USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT 2,4-DICHOROPHENOXYACETIC ACID DIMETHYLAMINE SALT (2,4-D DMAS)

June 2013

By
Shifang Fan
Environmental Scientist

STATE OF CALIFORNIA
Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, California, 95814

USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT 2,4-DICHLOROPHENOXYACETIC ACID DIMETHYLAMINE SALT

A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-D dimethylamine salt (2,4-D DMAS), and the reported historical uses as pesticides in California. The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

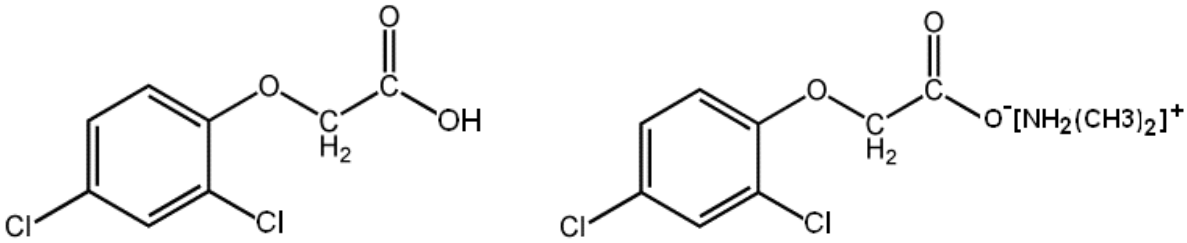
Physical-Chemical Properties

2,4-D is a chlorinated phenoxy compound (Figure 1a). It has been used since 1948 as a systemic herbicide by causing uncontrolled cell division in vascular tissue (NPIC, 2010). 2,4-D selectively controls a wide variety of broadleaf weeds and aquatic weeds in cultivated crops, pasture, rangeland, forest, parks, home garden, and aquatic vegetation.

2,4-D is a weak acid. There are many 2,4-D derivatives such as various 2,4-D acids, esters, amines, and other salts which vary in their physical and chemical properties and environmental behaviors. Each derivative is a different active ingredient (a.i.) of a range of pesticide products. When most of these derivatives are applied to different field and aquatic environments, the parent herbicidal 2,4-D is one of their initial degradation products.

Among all 2,4-D derivatives, 2,4-D DMAS is the one predominantly used in California agricultural practice. This recommendation is focused on fate of 2,4-D DMAS in air unless otherwise specified in the context. Chemical structure of 2,4-D DMAS is depicted in Figure 1b.

Figure 1. Chemical structure of 2,4-D and 2,4-D DMAS



a. 2,4-D b. 2,4-D DMAS

2,4-D is white to brownish crystalline solid and 2,4-D DMAS are formulated as crystal, powder, or liquid. Both 2,4-D DMAS and 2,4-D were water soluble and non-volatile. Based on their vapor pressures and Henry's law constants (Table 1), 2,4-D DMAS is more soluble and slightly lower in vapor pressure than 2,4-D. The solubility is pH dependent (Table 1). In USEPA's document, vapor pressure,

Henry's law constant and octanol/water partition coefficient for 2,4-D DMAS are "Not reported. Dissociates rapidly to acid" (USEPA, 2004).

Table 1, Physical and chemical properties of 2,4-D and 2,4-D DMAS

Common Name	2,4-D	2,4-D DMAS
Chemical Name	2,4-dichlorophenoxyacetic acid	2,4-dichlorophenoxyacetic acid dimethylamine salt
Chemical Name (IUPAC)	(2,4-dichlorophenoxy)acetic acid	2,4-D-dimethylammonium
CAS Registry Number	94-75-7	2008-39-1
EPA Chemical Code	030001	030019
DPR Chemical Code	636	806
Chemical Family	Chlorophenoxy herbicide	Chlorophenoxy herbicide
Chemical Formula	C8H6Cl2O3	C10H13Cl2O3N
Molecular Mass	221.04	266.12
Usage	Herbicide	Herbicide
Physical Form	Crystalline solid[NPIC]	Crystal or powder[APVMA, 2004] Aqueous liquid[NPIC]
Color	White to brown[NPIC]	white to brown[APVMA, 2004] Amber[NPIC]
Odor	Odorless	Slight amine odor
Melting point	140.5 ^{o}C	85-87 ^{o}C
Solubility (25 ^{o}C)	27.6 g/l[DPR] pH5: 29.9 g/l[NPIC] pH7: 44.6 g/l[NPIC] pH9: 43.1 g/l[NPIC]	657 g/l[DPR] pH5: 321 g/l[NPIC] pH7: 729 g/l[NPIC] pH9: 664 g/l[NPIC]
Vapor pressure (25 ^{o}C)	1.4×10^{-7} mmHg[DPR]	1.0×10^{-7} mmHg[DPR]
Henry's Law Constant* (25 ^{o}C)	1.5×10^{-12} atm-m^3/mol	5.3×10^{-14} atm-m^3/mol
Octanol/water partition coefficient (log K_{OW})	pH5-7: 0.092-2.14[DPR] pH5: 2.14[NPIC] pH7: 0.177[NPIC] pH9: 0.102[NPIC]	<1[DPR] pH5: 2.14[NPIC] pH7: 0.177[NPIC] pH9: 0.102[NPIC]
Adsorption coefficient (Koc)	45.5 cm^3/g[DPR] 20-136[NPIC]	45.5 cm^3/g[DPR] 72-136[NPIC]

NPIC: National Pesticide Information Center. 2,4-D technical fact sheet http://npic.orst.edu/factsheets/2,4-DTech.pdf

DPR: Department Pesticide Regulation. Pesticide chemistry database. http://em/docs/pubs/chem/allchems_pestchem.pdf and http://environmental-monitoring/pestchem/onecompoundoutput.cfm

*Henry's law constant is calculated from vapor pressure and the solubility values reported by DPR.

[†]Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

Environmental Fate

2,4-D DMAS exits in environments only due to pesticide applications or contaminations. It is not persistent under most environmental conditions. After being applied to field or aquatic environments, 2,4-D DMAS rapidly (<3 minutes) dissociates to 2,4-D and dimethyl ammonium. In many instances this conversion occurred in the pesticide tank mix. Analytical methods are unable to separate 2,4-D DMAS from 2,4-D in field studies. Therefore, 2,4-D data is used as a surrogate for 2,4-D DMAS environmental fate data (USEPA, 2004). In the following fate discussion the term 2,4-D DMAS/2,4-D will be used for the 2,4-D DMAS.

The main transformation (degradation) routes of 2,4-D DMAS/2,4-D in the environment are biological or abiological dissociation, hydrolysis, oxidation, and photolysis. The main transportation routes are application drift, precipitation, run off, and leaching.

The primary source of 2,4-D DMAS/2,4-D in air is through application drift. In the USEPA's risk assessment for 2,4-D, spray drift exposure is assumed to be 1% of the application rate from ground and overhead chemigation applications, 5% from aerial, airblast, and forced-air applications with an application efficiency of 60%. Drift is assumed not to occur with granular pesticides applications (USEPA, 2005).

A field study of 2,4-D drift showed that 3 to 4% of the material sprayed drifted as droplets and no significant amount was found in vapor or particulate samples (Grover, et al., 1972). In another field study, dimethylamine and diethylamine salts of 2,4-D were applied at a rate of 1.9 lb/ac of active ingredient at spray heights of 10 feet and crosswinds of 2 to 16 mph, were detected at concentrations of 0.17 to 0.20 mg/filter 200 feet downwind from the application site (USEPA, 2004). In a study of control on Eurasian watermilfoil and drift of 2,4-D DMAS, the drift was enough in one of the two test plots to reduce the effectiveness of the 2,4-D DMAS application (Julin and Harry, 1986).

Small amounts of 2,4-D that get into the air is subject to photo-oxidation with hydroxyl radicals with estimated half-life of one day. 2,4-D in the air may also dissolve into water droplets and deposit back to the ground (Walters, 1999).

Microbial oxidation and mineralization of 2,4-D in soil involves hydroxylation, cleavage of the acid side-chain, decarboxylation, and ring opening (NPIC, 2010). Soil degradates include 2,4-DCP and 2,4-dichloroanisol (2,4-DCA) or incorporate into soil organic matter and microbial biomass. The major volatile degradate from soil is CO_2 (USEPA, 2004). 2,4-D photodegradation half-life in soil was 68 days. Photodegradates of 2,4-D were identified as 1,2,4-benezenetriol (37% of applied) and CO_2 (25% of applied) (USEPA, 2004).

B. 2,4-D DMAS PESTICIDE USE IN CALIFORNIA

Currently, 258 products containing the active ingredient 2,4-D DMAS are actively registered in California. Formulations include liquid concentrate, emulsifiable liquid concentrate, flowable concentrate, soluble powder, dust/powder, granular/flake, etc. Table 2 summarizes active ingredient content and maximum label application rate for major 2,4-D DMAS products currently used in California. 2,4-D DMAS can be applied with aircraft, helicopter, backpack sprayer, band sprayer, boom

sprayer, granule applicator, hand held sprayer, injection equipment, tractor-mounted granule applicator, and tractor-mounted sprayer, etc. Application methods include ground, aerial, airblast, and chemigation, etc. Timing of 2,4-D DMAS application includes pre-emergence, emergence, post-emergence, pre-harvest, and pre-plant, etc.

Statewide use of 2,4-D DMAS from 2008 to 2010 was 1,292,027 pounds (DPR, 2010). The annual use ranged between 410,000 and 450,000 pounds. The top eight use counties were Kings (11.9%), Imperial (11.5%), Fresno (10.7), Stanislaus (9.5%), San Joaquin (7.3%), Merced (6.9%), Tulare (6.4%), and Solano (5.0%). The annual use of the top eight counties accounted for 68% to 71% of the statewide annual use (Table 3). Table 4 lists 2,4-D DMAS use by total pounds of active ingredient applied to the top 10 crops. The top five use crops were almond (23.1%), wheat (19.3%), uncultivated agricultural areas (10.6%), walnut - English walnut and Persian walnut (3.6%), and grapes (3.6%). The top five use months were February (35.2%), January (15.3%), March (15.0%), April (7.1%), and June (7.1%) (Table 5). About 73.3% of the statewide use was by ground applications and 26.1% by aerial applications (Table 6). Figure 3 shows the estimated cumulative percentile distribution for the pounds of active ingredient used, treated acreage, and application rate of individual 2,4-D DMAS applications during 2008-2010.

Table 2. Summary of active ingredient content and maximum application rate for 2,4-D DMAS products at annual use of 4000 pounds or higher during 2008-2010 in California

Product	**Active ingredient** %	**Maximum label rate** (pounds a.e.*/acre)
NUFARM WEEDAR 64 BROADLEAF HERBICIDE	46.8	4
RIVERDALE DRI-CLEAN HERBICIDE	96.9	5
AMINE 4 2,4-D WEED KILLER	46.5	4
RIVERDALE SOLUTION WATER SOLUBLE	96.9	5
ORCHARD STAR	46.8	2
WEEDAR 64 BROADLEAF HERBICIDE	46.8	4
2, 4-D AMINE 4 HERBICIDE	46.8	4 8 (right of way)
NUFARM ORCHARD CLEAN 4L BROADLEAF HERBICIDE	46.8	4
AGRISOLUTIONS 2,4-D AMINE 4	47.3	4
ORCHARDMASTER CA BROADLEAF HERBICIDE	33.2	1.4
GORDON'S ORCHARD MASTER CA BROADLEAF HERBICIDE	33.2	1.4
SABER CA	46.6	4
SOLUTION WATER SOLUBLE	96.9	5

*acid equivalent-the acid portion of the active ingredient (as in this case 2,4-D of 2,4-D DMAS, for example) or the portion of a pesticide formulation that could be theoretically converted back to or yield of the corresponding or parent acid, the herbicidal active portion of the formulation. The acid equivalent for each formulation is indicated on the product label.

Table 3. Annual 2,4-D DMAS use by county in years of 2008-2010
(Pounds of Active Ingredient)

County/Year	2008	2009	2010	Total
Kings	54,874	45,920	53,172	153,966
Imperial	54,896	49,879	44,366	149,141
Fresno	41,973	45,582	51,082	138,637
Stanislaus	37,782	41,679	43,369	122,830
San Joaquin	28,812	26,649	38,476	93,937
Merced	23,823	27,664	37,674	89,160
Tulare	27,981	28,184	26,000	82,165
Solano	27,365	15,952	20,824	64,140
Yolo	16,347	11,724	16,383	44,454
Glenn	16,500	13,236	14,097	43,832
Sacramento	13,024	17,445	11,512	41,981
Butte	13,578	12,727	8,965	35,271
Madera	5,817	12,519	9,198	27,535
Sutter	8,429	7,916	8,798	25,143
Tehama	6,393	9,878	8,381	24,652
Colusa	6,840	8,970	6,026	21,836
San Luis Obispo	6,065	4,648	8,840	19,553
Kern	4,655	1,658	6,754	13,067
Riverside	6,336	2,042	1,925	10,302
Siskiyou	1,317	4,638	4,224	10,179
OTHER 33 COUNTIES	28,761	26,449	25,035	80,245
Statewide use	**431,566**	**415,358**	**445,103**	**1,292,027**
Top eight counties use	297,506	281,510	314,963	893,978
Percent of top eight counties to statewide use	68.9%	67.8%	70.8%	69.2%

Table 4. Statewide use of 2,4-D DMAS by top ten crops in years of 2008-2010
(Pounds Active Ingredient)

Crop/Year	2008	2009	2010	2008-2010	% Total
ALMOND	90,286	103,412	104,981	298,679	23.1
WHEAT, GENERAL	94,423	87,535	67,994	249,952	19.3
UNCULTIVATED AGRICULTURAL AREAS	47,169	37,039	52,133	136,341	10.6
WALNUT (ENGLISH WALNUT, PERSIAN WALNUT)	137,22	16,649	16,315	46,686	3.6
GRAPES	15,487	13,351	17,343	46,181	3.6
BERMUDAGRASS (FORAGE - FODDER)	9,883	12,321	21,550	43,754	3.4
PEACH	12,503	12,079	12,247	36,829	2.9
FORAGE - FODDER GRASSES (ALL OR UNSPEC) (HAY)	12,808	7,852	12,223	32,883	2.5
GRAPES, WINE	8,989	8,638	9,790	27,416	2.1
PASTURES (ALL OR UNSPEC)	8,909	8,414	8,871	26,194	2.0
OTHER 67 CROPS	117,388	108,068	121,656	347,111	26.9
TOTAL	**431,566**	**415,358**	**445,103**	**1,292,027**	**100**

Table 5. Monthly statewide use of 2,4-D DMAS in years of 2008-2010
(Pounds Active Ingredient)

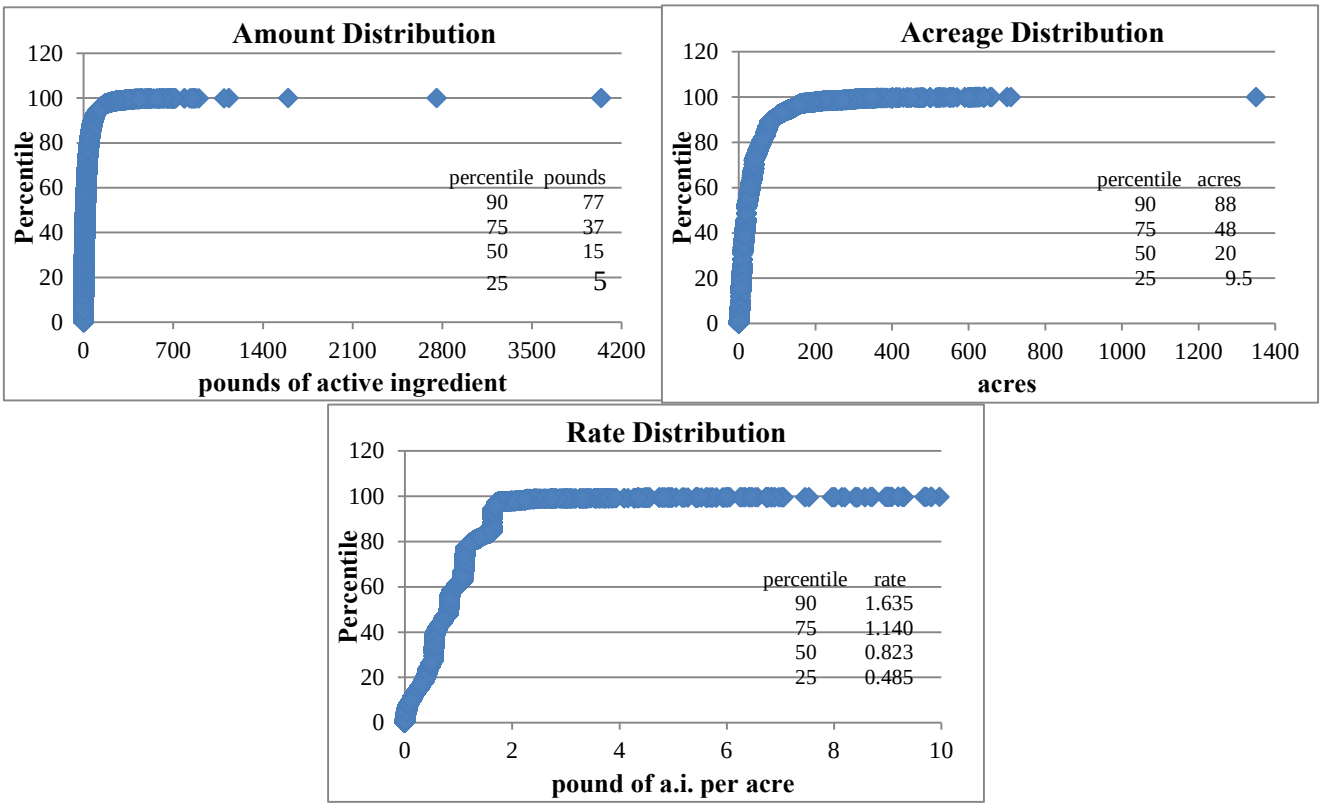
Month/Year	2008	2009	2010	Total
February	171,542	120,557	162,726	454,825
January	50,011	80,950	66,364	197,326
March	69,347	60,661	64,252	194,260
April	29,652	32,705	29,904	92,261
June	31,189	30,039	30,144	91,372
May	22,138	26,388	25,887	74,414
December	21,347	22,761	15,500	59,608
November	11,690	21,256	22,198	55,143
July	12,271	10,048	12,617	34,935
October	6,417	5,267	7,599	19,283
August	4,392	3,564	5,858	13,814
September	1,571	1,161	2,055	4,787
Total	**431,566**	**415,358**	**445,103**	**1,292,027**

Table 6. Statewide use of 2,4-D DMAS by application methods in years of 2008-2010
(Pounds Active Ingredient)

Method/Year	2008	2009	2010	2008-2010	% Total
Ground	301,777	316,268	328,744	946,789	73.3
Aerial	124,623	98,756	114,448	337,827	26.1
Other	5,165	334	1,911	7411	0.6

Figure 3. Estimated cumulative percentile distribution of the application amount, treated acreage, and application rate

Percentile	Amount (pound a.i.)	Area (acre)	Rate (pound/acre)
90	77	88.0	1.635
75	37	48.0	1.140
50	15	20.0	0.823
25	5	9.5	0.485



C. AIR MONITORING RECOMMENDATIONS

Merced County is one of the top eight counties for 2,4-D DMAS use in years of 2008-2010 (Table 2). Recent phytotoxicity in nearby crops possibly due to drift of 2,4-D DMAS applications was reported in Merced County. DPR requests that ARB conduct a field application air monitoring for any formulation of 2,4-D during 2013 in Merced County to enable DPR to address both human exposure as well as phytotoxicity. Based on a preliminary assessment of the toxicology data, DPR requests the target quantitation limit of **4 µg/m^3** for 2,4-D DMAS/2,4-D (Reardon, 2013). DPR recommends close coordination with the Merced County agricultural commissioner or the registrant, and local agencies and organizations to select the most appropriate sampling sites and timing for the air monitoring of 2,4-D DMAS application. If a sampling site is located on a private property, permission from the property owner must be obtained before the monitoring starts.

DPR recommends monitoring an application to a field at least 10 acres in size, preferably greater than 20 acres. The application rate should be at least 1 pound a.i./acre.

The sampling locations must have enough clearance for sampler placement and airflow. Ideally, samplers should be placed a minimum of 20 meters from the application area. At least eight samplers should be located around the field, one on each side and one at each corner. An extra sampler should be collocated at downwind sampling location. The collocated sample will be collected at this site during each sampling interval. Prior to application, at least two background samples should be collected for 18-24 hours duration.

Air samples should be taken before, during, and after application and for three Daytime/Overnight sampling periods as in the following schedule.

Sample period begins	**Sample duration time**
Background (pre-application)	Minimum 18 – 24 hours
Application	Start of application until 1 hour after end of application
1 hour after ending of application (post-application)	1 hour after end of application until 1 hour before sunset
1 hour before sunset	Overnight* until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise

*All overnight samples must include the period from one hour before sunset to one hour after sunrise.

For quality assurance field spikes, trip spikes, and trip blanks should be prepared in the laboratory and handled as the same as the field samples.

DPR requests the following information to be included in the monitoring report:

1) an accurate record of the application site, including topographic features
2) an accurate record of the positions of the monitoring equipment with respect to the application site, including the exact direction and distance of the samplers from the edge of the application site
3) an accurate record of pesticide application, including identity and quantity of pesticide applied, application starting and ending time, method, and application rate, etc.
4) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles with respect to North (identified as either true or magnetic North)
5) if applicable, meteorological data collected at 1-minute intervals including wind speed and direction, humidity, air temperature, and comments regarding degree of cloud cover.

D. SAFETY RECOMMENDATIONS

The following precautions are stated on the product labels and material safety data sheets. Most statements pertain to applicators. Therefore, these precautions are reference for monitoring staff.

Product labels for the 2,4-D DMAS carry a DANGER warning. 2,4-D DMAS may be hazardous to humans and domestic animals. It is corrosive and may cause irreversible eye damage if get in eyes. Avoid contact with skin or get on clothing. It is harmful if swallowing. Prolonged or frequently repeated skin contact may cause allergic reactions in some individuals.

Personal protection equipment includes long-sleeved shirt and long pants, shoes and socks, chemical resistant gloves or apron when exposed to the concentrate, and protective eyewear (goggles or face shield).

E. REFERENCES

APVMA, 2004. Australian Pesticides and Veterinary Medicines Authority. Standard for 2,4-D-dimethylamine Salt Active Constituent, Version 1, August. Australia. http://www.apvma.gov.au/products/constituents/standards/standard_2,4-D-dimethylamine_salt.php

DPR. 2010. California Pesticide Information Portal (CALPIP), Department Pesticide Regulation, Cal EPA. Sacramento, CA http://calpip.cdpr.ca.gov/main.cfm

DPR. 2011. Air Screening Levels for DPR Prioritization Purposes. Medical Toxicology Branch.

Grover, R., J. Maybank, and K. Yoshida. 1972. Droplet and vapor drift from butyl ester and dimethylamine salt of 2,4-D. Weed Sci. 20:320–324. http://www.jstor.org/pss/4041965

Julin, K.S., and L.G. Jr. Harry. 1986. Drift of 2,4-D DMA and control of Eurasian Watermilfoil in Lake Osoyoos. Lake and Reservoir Management, Volume 2, Issue 1, pages 372 – 376.

NPIC. 2010. National Pesticide Information Center. 2,4-D technical fact sheet. http://npic.orst.edu/factsheets/2,4-DTech.pdf

Reardon, C. 2013. Proposed Toxic Air contaminant Monitoring for 2012 and 2013 Addendum. Department of Pesticide Regulation, Cal EPA. Sacramento, California. http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/2413_goldstene.pdf

USEPA. 2004. Environmental Fate and Effects Division's risk assessment for the reregistration eligibility document for 2,4-Dichlorophenoxyacetic Acid (2,4-D). http://www.epa.gov/espp/litstatus/effects/24d/attachment-b.pdf

USEPA. 2005. Reregistration Eligibility Decision for 2,4-D. http://www.24d.org/govtrev/2,4-D%20RED%20FINAL%2007-25-05.pdf

Walters, J., 1999. Environmental fate of 2,4-dichlorophenoxyacetic acid. Environmental Monitoring Brunch, Department of Pesticide Regulation, CalEPA. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/24-d.pdf