alameda whipsnake from the use of the chemical. Given the LAA determination for the Alameda whipsnake and potential modification of its designated critical habitat, a description of the baseline status and cumulative effects for the Alameda whipsnake is provided in **Attachment 1**.

A summary of the risk conclusions and effects determinations for the Alameda whipsnake and its critical habitat, given the uncertainties discussed in Section 6, is presented in **Tables 7.1** and **7.2**.

<b>Table 7.1. Effects Determination Summary for Effects of Acrolein on the Alameda Whipsnake</b>		
<b>Species</b>	<b>Effects Determination <sup>1</sup></b>	<b>Basis for Determination</b>
Alameda whipsnake	LAA	<b>Potential for Direct Effects</b> Acute risk LOCs exceeded for reptiles. Chronic toxicity data are not available for birds and reptiles and as such, risk is presumed.
		<b>Potential for Indirect Effects</b> Acute risk LOCs exceeded for birds, reptiles, and amphibians that serve as prey for the whipsnake. Chronic toxicity data are not available for birds, reptiles, and amphibians, and as such, chronic risk is presumed for these prey items. No toxicity data are available for terrestrial invertebrates that serve as prey for whipsnakes and as such, risk is presumed.

<sup>1</sup> No effect (NE); May affect, but not likely to adversely affect (NLAA); or May affect, likely to adversely affect (LAA)

<b>Table 7.2. Effects Determination Summary for the Critical Habitat Impact Analysis</b>		
<b>Designated Critical Habitat for:</b>	<b>Effects Determination <sup>1</sup></b>	<b>Basis for Determination</b>
<b>Alameda whipsnake</b>	<b>HM<sup>1</sup></b>	Acute risk LOCs exceeded for birds and reptiles that serve as prey for the whipsnake. Chronic toxicity data are not available for birds and reptiles and as such, chronic risk is presumed for these prey items. No toxicity data are available for terrestrial invertebrates that serve as prey for whipsnakes and as such, risk is presumed. No toxicity data are available on the effects of acrolein on terrestrial plants and risk is presumed for plants that make up the habitat of the whipsnake.

<sup>1</sup> Habitat Modification or No effect (NE)

Based on the conclusions of this assessment, a formal consultation with the U.S. Fish and Wildlife Service under Section 7 of the Endangered Species Act should be initiated to seek concurrence with the LAA determinations and to determine whether there are reasonable and prudent alternatives and/or measures to reduce and/or eliminate potential incidental take.

When evaluating the significance of this risk assessment's direct/indirect and adverse habitat modification effects determinations, it is important to note that pesticide exposures and predicted risks to the whipsnake and its resources (*i.e.*, food and habitat) are not expected to be uniform across the action area. In fact, given the assumptions of drift and downstream transport (*i.e.*, attenuation with distance), pesticide exposure and associated risks to the whipsnake and its resources are expected to decrease with increasing distance away from the treated field or site of application. Evaluation of the implication of this non-uniform distribution of risk to the whipsnake would require information and assessment techniques that are not currently available. Examples of such information and methodology required for this type of analysis would include the following:

- Enhanced information on the density and distribution of Alameda whipsnake life stages within the action area and/or applicable designated critical habitat. This information would allow for quantitative extrapolation of the present risk assessment's predictions of individual effects to the proportion of the population extant within geographical areas where those effects are predicted. Furthermore, such population information would allow for a more comprehensive evaluation of the significance of potential resource impairment to individuals of the whipsnake.
- Quantitative information on prey base requirements for the whipsnake. While existing information provides a preliminary picture of the types of food sources utilized by the whipsnake, it does not establish minimal requirements to sustain healthy individuals at varying life stages. Such information could be used to establish biologically relevant thresholds of effects on the prey base, and ultimately establish geographical limits to those effects. This information could be used together with the density

data discussed above to characterize the likelihood of adverse effects to individuals.

- Information on population responses of prey base organisms to the pesticide. Currently, methodologies are limited to predicting exposures and likely levels of direct mortality, growth or reproductive impairment immediately following exposure to the pesticide. The degree to which repeated exposure events and the inherent demographic characteristics of the prey population play into the extent to which prey resources may recover is not predictable. An enhanced understanding of long-term prey responses to pesticide exposure would allow for a more refined determination of the magnitude and duration of resource impairment, and together with the information described above, a more complete prediction of effects to individual whipsnakes and potential modification to critical habitat.

## 8. References

- Atkins. E.L., E.A. Greywood, and R.L. MacDonald. 1975. Toxicity of pesticides and other agricultural chemicals to honey bees. Laboratory studies. Univ. of Calif., Div. Agric. Sci. Leaflet 2287. 38 pp. (MRID# 00036935).
- Baker Petrolite Corporation. 2006. *Magnacide H herbicide Application by State*. Submitted by Baker Petrolite Corporation. (MRID 46976913)
- Baker Performance Chemicals. 1986 *Washington Magnacide H Monitoring Report*. Submitted by Baker Petrolite, Bakersfield, CA. (MRID 47008404)
- 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. (MRID 47008403)
- Burns, L.A. 1997. Exposure Analysis Modeling System (EXAMSII) Users Guide for Version 2.97.5, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA.
- 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. (MRID 46976916)
- Carsel, R.F., J.C. Imhoff, P.R. Hummel, J.M. Cheplick and J.S. Donigian, Jr. 1997. PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.0; Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA.

- 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. (MRID 43037301).
- Conn, R. 1990. *Baker Performance Chemicals Inc. Phase 3 Summary of MRID 00117672. Determination of LD<sub>50</sub> Acrolein - Bobwhite Quail: Project K-1524.* Prepared by MBA Laboratories, Inc. 10 p. (Accession Number 92001003)
- Cornell University. 2011. All About Birds, The Cornell Lab of Ornithology website, [http://www.allaboutbirds.org/guide/ring-billed\\_gull/lifehistory](http://www.allaboutbirds.org/guide/ring-billed_gull/lifehistory)
- David, R. 1989. *Acute Oral Toxicity Study of Acrolein, Inhibited in Rats: Final Report: Study G-7230.220.* Unpublished study prepared by Microbiological Associates, Inc. 87 p. (MRID 41257001)
- Fletcher, J.S., J.E. Nellessen, and T.G. Pfleeger. 1994. Literature review and evaluation of the EPA food-chain (Kenaga) nomogram, and instrument for estimating pesticide residues on plants. *Environmental Toxicology and Chemistry* 13 (9):1383-1391.
- Ghilarducci, D. P. and Tjeerdema, R. S. 1995. Fate and Effects of Acrolein. *Reviews of Environmental Contamination and Toxicology* **144**: 95-146
- 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. (MRID 40945401)
- 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. (MRID 41869101)
- Hoerger, F., and E.E. Kenaga. 1972. Pesticide residues on plants: Correlation of representative data as a basis for estimation of their magnitude in the environment. *In* F. Coulston and F. Korte, *eds.*, *Environmental Quality and Safety: Chemistry, Toxicology, and Technology*, Georg Thieme Publ, Stuttgart, West Germany, pp. 9-28.
- 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.

- 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. (MRID 47008401)
- Jacobson, Brian. 1991. *Magnitude of Residue for Acrolein in Potable Water – Arizona Site*. Unpublished study performed by ABC Laboratories, Columbia, MO. ABC Report No. 38983. Submitted by Baker Performance Chemicals, Houston, TX. (MRID 41855401)
- Jacobson, Brian. 1991. *Magnitude of Residue for Acrolein in Potable Water – Arizona Site*. Unpublished study performed by ABC Laboratories, Columbia, MO. ABC Report No. 38983. Submitted by Baker Performance Chemicals, Houston, TX. (MRID 41855401)
- Karvonen, T., Koivusalo, H., Jauhiainen, M., Palko, J. and Wepling, K. 1999. A hydrological model for predicting runoff from different land use areas, *Journal of Hydrology*, 217(3-4): 253-265.
- Matherly, R. Hackerott, J. Nguyen, N. 1987 Octanol/Water Partition Coefficient of Acrolein: Study No. RD0008.287. Unpublished study prepared by Baker Performance Chemicals. 24 p. (MRID 40840604)
- 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. (MRID 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. (MRID 42183301)
- 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. (MRID 47008407)
- 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. (MRID 46976905)
- 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. (MRID 40840602).
- Salma, Tauseef. 2001. *Henry's Law Constant for Acrolein*. Baker Petrolite Internal Memorandum to Miles Rhea, dated January 4, 2001.
- Smith, A. M. 1993. (*<sup>14</sup>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. (MRID 42949201)
- Smith, A. 1993. (*<sup>14</sup>C-Acrolein*)--*Determination of the Aerobic Aquatic Metabolism* Final Report: Lab Project Number: 91-3-3747: 12167-0789-6100-750. Unpublished study prepared by Springborn Laboratories, Inc. 125 p. (MRID 43227101)
- Smith, Curtis W. 1962. *Acrolein*. John Wiley and Sons, London.
- Sunzenauer, I., E. Fite, T. Barry, H. Nelson, E. Odenkirchen, and D. 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 Advisory 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](http://www.epa.gov/oppefed1/ecorisk/fifrasap/rra_title_cont.htm)
- Tucker, R.; Hudson, R. 1970. *Acrolein: Acute Oral LD<sub>50</sub> 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. (MRID 00117668)
- U.S. Environmental Protection Agency (U.S. EPA). 1993. *Wildlife Exposure Factors Handbook, Volume I of II*. EPA/600/R-93/187a, December 1993.
- U.S. EPA. 1998. *Guidance for Ecological Risk Assessment*. Risk Assessment Forum. EPA/630/R-95/002F, April 1998.
- U.S. EPA. 2004. *Overview of the Ecological Risk Assessment Process in the Office of Pesticide Programs*. Office of Prevention, Pesticides, and Toxic Substances. Office of Pesticide Programs. Washington, D.C. January 23, 2004.
- U.S. EPA. 2008. *Environmental Fate and Ecological Risk Assessment Chapter (DP Barcode D354775)* in *Support of Phase VI of the Reregistration Eligibility*



- Decision on Acrolein (PC Code 000701). Office of Prevention, Pesticides, and Toxic Substances. Office of Pesticide Programs. Washington, D.C. July 2008.
- U.S. EPA. 2009. Ambient Aquatic Life Water Quality Criteria for Acrolein, Office of Water, Office of Science and Technology, Washington, D.C. July 2009.
- U.S. EPA. 2011. Risks of Bromethalin Use to Federally Threatened Alameda Whipsnake (*Masticophis lateralis euryxanthus*) and the Federally Endangered Salt Marsh Harvest Mouse (*Reithrodontomys raviventris*), Office of Pesticide Programs, Environmental Fate and Effects Division, Washington, D.C. March 25, 2011.
- U.S. Fish and Wildlife Service (USFWS) and National Marine Fisheries Service (NMFS). 1998. Endangered Species Consultation Handbook: Procedures for Conducting Consultation and Conference Activities Under Section 7 of the Endangered Species Act. Final Draft. March 1998.
- USFWS. 1996. Endangered and threatened wildlife and plants: determination of threatened status for the California red-legged frog. Federal Register 61(101): 25813-25833.
- USFWS/NMFS. 2004. 50 CFR Part 402. Joint Counterpart Endangered Species Act Section 7 Consultation Regulations; Final Rule. FR 47732-47762.
- Willis, G.H. and L.L. McDowell. 1987. Pesticide Persistence on Foliage in Reviews of Environmental Contamination and Toxicology. 100:23-73.