Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

M E M O R A N D U M

Arnold Schwarzenegger
Governor

TO: Linda O'Connell **HSM-10002**
Senior Environmental Scientist
Worker Health and Safety Branch

FROM: Lillian J. Kelly *(original signed by L. Kelly)*
Environmental Scientist
(916) 323-2837

DATE: January 26, 2010

SUBJECT: ACROLEIN INITIAL SCOPING DOCUMENT

Attached is the Acrolein Initial Scoping Document. Available documents and data reviewed were the Department's list of actively registered products (currently two), use and sales data, formulations and uses, pesticide illness reports, and the United States Environmental Protection Agency's Reregistration Eligibility Decision for Acrolein, September 2008, and Acrolein RED Amendment, August 2009.

California Environmental Protection Agency
Department of Pesticide Regulation
Worker Health and Safety Branch

HSM-10002

ACROLEIN
INITIAL SCOPING DOCUMENT
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Lillian J. Kelly, Environmental Scientist
Human Health Mitigation Program
1001 I Street P.O. Box 4015, Sacramento, CA 95812-4015
(916) 323-2837; Fax (916)445-4280 **www.cdpr.ca.gov**

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I. SUMMARY

Acrolein is a California Environmental Protection Agency (Cal/EPA) Department of Pesticide Regulation (DPR) restricted material and a United States Environmental Protection Agency (U.S. EPA) restricted use pesticide. It is used to control submersed and floating weeds and algae in irrigation canals, and to control bacteria and fungi in oilfield water injection systems. Two products correspond to these two uses: MAGNACIDE® H Herbicide and MAGNACIDE® B Microbiocide, respectively. Both products are registered for use in California. Approximately one quarter of a million pounds of acrolein were used annually in California for the period 2003-2007. The predominant use was non-production agricultural rights-of-way. Since 1999, DPR Worker Health and Safety Branch (WH&S) Pesticide Illness Surveillance Program (PISP) has not received any report of illness associated with acrolein.

The U.S. EPA completed a Reregistration Eligibility Decision (RED) document for acrolein in September 2008. The RED identified potential exposure scenarios associated with use of the herbicide. Potential risk levels of concern are associated with short-term inhalation exposure. In September 2009, U.S. EPA posted an Amendment in the docket which revised the mitigation requirement from two to one certified applicator onsite during the application and added the requirement for the applicator to maintain contact with the organization no less than every two hours (U.S. Environmental Protection Agency, 2008). Baker Petrolite Corporation is the sole registrant of the technical grade active ingredient (95% pure acrolein). Provided Baker Petrolite Corporation amends the MAGNACIDE® H Herbicide label, incorporates mitigation measures, and submits required data, acrolein is eligible for reregistration.

II. PURPOSE

The Birth Defect Prevention Act of 1984 (Food and Agricultural Code Division 7, Chapter 2, Article 14, Section 13121) requires DPR to review the toxicology of all active ingredients currently registered in California. Acrolein is one of the high priority pesticides on DPR's list of active ingredients for risk characterization (Patterson, 2009). This Initial Scoping Document lays the groundwork for assessing the adequacy of existing protective measures listed on pesticide product labels. It is prepared in support of WH&S Human Health Assessment Program's Exposure Assessment Document which is an integral part of DPR's risk characterization process.

III. REGULATORY HISTORY / STATUS

Brief description

Acrolein is a Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) List B, non-food use pesticide. In 1959, acrolein was registered as a biocide to kill bacteria that accumulate within pipes of petroleum producing systems. In 1975, it was registered as an herbicide for control of submerged and floating aquatic weeds and algae in irrigation canals and irrigation reservoirs. Agriculture irrigation-use occurs only in 15 states in the Great Plains and western states. Physical/ chemical properties for the products are listed in the individual product manuals (Baker

Petrolite Corporation, 2005) (Baker Petrolite Corporation., 1999). The manuals are labeling requirements.

Applicable regulations

Federal and State codes applicable to acrolein are given in Tables 1.A. and 1.B. California Special Local Need (SLN) 930006 for use in underground burrowing systems was cancelled by U.S. EPA in 2006 (U.S. Environmental Protection Agency, 2006) (U.S. Environmental Protection Agency, 2005) and inactivated by DPR in 2008.

Table 1.A. Federal Laws and Regulations Applicable to Acrolein

Laws	FIFRA Registration Type : **Two Section 3 Regular and One Section 24c Special Local Need (SLN)**	FIFRA Reregistration Eligibility Decision (RED) : **Issued September 2008**	FFDCA Tolerance Reassessment Eligibility Decision (TRED) : **Not Applicable - No Food Use**	FQPA Susceptibility of Children : **Not Applicable - No Residential Use**	FQPA Cumulative Risk : **Not Applicable**
Title 40 CFR	Part 162.151(i) : **California SLN 780039 for use in irrigation water reservoirs** Part 152.175 Restricted Use Pesticide : **Acrolein** Part 170 Worker Protection Standard : **Established in the RED; includes OSHA 29 CFR Part 1910.134** Part 156 Labeling Requirements : **MAGNACIDE® H Herbicide**				

FIFRA: Federal Insecticide, Fungicide, and Rodenticide Act, 1947 [Section 3(c)(5)(D) and Section 2(bb)]; Amended 1988 to require Reregistration of pesticides registered before 11/1/1984 [Section 4(g)(2)(A)].
FFDCA: Federal Food, Drug, and Cosmetic Act, 1938; Amended 1996 to require a safety determination of no harm from aggregate (inhalation, oral, and dermal) exposures [Section 408(b)(2)(A)(ii)].
FQPA: Food Quality Protection Act, 1996 [Section 408(b)(2)(C)(i) and (ii)].
CFR: Code of Federal Regulations
OSHA: Occupational Safety and Health Administration

Table 1.B. California Laws and Regulations Applicable to Acrolein

	Restricted Material	**Toxic Air Contaminant**	Groundwater Protection List	Proposition 65 List
Yes / No	**Yes**	**Yes**	No	No
Law	FAC Div 7, Ch 3, Art 1.5, Section 14001	FAC Div 7, Ch 3, Art 1.5, Section 14021(b)	FAC Div 7, Ch 2, Art 15, Section 13145(d)	HSC Section 25249.5
Title 3, Title 27	3 CCR 6400	3 CCR 6860	3 CCR 6800(b)	27 CCR 25000-27001

FAC: California Food and Agricultural Code
HSC: California Health and Safety Code
CCR: California Code of Regulations

As a toxic air contaminant, Cal/EPA Office of Environmental Health Hazard Assessment (OEHHA) developed acute and chronic reference exposure levels (RELs) for non-cancer health impacts of acrolein. The acute inhalation REL is 2.5 micrograms per cubic meter ($\mu g/m^3$) and the chronic inhalation REL is 0.35 $\mu g/m^3$ (Office of Environmental Health Hazard Assessment, 2008). Acrolein is a byproduct of fires and is one of several acute toxicants to firefighters. Sources noted by OEHHA are combustion of fossil fuels, tobacco/cigarette smoke, and pyrolyzed animal and vegetable fats.

California regulatory status

In May 2009, acrolein was delisted from the California Groundwater Protection List because the re-determined value for anaerobic soil metabolism no longer exceeds the specific numerical value criteria. The DPR risk characterization for acrolein is pending.

Federal regulatory status

The RED summarized key features and findings of the human health risk assessment and of the environmental fate and ecological risk assessment. Findings regarding potential exposure scenarios, aggregate and cumulative risks, and the risk management and regulatory decision are as follow.

U.S. EPA Exposures Scenarios

Three potential inhalation exposure scenarios are associated with use of MAGNACIDE® H Herbicide:

- application interval, a new scenario consisting of the time after set-up and before break-down when personal protective equipment (PPE) has been removed; the interval ranges between 30 minutes to 8 hours
- post-application, occupational
- post-application, bystander.

Potential risk levels of concern are associated with short-term inhalation exposure. The RED reported results of two acrolein ambient air monitoring studies which the California Air Resources Board (CARB) conducted at the request of DPR (California Air Resources Board, 2005) (California Air Resources Board, 2007). The CARB conducted a third ambient air monitoring study at DPR's request which was available after the RED was released (California Air Resources Board, 2008). The following acrolein concentrations were detected in the third study: five minutes before the application, 1 to 2 parts per billion (ppb) at background locations; during the application, 7.3 ppb as the highest concentration at 65 feet (ft) from the canal and 0.3 miles downstream. The second highest concentration was 6.8 ppb at 18 ft from the canal's water and 3.5 miles downstream; the report noted that diesel tractors passed by 35 times during this sampling. The application rate was 1.8 parts per million (ppm) over three hours. The data were of high quality and indicated that highest potential risks are to persons standing adjacent to a treated canal. However, the data are insufficient to determine appropriate dimensions of a restricted area.

Aggregate and Cumulative Risks

The U.S. EPA did not conduct an aggregate risk assessment because there are no anticipated drinking water or dietary exposures to residues of acrolein, no registered food or feed uses, and no residential use. The U.S. EPA did not assume acrolein had a common mechanism of toxicity with other substances and therefore did not conduct a cumulative risk assessment.

U.S. EPA Risk Management and Regulatory Decision

No changes to the label or use pattern are required for MAGNACIDE® B Microbiocide based on assumptions of completely closed delivery and use systems. The MAGNACIDE® H Herbicide label must be revised to specify PPE and respirator type with fit testing, medical qualification, and training. Baker Petrolite Corporation's training (Baker Petrolite Corporation, 2008) is

required annually instead of every three years. To reduce bystander exposure, posting of the application is required and applications are only permitted where "no swimming" signs are posted. Three misleading health statements specified in the RED must be deleted from the MAGNACIDE® H Herbicide Manual. Application restrictions are specified in the September 2009 Amendment. The registrant must submit product-specific and generic data for acrolein. Provided requirements are implemented, acrolein is eligible for reregistration.

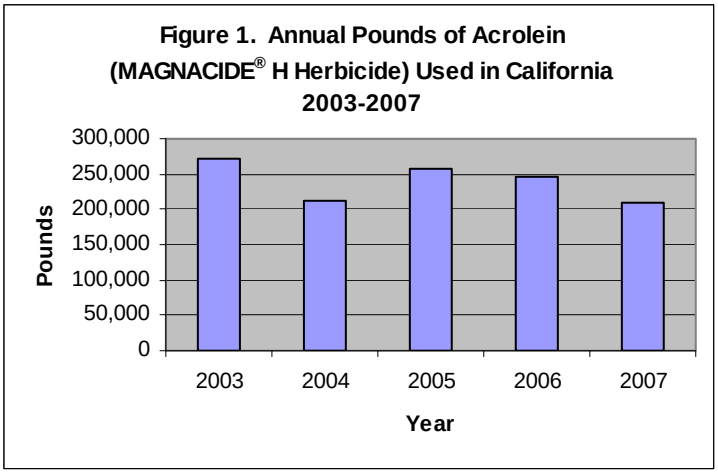
IV. PESTICIDE USE and SALES

The U.S. EPA estimated that approximately one million pounds of acrolein are used annually in the United States. In California, MAGNACIDE® B Microbiocide use in oil wells is classified as non-agricultural, industrial and is not required to be reported. The DPR Pesticide Use Report data show that on average approximately one quarter of a million pounds of acrolein have been used annually for the 5-year period 2003-2007, and that acrolein accounts for less than 1% of total pesticide sales for the period (Table 2, Figure 1).

Table 2. Acrolein (MAGNACIDE® H Herbicide) Use and Sales Data 2003–2007
California Department of Pesticide Regulation

Year	Pounds Acrolein Applied			Total Pounds of Acrolein Applied (a)	Total Pounds of Acrolein Sold (b)	Total Pounds of Pesticides Sold	% Acrolein of Total Pesticide Sales
	Aquatic Areas, Irrigation Systems	Rights of Way	Other				
2003	19,716	241,287	11,730	272,733	401,503	661,488,765	0.06
2004	17,159	190,157	3,696	211,012	470, 833	667,103,789	0.07
2005	26,097	229,833	1,264	257,194	521,719	611,368,382	0.08
2006	23,445	222,824	176	246,445	1,033,843	742,761,450	0.14
2007	19,144	187,626	2,436	209,206	1,196,942	677,920,963	0.18
Total	105,441	1,071,730	19,299	1,196,590			

(a) California Department of Pesticide Regulation, Pesticide Use Report database; latest access August 11, 2009. www.cdpr.ca.gov/docs/pur/purmain.htm (b) California Department of Pesticide Regulation, Mill Assessment database; latest access March 23, 2009. www.cdpr.ca.gov/docs/mill/nopdsold.htm
Other = Landscape maintenance, uncultivated agricultural and non-agricultural areas, structural and vector pest control. Note: DPR deactivated use of acrolein in underground burrowing systems in 2008.



California Department of Pesticide Regulation, Pesticide Use Report database, latest access August 11, 2009 www.cdpr.ca.gov/docs/pur/purmain.htm

The top five counties reporting use of acrolein in the 5-year period are ranked in Table 3.

Table 3. Top Five Counties With Highest Use of Acrolein (MAGNACIDE® H Herbicide) in California, 2003–2007

County	Average Pounds Acrolein Used	% Average Total Annual Use
Kern	75,606	31.59
Fresno	51,576	21.55
Stanislaus	42,065	17.57
Merced	21,465	8.96
San Joaquin	11,008	4.59
Total	201,720	84.28

V. FORMULATIONS and USES

Acrolein is not applied directly to agricultural crops. Both MAGNACIDE® H Herbicide and MAGNACIDE® B Microbiocide are formulated as pressurized liquid packaged under a nitrogen blanket with 95% acrolein and contain 6.7 pounds of active ingredient per gallon. Applications are made using specifically designed equipment supplied and maintained by Baker Petrolite Corporation.

MAGNACIDE® H Herbicide is forced from the container with nitrogen gas directly into the irrigation canal water over a period of 30 minutes to 8-hours. The treated water proceeds down the irrigation system in a "wave." The MAGNACIDE® H Herbicide Monitor is a hand-held colorimeter instrument that measures the concentration of acrolein in treated irrigation waters with an accuracy of 0.1 ppm. Results are read directly off the monitor's scale in the range of 0.25 to 15.0 ppm. Appropriate treatment requires calculation of the following:

- weed growth condition, standardized in a chart in the manual
- canal flow rate, stated as cubic feet per second
- temperature of the water to be treated, since MAGNACIDE® H Herbicide is less soluble in water temperatures below 60^{o} Fahrenheit
- application time desired.

Water treated with MAGNACIDE® H Herbicide must either be used for irrigation of fields (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. California's SLN 780039, registration type 24(c), is registered under MAGNACIDE® H Herbicide for use in reservoirs and impounded water.

California is the third largest oil-producing state in the United States. Kern County provides 66% of all oil production in California and 10% of the total oil production in the country (San Joaquin Geological Society, 2008). Application of MAGNACIDE® B Microbiocide in oilfields occurs in a closed system described as follows (Dickinson, 2009). Production wells yield oil, gas, and water. All fluids from production wells go to a tank farm, which is a collection of tanks (with vapor recovery) that separate and purify the oil, gas and water. The clean oil goes to the refinery, the clean gas goes to the gas company, and the clean water is re-injected into the same oil reservoir. This step of the process is called secondary oil recovery or waterflooding, and the well in which fluids are injected is called an injection well. The water from the injection well physically moves

Photograph of an oilfield acrolein application showing a portion of a tank farm in the background. Courtesy of Baker Petrolite Corporation.

oil to the adjacent production wells. Typically there are many production wells to a few injection wells. Chemical and microbiological factors hamper smooth operation of the waterflood system. MAGNACIDE® B Microbiocide kills bacteria in the water that cause corrosion and plugging of the injection wells. It is introduced upstream to treat as much of the system as possible before the water reaches the wellhead. It is added to the water at a storage tank, heater treater, separation tank, filter, or at the producing or injecting wellhead. Dosages of MAGNACIDE® B Microbiocide depend on the type of treatment desired (continuous, slug, or well squeeze) and range from 5 to 12,000 ppm. Only Baker Petrolite Corporation employees apply MAGNACIDE® B Microbiocide in oilfield operations.

VI. LABEL REQUIREMENTS

In October 2008, DPR received revised labels of both products. In December 2008, DPR accepted the revised MAGNACIDE® B Microbiocide label dated January 2004. The manual on file with DPR is dated September 1999. In April 2009, DPR accepted the MAGNACIDE® H Herbicide label dated February 2004 and manual dated March 2005.

a. MAGNACIDE® H Herbicide and MAGNACIDE® B Microbiocide are registered for retail sale to and use only by Certified Applicators or persons under their direct supervision and only for those uses covered by the Certified Applicator's certification.

b. Both product labels display the signal word "Danger" with the skull and crossbones and "Poison". Both labels advise the physician to treat exposed areas as a chemical burn and to keep the exposed person under observation for 24-hours. Both labels also display the Department of Transportation placards for inhalation hazard and flammable liquid.

c. Both product labels require the following PPE: 1) when setting up and breaking down application equipment, a full-face air purifying respirator with organic vapor (OV) cartridges approved by the National Institute of Occupational Safety and Health (NIOSH) and butyl rubber gloves; 2) for visual inspection during treatment, chemical splash goggles.

d. There is no maximum application rate specified on either label.

e. There is no maximum number of applications per year and no minimum re-treatment interval specified on either label.

f. Restricted entry interval (REI) – Not applicable.

g. Pre-harvest interval (PHI) – Not applicable.

h. Both product labels have specific environmental restrictions to prevent toxicity to fish and wildlife.

The RED requires the following changes to the MAGNACIDE® H Herbicide label: PPE is extended to include the application interval, replacing chemical splash goggles with a NIOSH approved full-face respirator with either OV removing cartridges with a prefilter approved for pesticides (TC-23C) or a canister approved for pesticides (TC-14G). Respirator fit testing, medical qualification, and training is required. Engineering controls for a closed system to prevent dermal and inhalation exposures, and a device that will limit drippage to no more than 2 milliliters/disconnect must be used. MAGNACIDE® H Herbicide applications must be made during daylight hours, with posting of the application site and equipment areas as specified, and only in canals with posted "no swimming" signs. Application restrictions added are a maximum application rate of 15 ppm and a minimum re-treatment interval of 2-weeks. Per the RED Amendment, acrolein use will be restricted to a maximum of 8-applications per application point per calendar year, and one certified applicator must be onsite during the application and in contact with the organization no less than every 2-hours.

The U.S. EPA expects to issue Data Call-In (DCI) requirements for acrolein by the end of 2009. Typically the U.S. EPA estimates a period of three to four years for completion of this phase of the RED requirements, however, the time period may extend. Label amendments are contingent upon completion of DCI requirements.

VII. POTENTIAL EXPOSURE SCENARIOS

Potential exposure scenarios associated with registered use of a pesticide are classified as occupational and non-occupational. Both classifications include handler and non-handler potential exposure scenarios. The handler is involved in all aspects of the pesticide application. Non-handlers are individuals not involved in the application but whose work brings them in proximity with the application, treated area or storage area. Residential use is non-occupational and potential exposure may occur as a handler or non-handler. Bystander exposure may be occupational or non-occupational and occurs when an individual incidentally comes in contact with a pesticide that moves offsite during or following application.

Occupational, Handler
The greatest potential exposure associated with application of MAGNACIDE® H Herbicide is to the occupational handler and by both the inhalation and dermal routes. Since acrolein is applied under pressure, there is potential for valve leaks or hose breaks, especially at the collar of the tank. MAGNACIDE® B Microbiocide is applied in a closed system, only in oilfields, and only by Baker Petrolite Corporation employees.

Occupational, Non-Handler
Office personnel in proximity to acrolein storage areas may be exposed to the vapors.

Non-Occupational - *Residential*
Not applicable. There are no residential uses of acrolein.

Bystander
Fieldworkers adjacent to rights-of-way during applications in canals, residents living downwind of irrigation canals during applications, and individuals or workers in public areas (golf courses, recreational parks) near canals or reservoirs during treatment may be exposed to acrolein vapors.

VIII. PESTICIDE ILLNESS REPORTS

PISP illness reports
Since 1999, PISP has not received any report of illness associated with the use of acrolein. During the period 1983 through 1999, PISP received 14 illness reports. Symptoms noted included eye irritation, skin contact, and smelling an odor. A Table of case information is provided in the Appendix of this document.

Illnesses from other States
The U.S. EPA consulted five databases for Public Health / poisoning incident data associated with acrolein and reported the following case numbers in the RED:

- The U.S. EPA's Office of Pesticide Programs Incident Data System identified a total of seven exposures from 1999 through 2007. One exposure in 1999 and one in 2007 resulted in death of the certified applicator. While both men were not wearing PPE, the activity in each case may have occurred during the application interval. One was not observed at the hospital for the 24-hour period as advised on the label and died at home during the night. The other man died in the hospital within 36 hours.
- The PISP reported 14 cases (Appendix of this document).
- The Poison Control Centers reported a total of 47 cases from 1993 through 2003.
- The NIOSH Sentinel Event Notification System for Occupational Risks (SENSOR) reported only one case for the period 1998 to 2003, a duplicate from the PISP data.
- The National Pesticide Telecommunications Network reported no exposures to acrolein for the period 1984-1991.

Review of published literature
In 2002, a 55-year old man in Germany died within 100 minutes of ingesting 250 milliliters of a weed killer that contained allyl alcohol, which is metabolized to acrolein. Acrolein causes cardiotoxicity and leads to cardiac arrest. The acrolein concentration in the man's blood was 7.2 milligrams/liter, which is within the cardiotoxic concentration range. At autopsy, bloody reddish fluid was found in the mouth, larynx, esophagus, and trachea. All internal organs exhibited a strong pungent odor (Toennes *et al.*, 2002).

IX. REFERENCES

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X. APPENDIX

Illnesses Associated With Use of Acrolein 1983–2007, California Department of Pesticide Regulation

No.	Year	Case	Ag / Non-Ag	Site	Type of Illness	Narrative Description
1	1983	Definite	Non-Ag	Unknown	Eye	After injecting material into a canal water, applicator flushed lines; residual material splashed on his face mask. When he took the mask off, some material dripped from the mask into his eyes.
2		Definite	Ag	Unknown	Skin	Employee was sprayed with Magnacide when a line backed up, spraying material out of a vent valve.
3		Possible	Non-Ag	Unknown	Systemic	Exposed to vapors created in a holding tank containing Magnacide B while working on an oil rig.
4	1985	Definite	Non-Ag	Unknown	Systemic	A Police Officer was exposed while cordoning a spill site at the Magna plant.
5		Definite	Non-Ag	Unknown	Systemic	A Police Officer was exposed while directing traffic at the Magna plant spill.
6		Definite	Ag	Unknown	Systemic	Irrigator was exposed to Magnacide while breaking pipe lines.
7	1986	Definite	Ag	Unknown	Skin, Eye	2 Flood Control employees were working on well pumps located next to a reservoir which was being treated with Magnacide H. Notice of Violation issued for failure to submit a Notice of Intent.
8		Definite	Ag	Unknown	Skin, Eye	2nd Flood Control employee as above.
9		Possible	Ag	Irrigation systems (Ditches, Canal Banks)	Systemic	A Water District maintenance crewman smelled the pesticide odor while monitoring an application to a canal.
10	1987	Possible	Non-Ag	Unknown	Systemic	An office worker in close proximity to equipment used for applying acrolein smelled the substance. She became ill after 2 hours near the equipment.
11	1993	Definite	Ag	Irrigation systems (Ditches, Canal Banks, etc.)	Eye	While putting a new end on a hose, a worker was splashed in the left eye with liquid/gas from the hose. Punctate keratitis observed. Eye protection was not worn.
12	1997	Probable	Non-Ag	Irrigation systems	Eye, Respiratory	An Oil Well Operator went to check on a well. He breathed pesticide vapors from a leaking water line, developed symptoms and left immediately. The pesticide suppresses algae growth in water injected into the oil field.
13	1998	Definite	Non-Ag	Irrigation systems	Skin	An Irrigation District employee exposed himself to acrolein while trying to shut off a tank valve. The application hose got hung up and broke off at the collar of the tank. His sleeve was soaked with acrolein resulting in burns to his right arm.
14	1999	Probable	Ag	Soil	Eye, Systemic	As a Research Employee measured acrolein into a graduated cylinder, her eyes began to water and burn. She wore a full face respirator while working and is unaware of how she got exposed.

Data provided by Dr. Louise Mehler, April 4, 2008. As of December 2009 there are no reports associated with use of acrolein since 1999.
Definite = both physical and medical evidence document exposure and consequent health effects. Probable = limited or circumstantial evidence supports a relationship to pesticide exposure. Possible = evidence neither supports nor contradicts a relationship.
Ag = Agricultural use and indicates pesticide use intended to contribute to production of an agricultural commodity.
Type of Illness = characterization of signs and symptoms. Prior to 1989, "systemic" was used to characterize all symptoms other than or in addition to eyes and/or skin. The Department of Pesticide Regulation Pesticide Illness Surveillance Program database may be accessed at www.cdpr.ca.gov/calpiq.