Use Information and Air Monitoring Recommendation for the Active Ingredient Methyl Isothiocyanate in California: Seasonal Ambient Monitoring in Fresno County

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By

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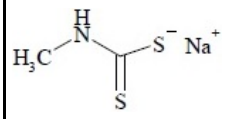
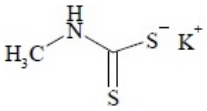
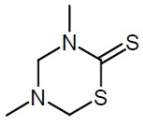
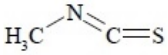
A. INTRODUCTION

The California Department of Pesticide Regulation (DPR) provides this recommendation to assist the California Air Resources Board (ARB) with the selection of appropriate locations to perform seasonal ambient air monitoring in Fresno County for the pesticide active ingredient methyl isothiocyanate (MITC) as part of the proposed monitoring included in the 2016 Budget Act. This recommendation also includes general information regarding the physical-chemical properties and the top agricultural pesticide uses of MITC and its precursors in California.

MITC is a highly volatile compound with broad, non-selective biocidal activity which results from the breakdown of three chemical precursors in water (US EPA 2009). MITC is the active ingredient (a.i.) produced by its precursors for fumigant purposes. Table 1 lists physical and chemical properties of MITC and its precursors. Due to its high volatility, MITC readily leaves soil and enters the atmosphere where it is susceptible to gas phase photolysis and observed to have a half-life ranging from approximately 9 to 13 hours (Collins 2016).

Table 1: Physical and chemical properties of metam sodium, metam potassium, dazomet, and MITC (Taken from Collins 2016).

	Compound			
Chemical Structure				
Chemical Name	Metam sodium	Metam potassium	Dazomet	Methyl isothiocyanate
IUPAC Name	sodium;N-methylcarbamodithioate	potassium;N-methylcarbamodithioate	3,5-dimethyl-1,3,5-thiadiazinane-2-thione	methylimino(sulfanylidene)methane
Molecular Formula	$C_2H_4NS_2Na$	$C_2H_4NS_2K$	$C_5H_{10}N_2S_2$	C_2H_3NS
CAS Registry Number	137-42-8	137-41-7	533-74-4	556-61-6
Physical State at 25 °C and 1 atm	Crystalline solid	Crystalline solid	Crystalline solid	Crystalline solid
Molecular Weight (g/mol)	129.18	145.29	162.3	73.12
Boiling Point (°C)	Decomposes	Decomposes	Decomposes	119
Melting Point (°C)	Decomposes	Decomposes	104 - 105	36
Vapor Pressure at 25 °C	Non-volatile	Non-volatile	9.88×10^{-6} mmHg	16.0 mmHg
Water Solubility at 25 °C	9.63×10^{4} ppm	N/A	3.63×10^{3} ppm (20°C)	8.61×10^{3} ppm
Density (g/mL)	1.1648 (20 °C)	N/A	1.3 (20 °C)	1.069 (25 °C)
Henry's Law Constant 25 °C	N/A	N/A	2.66×10^{-10} atm·m^3/mol	1.79×10^{-4} atm·m^3/mol
Octanol/Water Partition Coefficient (K_{ow})	<10	N/A	4.3	8.7, 15.8 - 23.5
Koc	N/A	N/A	52	3-14.5

MITC has been shown to be toxic to non-target plants, aquatic invertebrates, fish, birds, and mammals (EPA 2009). For handlers, workers, and bystanders associated with the soil uses of MITC, the main risk of exposure is acute inhalation as a result of fumigant off-gassing. The human health risk assessment for MITC shows that acute inhalation exposures of 22 ppb or greater for a 1 to 8 hour time period for bystanders and handlers could pose risks of concern (EPA 2009). The primary complaint of those exposed to MITC is irritation of the eye. Additionally, reports of systemic or respiratory effects have also been documented.

B. Pesticide Use Summary

MITC results from the breakdown of dazomet, metam sodium, or metam potassium at the immediate site of application. Therefore, the MITC use amount in this document refers to the sum of the a.i. produced from the use of the three MITC precursors. Use information was obtained for the calendar years 2012 – 2014 from the Pesticide Use Report (PUR) database maintained by DPR. The annual use by the top 15 counties in the state is ranked and displayed in Table 2 for the years of 2012 – 2014. Total use was highest in Kern, Fresno, Merced, Kings, and Ventura Counties (DPR 2016). Table 3 organizes the annual use of MITC for specific applications, with agricultural applications (carrots, tomatoes for processing, potatoes, etc.) being the dominant use for MITC fumigations in the state.

Total MITC use statewide as a cumulative total for each township during 2012 – 2014 is displayed in Figure 1. Statewide use data is illustrated at the township level (6x6 mile area) to better highlight areas of high use in California. Additionally, use within Fresno County is shown in Figure 2 at a resolution of 1 square mile sections (section level) as defined by Public Land Survey System (PLSS) and displays California Irrigation Management Information System (CIMIS) meteorological data from 2012 – 2014 for CIMIS Station 80 near Fresno State University. Meteorological data is represented as a wind rose to indicate the percent of time that wind is blowing from each direction.

Table 2. Annual MITC reported use (pounds a.i.) by county and year in California during 2012 – 2014[1] (DPR 2016).

County	2012	2013	2014	Total
Kern	4,260,000	5,220,000	3,596,000	13,076,000
Fresno	3,926,000	3,502,000	2,665,000	10,093,000
Merced	754,000	915,000	1,345,000	3,014,000
Kings	716,000	737,000	718,000	2,172,000
Ventura	1,078,000	453,000	349,000	1,881,000
Santa Barbara	1,067,000	222,000	186,000	1,474,000
Stanislaus	468,000	468,000	438,000	1,374,000
Riverside	714,000	284,000	258,000	1,256,000
Los Angeles	376,000	574,000	232,000	1,181,000
Imperial	1,031,000	8,000	0	1,039,000
Santa Clara	266,000	259,000	306,000	831,000
Madera	457,000	155,000	151,000	763,000
Monterey	190,000	199,000	368,000	756,000
San Joaquin	352,000	171,000	172,000	695,000
San Luis Obispo	137,000	249,000	238,000	625,000

[1]Numbers are rounded to hundreds

Table 3. Annual reported use of MITC by application and year in California during 2012 – 2014[1] (DPR 2016).

	Pounds a.i.			
Application	**2012**	**2013**	**2014**	**Combined**
Carrots, General	5,587,000	4,776,000	3,441,000	13,804,000
Tomatoes, for Processing/Canning	3,013,000	2,225,000	2,116,000	7,354,000
Potato (White, Irish, Red, Russet)	1,467,000	1,346,000	968,000	3,780,000
Peppers (Fruiting Vegetable - Bell, Chili, etc.)	1,325,000	815,000	711,000	2,851,000
Soil Application, Preplant - Outdoor (Seedbeds, etc.)	362,000	1,115,000	1,245,000	2,722,000
Onion (Dry, Spanish, White, Yellow, Red, etc.)	1,020,000	947,000	388,000	2,356,000
Strawberry (All or Unspec)	1,153,000	549,000	458,000	2,160,000
Sweet Potato	465,000	546,000	808,000	1,818,000
Uncultivated Agricultural Areas (All or Unspec)	275,000	319,000	217,000	812,000
Tomato	309,000	242,000	183,000	734,000
Statewide Total for All Applications	16,784,000	14,389,000	11,995,000	43,168,000
Total for Top Ten Applications	**14,976,000**	**12,879,000**	**10,535,000**	**38,390,000**
Percent of Statewide Total	**89.2**	**89.5**	**87.8**	**88.9**

[1]Numbers are rounded to hundreds

The top five counties with the highest use of MITC for 2012 – 2014, listed in decreasing order, were: Kern, Fresno, Merced, Kings, and Ventura. Table 4 lists pounds of a.i. applied by month for the top five counties between 2012 – 2014. Peak use is observed to be seasonal for all counties with unique peak periods for each county. Figure 3 charts the distribution, by month, of the total use of MITC for 2012 – 2014 in the top five counties. Use in Fresno County peaks during the months of January to March. Figure 4 charts the distribution, by week, of the total use of MITC during individual years for Fresno County. For Fresno County, peak use occurs starting the middle of January and continues for 12 weeks (between weeks 3 – 14 of the year).

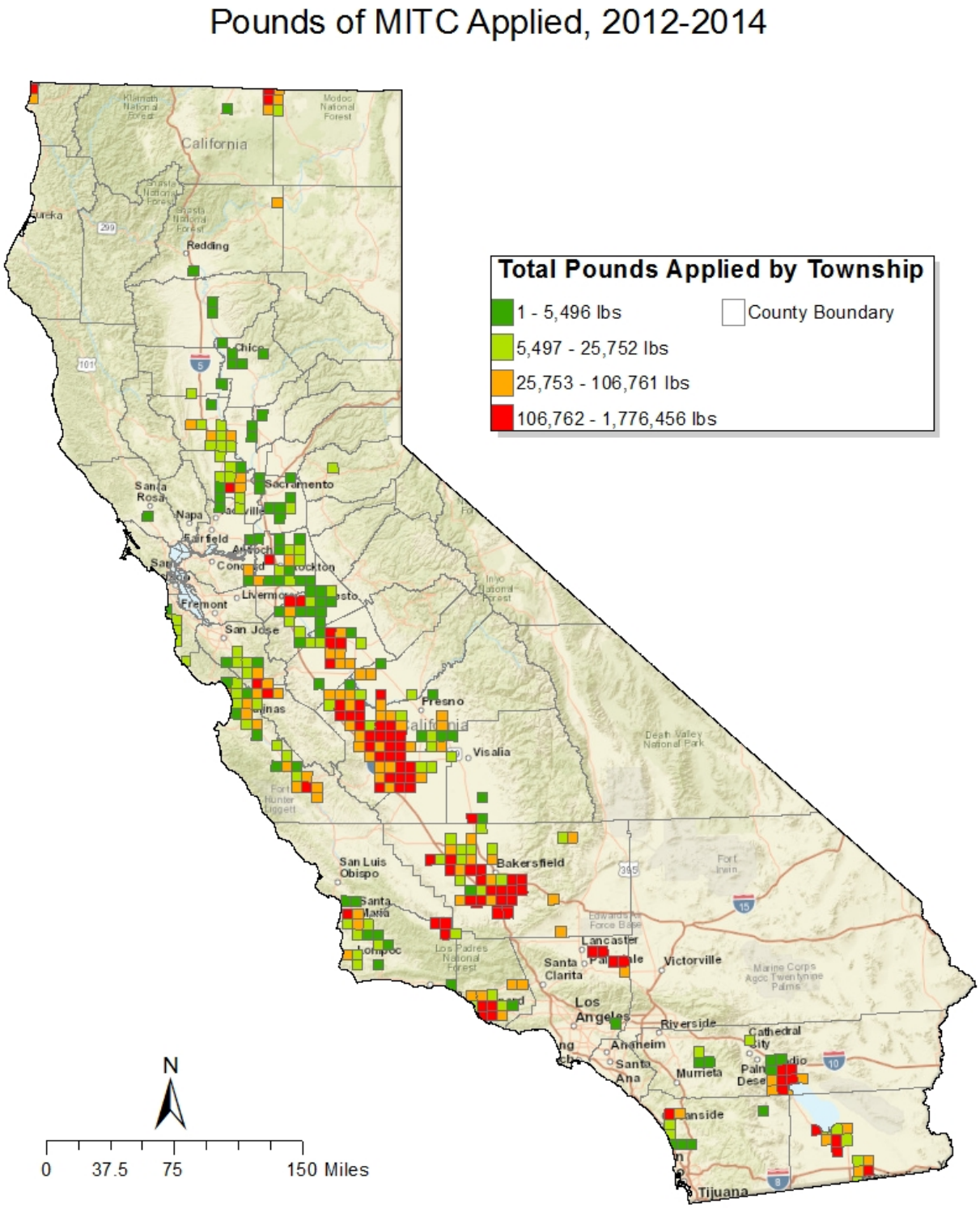


Figure 1. Reported use of MITC (pounds of a.i.) applied by township (6x6 miles) in California for 2012 – 2014.

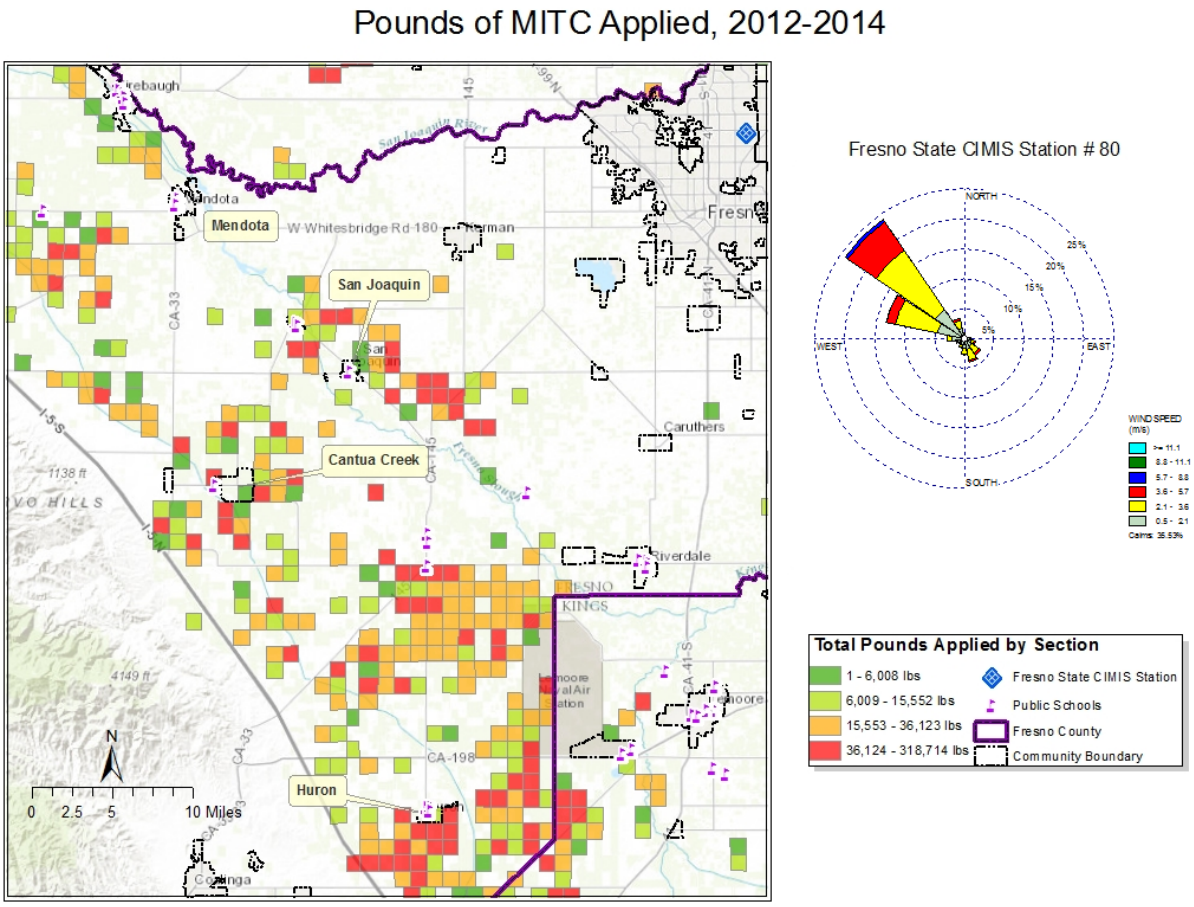


Figure 2. Focused map of Fresno county showing reported use of MITC (pounds of a.i.) by section for 2012 – 2014. Wind roses provided by data from the California Irrigation Management Information System (CIMIS) station 80 near Fresno State University for 2012 – 2014.

Table 4. Reported use of MITC (pounds of a.i.) by month during 2012 – 2014 for the top five counties with highest MITC use in California[1].

County	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
	2012	367,000	296,000	117,000	16,000	20,000	323,000	1,522,000	738,000	54,000	123,000	513,000	171,000
Kern	2013	581,000	271,000	38,000	26,000	25,000	262,000	1,514,000	829,000	76,000	480,000	746,000	373,000
	2014	271,000	160,000	44,000	28,000	23,000	301,000	977,000	600,000	33,000	247,000	446,000	465,000
	2012	579,000	1,141,000	664,000	205,000	11,000	42,000	32,000	66,000	14,000	510,000	347,000	315,000
Fresno	2013	508,000	1,152,000	642,000	106,000	12,000	1,000	30,000	85,000	0	356,000	153,000	458,000
	2014	400,000	915,000	494,000	132,000	23,000	0	8,000	105,000	75,000	216,000	234,000	63,000
	2012	2,000	93,000	225,000	233,000	0	83,000	56,000	1,000	0	4,000	2,000	57,000
Merced	2013	25,000	69,000	310,000	209,000	32,000	197,000	4,000	2,000	2,000	4,000	27,000	35,000
	2014	18,000	153,000	361,000	409,000	46,000	229,000	22,000	41,000	24,000	19,000	5,000	18,000
	2012	70,000	115,000	123,000	6,000	0	0	30,000	0	0	167,000	106,000	99,000
Kings	2013	58,000	160,000	6,000	21,000	0	0	0	72,000	39,000	202,000	79,000	102,000
	2014	87,000	91,000	51,000	0	0	0	0	20,000	27,000	244,000	78,000	121,000
	2012	0	0	40,000	0	2,000	258,000	157,000	172,000	422,000	1,000	25,000	1,000
Ventura	2013	0	0	34,000	19,000	57,000	112,000	7,000	25,000	198,000	1,000	0	0
	2014	1,000	0	0	0	13,000	44,000	85,000	3,000	201,000	1,000	0	0

[1]Numbers are rounded to hundreds

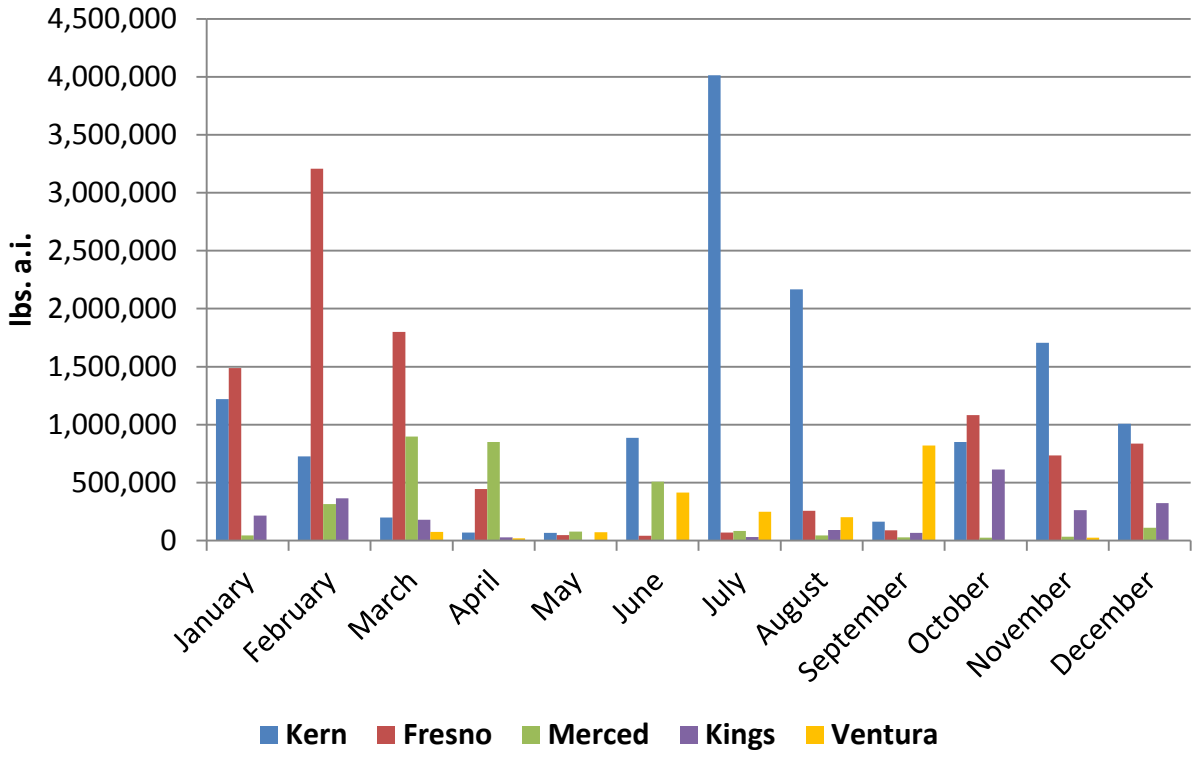


Figure 3. Reported use of MITC (pounds of a.i.) by month during 2012 – 2014 for the top five California counties.

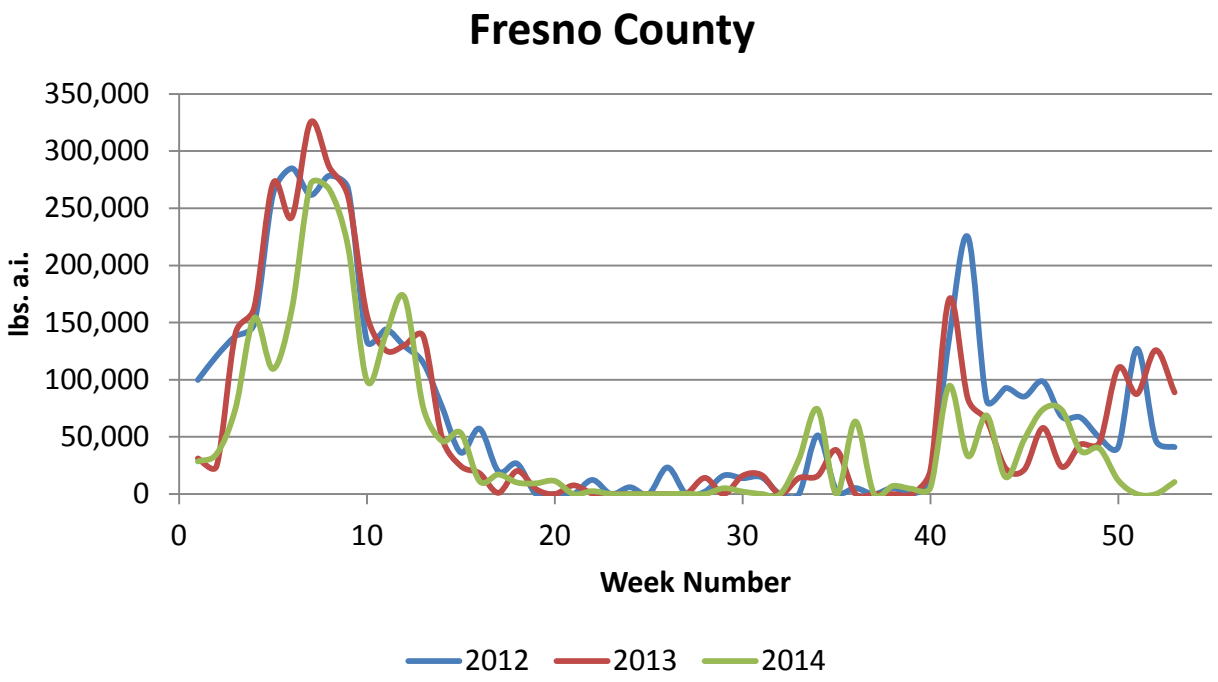


Figure 4. Reported use of MITC (pounds of a.i.) by week during 2012 – 2014 for Fresno County.

C. RECOMMENDATIONS

Ambient Air Monitoring

DPR is most interested in considering monitoring in counties where MITC use is highest: Kern and Fresno Counties. DPR is currently conducting ambient air monitoring for MITC in Kern County as part of the Air Monitoring Network which has been ongoing since 2011 (Tuli et al. 2015). Therefore, DPR requests that ARB conduct seasonal ambient monitoring for MITC in 4 – 8 locations within Fresno County near areas of high Metam Potassium, Metam Sodium, and Dazomet use (Figure 2; Table 5), as well as in one background site located away from areas of use.

DPR recommends that monitoring sites be located on schools or other public properties, near the edge of the community, and downwind of high use areas (Figure 2). Monitoring should be conducted over a 12-week period corresponding to the high-use MITC season in this region, which occurs during the months of January through April (weeks 3 – 14 of the year). At each sampling site, DPR recommends four 24-hour samples per week should be collected in sequence during each week of the 12-week sampling period. For each week, the four day sampling period should begin on randomly chosen days over the full seven-day week, including weekends. In addition to the primary samples, replicate (co-located) samples are needed for at least 10% of total samples collected during the 12 week period. Field spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and monitoring study conditions (e.g., air flow rates, sample transportation and storage) as those occurring at the time of ambient air sampling. DPR recommends target 24-hour quantitation limits of at least 0.004 ppb for MITC (ARB 2002).

DPR requests that ARB provide the following information in its ambient air monitoring report submitted to DPR:

1. Location of each sampler (if at a school, location of sampler within school grounds);
2. Sampling height and any information relevant to the study (presence of trees, buildings, particular industrial or commercial facilities and activities);
3. Proximity of the sampler to treated or potentially treated fields, including distance and direction;
4. Latitude and longitude coordinates for sampling sites, including the Datum used (e.g., NAD 27 or NAD 83); and
5. A map of the monitoring site locations and photographs of sample locations.

Suggested Communities for Air Monitoring

DPR considered 1,267 communities, including all cities and census designated places (CDPs) in California, except those within the urban counties of Los Angeles, Orange, San Diego, and San Francisco (Andrews and Verder-Carlos 2014).

DPR evaluated and rated each of the 1,267 California communities using the following criteria:

a) Regional use density (lbs of a.i. used) during 2012 – 2014 (between 1 and 5 miles outside community boundary);
b) Local use density (lbs of a.i. used) during 2012 – 2014 (within 1 mile outside community boundary);
c) Community use density (lbs of a.i. used) during 2012 – 2014 (within the community boundary);

Rankings were given to the communities within Fresno County according to the statewide rankings of the 1,267 communities evaluated. Table 5 summarizes the results of the evaluation of pesticide use and the Office of Environmental Health Hazards Assessment's (OEHHA) CalEnviroScreen 2.0 (CES 2.0) Population Characteristics percentile for those communities. For any California census tract, the CES 2.0 Population Characteristics percentile factors the following parameters: percent of children and elderly in the population, percent of low birth-weight births, and the rates of asthma emergency department visits, educational attainment, linguistic isolation, poverty, and unemployment (OEHHA, 2014).

DPR is recommending ARB to conduct air monitoring in communities where high MITC use occurs, guided by the community rating from Table 5, and where the CES 2.0 Population Characteristics percentiles are the highest. DPR suggests that consideration should go to the communities of Huron, Del Rey, and Cantua Creek as these communities are ranked highly for both MITC use and environmental justice factors. Multiple sampling locations may be placed within a single community. DPR recommends that ARB select an additional monitoring site distant to MITC applications for rural background samples.

Table 5. Pesticide use and environmental Justice Factors Ratings for Communities in Fresno County near high MITC use areas during 2012 – 2014.

Community Name	MITC Use		CES 2.0 Population Characteristics	
	Statewide Rank[1]	County Rank[2]	Percentile	Rank[3]
Huron City	6	1	93	3
Del Rey CDP	6	1	93	3
Cantua Creek CDP	9	3	82	5
Mendota City	9	3	82	5
San Joaquin City	16	5	82	5
Tranquility CDP	18	6	82	5
Three Rocks CDP	41	7	94	2
Coalinga City	56	8	64	10
Firebaugh City	57	9	81	9
Lanare CDP	67	10	97	1

[1] Community pesticide reported use ranking is out of possible 1,267 California communities evaluated.
[2] Fresno County community rankings based on reported MITC use, with lower numbers indicate higher nearby pesticide use.
[3] Rankings for the top MITC reported use communities in Fresno County, with lower numbers indicating higher environmental justice priority.

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