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Fresno, Kings, Madera & Tulare Counties

AGRICULTURAL PERSONNEL MANAGEMENT PROGRAM

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Environmental Concerns Part of Pesticide Handler Training

California employers must assure employees handling pesticides have been trained according to Title 3 CCR, Subchapter 3 "Pesticide Worker Safety." Section 6724 requires that training for each pesticide or *chemically similar group* must cover, among other subjects, "environmental concerns such as drift, runoff, and wildlife hazards." Similarly, **federal** regulations (40 CFR Part 170 § 170.230) require that pesticide safety training for handlers convey information on "environmental concerns such as drift, runoff, and wildlife hazards" – as one of thirteen prescribed topics.

This writing provides a reference for pesticide safety instructors and/or farm managers relating to ***pesticides' environmental hazards****. In 2002, California had about 920 registered pesticide active ingredients used in approximately 12,038 pesticide products; a year earlier, 890 active ingredients were registered for use in 11,592 products.*

Aside from product labels, Material Data Safety Sheets (MSDSs) may provide *precautionary* ecological information. Although the American National Standards Institute and the Chemical Manufacturers Association both recommended inclusion of ecotoxicity data for fish, invertebrates, plants, and microorganisms, OSHA does not mandate this information as part of MSDSs. In some cases, though, manufacturers do include "ecological" toxicity data and sometimes information on persistence and degradation, soil mobility, bioaccumulation, and photochemical degradation by sunlight. Some manufacturers simply say "data not given" or "data not available" (usually MSDS Section 12). Others advise that you write or call for this information.

Many MSDSs and product labels are at http://www.cdms.net/pfa/LUpdateMSG.asp. Supplemental *ecological* and other technical information for many pesticides has been organized by cooperative extension services (with one-time USDA funding) as Pesticide Information Profiles (PIPs) at http://ace.orst.edu/info/extoxnet/pips/ghindex.html. (This site still gets over 1.5 million hits per year.)

Some MSDSs contain ecological information in plain-English. Here is **part** of the Section 12 *Summary of Effects* for an insecticide product with active ingredient **endosulfan**. *This pesticide is toxic to fish, birds, and other wildlife. Birds feeding on treated areas may be killed… Due to the risk of runoff and drift, do not apply within a distance of 300 feet of lakes, ponds, streams… Do not contaminate water by cleaning of equipment or disposal of equipment wash waters. This product must not be used in areas where impact on threatened or endangered species is likely...* [In California, use of endosulfan and other pesticides is regulated through the restricted materials permit program administered on the local level by the county agricultural commissioners. USEPA Endangered Species Protection "Interim Measures Bulletins" for each California county are at http://www.cdpr.ca.gov/docs/es/index.htm.]… *This product is toxic to bees exposed to direct application. Applications should be timed to coincide with periods of minimum bee activity, usually between late evening and early morning.*

Some manufacturers add *technical* measures of fish, avian, bee and other organism toxicity to precautionary text in Section 12. For example, one company reports the following data for a pesticide product with active ingredient endosulfan.

***Fish** Toxicity:* *96 hour LC_{50} Rainbow trout – 1.4 µg/L*
96 hour LC_{50} Bluegill – 1.2 µg/L
***Bee** Toxicity:* *Moderately toxic.*

***Avian** Toxicity:* *Oral LD_{50} Bobwhite quail – 800 mg/Kg*
Oral LD_{50} Mallard duck – 220 mg/Kg
NOTE: *One µg/L (microgram per Liter) = .001 mg/L = 1 part per billion*

(LC_{50} is the statistically derived estimate of concentration expected to cause 50% lethality. LD_{50} is the statistically derived estimate of oral dose expected to result in 50% lethality.) Following are active ingredient toxicity ranges for certain wildlife classes.

Bird: Acute Oral (mg/kg) LD_{50}	
Practically Nontoxic	>2000
Slightly Toxic	501-2000
Moderately Toxic	51-500
Highly Toxic	10-50
Very Highly Toxic	<10

Bird: Dietary (ppm in diet) LD_{50} (8-day)	
Practically Nontoxic	>5000
Slightly Toxic	1001-5000
Moderately Toxic	501-1000
Highly Toxic	50-500
Very Highly Toxic	<50

Fish: (ppm – mg/L) LC_{50} (96-hour)	
Practically Nontoxic	>100
Slightly Toxic	10-100
Moderately Toxic	1-10
Highly Toxic	0.1-1
Very Highly Toxic	<0.1

Bee:		
Highly Toxic:	*(LD_{50} = 0.001 to 1.99 µg/bee)*	Kills on contact during application and for one or more days after.
Moderately Toxic:	*(LD_{50} = 2.0 to 10.99 µg/bee)*	Kills bees if applied over them. Can be used with limited danger to bees if not applied over bees in the field or hives. Correct dosage, timing, and method of application are essential.
Practically Nontoxic:		Relatively nontoxic. Can be used with few precautions with minimum injury to bees.

Persistence … The soil *half-life* is a measure of the persistence of a pesticide in soil. Pesticides can be categorized on the basis of their half-life as nonpersistent, degrading to half the original concentration in less than 30 days; moderately persistent, degrading to half the original concentration in 30 to 100 days; or persistent, taking longer than 100 days to degrade to half the original concentration. A "typical soil half-life" value is an approximation and may vary greatly because persistence is sensitive to variations in site, soil, and climate. The *PIP* for **carbaryl** says this about *environmental fate*:

- *Breakdown in soil and groundwater: Carbaryl has a **low** persistence in soil. Degradation of carbaryl in the soil is mostly due to sunlight and bacterial action. It is bound by organic matter and can be transported in soil runoff. Carbaryl has a half-life of 7 to 14 days in sandy loam soil and 14 to 28 days in clay loam soil. Carbaryl has been detected in groundwater in three separate cases in California.*
- In contrast, the *PIP* for **endosulfan** says: *Endosulfan is **moderately** persistent in the soil environment with a reported average field half-life of 50 days. The two isomers have different degradation times in soil. The half-life for the alpha-isomer is 35 days, and is 150 days for the beta-isomer under neutral conditions. These two isomers will persist longer under more acidic conditions. The compound is broken down in soil by fungi and bacteria.*

Bio-accumulation … is the absorption and concentration of a chemical in plants or animals. A measure of the tendency for a chemical to accumulate is the bioconcentration factor, the ratio of the concentration of a substance in a living organism (mg/kg) to the concentration of that substance in the surrounding environment (mg/l for aquatic systems).

The bioaccumulation for **endosulfan** may be significant; in the mussel (Mytelus edulis) the compound accumulated to 600 times the ambient (background) water concentration.

Water solubility … If an active ingredient is water soluble it is not apt to remain in one place or one organism, but may percolate through living and inert materials into ground and surface water, traveling as far as its persistence in original form or transformation products will allow it. *Scales* for rating solubility of toxic materials vary. The key is **how much** must be taken up by the solvent to be hazardous to water resources and organisms exposed to it.

From an environmental perspective, only materials with solubility (at 20 to 30°C) of less than 1 part per million (1 mg/L) are deemed *insoluble*. (Endosulfan has a solubility of only .32 ppm.) Slightly soluble pesticides range from 1 to 100 mg/L; soluble from 100 to 10,000 mg/L; pesticides with solubility over 10,000 mg/L are considered *very* soluble.

Water solubility of active ingredients on California's "Section 6800(a)" list that have been found in groundwater — due to *legal* agricultural use — range from 5 mg/L **(simazine)** to 33,000 mg/L **(hexazinone)**. The current "groundwater list" is part of regulations at http://www.cdpr.ca.gov/docs/inhouse/calcode/chapter_.htm.

Pesticide *breakdown products* have different characteristics (but may have similar or greater toxicity) than the parent material. **Mancozeb** has a water solubility of only 6 mg/L. However, its major metabolite, **ETU** (ethylenethiourea), has greater tendency to be mobile due to its high water solubility and weak adsorption in soil. ETU (a potential groundwater contaminant) is characterized as a carcinogen, mutagen (chromosome damage), teratogen (embryo damage), and goiterogen (thyroid damage). The solubility of a pesticide and its adsorption (attachment) to soil particles are inversely related. This means that as solubility increases, its adsorption decreases.

Soil sorption … One of the most useful indices for quantifying pesticide sorption on soils is the partition coefficient (K_{oc}). The K_{oc} value is the ratio of pesticide concentration in the sorbed-state (that is, bound to soil particles) and the solution-phase (that is, dissolved in the soil-water). Thus, for a given amount of pesticide applied, the smaller the K_{oc} value, the greater the concentration of pesticide in solution. Pesticides with small K_{oc} values are more likely to be leached compared to those with large K_{oc} values.

K_{oc} values of *less than 500* indicate little or no adsorption and a potential for leaching. K_{oc} values (sandy loam) for **simazine** and **hexazinone**, both on the "groundwater protection list" are 114 and 54, respectively. Both are moderately persistent in soil. When considering the impact on groundwater, half-lives and K_{oc}s are particularly important when: (1) the application site of a pesticide has soils with low organic matter; the site is underlain with very permeable subsoil or a high water table; or (3) when fractured or porous bedrock is located at a shallow depth under the application site.

Pesticides in surface water … From 1992-95, the U.S. Geological Survey detected seven pesticides at levels exceeding criteria for aquatic life in the San Joaquin-Tulare Basins. These pesticides were herbicides **diuron** and **trifluralin**, and insecticides **azinphos-methyl**, **carbaryl**, **chlorpyrifos**, **diazinon**, and **malathion**. Forty percent of these exceedances were attributed solely to diazinon. http://water.usgs.gov/pubs/circ/circ1159/ Most of these active ingredients have "low" or "very low" pesticide *movement ratings* (to groundwater), and **high** K_{oc} measures (median 1,000), based on the OSU Extension pesticide properties database at http://ace.orst.edu/info/npic/ppdmove.htm (another helpful reference).

Air Quality Issues

Volatility … Many pesticides can escape from soils as gases. Some can be drawn from the soil and enter the atmosphere with evaporating water. Pesticide particles in the atmosphere can come back to earth in rain, snow, or dust fall. They then can leach into ground water or be carried by runoff into surface water. Airborne transport of pesticides is probably the principal method for their widespread dispersion in the environment.

Vapor pressures on MSDSs are usually stated in millimeters of mercury (mmHg) at 20°C (68°F). [1 mmHg=133,000 mPa (milliPascals)] The higher the vapor pressure, the greater the material's tendency to evaporate into the atmosphere. The vapor pressures of most pesticides will change with temperature to a degree equivalent to an increase in volatility of about *three to four times* for each 10°C increase in temperature. A scale for rating volatility follows.

Volatility Rating	Vapor Pressure at 20 to 30°C (room temperature)
Nonvolatile	Less than 1 x 10^{-7} mmHg (.0000001 millimeters of mercury)
Slightly volatile	10^{-7} to 10^{-4} mmHg (.0000001 to .0001 mmHg)
Volatile	10^{-4} to 10^{-2} mmHg (.0001 to .01 mmHg)
Highly volatile	Greater than .01 mmHg

The vapor pressure for **1,3-dichloropropene** is 28 mmHg at 25°C (77°F); **for metam-sodium** it is 24 mmHg. Both soil fumigants are on California's "Toxic Air Contaminant List" (amended 2003). TAC pesticides are those determined to be "an air pollutant that may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health."

Crop producers *pulling their weight* in cleaning the air… The reported pounds of pesticides used on DPR's TAC list in the eight-county **San Joaquin Valley Unified Air Pollution Control District** trended from 22,145,530 in 1995 to 10,837,669 in 2001 – a **marked** decline of 51 percent over the period. In contrast, the number of jobs in the air management district's agricultural production industry (annual average) fell only 3% from 1995 to 2001 (California Employment Development Department). In 2001, TAC pesticides made up **only 13%** of total pesticides used in the SJV air basin, down from 18% in 1995. The table below shows changes in use and the "commodities" that accounted for over 50 percent of use of each TAC pesticide in 2001.

TAC active ingredient	Action	Use: 1995	2001	% change	Major "commodities"
metam-sodium	Fumigant	9,131,528	4,968,824	-46	tomato (processing), carrot
1,3-dichloropropene	Fumigant	376,770	2,482,643	+559	preplant, sweet potato
methyl bromide	Fumigant	6,782,766	1,040,632	-85	preplant, nursery (outdoor)
trifluralin	Herbicide	924,521	481,246	-48	cotton, alfalfa
chlorine	Bactericide	592,308	293,648	-50	carrot packing sheds
tribufos	Defoliant	861,619	242,099	-72	cotton (100%)
acrolein	Herbicide	264,932	199,905	-25	rights-of-way, water area
maneb	Fungicide	548,622	180,786	-67	almond, lettuce
carbaryl	Insecticide	1,194,207	176,975	-85	orange, tomato, apple
mancozeb	Fungicide	355,240	164,812	-54	grape, tomato, potato
Other		1,113,017	606,099	-46	
Total		**22,145,530**	**10,837,669**	**-51**	

Includes counties of Fresno, Kern, Kings, Madera, Merced, San Joaquin, Stanislaus, and Tulare. (Land area totals 24,843 square miles.)

Significant *counter-trends* … Although pounds of TACs dropped notably in the San Joaquin air basin from 1995 to 2001, pounds of metam-sodium used in Merced County jumped 75% (83,029 lbs.) in processing tomatoes. In Kings County, use of metam-sodium in dry onions and processing tomatoes increased by 207,128 pounds or 2.5 times. Also in Merced County, use of 1,3-dichloropropene has grown from 61,707 lbs. in 1995 to 513,936 lbs. (2001) in sweet potatoes.

Another air issue ... Many pesticide products contain **volatile organic compounds** (VOCs) that contribute to the formation of smog. The DPR has worked with the state Air Resources Board to put together a State Implementation Plan under the federal Clean Air Act to reduce emissions of all sources of VOCs, including pesticides, in *non-attainment air basins* of the state. DPR's contribution to the plan included accurate data on the amount of VOCs in pesticides and the ability to inventory the use of those pesticides through pesticide use reporting. Pesticide use reporting data are at http://www.cdpr.ca.gov/docs/pur/purmain.htm.

In the San Joaquin Valley air basin, the active ingredients contributing 60% of VOC emissions in 2001 were (1) **metam-sodium** (Vapam), (2) **1,3-dichloropropene** (Telone), (3) **methyl bromide**, and (4) **chlorpyrifos**. Rounding out the top ten contributors to 2001 VOC emissions in the SJV are (5) **oxyfluorfen**, (6) **glyphosate** (isopropylamine salt), (7) **trifluralin**, (8) **pendimethalin**, (9) **acrolein**, and (10) **sulfur**. Approximately 90% of pesticide VOC emissions were attributable to agricultural use as compared to 10% from commercial structural pesticide applications.

The pesticide VOC inventory is calculated annually each year using pesticide product emission potential (EP) data. The EP is that fraction of a product that is assumed to potentially contribute to the atmospheric VOCs. The EPs for fumigant products with active ingredients 1,3-dichloropropene and methyl bromide are generally 100 percent. Median EP of 18 products with active ingredient metam-sodium, however, was only 24%. Metam-sodium and 1,3-dichloropropene are pesticides known to the State of California to cause cancer (on the Proposition 65 list). Metam-sodium is also listed as a chemical known to cause birth defects or reproductive harm.

References: Crop Protection Handbook, Meister Publishing Co., 2003; and Basic Guide to Pesticides - Their Characteristics and Hazards, Rachel Carson Council, 1992.

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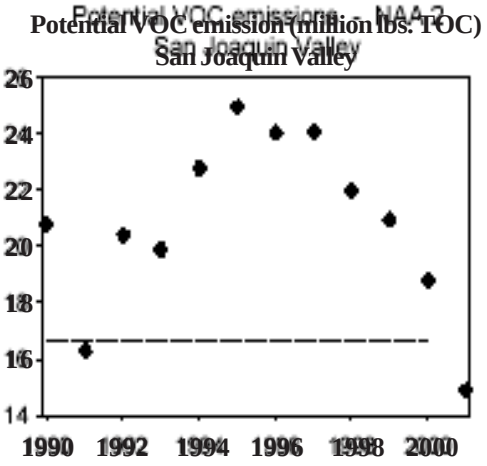
Estimated EPs for products containing the herbicide chlorpyrifos varied considerably among products and formulations. The EPs for products containing chlorpyrifos ranged from none to 51%. The most popular product used in 2001 containing chlorpyrifos (Lorsban 4-E) has an EP of 51%. Chlorpyrifos is used mainly in cotton, almonds, and alfalfa, and is one of several organophosphates detected in 2000 in trace amounts in frogs in west-facing habitats in the high Sierras near Yosemite.

Total pounds of chlorpyrifos used in the 8-county San Joaquin Valley air basin dropped from 2,401,537 pounds in 1995 to 1,036,131 pounds in 2001 – **a decline of 60 percent**.

Although 10,699,044 pounds of "petroleum oil, unclassified", were used as pesticides in the SJV air district in 2001 (down 9% from 1995), the EPs for these products are all under 2%.

More good news ... The Pesticide Potential Volatile Organic Compounds Emissions decline to a level of 13.9 million pounds Total Organic Gases (TOG) in 2001 **achieves,** for the first time, the 2005 goal of 80% of estimated 1990 emission levels. The downward trend for the San Joaquin Valley, and estimated 2001 emissions by month, are charted in a DPR summary memo at http://www.cdpr.ca.gov/docs/pur/vocproj/vocsumm.htm. However, it's clear that future (permitted) fumigant use in the San Joaquin Valley will play a major role in determining if pesticide VOC emissions "stay on target."



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Sincerely,

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