USE INFORMATION, APPLICATION MONITORING AND AMBIENT AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT 3,4-DICHLOROPROPIONANILIDE (PROPANIL) AND BREAKDOWN PRODUCT 3,4-DICHLOROANILINE

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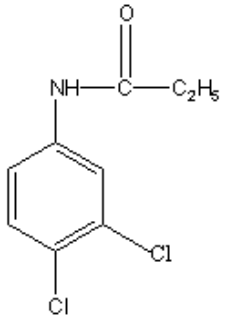
A. BACKGROUND

This recommendation contains general information on physical-chemical properties of propanil and its' breakdown product, 3,4-dichloroaniline and propanils' reported historical uses as a pesticide 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

Figure 1. Chemical structure of propanil.



Propanil (Chemical name: *N*-(3,4-dichlorophenyl) propanamide; Molecular formula: $C_9H_9Cl_2NO$) (Figure 1) is a colorless odorless crystal (Tomlin, (ed.) 1994). The solubility in water is 0.13 g/l (25^0C) (Tomlin, (ed.) 1994). Propanil is rapidly broken down in water by sunlight; photolysis DT_{50}: 12-13 h (Tomlin, (ed.) 1994). Table 1 lists physical-chemical properties of propanil. Rohm & Hass Co. introduced the product, and there are several other current manufacturers. The low vapor pressure indicates that the potential to become vapor when applied is low. However, drift of propanil during peak use periods is a well-documented problem (Barry and Walters, 2002).

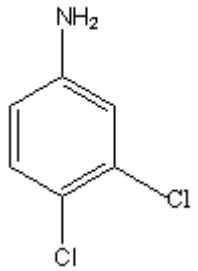
Table 1. Physical and chemical properties of propanil (Tomlin, (ed.) 1994, The Crop Protection Handbook, 2005, EXTONET, 1993, DPR, 2006, Spectrum, 2008 and U.S. EPA, 2003.).

Chemical name	propanil
Trade names†	Duet, Propanil 4, Riceshot, Stam , Wham, Super Wham
CAS Registry number	709-98-8
Molecular formula	$C_9H_9Cl_2NO$
Molecular weight	218.1 g/mol
Melting point	91.5 ^{0}C
Vapor pressure	2.6 x 10^{-7} mm Hg (torr) at 30 ^{0}C
Specific gravity	1.41 g/cm^3 (22 ^{0}C)
Water solubility	0.13 g/l (25 ^{0}C)
Henry's Law Constant	4.5X10^{-9} atm-m^3/mole at 25 ^{0}C
Soil particle adsorption	149 –220 (K_{OC})
Octanol / Water Partition Coefficient (log K_{OW})	3.3
Hydrolysis half-life	Short half-life in water; less than a day
Soil half-life	1-3 days (microbial degradation)

† Disclaimer: The mention of commercial products, their sources, or their use in connection with material reported herein should not be considered as either an actual or implied endorsement of such products.

Figure 2

Chemical structure of 3,4-Dichloroaniline.



3,4-Dichloroaniline is the major breakdown product of propanil due to microbial acylamidase hydrolysis (Tomlin (ed.), 1994). In rice plants, propanil is rapidly hydrolyzed to yield free 3-4-Dichloroaniline, which binds to lignin in rice leaves (Yih, et.al. 1968). 3,4-Dichloroaniline is also manufactured as a commercial product. 3,4-Dichloroaniline has an estimated atmospheric half-life of 9 hours (European Commission, 2006).

Table 2. Physical and chemical properties of 3,4-Dichloroaniline (International Chemical Safety Cards: 0144), European Commission, 2006, and Hazardous Substances Data Bank, 1999.

Chemical name	3,4-Dichloroaniline
CAS Registry number	95-76-1
Molecular formula	$(C_6H_3)Cl_2(NH_2)$
Molecular mass	162.0 g mol^{-1}
Boiling point	272 ^{0}C
Melting point	72 ^{0}C
Vapor pressure	15.012 x 10^{-3} mm Hg (20^{0}C)
Relative density	1.36 g cm^3 (water = 1)
Water solubility	580 mg/l at 20 ^{0}C
Henry's Law Constant	1.9 x 10^{-6} atm-m^3/mole at 25 ^{0}C
Soil particle adsorption	bound to soil 80% K_{OC} 239 (sand)-800 (silt loam)
Field dissipation half-life	in soil 1.5 days
Octanol / Water Partition Coefficient (log K_{OW})	2.69

B. CHEMICAL USES OF PROPANIL IN CALIFORNIA

Propanil is an acetanilide postemergence herbicide with no residual effect. It is used against a variety of grasses and broad-leaved weeds in rice. It is available as emulsifiable concentrate, liquid and dry flowable, low volume, and ultra low volume (ULV) formulations (Meister (ed.), 1992).

Thirteen propanil containing products are registered in California as of February 2008 (DPR, 2006). Commercial products may come as pre-mixes with another active ingredient or as pure propanil. The signal word can be "Caution" or "Warning". The label identifies compatible and incompatible products, amounts, and their mixing order. In rice, the maximum recommended rate per application is 6.0 lbs active ingredient (a.i.) per application per acre or 8.0 lbs a.i. per acre per season. This is a mitigation measure to reduce the likelihood of drift. This pesticide is applied to foliage of target plants using ground equipment such as tractor-mounted sprayers or aerially. Both helicopters and fixed-wing aircrafts are used in aerial applications. Aerial applications are considered more problematic than ground applications. A report by Barry and Walters (2002) shows that frequent and significant amounts of propanil may be present in and around application sites during the peak application months due to high frequency of applications concentrated in few counties. Sensitivity of prunes to propanil, high frequency of aerial applications coupled with wind cause the field problem. There is a prune foliage residue threshold of 0.1 ppm when propanil is in use (Akesson, 1986).

As a post emergent herbicide on rice, it is recommended to apply on completely drained or fields with minimal standing water. Propanil should not be applied to standing water. It controls a variety of grassy weeds and sedges in young rice fields. If used as an emergency control of grown weeds, recommendations differ. Water from treated rice fields should be held as given in the label. Special precautions have to be taken to prevent potable water source contaminations. Also propanil should not be used if contamination of down-stream Catfish farms cannot be mitigated. Shrimp are sensitive to this pesticide. Propanil has the potential of contaminating shallow ground water due to seepage through cracks in rice paddies.

Total annual use of propanil in California is given in Table 3. The total use of propanil for the years 2004, 2005, and 2006 have been around 1.7, 1.4, and 1.5 million pounds of a.i. respectively. A few pounds used in Riverside County are omitted from this report. The highest use county was Colusa with about 400,000 lbs of a.i. or 26% of the total state use for this period. Sutter County was the second highest user at 20% of the total use. Glenn County was a close third. The use of propanil during this 3-year period has been fairly stable. Few Counties show greater than 50% variability between years.

Table 3. Propanil use (pounds a.i.) from 2004, to 2006.

	Propanil Use_Pounds ai			
County	**2004**	**2005**	**2006**	**County Total**
COLUSA	404,181	375,680	397,173	1,177,034
SUTTER	315,661	273,950	326,246	915,858
GLENN	323,050	283,482	302,563	909,095
BUTTE	304,445	242,238	252,135	798,819
YOLO	120,203	92,443	89,916	302,562
YUBA	87,429	60,364	65,481	213,274
PLACER	49,460	25,235	23,710	98,405
SACRAMENTO	31,278	23,158	14,979	69,415
MERCED	20,922	16,698	9,779	47,400
SAN JOAQUIN	23,015	8,886	10,384	42,284
FRESNO	7,588	12,041	0	19,629
STANISLAUS	4,566	3,956	4,812	13,333
Year Total	**1,691,800**	**1,418,131**	**1,497,177**	**4,607,108**

Table 4. Monthly use-pattern of propanil for years 2004, 2005, and 2006.

	Propanil Use_Pounds a.I.				
County	**Year**	**MAY**	**JUN**	**JUL**	**Year Total**
BUTTE	2004	21,904	264,752	17,309	304,445
	2005	8,115	116,945	117,178	242,238
	2006	0	116,253	135,760	252,135
COLUSA	2004	27,920	360,591	15,451	404,181
	2005	18,116	234,077	123,367	375,680
	2006	5,677	231,758	159,738	397,173
FRESNO	2004	4,677	2,830	81	7,588
	2005	0	11,048	993	12,041
GLENN	2004	32,780	279,703	10,567	323,050
	2005	6,254	218,729	57,927	283,482
	2006	72	230,806	71,685	302,563
MERCED	2004	505	15,965	4,453	20,922
	2005	250	7,279	9,170	16,698
	2006	0	5,179	4,600	9,779
PLACER	2004	4,694	39,066	5,140	49,460
	2005	0	13,901	11,212	25,235
	2006	0	10,931	12,658	23,710
SACRAMENTO	2004	1,748	22,369	7,162	31,278
	2005	0	11,314	9,921	23,158
	2006	0	3,343	10,402	14,979
SAN JOAQUIN	2004	790	21,945	280	23,015
	2005	940	4,581	3,234	8,886
	2006	0	7,940	2,444	10,384
STANISLAUS	2004	144	4,202	220	4,566
	2005	0	1,457	2,379	3,956
	2006	0	1,981	2,831	4,812
SUTTER	2004	23,656	244,708	47,197	315,661
	2005	8,422	160,650	103,689	273,950
	2006	4,222	184,511	134,634	326,246
YOLO	2004	700	99,943	18,936	120,203
	2005	284	26,068	65,089	92,443
	2006	0	28,074	61,519	89,916
YUBA	2004	25,919	58,883	2,222	87,429
	2005	10,436	37,071	12,856	60,364
	2006	1,196	47,381	16,657	65,481
Month Total		**209,419**	**3,126,231**	**1,258,959**	**4,607,108**
Month Average		**6,159**	**91,948**	**37,028**	

Table 4 gives the monthly use pattern in each county for 2004 - 2006. June was the highest use month, and July was a distant second. There were sporadic uses in January, March, and April in some years. In the month of August use was higher than these three months, but less that 1% of the total use. It is also evident from both tables (3 and 4) that Sacramento Valley counties are the dominant users.

C. APPLICATION SITE AIR MONITORING RECOMMENDATION

Table 5. Total pounds (a.i.) air applied, % air applied, pounds ground applied, and county totals of propanil for June and July during years 2005 and 2006.

Year	County	Air applied pounds a.I.	% Air applied	Ground applied pounds a.I.	County total pounds a.I.
2005	COLUSA	129,581	34	246,098	375,680
	GLENN	70,770	25	212,712	283,482
	SUTTER	46,123	17	227,827	273,950
	BUTTE	99,437	41	142,801	242,238
	YOLO	54,152	59	38,261	92,443
	YUBA	93	0	60,271	60,364
	PLACER	13,194	52	12,040	25,235
	SACRAMENTO	16,461	71	6,697	23,158
	FRESNO	12,041	100	0	12,041
	MERCED	16,698	100	0	16,698
	SAN JOAQUIN	4,882	55	4,004	8,886
	STANISLAUS	3,724	94	232	3,956
2005 Total		**467,156**	**33**	**950,945**	**1,418,131**
2006	COLUSA	132,995	33	264,178	397,173
	SUTTER	68,565	21	257,682	326,246
	GLENN	86,238	29	216,325	302,563
	BUTTE	92,865	37	159,270	252,135
	YOLO	77,219	86	12,688	89,916
	YUBA	3,390	5	62,091	65,481
	SACRAMENTO	14,979	100	0	14,979
	SAN JOAQUIN	7,154	69	3,230	10,384
	MERCED	9,689	99	90	9,779
	STANISLAUS	3,872	80	940	4,812
2006 Total		**510,459**	**34**	**986,709**	**1,497,177**

The percentage of aerial applied propanil is significant (Table 5). The leading counties' aerial applied propanil was close to 34% of the total applied during the last two years reported here. In the same years, the average application size was 71.5 acres with a range of 0.02-492 acres. DPR therefore recommends monitoring an aerial application to a site of around 70 acres. If a site of this size cannot be located, smaller site is acceptable but must be at least 10 acres.

DPR recommends monitoring of 3,4-dichloropropionanilide (propanil) and its breakdown product, 3,4-dichloroaniline. A minimum of eight primary samplers per chemical should be positioned around the application site. At least two background samples should be collected for 12-24 hours, just prior to application. Assuming that the field has four sides, one sampler per chemical is placed at the middle of each side, and one sampler per chemical at each corner. In addition, DPR also requests that two additional samplers be set up adjacent to two of the primary samplers, preferably on opposite sides, and equipped with a sample tube and particulate filter to monitor for particulates. The two particulate samples are to be collected during each sampling interval similar to the primary samples. Ideally samplers should be placed at a minimum of 20 meters from the application area. The recommended target quantitation limit for both chemicals is 1.0 $\mu g/m^3$. DPR recommends coordination with the county agricultural commissioner to select the most appropriate sampling sites. Follow all the requirements in the product label. If a site is located on a private property, permission from the property owner must be obtained. Air samples should be taken before, during, and after application and for three Daytime/Overnight sampling periods as given in the following schedule.

Sample period begins:	**Sample duration/time**
Background (pre-application)	Minimum 12-24 hours
Application	Start of application until 1 hour after end of application
End 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 (1st overnight sample)
1 hour after sunrise	Daytime until one hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise (2nd overnight sample)
1 hour after sunrise	Daytime until one hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise (3rd overnight sample)

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

Field spikes should be prepared in the laboratory and run in the field with the samples for quality assurance. Trip blanks should also be included and handled the same way as the regular samples.

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

1) an accurate report 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 exact direction and distance of the samplers from the edge of the application site.

3) an accurate record of pesticide application, including application rate or quantity of the pesticide applied, application starting and ending time, and method, 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.

Figure 3. Sacramento valley region propanil use (pounds a.i.) in June of 2005 and the 16 target communities (All maps courtesy of Rosemary Neal, Staff Environmental Scientist, DPR).

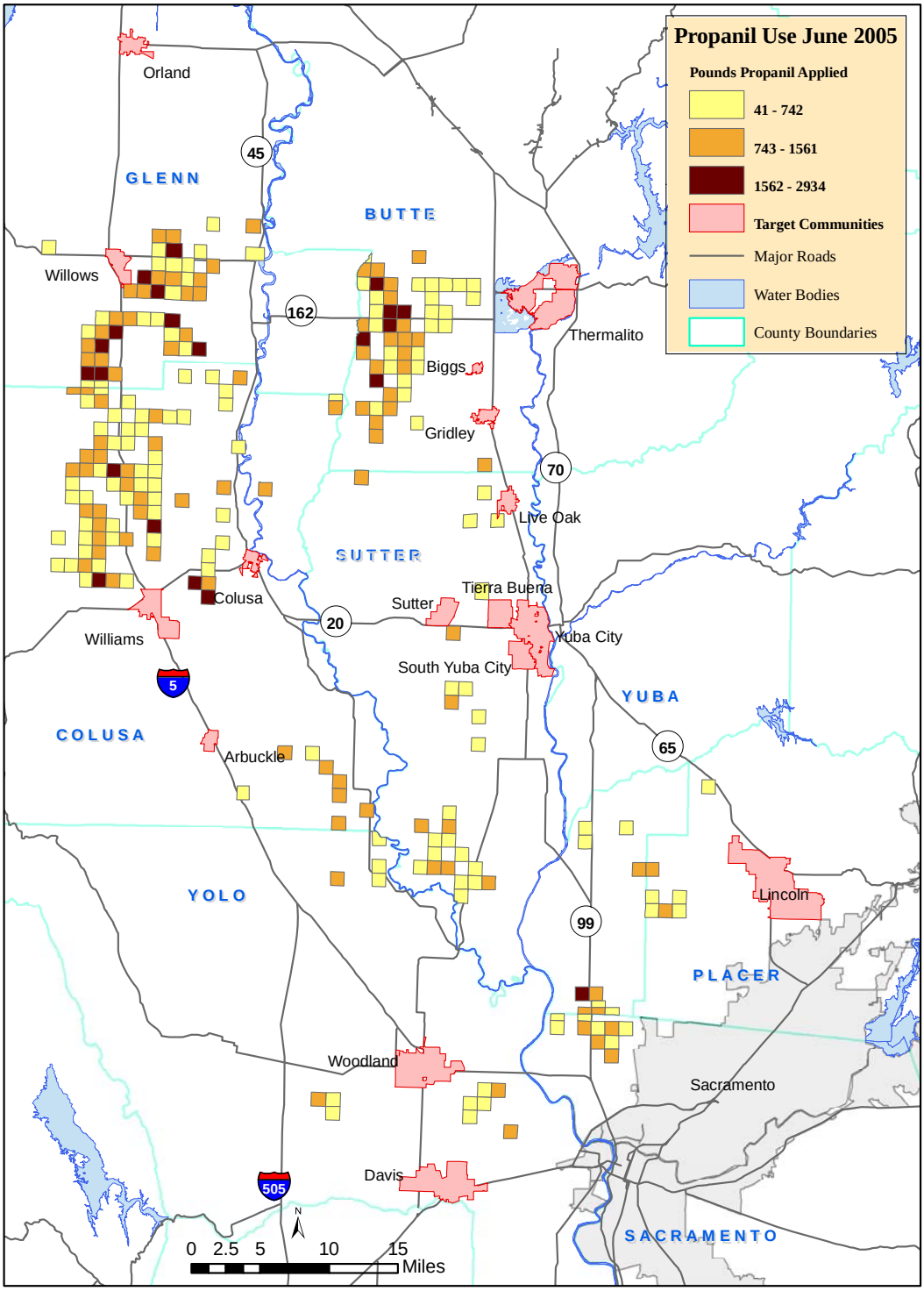


Figure 4. Sacramento valley region propanil use (pounds a.i.) in July of 2005 and the 16 target communities.

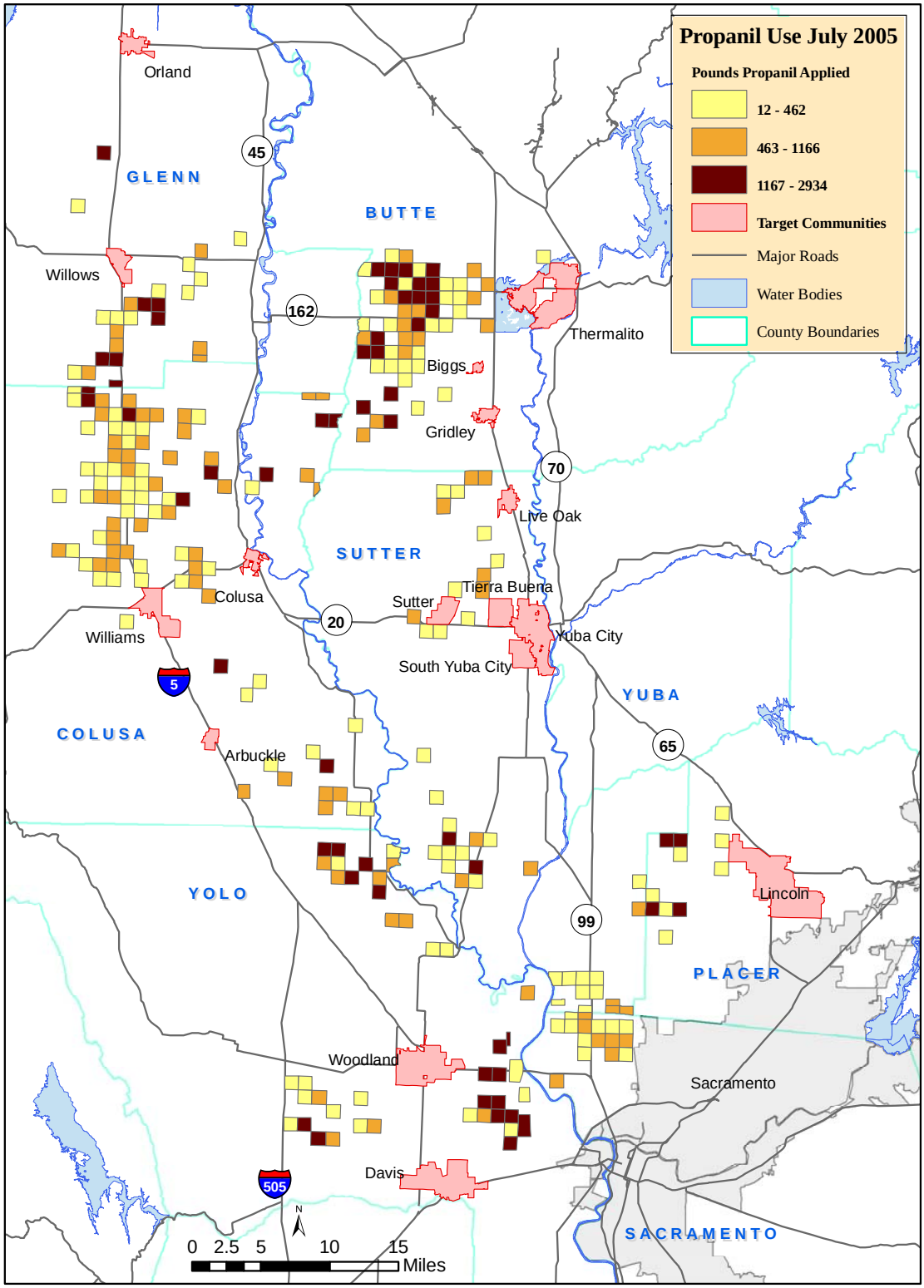


Figure 5 Sacramento valley region propanil use (pounds a.i) in June 2006 and the 16 target communities.

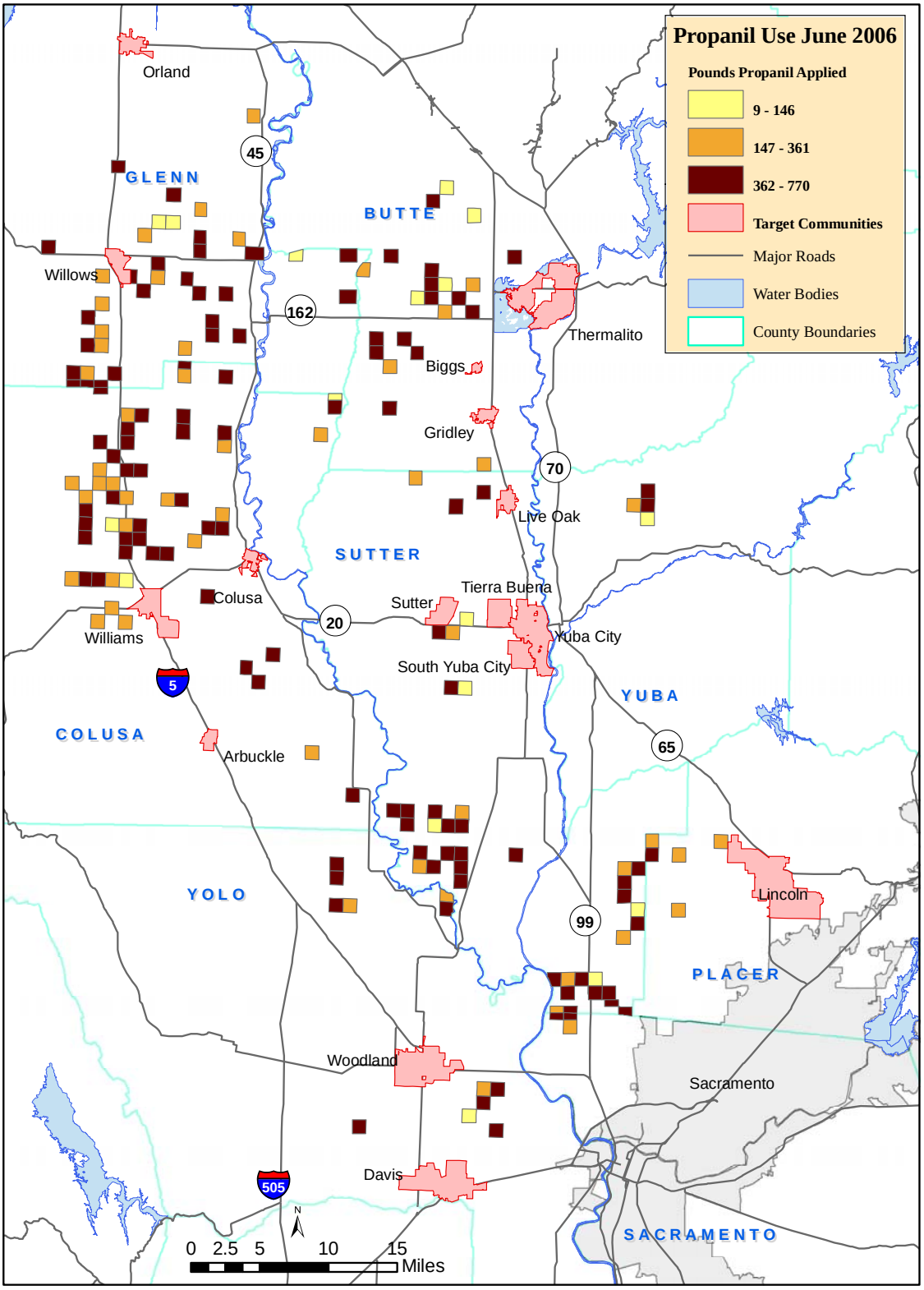
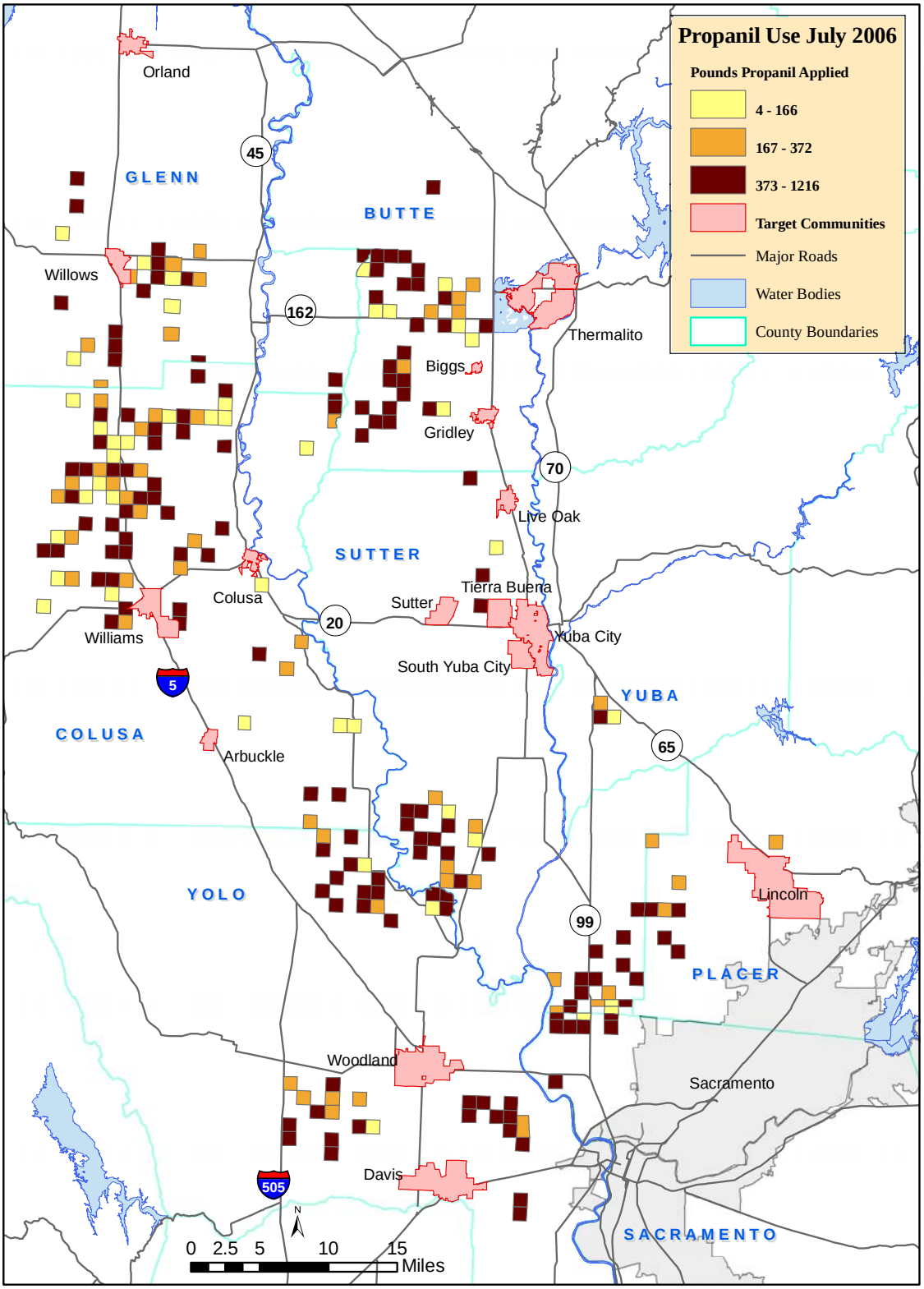


Figure 6 Sacramento valley region propanil use (pounds a.i) in July 2006 and the 16 target communities.



D. AMBIENT AIR MONITORING RECOMMENDATIONS

As part of the Cal/EPA Environmental Justice (E.J.) Action Plan, DPR recommends ambient air monitoring of 3,4-dichloropropionanilide (propanil) and the breakdown product 3,4-dichloroaniline, in rural communities to address the environmental risk factors that impact children's health.

Being at close proximity to agricultural fields, California rural communities may have elevated levels of propanil in the air relative to urban communities. The selection of communities is based on data that are statistically valid and objective. Figures 3 and 4 show propanil use during peak months, June and July respectively, for the year 2005. Similarly, Figures 5 and 6 show propanil use in 2006. DPR selected 16 communities in Glenn, Butte, Sutter, Colusa, Yuba, Placer, and Yolo counties based on their proximity to propanil applications. These communities are identified by name in the 2000 U.S. Census (U.S. Census Bureau, 2000), and are also included in a spatial dataset given by the U.S. Census Bureau for use in a Geographic Information Systems (GIS).

These 16 communities were rated on the following categories and subcategories.

- Environmental justice factors
    - Population density of children (less that 18 years old) per square mile
    - Median family income
    - Hispanic population percentage
    - Non-white population percentage
- Pesticide use
    - Regional (within 5 mile radius of community) use density of propanil
    - Local (within 1 mile radius of community) use density of propanil

Using the data from the 16 communities, they were ranked for each category of the four E.J. factors. Median family income was ranked from lowest to highest, and the other 3 were ranked from highest to lowest. Then the four ranks of each community were added, getting one value per community. These values were ranked again from highest to lowest. These rank values were then rated; giving the highest four values the rating of four. The next highest four values were rated as three, and so on. The GIS based regional and local pesticide use subcategories followed the same criterion as the last three E. J. factors. The four individual rankings for pesticide use in 2005, and 2006, both within a 1-mile and 5-mile radius of each community were added to obtain a single propanil use rank per community. Similar to the E.J. ratings, the propanil use ranks were rated from four to one, four being the highest use group. The propanil rating and E.J. factor ratings were summed and then placed into four groups for a total rating. This method gave equal weights to E.J. factors and pesticide use values (Table 6). The five ambient-air monitoring sites should be located in areas where the propanil rank is high and the overall ratings are among the highest.

Table 6. The ranks and ratings of communities based on propanil use and their environmental justice factors.

Target Community	Propanil Rank	Propanil Rating	EJ Factor Rating	Total Rating
Willows	16	4	4	4
Williams	15	4	2	4
Woodland	14	4	4	4
Thermalito	13	4	1	3
Live Oak	12	3	4	4
Lincoln	11	3	2	3
Sutter	10	3	1	1
Tierra Buena	9	3	2	3
Colusa	8	2	3	3
Biggs	7	2	3	3
Davis	6	2	3	3
Gridley	5	2	2	1
South Yuba City	4	1	4	3
Yuba City	3	1	3	1
Arbuckle	2	1	4	3
Orland	1	1	2	1

Six sampling sites (five air monitoring sites and one urban background site) should be selected in relatively high population areas or areas frequented by people such as schools or school district offices, fire stations, or other public buildings. Background samples should be collected in an area away from propanil use. At each sampling site, four 24-hour samples per week, of both, propanil and its breakdown product should be collected. Since the peak use months were June followed by July, it is recommended that monitoring is conducted for 8 weeks from late May to late July. In addition to the primary samples, replicate samples are needed for four 24-hour periods at each sampling site. Field spike samples should be collected in the same environment. Target 24-hour quantitation limit of 1.0 $\mu g/m^3$ is recommended for both chemicals. DPR also requests that an additional sampler be set up at one of the sites that is equipped with a sample tube and particulate filter to monitor for particulates. The particulate sample is to be collected during each sampling interval similar to the primary sample. Additionally, DPR requests that ARB provides in the ambient air monitoring report: 1) the proximity of the sampler to the treated or potentially treated fields, including the distance and direction, 2) distance of the sampler from ground level, and 3) a map of the monitoring site locations.

E. SAFETY RECOMMENDATIONS

The commercial products that contain propanil as an active ingredient carry the signal word, “Caution” or “Warning”. Applicators and handlers must wear the label recommended Personal Protective Equipment (PPE) and follow recommended procedures. Applicators and other handlers must wear long sleeved shirt and long pants, chemical resistant gloves made of any waterproof material, shoes plus socks, and protective eye wear. It is also recommended to 1). Wash hands before eating, drinking, chewing tobacco or using the toilet. 2). Remove clothing/PPE immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing. 3). Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change to clean clothing. Restricted entry interval for unprotected workers is 24 hours.

F. REFERENCES.

1. Akesson, N. B. 1986. Calculations for relating the prune tree responses to propanil with air borne and fallout residues. Memorandum dated May 20, 1986.

2. Barry, T. and J. Walters. 2002. Characterization of propanil prune foliage residues as related to propanil use patterns in Sacramento Valley, California. Environmental Monitoring Branch, Department of Pesticide Regulation. EH02-4.

3. Crop Protection Handbook. 2005. Willoughby, OH. Meister Publishing Company.

4. DPR. 2006. Product/Label Database <http://www.cdpr.ca.gov/docs/label > Verified on 01-22-2008.

5. European Commission. 2006. 3,4-Dichloroaniline Summary Risk Assessment Report. European Commission, Director General Joint Research Center, Institute for Health and Consumer Protection. European Chemicals Bureau, 1-21020 Ispra (VA) Italy. Available online at: <http://ecb.jrc.it/documents/Existing-Chemicals/RISK_ASSESSMENT/SUMMARY/34dichloroaniline_DCAsum048.pdf> Verified on 02-25-2008.

6. EXTONET. 1993. PMEP: Propanil, Publication Date: 9/93. Pesticide Safety Education Program. 5123 Comstock Hall, Cornell University, Ithaca, NY 14853-0901. Available online at: < http://extoxnet.orst.edu >Verified on 01-22-2008.

7. Hazardous Substances Data Bank. 1999. 3,4-Dichloroaniline, Available online at: http://www.chematlas.com/Document.aspx?file=\HSDB\FILES\HSDB1319.XML Verified on 05-09-08.

8. Meister, R. T. (ed.). 1992. Farm Chemicals Handbook ’92. Meister Publishing Company. Willoughby, OH.

9. Spectrum. 2008. Chemical Fact sheet, Propanil. Available online at: <http://www.speclab.com/compound/c709988.htm> Verified on 01-22-2008.

10. Tomlin, C. (ed.). 1994. The Pesticide Manual, Tenth edition. Crop Protection Publications. The British Crop Protection Council, 49 Downing Street Franham, Surrey GU9 7PH, United Kingdom.

11. U.S. Census Bureau. 2000. Available online at: American Fact Finder; <http://factfinder.census.gov>.

12. U.S. EPA, 2003. Registration Eligibility Docket (7502C), US Environmental Protection Agency, Ariel Rios Building, 1200 Pennsylvania Avenue, NW, Washington, DC 20460-0001. Available online at <http://www.epa.gov.pesticides/reregistration/status.htm>.

13. Yih, R. Y., D. H. McRae, and H. F. Wilson. 1968. Metabolism of 3’, 4’-Dichloropropioanilide: 3,4-Dichloroaniline-Lignin Complex in Rice Plants. Science, 161:376-377