

Acrolein: Environmental Fate and Ecotoxicology

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Kenneth D. King



Air Program
Environmental Monitoring Branch
California Department of Pesticide Regulation
1001 I Street
Sacramento, CA, 95812
www.cdpr.ca.gov

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1 Introduction

Acrolein, also known as acrylaldehyde, allyl aldehyde, ethylene aldehyde, propenal, and prop-2-enal, is a volatile colorless liquid with a pungent odor. Acrolein was registered as an herbicide with the United States Environmental Protection Agency (U.S.EPA) in 1975 after previously being registered as a biocide in 1959 (USEPA, 2008). Acrolein is mainly used for the control of aquatic weeds and algae in irrigation canals and for the control of algae, aquatic plants, and mollusks in industrial recirculating water systems, cooling towers, treatment ponds, and irrigation channels (Ghilarducci and Tjeerdema, 1995). There are two products actively registered with the California Department of Pesticide Regulation (DPR), which date to 1970 and 1972 (DPR, 2016a). This report summarizes the most current knowledge on the environmental fate, physico-chemical properties of acrolein, an overview of current regulations, as well as spatial (both county and site type) and temporal patterns in reported agricultural use in California.

2 Physical and Chemical Properties

Acrolein is a highly flammable, reactive, volatile colorless liquid at room temperature and pressure (Figure 1) (Ghilarducci and Tjeerdema, 1995). It is an unsaturated aldehyde and exhibits both electrophilic and nucleophilic behavior (Ghilarducci and Tjeerdema, 1995). The combination of a carbonyl group ($R-C=O$) and a vinyl ($R-C=C$) group within the molecular structure of acrolein results in high reactivity (Ghilarducci and Tjeerdema, 1995). This introduces hazards in storage and handling, particularly from spontaneous polymerization (Ghilarducci and Tjeerdema, 1995). Common reactions of acrolein include Diels-Alder condensation, dimerization-polymerization, addition to the $C=C$ bond, carbonyl additions, reductions, and oxidations (WHO, 1992). At room temperature, when catalyzed by ultraviolet light, acrolein is subject to highly exothermic polymerization (Ghilarducci and Tjeerdema, 1995). The aqueous 97% w/w technical grade active ingredient (TGA) is the most pure form typically available (Shaner, 2014). The TGA is described as having a pungent odor (Shaner, 2014). Table 1 shows the physical and chemical properties of acrolein.



Figure 1: Chemical structure of acrolein

Table 1: Physical and chemical properties of acrolein

Property	Value	Reference
Common Name	Acrolein	
IUPAC Name	2-propenal	
Other Names	acraldehyde, acrylaldehyde, acrylic aldehyde, allyl aldehyde, ethylene aldehyde, propenal, prop-2-enal, prop-2-en-1-al	
CAS #	107-02-8	
CAS # (deleted)	25314-61-8	
Molecular Formula	C ₃ H ₄ O	
Molecular Weight	56.06 g/mole	
Description	TGAI: Colorless liquid, pungent odor	Shaner, 2014
Density	TGAI: 0.847 g/mL @ 15.6°C	Shaner, 2014
Melting Point	-86.9°C	Shaner, 2014
Vapor Pressure	28 x 10 ³ Pa @ 20°C	Shaner, 2014
Boiling Point	52.7 °C	Shaner, 2014
Solubility	208 g/L @ 20°C	Howard, 1989
Log K _{ow}	0.9	WHO, 1992
K _{oc}	Average 0.5 mL/g	Shaner, 2014
Henry's Law	4.4 x 10 ⁻⁶ atm-m ³ /mol	Howard, 1989

3 Use Profile

3.1 Acrolein Applied as a Pesticide

Acrolein is injected below the surface of irrigation canals for the control of submerged and floating aquatic weeds (Shaner, 2014). It is used at aqueous concentrations as high as 10 mg/L in industrial recirculating water systems, cooling towers, treatment ponds, and irrigation channels for the control of algae, aquatic plants, and mollusks (Ghilarducci and Tjeerdema, 1995). It is also used to control microbial growth in subsurface feed lines, wastewater, hydrocarbon fuels, and oil wells (Ghilarducci and Tjeerdema, 1995). It is used in the paper industry at 0.4-0.6 mg/L to control slime formation (Ghilarducci and Tjeerdema, 1995).

Beginning in 1990, California agricultural applicators have been required to report the use of any registered pesticide to DPR and to the County Agricultural Commissioner presiding over the county in which the application occurred. DPR collects this data and stores it in the Pesticide Use Report (PUR) database. Information in this database includes, but is not limited to, application date, pounds of AI applied, area treated, formulation applied, and location (DPR, 2016b). Where possible, the location of the application is specified using meridian, township, range, and section data to obtain a resolution of approximately one square mile (DPR, 2016b). Limitations of the data in the PUR are the exclusion of home-and-garden uses, as well as most industrial and institutional uses, which are the primary exceptions to this reporting requirement (DPR, 2016b). The summed use, in terms of lbs of AI, is shown in Figure 2.

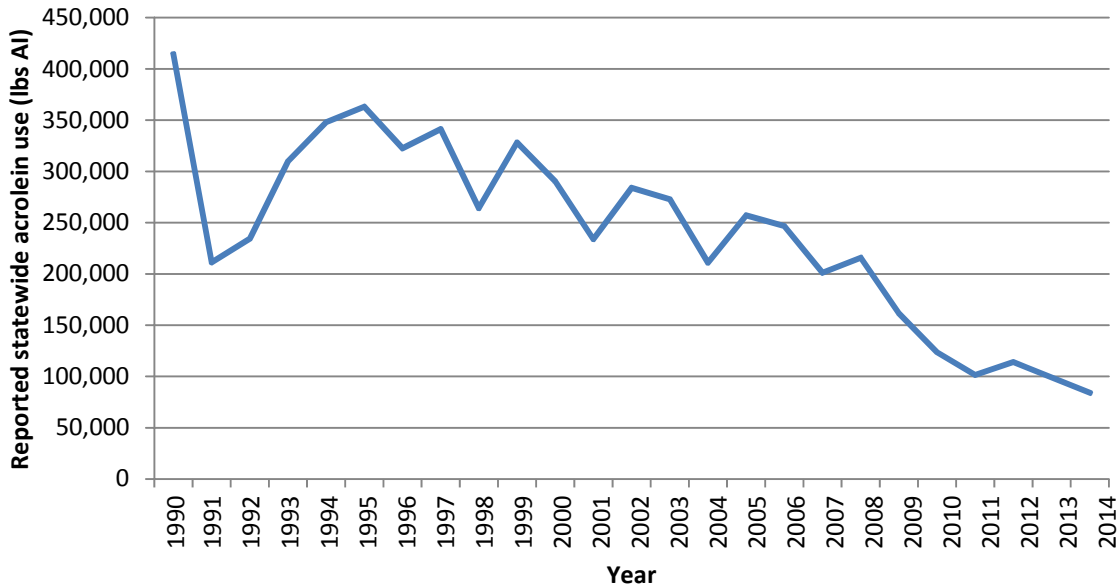


Figure 2: Statewide reported use of acrolein in terms of pounds of AI per year

There have been two formulations of acrolein reported as used in the PUR since 1990, Magnacide H and Magnacide B (DPR, 2016b). Since January of 2000, all reported uses of acrolein have been of the Magnacide H formulation (DPR, 2016b). The last reported use of Magnacide B in the PUR was in 1992, and the highest use of that formulation in any year (1991) accounted for less than 0.4% of total reported acrolein used in 1991 in terms of pounds of AI applied (DPR, 2016b).

Application of Magnacide is via introduction directly into irrigation systems from the container by forced nitrogen gas (Alligare, 2013) to reach concentrations of up to 15 ppm. Calculations using water volume, temperature, velocity, quality, and weed density are used to produce a “wave” which will travel downstream and bathe weeds at a sufficient concentration and exposure time (Alligare, 2013). In the PUR database, these irrigation canal applications were most commonly reported as either rights of way or aquatic areas (DPR, 2016b).

The county with the highest reported use of acrolein (pounds of AI applied) in 2014 was Stanislaus County followed by Fresno County and Kern County (DPR, 2016b). These three counties accounted for 70.7% of acrolein use (in terms of lbs AI) in 2014 (27.7%, 24.5%, and 18.5%, respectively). Use of acrolein has been generally decreasing since 1990 as shown in Figure 2 (DPR, 2016b). Use by county is shown for 1990-2014 in Figure 4. Table 3 details annual use in the 16 counties reporting any use of acrolein in the 5 most recent years for which records are available in terms of pounds of AI, while Table 4 presents this information in terms of number of applications.

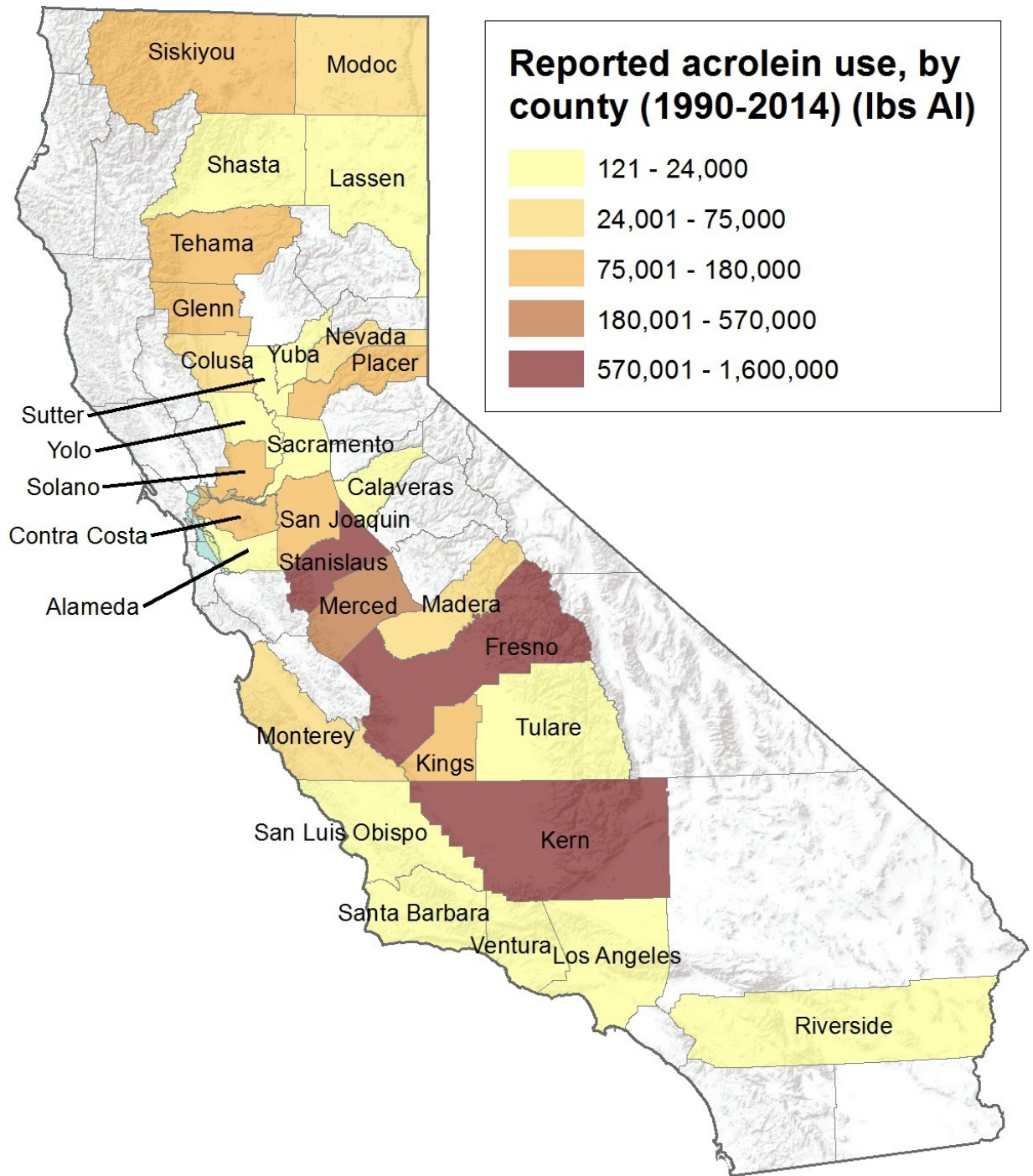


Figure 3: Use of acrolein as reported in PUR by pounds AI applied per county from January 1, 1990 through December 31, 2014

Table 2: Reported use of acrolein by county (pounds of AI applied)

County	Pounds of Acrolein AI Used*					
	2010	2011	2012	2013	2014	2010-2014
Kern	21,800	32,500	44,500	26,600	15,600	141,000
Stanislaus	32,400	27,600	22,800	26,100	23,400	132,100
Fresno	17,700	17,100	14,100	13,100	20,600	82,600
San Joaquin	15,200	8,800	7,900	8,100	10,900	50,900
Glenn	13,300	5,500	8,300	6,100	6,000	39,100
Merced	4,800	1,800	2,000	4,900	3,600	17,100
Contra Costa	3,200	3,600	4,200	5,900	0	16,800
Tehama	3,600	1,100	3,000	3,000	0	10,700
Colusa	7,400	1,100	1,500	300	400	10,600
Siskiyou	2,100	200	2,200	2,000	1,000	7,500
Shasta	1,100	200	1,100	1,100	800	4,400
Santa Barbara	0	700	1,100	1,200	1,100	4,100
Riverside	200	500	1,100	500	700	2,900
Placer	900	900	0	0	0	1,800
San Luis Obispo	0	100	100	100	100	400
Madera	0	0	400	0	0	400
Total	123,700	101,400	114,100	99,000	84,200	522,500

*Rounded to nearest hundred

Table 3: Number of reported acrolein applications by county

County	Number of Applications of Acrolein					
	2010	2011	2012	2013	2014	2010-2014
Kern	20	24	24	20	13	101
Stanislaus	19	18	16	18	10	81
Fresno	17	6	6	5	14	48
Merced	11	8	7	11	9	46
Santa Barbara	0	8	11	12	9	40
San Joaquin	8	6	7	8	6	35
Glenn	7	5	7	6	4	29
Shasta	5	3	7	7	4	26
Siskiyou	7	1	7	7	3	25
Contra Costa	7	4	5	7	0	23
Riverside	1	2	5	3	5	16
Tehama	4	3	1	2	0	10
Colusa	3	1	3	1	1	9
Placer	2	2	0	0	0	4
San Luis	0	1	1	1	1	4
Madera	0	0	2	0	0	2
Total	111	92	109	108	79	499

Examination of the reported use of acrolein by month over the five most recent years for which records are available reveals peak use occurs in July during the years 2010 to 2014, with the exception of 2012 (DPR, 2016b). During the 2012 calendar year reported use of acrolein peaked during June (DPR, 2016b). This is consistent with an increase in algae and aquatic weed growth during the summer months. Evaluation of each year consistently shows peak use during the summer months and little to no use during the winter months, with transitional periods during the spring and autumn months (DPR, 2016b). These monthly trends are represented in Figure 4 and detailed in Table 5.

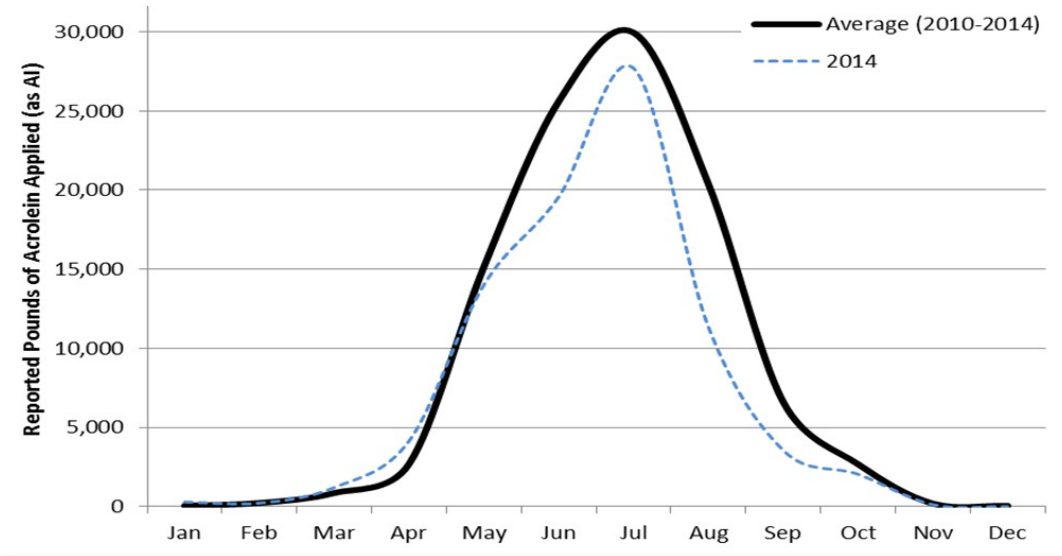


Figure 4: Seasonal use of acrolein in 2014 and averaged across 5 years with most recent data

Table 4: Use of acrolein (pounds AI) by month

Month	Sum of Use per Month by Year (lbs AI)*					Average (2010-2104)
	2010	2011	2012	2013	2014	
Jan	0	0	0	0	300	100
Feb	200	200	500	0	200	200
Mar	700	1,000	300	1,100	1,200	900
Apr	3,100	1,500	2,700	2,100	4,200	2,700
May	10,400	12,200	17,200	21,900	14,000	15,200
Jun	37,200	14,800	32,400	24,100	19,600	25,600
Jul	40,300	32,000	23,500	26,200	27,700	29,900
Aug	21,700	27,000	25,700	16,200	11,300	20,400
Sep	7,800	9,800	6,600	5,400	3,600	6,600
Oct	1,900	2,700	4,800	2,000	2,000	2,700
Nov	400	200	200	0	100	200
Dec	0	0	300	0	0	100

*Rounded to nearest hundredth

3.2 Non-Pesticide Sources of Acrolein

Beyond the use of acrolein as a pesticide, pyrolysis of organic compounds is a major source of atmospheric acrolein (Ghilarducci and Tjeerdema, 1995). Automobile exhaust, cigarette smoke, structural and vegetation fires, emissions from cooking and manufacturing can result in pyrolysis of acrolein (Ghilarducci and Tjeerdema, 1995). The majority of exposure to acrolein is a result of incomplete combustion; thus, the primary route of human exposure will be through inhalation (Ghilarducci and Tjeerdema, 1995). Acrolein also occurs as a product of the photooxidation of hydrocarbon pollutants in the air such as propylene and 1,3-butadiene (Faroon et al., 2008). Additionally, acrolein occurs as a metabolite of allyl alcohol, allylamine, spermine, spermidine, and cyclophosphamide (an anticancer drug) (Ghilarducci and Tjeerdema, 1995).

In 2004 the annual statewide emissions of acrolein from mobile, stationary, and natural sources (which did not include atmospheric transformation of 1,3-butadiene) reported in the California Toxics Inventory were an estimated 2,242 tons, contributing to a statewide ambient level of 0.53 ppb (1.22 $\mu\text{g}/\text{m}^3$) (ARB, 2008b).

4 Environmental Fate and Degradation

4.1 Environmental Fate and Degradation in Air

Tropospheric removal of acrolein is dominated by reaction with free radicals, particularly $\cdot\text{OH}$ (hydroxyl radical) (Ghilarducci and Tjeerdema, 1995). The reactions are likely due to nucleophilic attack on the carbonyl or the β -carbon of the aldehyde and rates are highly dependent on the concentration of free radicals (Ghilarducci and Tjeerdema, 1995). Diurnal variation of $\cdot\text{OH}$ will result in variation of oxidation rates throughout the day (Ghilarducci and Tjeerdema, 1995). Due to this variation measured atmospheric residence times have varied between 13.5 to 20 hours in the presence of hydroxyl radicals (Edney et al., 1981; Lyman *et al.*, 1982). A strong correlation of the concentration of hydroxyl radicals in the troposphere to seasonal variations in solar radiation has also been observed (Rohrer and Berresheim, 2006). These annual hydroxyl radical concentration peaks coincide with the months of highest reported agricultural use of acrolein (Rohrer and Berresheim, 2006; DPR, 2016b). Minor reactions with NO_x and O_3 will also contribute to the removal of atmospheric acrolein (Ghilarducci and Tjeerdema, 1995). Degradates include carbon monoxide, carbon dioxide, formaldehyde, glycoaldehyde, ketene, and peroxypropenyl nitrate (Ghilarducci and Tjeerdema, 1995). The atmospheric degradation pathway of acrolein by photooxidation is shown in Figure 5.

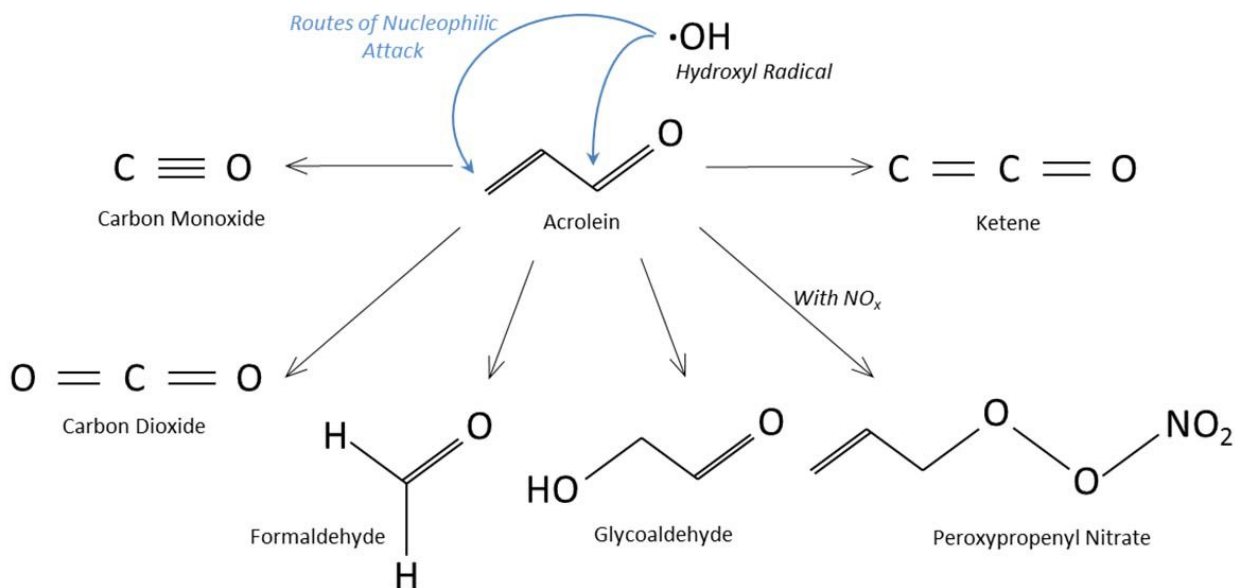


Figure 5: Atmospheric degradation of acrolein by way of photooxidation (adapted from Ghilarducci and Tjeerdema, 1995)

When acrolein in the vapor phase was exposed to light at 313 nm, 193 nm, 250-350 nm, and natural sunlight photolysis occurred with CO , C_2H_4 , $\cdot\text{C}_2\text{H}_3$, and $\text{HCO}\cdot$ as breakdown products (Ghilarducci and Tjeerdema, 1995). Additionally, at 230 nm methylketene has been detected as a photolytic product of acrolein (Johnstone and Sodeau, 1992).

Acrolein has also been detected in small amounts in rainwater, indicating wet deposition as a mechanism of removal from the atmosphere (Grosjean, 1983).

4.1.1 Air Monitoring

In July of 2007 the California Air Resources Board (ARB) conducted monitoring of an application of acrolein to an irrigation ditch west of Lost Hills, CA at the request of DPR (ARB, 2007). Twenty 4.25-hour integrated air samples were collected at distances ranging from 18 to 65 feet from each side, at points from 0 to 1 mile and 3.5 to 4.5 miles downstream of the application (ARB, 2008a). The highest measured concentration was 7.3 ppb ($16.8 \mu\text{g}/\text{m}^3$), followed by 6.8 ppb ($15.6 \mu\text{g}/\text{m}^3$), with a background ambient concentration of 1.0 to 2.0 ppb (2.3 to $4.6 \mu\text{g}/\text{m}^3$) (ARB, 2008a).

The Annual Statewide Toxics Summary released by ARB shows statewide average (mean) annual acrolein concentrations between 0.43 and 0.93 ppb (0.99 to $2.13 \mu\text{g}/\text{m}^3$) (ARB, 2016a). The maximum detected concentration reported in the Toxics Summary is 16 ppb ($36.71 \mu\text{g}/\text{m}^3$) (ARB, 2016a). This data consists of 5,850 observations taken between mid-2003 and 2015 (ARB, 2016a).

In February 2011, DPR began the Air Monitoring Network (AMN), which conducted weekly monitoring of three agricultural communities for multiple pesticides and pesticide breakdown products, which included acrolein (DPR, 2013). Due to the large amount of non-pesticidal sources of acrolein as well as some uncertainty in the use of the analytical method to determinate acrolein concentrations, DPR discontinued monitoring for acrolein as part of the AMN in 2012 (DPR, 2013). With this caveat, the average detected concentration among the monitored communities was 1.2 $\mu\text{g}/\text{m}^3$, with the highest observation, 9.7 $\mu\text{g}/\text{m}^3$, occurring in Salinas in December 2011 (DPR, 2012). These averages are consistent with statewide average levels of acrolein reported in ARB's Annual Statewide Toxics Summary.

Additionally, Magnacide H field air monitoring samples from three test locations were collected in 2002 and were included in US EPA's 2008 Reregistration Eligibility Decision for Acrolein (US EPA, 2008). Air monitoring results from this study ranged from not detected to 63 ppb. The 63 ppb concentration however, was reported as the result of an apparent equipment leak during the air monitoring period.

4.2 Environmental Fate and Degradation in Soil

Acrolein is weakly adsorbed to soil as indicated by a soil sorption coefficient (K_{oc}) value of 0.5 mL/g (Shaner, 2014). As such, volatilization is predicted from dry soil while extensive leaching is predicted in moist soil (Howard, 1989). In sediment, both aerobic and anaerobic degradation appear to share hydrolysis as an early step (Shaner, 2014). Half-lives of 4.2 hours were observed in aerobic soil conditions, while 11 days was observed in anaerobic soil conditions (Shaner, 2014).

4.3 Environmental Fate and Degradation in Water

In natural waters, at rates suggested for herbicidal use, acrolein persisted up to 6 days, depending on temperature (Ghilarducci and Tjeerdema, 1995). In one study, an application to an irrigation canal and lateral infested with aquatic plants at the highest label permitted rate resulted in a concentration of 15 ppm for a period of 2 hours, and calculated dissipation half-lives of 275 minutes in the canal, and 54 minutes in the lateral (Faroon et al., 2008). Other studies have reported half-lives as high as 21 days which was observed to be temperature dependent, 10 hours in weeded canals, and 7.5 hours in non-weeded canals (Ghilarducci and Tjeerdema, 1995; Shaner, 2014).

Volatilization of acrolein is one of the major removal processes for acrolein in surface water (Ghilarducci and Tjeerdema, 1995). One study measured 10% volatilization of initial concentrations of a combination of aldehydes, including acrolein (Bowmer *et al.*, 1974). However a lack of turbulence may result in the figure from this study being lower than those occurring under field conditions (Bowmer *et al.*, 1974).

Though not the only means of elimination in aquatic systems, reversible, first-order hydration appears to be a significant pathway (Ghilarducci and Tjeerdema, 1995). Ninety-two percent of acrolein was found to exist in the hydrated form, 3-hydroxypropanal, under laboratory

conditions at 20°C (Bowmer *et al.*, 1974). Photolysis of acrolein is not expected due to this hydration resulting in the elimination of chromophores (Mabey, 1982).

In water, acrolein can be oxidized or reduced to form acrylic acid or allyl alcohol, respectively (Figure 6) (Shaner, 2014). Further reaction yields oxalic acid and carbon dioxide. The half-life of acrolein in water is subject to temperature and pH (Shaner, 2014). Acrolein does not contain any hydrolyzable groups (Ghilarducci and Tjeerdema, 1995).

Acrolein is also subject to downstream movement in irrigation canals and was detected at concentrations as high as 100 µg/L measured 64 km downstream of the point of application (Ghilarducci and Tjeerdema, 1995).

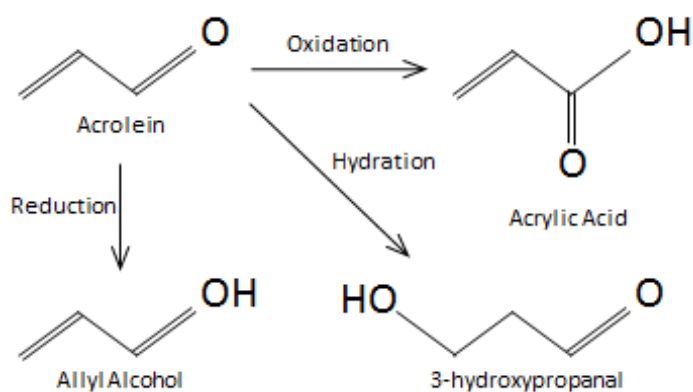


Figure 6: Degradates of acrolein in water

4.3.1 Aquatic Organisms

Reversible hydration to 3-hydroxypropanal will also cause acrolein to be available for removal via biotransformation (Ghilarducci and Tjeerdema, 1995). A significant degree of biodegradation of acrolein or 3-hydroxypropanal appears to occur (Ghilarducci and Tjeerdema, 1995). Comparison of acrolein degradation in sterilized and unsterilized water produced half-lives of 43 hours and 29 hours, respectively (Ghilarducci and Tjeerdema, 1995).

Acrolein is toxic to fish and wildlife (Shaner, 2014). Control of aquatic plants is the main use of acrolein (Ghilarducci and Tjeerdema, 1995). This is accomplished through destruction of the integrity of cell membranes through its reactivity (Ashton and Crafts, 1981). Enzyme systems in the cell may also be disrupted by the affinity of acrolein for sulfhydryl groups (WSSA, 1983). These effects occur in species such as water hyacinth (*Eichhornia crassipes*) at concentrations as low as 50-600 ppm (Ghilarducci and Tjeerdema, 1995). These effects are temperature dependent, occurring more rapidly at higher temperatures (Ghilarducci and Tjeerdema, 1995).

The physical and chemical properties of acrolein suggest low potential for bioaccumulation (Ghilarducci and Tjeerdema, 1995). Bioconcentration factor estimated from K_{ow} is 0.6 (Lyman *et al.*, 1982).

5 Regulation

Acrolein is a Restricted Use Pesticide (RUP) due to its high acute toxicity (U.S.EPA, 2008). RUP status means that the pesticide has been deemed to have a higher than average potential for harm to public health, workers, domestic and wild animals, other crops, and the environment (DPR, 2016c). Due to this potential for harm, with some exceptions, restricted use pesticides must be purchased and applied by or under the supervision of a certified applicator with a time and site specific permit from the County Agricultural Commissioner (CAC) (DPR, 2016c). This allows the CAC to assess the potential effects, prior to the application of the RUP (DPR, 2016c). These permits may be denied, or feasible alternatives may be required by the CAC (DPR, 2016c).

Use of acrolein as a pesticide is regulated nationally under the Federal Insecticide, Fungicide, Rodenticide Act (FIFRA) and was first registered by the U.S.EPA in 1959 (U.S.EPA, 2008). Acrolein was first publicly used as an herbicide in 1960 (Ghilarducci and Tjeerdema, 1995). In California there are two active registrations of products containing acrolein as an active ingredient which date to 1970 and 1972 (DPR, 2016d).

ARB recognized acrolein as a toxic air contaminant (TAC)¹ in 1993, in accordance with the California Health & Safety Code Division 26 §39657(b) (ARB, 2008b). Even earlier, acrolein was listed as a federal hazardous air pollutant (HAP) under the Clean Air Act (42 U.S.C. Section 7412(b)) (ARB, 2016b). Additionally, OEHHA lists acrolein as a TAC that may disproportionately impact children, in accordance with Cal. Health & Safety Code Div. 26 §39669.5 (ARB, 2008b).

At the federal level, the US Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit (PEL) of 0.25 mg/m³ time weighted average (TWA) for 8-hour periods in maritime, construction, and general occupational settings (OSHA, 2016).

Additionally, section 202(l)(2) of the Clean Air Act requires US EPA to set standards to control HAPs from motor vehicles, motor vehicle fuels, or both (US EPA, 2007). To meet this requirement US EPA issued a rule² in 2007 to finalize standards to reduce acrolein alongside other Mobile Source Air Toxics (MSATs) (US EPA, 2007). MSATs account for 74% of the outdoor non-cancer (respiratory) risk evaluated in the National-Scale Air Toxics Assessment (NATA) conducted by US EPA in 1999 (US EPA, 2007). Acrolein accounts for the majority of this risk, followed by formaldehyde (US EPA, 2007). Sources of MSATs include motor vehicles, aircraft, locomotives, ships, as well as the engines of non-road equipment used in lawn, garden,

¹The Cal. Health & Safety Code Div. 26 §39655 defines a TAC as an air pollutant which may cause or contribute to an increase in mortality or in serious illness, or which may pose a present or potential hazard to human health

²40 CFR Parts 59, 80, 85, and 86; [EPA-HQ-OAR-2005-0036; FRL-8278-4] "Control of Hazardous Air Pollutants From Mobile Sources"

farming, and construction (US EPA, 2007). These MSATs present increased risk to those in vehicles, near roads, or in homes with attached garages (US EPA, 2007). The specific standard relating to combustion products limits emissions from passenger vehicles during operation at cold temperatures (US EPA, 2007). Previously, testing of non-methane hydrocarbon was typically performed at 75°F while the new standard will lower this to 20°F (US EPA, 2007). This was phased in from 2010 to 2013 for lighter vehicles and 2012 to 2015 for heavier vehicles (US EPA, 2007). These finalized standards are projected to reduce acrolein as a MSAT by 317 tons in the year 2020 (US EPA, 2007).

6 Summary

Acrolein has several sources beyond its use as a pesticide. Foremost among these is incomplete combustion of organic compounds. Reported agricultural use of acrolein as a pesticide has followed a decreasing trend since 2000. Reported use of acrolein has been dominated by applications to rights-of-way in both terms of pounds applied (as AI) and number of applications. Kern County, followed by Stanislaus and Fresno Counties, had the highest use during the period 2010-2014 in terms of both pounds of acrolein (as AI) and number of applications.

Once applied, some volatilization of acrolein to the atmosphere is likely from aquatic environments. In the atmosphere degradation is likely to be dominated by photooxidation, specifically by hydroxyl radicals. The periods of highest use of acrolein coincides with the yearly peak concentrations of these radicals which serve to degrade it. Observed atmospheric half-lives range from 13.5 to 20 hours. Low measured half-lives in experiments conducted in aquatic Californian conditions, as well as atmospheric conditions indicate a low environmental persistence of acrolein.

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