USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT MANCOZEB

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A. BACKGROUND

Pursuant to Food and Agricultural Code section 14022(c), the Department of Pesticide Regulation (DPR) submitted a request to the Air Resources Board (ARB) to monitor an application of the fungicide mancozeb and its breakdown product, ethylenethiourea (ETU) in 2014 (DPR, 2014).

This recommendation contains general information regarding the pesticide description and physical-chemical properties of mancozeb and ETU (Table 1) and the reported historical mancozeb use (2008-2012) in California. The DPR provides this information to assist the ARB in selection of appropriate location for conducting a mancozeb application air monitoring operation.

Pesticide Description and Physical-Chemical Properties

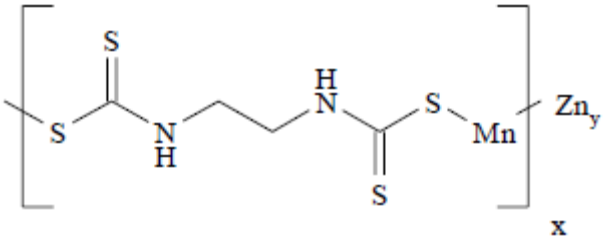
Mancozeb is a high molecular weight polymer composed of repeating single units containing manganese (Mn) and zinc (Zn) ions (Figure 1). It is not a naturally occurring compound, but a synthesized fungicide of ethylenebisdiothiocarbamate (EBDC) group. Mancozeb and two other EBDC fungicides, maneb and metiram, are all metabolized in the body or degrade in the environment to ETU and other intermediates (US EPA. 2005). They can be further broken down and mineralized to CO_2, metals, and other compounds. The chemical structure of ETU is depicted in Figure 1.

Mancozeb is a yellowish powder, practically insoluble in water and not volatile with negligible vapor pressure. It decomposes at 150-172 ^{o}C in acid and alkaline conditions, with heat, and upon exposure to moisture and air (US EPA, 2005).

ETU is a crystalline solid with a white to pale green color, and a faint amine odor. It is soluble in water and slightly soluble in methanol, ethanol, ethylene glycol, pyridine, acetic acid and naphtha. The estimated vapor pressure is 2.0×10^{-6} mm Hg at 25 ^{o}C (HSDB, 2014). When it is heated to decompose, nitrogen and sulfur oxides are emitted (US EPA. 2005).

Figure 1. The Chemical Structure of Mancozeb and ETU (copy from US EPA, 2005)

Mancozeb



ETU

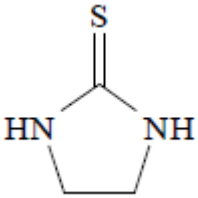


Table 1. Physicochemical Properties of Mancozeb and ETU*

Attribute	Mancozeb	ETU
Chemical name	Zn Mg ethylenebisdithiocarbamate	2-Imidazolidinethione
Chemical family	Dithiocarbamate	Imidazolidine-2-thione
Common name	Mancozeb	Ethylene thiourea
Trade name	Dithane 45®, Manzate 200®, Penncozeb®, Fore	NA-22®, NA-22-D®, Pennac CRA®, Robac-22®,
CAS number	8018-01-7	96-45-7
Molecular formula	$(C_4H_6MnN_2S_4)_x$ $(Zn)_y$ x:y~10:1	$C_3H_6N_2S$
Molecular weight	$(265.3)_x + (65.4)_y$	102.2
Appearance	Yellowish powder	white to pale green crystalline
Density	0.4 g/ml (25 °C)	1.4
Specific gravity	1.1 (20 °C)	
Vapor pressure	$1.3x10^{-10}$ mm Hg at 25 °C (ARS, 1995)	$2.0x10^{-6}$ mm Hg at 25 ^oC (HSDB, 2014)
Solubility in water	6-20 ppm at 25 ^oC (DPR, database)	20,000 ppm at 30 ^oC
Melting point	192-194 ^oC (ARS, 1995)	203-204 ^oC
Henry's law constant	$4x10^{-9}$ atm-m^3/mol (DPR database) $1.5x10^{-11}$ atm-m^3/mol (ARS, 1995)	$1.4x10^{-11}$ atm-m^3/mol (HSDB, 2014)
Octanol-water coefficient (Log Kow)	1.8 (DPR database) 1.3 (ARS, 1995)	0.2
Soil adsorption coefficient (Koc)	363-20,726 ml/g (ARS, 1995)	34-142 ml/g (Xu, 2000b)
Hydrolysis half-lives (25 °C)	<0.1-0.7 days at pH 9 (DPR database) 2.3 days at pH 7 (DPR database) 1.5 days at pH 5 (DPR database)	
Photolysis half-lives	3 hours in water (Xu, 2000a) < 3 hours in air (HSBD, 2014)	1-4 days (Xu, 2000b)
Soil metabolism half- lives	6-139 days (ARS, 1995)	1-7 days (Xu, 2000b)

*Data from USEPA, 2005 except for denoted.

Environmental Fate

Mancozeb is released in the environment mainly from pesticide application spray drift. It has a low potential to volatilize to air due to its negligible vapor pressure. It is relatively immobile in

soils due to its low solubility and moderately strong adsorption to most soils and sediment particles. The major transformation pathways are hydrolysis, photolysis and biodegradation in water and soils.

In air, mancozeb mainly exists in particulate phase. It can be transported and removed from air by wind erosion, deposition, hydrolysis, and photolysis. An ambient air monitoring study conducted in California by ARB (ARB, 1994a) found no detectable concentrations in any of the 57 samples analyzed, at a minimum detection limit of 0.025 $\mu g/m^3$ for a 24-hour sample. On the other hand, in a field application air monitoring study, of 28 samples collected during and 2, 6, 10, 22, 46, and 70 hours after an aerial mancozeb application in Kern County, California, approximately 68% had detectable results, ranging from 0.048 $\mu g/m^3$ to 1.81 $\mu g/m^3$ (ARB, 1994b). The maximum concentration (1.81 $\mu g/m^3$) occurred during the 1.5 hours application period. In another application study, mancozeb air concentrations decreased rapidly to < 1 $\mu g/m^3$ three hours post application (Garron *et al.*, 2009).

In water and soils, mancozeb is quickly hydrolyzed. Estimated half-life is 2 or less days in water over a range of pH 5-9 (R&H Company, 1987a; Lyman and Lacoste 1975). Aqueous photolysis studies estimated a half-life of 3 hours (R&H Company, 1987b). However, there was no photolytic degradation in a dry soil, under continuous exposure (24 hrs/day) to artificial sunlight, over a 30 days study (R&H Company, 1987c). Mancozeb has low soil persistence with estimated overall field dissipation half-life of 6-139 days (ARS, 1995). In a laboratory study, both biological and/or chemical degradation of mancozeb yielded EU via intermediates EBIS and ETU in both sterilized and unsterilized soils (R&H Company, 1987c and 1987d). The metabolites can be further biologically mineralized to CO_2 under aerobic condition in unsterilized soils. Half-life of less than 2 days was estimated in unsterilized aerobic soils (HSDB, 2014). Mancozeb and its degradates moderately-strongly bind to soils with adsorption coefficient (K_{oc}) varied from 363 to 20,726 cm^3/g (ARS, 1995). The bound residues degrade slowly in the environment. A study investigating long term effects of abundant mancozeb applications (2.5 kg $ha^{-1}week^{-1}$ for 10 years) on soil and surface-, subsurface-, and ground-water in a banana production region of tropical Mexico found high concentrations of ETU in surface and subsurface waters and Mn in soils (Geissen *et al.*, 2010).

ETU, the major degradate of concern, is released to environment by degradation of the EBDC fungicides from applications and also by various waste streams of production and use as a vulcanizing agent and chemical intermediate. The major transformation and transportation pathways are photodegradation, biodegradation, leaching, run-off, rain, and wind transportation in the environment.

In air, it exists in both vapor and particulate phases with its vapor pressure of 2.0×10^{-6} mm Hg. However it is not expected to volatilize from water to air since its high solubility (20,000 mg/l) results in its low Henry's Law constant of 1.4×10^{-11} atm-m^3/mol. ETU in vapor phase degrades via reaction with photochemically produced hydroxyl radicals and its estimated half-life is less than 3 hours (HSBD, 2014). Particulate phase ETU can be removed from the atmosphere by wet or dry deposition (HSDB 2014). Nash and Beall (1980) estimated half-life of ETU in air was 9 days in a microagroecosystem chamber (150 x 115 x 50 cm^3) study.

In water and soils, ETU is mobile and susceptible to leaching and run-off transportation based on its high solubility. It is persistent to hydrolysis, evidenced in a 90 days study over the pH ranges of 5-9 at room temperature or at 90 ^{0}C (Crucickshank and Jarrow, 1973). It is not likely to adsorb onto sediments and soils due to its high solubility and low adsorption affinity. Volatilization from water or moist soil surfaces is not significant. Photolysis is a major degradation pathway in water and soils. In aquatic photolysis studies using deionized and sterilized natural waters, ETU degraded in six of seven natural water samples when exposed to light (HSDB, 2014). Other photolysis studies with presence of photosensitizer indicated that ETU degraded more than 90% of 100 ppm ^{14}C-ETU after 6 hours exposed to UV light in distilled water (Rhode, 1977) and 95 % of 0.64 ppm ETU after 4 days in deionized water under a laboratory photoreactor, also 95% of 10 to 25 ppm ETU after 4 days exposed to sunlight (Ross and Crosby, 1973). When ETU adsorbed on silica gel at 100 or 1 µg/cm^2, 65% or 97% of the photosensitized ETU degradated under the sunlamp power of 300 and 3,300 µW/cm^2 after 8 or 20 hours, respectively (Crucickshank and Jarrow, 1973). The reported photolysis half-lives in natural water range from 1 to 4 days (Xu, 2000b). In soil, ETU can be chemically and biologically degraded with reported half-lives 1-7 days under field conditions (Miles and Doerge, 1991; Nash and Beall, 1980; Rhodes, 1977). Rapid degradation may limit ETU leaching, however, slow and steady ETU formation from mancozeb complex can make it available for leaching at low concentration (US EPA, 2005). This is evidenced by detectable ETU found at subsurface and ground water after repeated mancozeb applications for 10 years (Geissen *et al.*, 2010). Groundwater monitoring in California showed that only one of 80 wells sampled for ETU had a detectable concentration(0.725 ppb); but follow-up samples collected at this and proximate wells had no concentrations above the minimum detection limit of 0.578 ppb (Xu, 2000b).

B. MANCOZEB PESTICIDE USE IN CALIFORNIA

Mancozeb is a broad spectrum contact fungicide used on agricultural crops (various vegetables, fruits, and nuts), turf (golf courses, sod farms), and horticulture (ornamental plants, cut flowers). The statewide annual use of mancozeb (DPR, 2013) has greatly increased in recent years, ranging from 237,000 and 284,000 pounds in 2008 and 2009, to 706,000 pounds in 2010, to 1,002,000 and 1,068,000 pounds in 2011 and 2012.

The majority of mancozeb use occurred in four counties: Monterey, Fresno, San Joaquin, and Kern (Table 2). The monthly statewide use from 2008 to 2012 showed that the high use months were from March to June with the peak in April (Table 3). The monthly use pattern for the top four counties showed the peak use in April occurring in three of the four top use counties. However, in Monterey County, the high use was relatively evenly distributed from May to September (Figure 2).

Mancozeb was used in California mainly on walnut (27%), lettuce head or leaf (18%), onion (13%), processing and canning tomatoes (8%) and pear (8%) as shown on Table 4. For the top 4 use counties in 2008-2012, the top five crops were lettuce head or leaf (33%), onion (19%), walnut (12%), processing and canning tomatoes (9%) and potato (8%). About 74% of the statewide use was applied by ground applications and 24% by aerial applications (Table 5). Table 6 lists the mancozeb use (pounds of active ingredient), treated area size (acres), and application rate (pounds/acre) at different percentile for individual mancozeb applications during 2008-2012. Figure 3 plots the cumulative frequency distributions for all individual applications.

Table 2. Mancozeb use (pounds of a.i.) by top ten counties during 2008 – 2012

County	2008	2009	2010	2011	2012	Total
Monterey	8,818	3,873	9,903	186,876	227,901	437,372
Fresno	36,190	41,182	80,002	110,675	127,468	395,517
San Joaquin	9,445	11,872	74,756	67,732	84,425	248,229
Kern	34,448	23,611	47,706	59,404	53,100	218,268
Butte	129	382	57,434	37,211	89,685	184,842
Kings	17,607	25,144	47,206	54,954	29,090	174,002
Sacramento	28,805	32,879	32,637	35,593	34,153	164,067
Sutter	111	240	49,140	57,321	47,042	153,854
Tehama			34,059	54,569	33,970	122,598
Glenn	681	499	39,257	48,587	18,668	107,692

Table 3. Statewide mancozeb use (pounds of a.i.) by month during 2008 – 2012

Month	2008	2009	2010	2011	2012	Total
January	8,381	1,763	9,030	7,080	14,096	40,348
February	9,527	5,406	9,999	8,276	37,953	71,161
March	73,423	40,038	83,702	79,314	138,481	414,957
April	**83,283**	**81,432**	**326,195**	**274,750**	**402,719**	**1,168,378**
May	43,928	41,460	179,483	247,479	187,429	699,779
June	18,236	28,851	28,541	157,185	66,392	299,205
July	22,677	17,353	22,877	71,418	65,751	200,076
August	8,140	7,541	20,408	69,556	64,899	170,544
September	8,112	4,949	11,119	50,807	53,144	128,130
October	3,106	2,289	7,884	19,648	18,664	51,591
November	1,931	2,826	3,441	7,119	7,084	22,403
December	3,738	2,997	3,476	9,431	11,125	30,766

Figure 2. Monthly mancozeb use in top four counties during 2008-2012

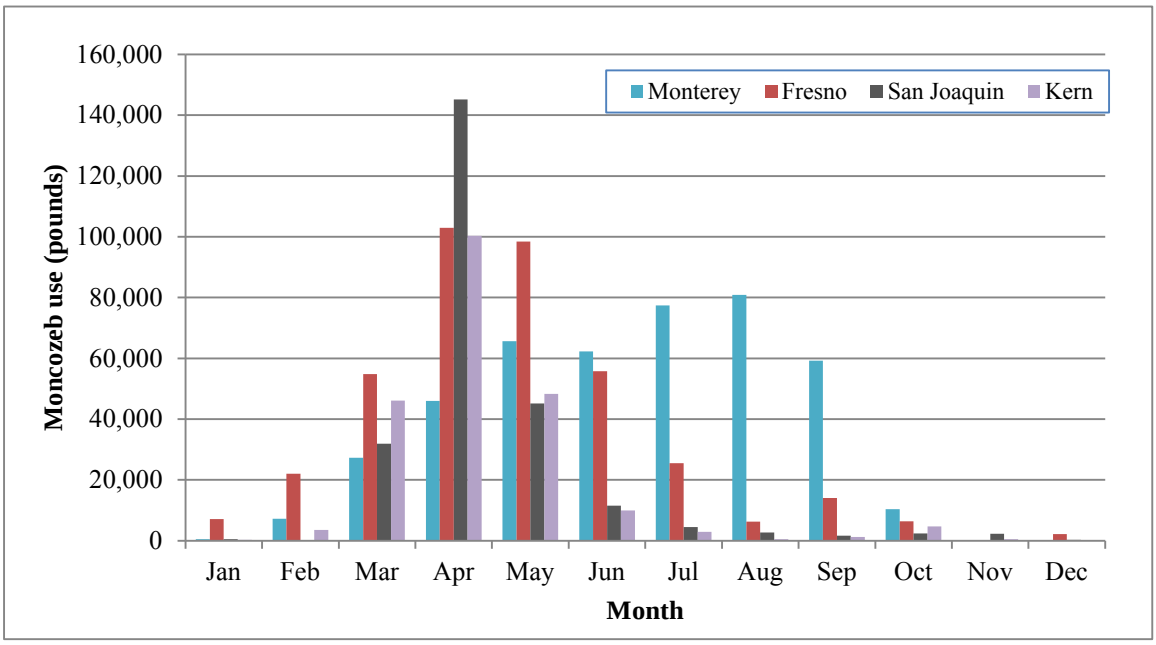


Table 4. Mancozeb use (pounds of a.i.) by top 10 crops during 2008 – 2012

Crop	2008	2009	2010	2011	2012	Total
English, Persian Walnut			281,464	313,898	308,357	903,718
Lettuce, Head or Leaf			9	222,583	332,973	555,565
Onion	60,050	64,710	105,035	124,814	102,186	456,794
Tomatoes for Canning	15,150	17,148	88,577	107,857	45,475	274,208
Pear	53,240	49,877	54,007	50,934	61,766	269,824
Grapes	36,788	20,998	33,717	29,447	33,117	154,067
Potato	26,624	18,742	22,918	33,015	35,098	136,396
Grapes for Wine	32,918	16,045	20,567	16,068	9,482	95,080
Apple	13,151	15,362	16,168	18,559	21,923	85,163
Ornamental Turf	20,357	12,165	24,620	9,538	9,796	76,476

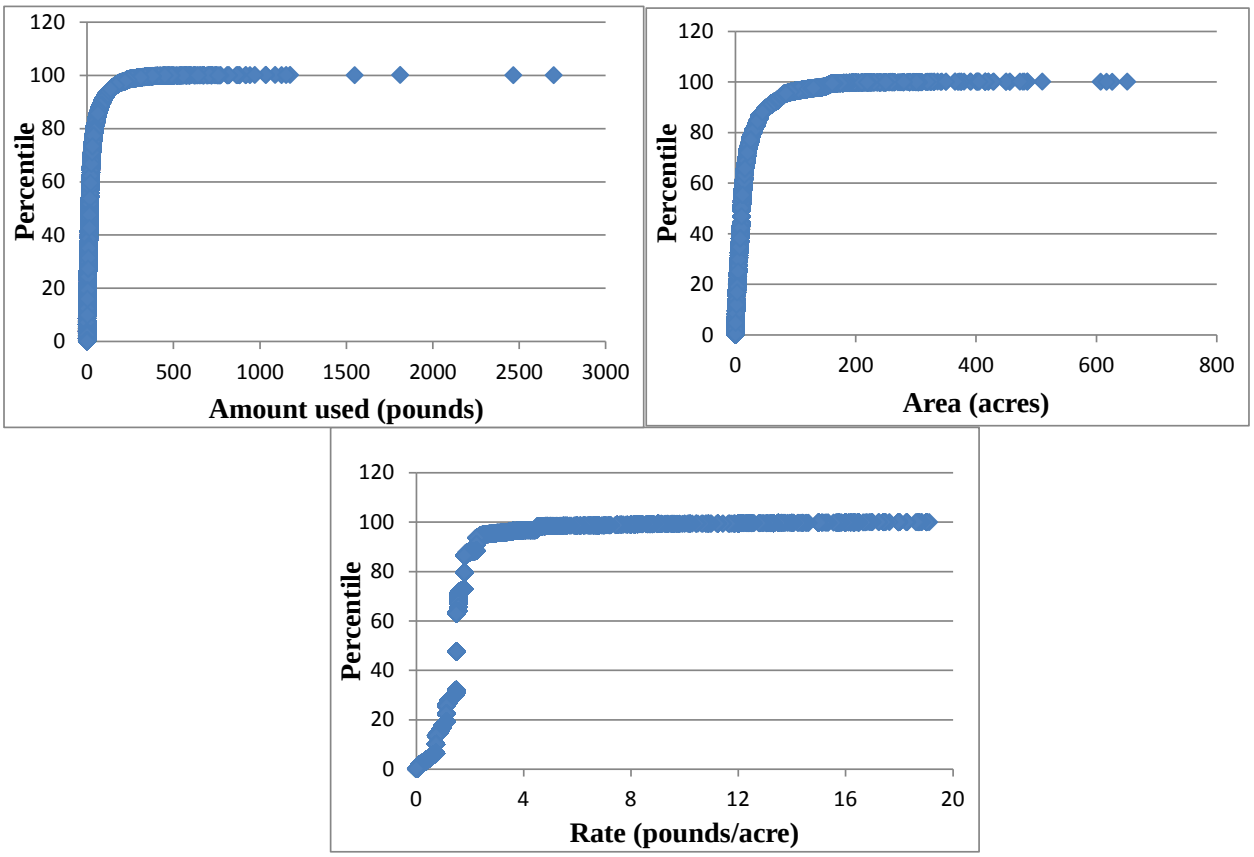
Table 5. Mancozeb use (pounds of a.i.) by application method during 2008 – 2012

Method	2008	2009	2010	2011	2012	Total
Ground	190,004	146,853	510,762	720,701	866,325	2,434,644
Aerial	79,747	78,214	184,411	264,922	191,044	798,337
Other	14,731	11,739	10,981	16,441	10,368	64,260

Table 6. Percentile distributions of mancozeb use for individual applications during 2008 – 2012

Attribute	Amount (pound)	Area (Acre)	Rate (pound/acre)
Maximum	2700	651	19.12
90th	90	54	2.25
75th	35	23	1.80
50th	16	10	1.50
25th	6	5	1.13
Minimum	0.000075	0.000023	0.000002

Figure 3. Cumulative distribution plots for individual applications during 2008 – 2012



C. AIR MONITORING RECOMMENDATIONS

DPR requests that ARB monitor a field application for mancozeb and its breakdown product ETU. Based on a preliminary assessment of the toxicology data, DPR requests a target quantitation limit of 0.08 µg/m^3 for mancozeb and 8 µg/m^3 for ETU (Reardon, 2014). DPR recommends close coordination with the county agricultural commissioner or the registrant, and local agencies and organizations to select the most appropriate sampling sites and time for the air monitoring. If a sampling site is located on a private property, permission from the property owner must be obtained before the monitoring starts.

DPR recommends ARB select a ground application on a field agricultural crop, at an application rate close to 2.25 pounds per acre, which is at the 90th percentile of all individual applications during 2008 – 2012 (Table 6). The application field size should be 20 acres or larger.

The sampling locations must have enough clearance for sampler placement and airflow. Samplers should be placed 10 to 15 meters from the application area. At least eight samplers should be located

around the field, four on each side and four 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/nighttime 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 mancozeb application, including quantity of mancozeb 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 precaution statements are reference for monitoring staff.

Product labels for the mancozeb carry a Caution warning. It is hazards to human and domestic animals. Keep out of reach of children. Harmful if swallowed, inhaled, or absorbed through the

skin. Avoid contact with skin, eyes, or clothing. Avoid breathing spray mist, Remove contaminated clothing and wash clothing before reuse. Cause moderate eye irritation

Personal protection equipment includes coveralls over long-sleeved shirt and long pants; chemical resistant gloves, such as nitrile rubber, natural rubber, or butyl rubber; shoes plus socks; and protective eyewear.

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