

**Department of Pesticide Regulation
Environmental Monitoring Branch
Groundwater Protection Program
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Study 335: Protocol for Groundwater Protection List Monitoring for Clothianidin and Thiamethoxam in High Use Areas

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INTRODUCTION

Clothianidin is a widely used neonicotinoid in California agriculture, mainly used for its insecticidal properties. It is both an active ingredient (AI) and a major degradate of the AI thiamethoxam. Agricultural use of clothianidin was first reported in California in 2008 and it is primarily used on wine grapes, cotton, almonds, broccoli, table and raisin grapes, lettuce, and other crops. Common application methods include spraying plant leaves to control piercing, sucking, and chewing insects and soil drenching for flowers, trees, and shrubs. Thiamethoxam is also a neonicotinoid insecticide used to protect agricultural crops against a broad range of insects that feed on roots, leaves, and other plant tissues. Its first reported agricultural use in California was in 2002 and it is primarily used on oranges, sunflowers, wine grapes, tomatoes, cotton, lettuce, and as a seed treatment. According to the U.S. Environmental Protection Agency (U.S. EPA), the largest agricultural use of clothianidin and thiamethoxam in the United States is in the form of seed treatments (U.S. EPA, 2020), especially on row crops such as corn, wheat, cotton, and soybeans. Seed treatment is not the focus of this study; however, the Department of Pesticide Regulation (DPR) will consider this type of use in later studies if clothianidin and thiamethoxam are detected in groundwater and further study is warranted.

Clothianidin and thiamethoxam both have properties that indicate they are mobile, persistent, and have the potential to migrate to groundwater requiring both AIs be placed on the Groundwater Protection List (GWPL), Title 3, California Code of Regulation (3CCR) section 6800(b), as identified pursuant to section 13145(d) of the California Food and Agricultural Code (FAC). In 2023, clothianidin was first detected in California groundwater by DPR's Groundwater Protection Program (GWPP). Samples collected from 62 wells during the annual monitoring of DPR's Well Network Study (Davalos, 2021) were analyzed with updated screens, resulting in 30.6% of the

wells sampled containing quantifiable or trace detections of clothianidin. Five percent of the sampled wells contained quantifiable detections of clothianidin above the analytical method reporting limit (RL). For thiamethoxam, one well sampled contained a trace detection and there were no quantifiable detections. Quantifiable detections refer to concentrations above the RL, while trace detections are measured concentrations above the method detection limit (MDL) but below the RL. To date, the highest concentration of clothianidin detected in groundwater in the Well Network Study was 0.317 ppb. Wells in the network are in areas susceptible to pesticide movement to groundwater within Fresno and Tulare counties.

DPR's GWPP has historically been implementing the Pesticide Contamination Prevention Act (PCPA), defined in Sections 13141-13152 of the FAC. The PCPA was originally enacted in 1985 under Assembly Bill 2021 and its purpose is to prevent pesticide pollution of the groundwater aquifers of the state. To fulfill the mandates of Section 13148, DPR's GWPP conducts groundwater monitoring of the pesticides on the GWPL in areas where they are primarily used to determine if these pesticides have migrated to groundwater.

In the proposed study, DPR will monitor groundwater concentrations of clothianidin and thiamethoxam throughout California, prioritizing areas of highest agricultural use and areas vulnerable to pesticide contamination. Areas with high agricultural use of pesticides and vulnerable groundwater often overlap with disadvantaged communities. Disadvantaged communities, especially those that rely on groundwater for drinking water, are at greater risk from impacts to groundwater. For this reason, DPR will primarily sample domestic wells.

OBJECTIVE

This study aims to identify the presence and concentrations of clothianidin and thiamethoxam in groundwater, especially in regions of California that have high agricultural use and are vulnerable to groundwater contamination. Samples will also be analyzed for other pesticides and degradates on the GWPL and included in DPR's analytical screens.

PERSONNEL

The Environmental Monitoring Branch (EMB) will conduct this study under the direction of the GWPP supervisor, Carissa Ganapathy. Key DPR staff assigned to this project include:

- Project Leaders: Auxilio Henda and Andrew Hawkins
- Senior Scientist: Nels Ruud, Ph.D.
- Laboratory Liaison: Vaneet Aggarwal, Ph.D.
- Analytical Chemistry: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Please direct questions regarding this study to Auxilio Henda (auxilio.henda@cdpr.ca.gov) or Andrew Hawkins (andrew.hawkins@cdpr.ca.gov).

STUDY PLAN

DPR's selection of areas to monitor for clothianidin and thiamethoxam will be based on a high relative amount of use of the insecticides in the surrounding area. The California Pesticide Use Reports (PUR) Database (CDPR, 2024) was queried for clothianidin and thiamethoxam usage data for every county in terms of total pounds applied. Reported use within each county was compared to generate a statewide ranking of all counties. Figures 1 and 2 show the top-ranked counties with the highest reported agricultural use of clothianidin and thiamethoxam, and Appendices 1 and 2 show the annual use by county. Figures 3 and 4 show the statewide annual reported use of each AI. Agricultural use of pesticides is reported on a section-basis, where a section is a one-square-mile area based on the California Public Land Survey System, allowing for targeted monitoring within counties.

The goal of the study is to sample at least 60 domestic wells across the state, with a primary focus on the counties with the highest use. DPR will also prioritize sections with significant use of one or both active ingredients, even in counties with low overall use, if certain factors are met. Sections will be compared and prioritized for monitoring based on the following factors:

1. High relative use of clothianidin and/or thiamethoxam within the section.
2. Shallow average depth-to-water within the section based on historical levels.
3. Previously reported detections of any pesticides in wells within or surrounding the section.
4. Sections that are identified by DPR as [Groundwater Protections Areas](#).
5. Available wells to sample based on existing records in the Well Inventory Database.

SAMPLING

Wells for sampling will be selected in the designated areas following the guidelines described in the Standard Operating Procedure (SOP) Number FSWA001.04 (Kocis, 2022). Domestic wells will be prioritized since they tend to be shallower and more accessible than irrigation or municipal wells.

ANALYTICAL METHODS

The California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry (CAC) will conduct chemical analysis of the groundwater samples. CDFA will analyze samples for clothianidin using the Triazine Screen (CDFA, 2023a), and thiamethoxam using the Multi-Analyte Screen (CDFA, 2023b). Clothianidin was added to the triazine screen method by the analytical laboratory and then validated due to higher selectivity and sensitivity after testing recoveries in both screens. The Multi-Analyte Screen includes both liquid chromatography-mass spectrometry (LC/MS) and gas chromatography-mass spectrometry (GC/MS) techniques. Thiamethoxam is analyzed with LC/MS instrumentation included in this method. DPR has determined that both analytical methods provide unequivocal identification of the chemicals (Aggarwal, 2023a and 2023b). The list of all pesticides to be analyzed and their respective reporting limits are listed in Tables 1 to 3.

The CDFA's laboratory will follow DPR's standard laboratory quality control procedures as outlined in SOP QAQC001.01 (Peoples, 2019). The laboratory will include quality control samples with each batch of field

samples analyzed, including blank samples (samples containing no pesticides) to check for contamination and fortified samples (blind spikes) to check precision and accuracy.

Table 1. Triazine Screen method detection limits (MDL) and reporting limits (RL) in ppb (EMON-SM-62.9, Revision 6) (CDFA, 2023a).

Analyte	MDL	RL
Deisopropyl-atrazine or Deethyl-simazine (ACET)	0.00185	0.02
Atrazine	0.00243	0.02
Bromacil	0.00223	0.02
Clothianidin	0.00139	0.02
Diaminochlorotriazine (DACT)	0.00209	0.02
Deethyl-atrazine (DEA)	0.00141	0.02
Desmethyl-norflurazon (DSMN)	0.00283	0.01
Diuron	0.00169	0.02
Hexazinone	0.00174	0.01
Metribuzin	0.00316	0.02
Norflurazon	0.00232	0.02
Prometon	0.00245	0.02
Prometryn	0.00251	0.02
Simazine	0.00267	0.02
Tebuthiuron	0.00252	0.02

Table 2. Multi-Analyte Screen (LC/MS) method detection limits (MDL) and reporting limits (RL) in ppb (EMON-SM-05-032, Revision 3) (CDFA, 2023b).

Analyte	MDL	RL
AIBA (2-amino-N-isopropyl benzamide)	0.00700	0.02
Alachlor	0.00100	0.03
Atrazine	0.00300	0.02
Azinphos-methyl	0.00600	0.05
Azoxystrobin	0.00200	0.02
Bensulide	0.00300	0.02
Bromacil	0.00400	0.02
Carbaryl	0.00300	0.02
Carbofuran	0.00100	0.02
Chlorantraniliprole	0.00200	0.02
Cyprodinil	0.00200	0.02
Diazinon	0.00200	0.03
Dimethenamide	0.00300	0.02
Dimethoate	0.00500	0.02
Diuron	0.00200	0.02
Ethofumesate	0.00400	0.03
Fenamiphos	0.00200	0.03
Fludioxonil	0.00400	0.03
Flupyradifurone	0.00400	0.02
Flutriafol	0.00200	0.02
Imidacloprid	0.00300	0.02
Isoxaben	0.00200	0.02
Linuron	0.00200	0.02
Mefenoxam/metalaxyl	0.00200	0.02
Methiocarb	0.00300	0.02
Metolachlor	0.00300	0.02
Methomyl	0.00500	0.02
Methoxyfenozide	0.00300	0.03
Metribuzin	0.00200	0.02
Myclobutanil	0.00400	0.02
Napropamide	0.00200	0.02
Norflurazon	0.00200	0.02
Oryzalin	0.00500	0.05
Prometon	0.00300	0.02
Propiconazole	0.00200	0.02
Pyraclostrobin	0.00200	0.02
Simazine	0.00300	0.02
Tebuthiuron	0.00200	0.02
Thiamethoxam	0.00600	0.02
Thiobencarb	0.00200	0.02
Uniconazole	0.00400	0.05

Table 3. Multi-Analyte Screen (GC/MS) method detection limits (MDL) and reporting limits (RL) in ppb (EMON-SM-05-032, Revision 3) (CDFA, 2023b).

Analyte	MDL	RL
Clomazone	0.00600	0.05
Dichlobenil	0.00500	0.03
Dichloran	0.00500	0.05
Disulfoton	0.00600	0.05
Ethoprophos	0.00400	0.03
Fonofos	0.00600	0.03
Malathion	0.00600	0.03
Parathion Ethyl	0.00600	0.03
Parathion Methyl	0.00400	0.03
Phorate	0.00400	0.03
Piperonyl Butoxide	0.00400	0.03
Prometryn	0.00600	0.03
Propanil	0.00600	0.05
Triallate	0.00500	0.03
Benfluralin	0.00400	0.05
EPTC (S-ethyl dispropylthiocarbamate)	0.00300	0.05

DATA ANALYSIS

Results from the samples will be used to assess the presence and concentrations of clothianidin and thiamethoxam in areas of agricultural use. DPR will provide a letter reporting the results to participating well users and publish an analysis of sampling results following the completion of the study. Detections in the prioritized and surrounding areas may be used to assess regional vulnerability to groundwater contamination. These results may trigger additional sampling, lead to expansion of Groundwater Protection Areas, or a formal review of the detected pesticide as outlined in Food and Agricultural Code Sections 13149-13151. Additionally, results from this study will be published to the Well Inventory Database during the annual update.

ESTIMATED TIMETABLE

- March 2024 through June 2025: Conduct sampling.
- Summer 2024 - fall 2025: Obtain and review analytical results from CDFa laboratory.
- Spring 2026: Complete report of findings and post to DPR’s website.
- Communication
 - Provide notice to the County Agricultural Commissioner two weeks prior to initiating monitoring in a county. Additional notice will be provided if there is a six-month lapse in monitoring within a county.
 - Provide results to the Well Inventory Database manager.
 - Provide results to participating well users within 90 days of receipt from the laboratory.

FIGURES

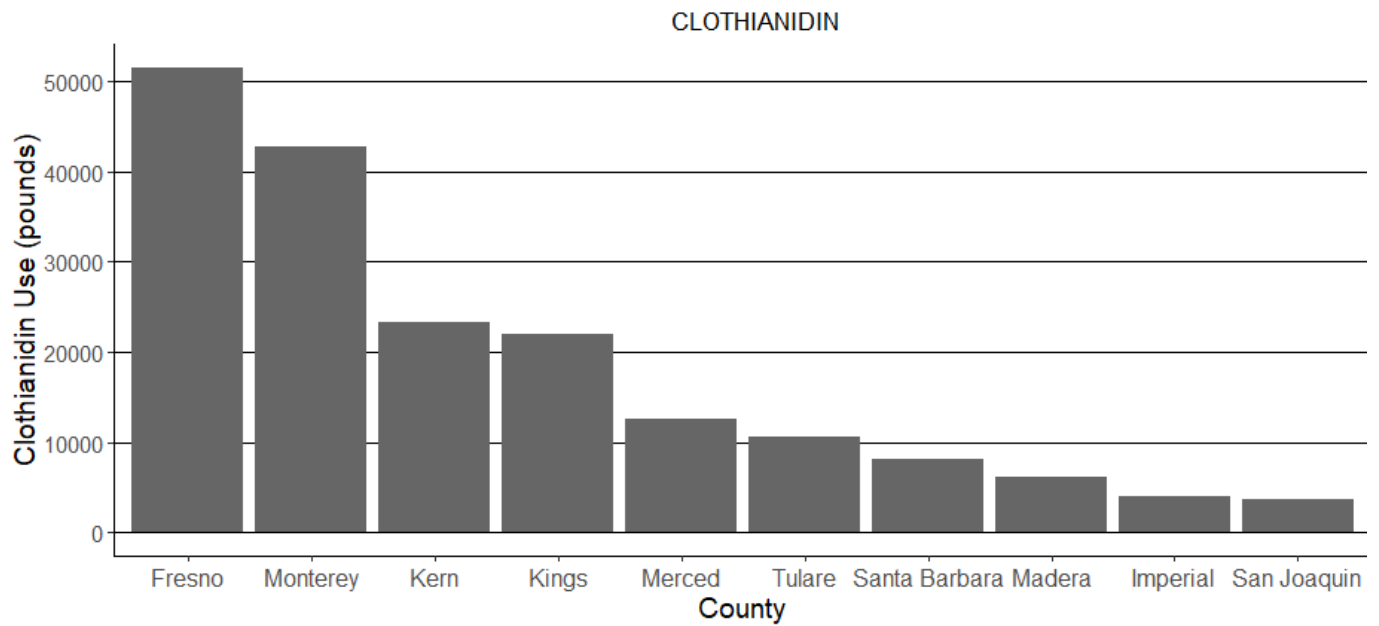


Figure 1. Total reported agricultural use of clothianidin in the top ten California counties.

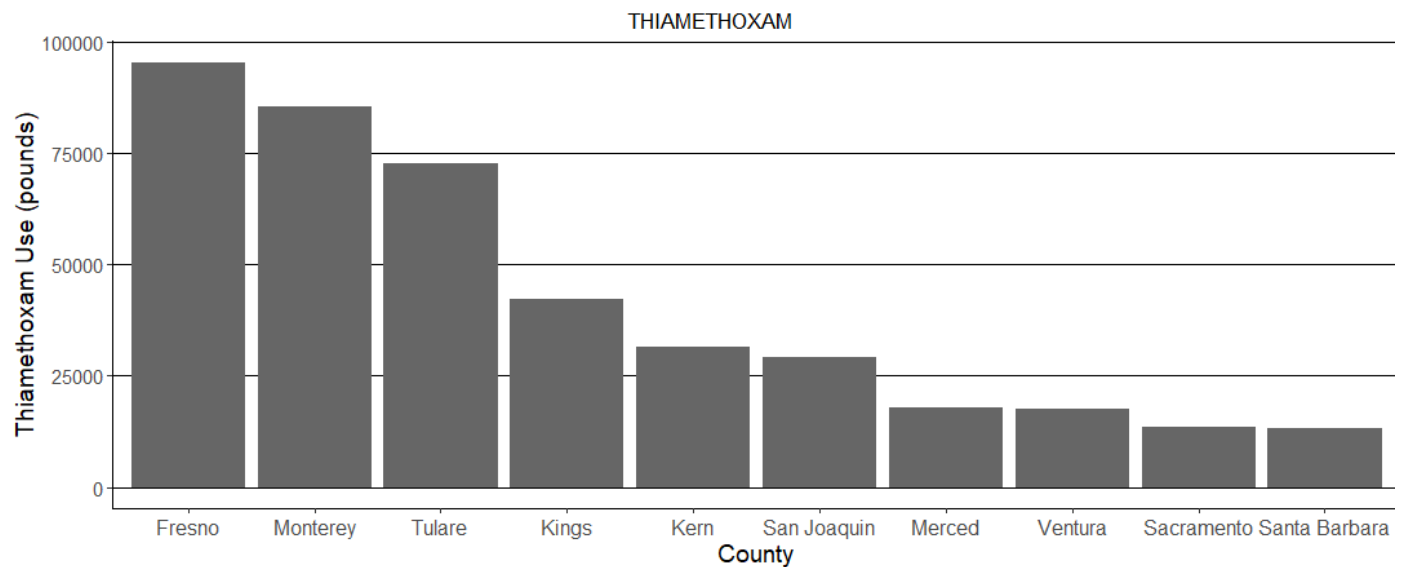


Figure 2. Total reported agricultural use of thiamethoxam in the top ten California counties.

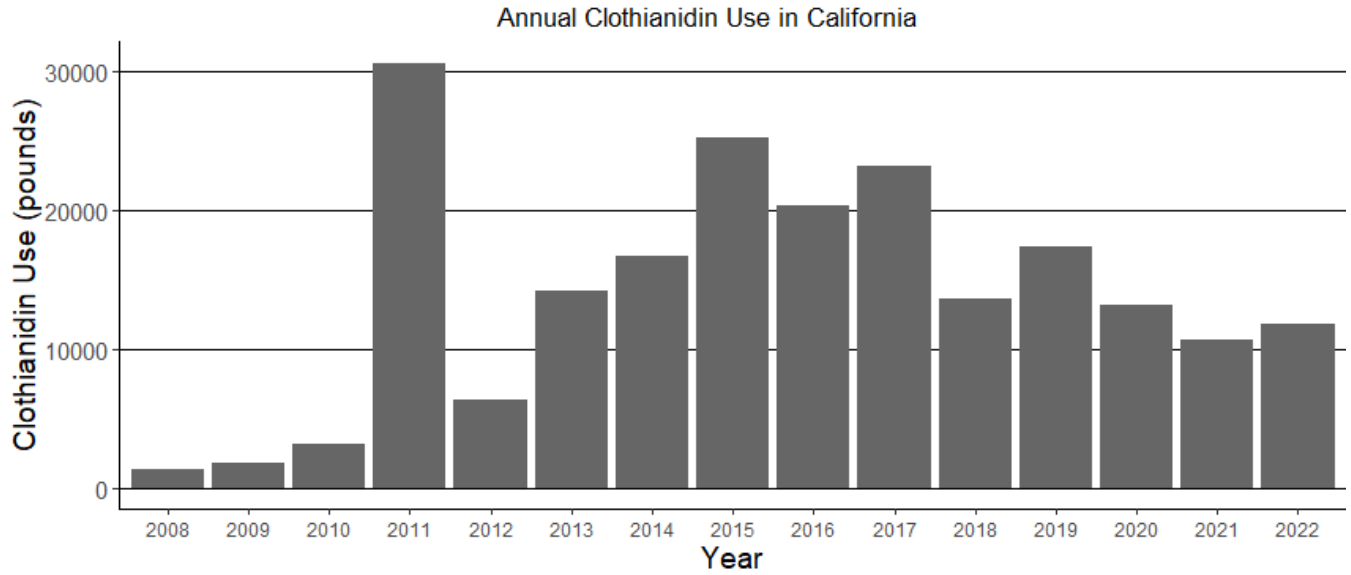


Figure 3. Statewide reported agricultural use of clothianidin from 2008 to 2022.

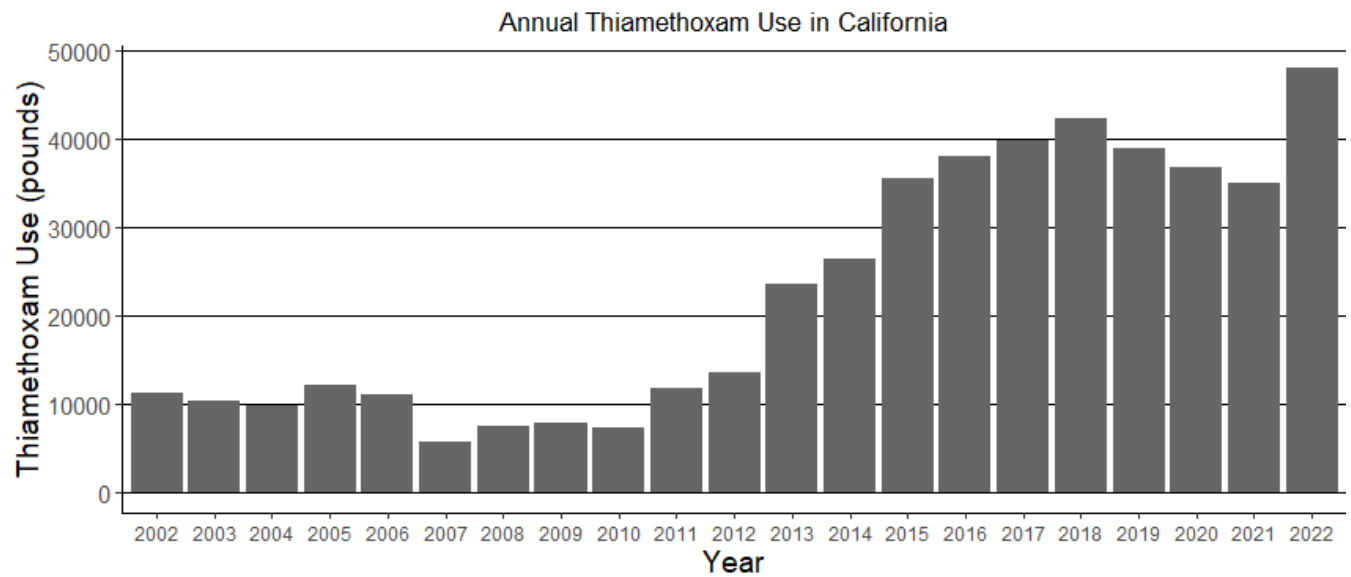


Figure 4. Statewide reported agricultural use of thiamethoxam from 2002 to 2022.

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APPENDIX 1. Annual clothianidin use (pounds) from 2008 to 2022 for counties with over 100 pounds total use. Counties are ordered by highest use.

County	2008	2009	2010	2011*	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	Total
Fresno	171	162	237	11318	1562	4163	3769	7755	4193	4653	2526	3639	2832	2179	2398	51557
Monterey	16	52	160	232	410	2186	4065	6054	4796	4658	3741	5651	3505	3353	3924	42803
Kern	657	755	665	2331	1021	1844	1915	2534	2140	4656	997	1384	909	669	870	23349
Kings		21		12356	183	706	677	1454	1185	1685	1089	1166	881	433	243	22052
Merced	11	118	119	1298	159	1051	417	963	1469	1988	1024	1406	1040	580	936	12579
Tulare	322	161	258	813	633	741	864	953	1598	1402	753	814	560	293	397	10562
Santa Barbara	24	18	138	187	505	108	889	1257	1021	736	611	672	571	714	658	8109
Madera		199	132	615	258	953	513	706	549	583	309	388	362	404	179	6150
Imperial				227	189	354	622	686	626	382	257	139	188	148	136	3954
San Joaquin	14	139	842	141	182	207	470	212	251	172	257	197	274	142	137	3637
Stanislaus			99	11		235	79	310	190	443	129	409	357	356	83	2701
Ventura				27	85	101	147	178	313	290	360	261	187	188	196	2333
Sonoma	24	36	101	129	45	47	37	264	239	194	213	263	277	203	129	2201
Sutter			1	210	224	106	165	111	60	186	160	131	296	262	227	2139
Napa	62	54	40	21	9	26	55	149	242	150	278	156	280	208	376	2106
San Luis Obispo	22	12	156	29	138	91	149	294	143	80	122	197	102	111	444	2090
Santa Clara				0	38	196	235	288	419	285	219	39	42	34	33	1828
San Benito					81	151	137	270	278	206	192	73	48	86	137	1659
Yolo			2	191	58	98	191	269	32	90	77	34	31	20	2	1095
Riverside		8	0	96	215	528	1	2	21	100	28	4	7	2	2	1014
Solano				34	65	107	257	71	163	89	21	20	17	33	12	889
Butte			1	1	49	69	195	132	89	51	49	19	59	33	72	819
Yuba				48	43	22	29	41	25	20	56	74	100	42	96	596
Tehama					47	3	200	91	7	13	26	13	23	43	12	478
Sacramento	11	24	110	2	2		25	8	171	24		13	55	16	5	466
Colusa				249	16		3	10	5	24	20	62	24	4	6	423
Glenn				85		37	96	51	2		17	16	0	11	8	323
Santa Cruz						26	44	63	74	20	46	11	13	10	2	309
Mendocino				7	3		293								1	304
Contra Costa		5	2			32	50	80	68	44	1	4				286
Placer				5	48	1			1	21		32		32		140
Los Angeles							102		0	0		6		1	1	110
El Dorado			0						18		11	38	14	20		101

*Note: The higher reported use of clothianidin in 2011 was confirmed to be from increased use on cotton.

APPENDIX 2. Annual thiamethoxam use (pounds) from 2002 to 2022 for counties with over 100 pounds total use. Counties are ordered by highest use.

County	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	Total
Fresno	3947	3739	3778	4647	5210	3211	3546	3839	2081	3139	2374	5206	4299	6266	6221	5694	5847	5291	5292	4894	6966	95487
Monterey	18	47	39	129	302	377	467	718	1296	2560	4088	5612	7661	7001	9304	7512	9169	8246	7399	6455	6970	85370
Tulare	305	378	373	548	314	131	70	98	72	245	1293	3643	4527	5952	7659	8477	9000	7890	7920	6551	7139	72585
Kings	4098	3003	2992	4504	3319	494	1183	655	1276	2293	1106	2135	1507	1875	1442	2279	2043	2584	1549	642	1212	42191
Kern	1123	1265	1088	818	372	47	130	245	78	258	328	1505	1231	2427	2856	3385	2837	2223	2556	2257	4537	31566
San Joaquin	3	149	39	228	384	424	395	523	504	1057	890	1186	1436	1947	1792	2431	2594	3055	2575	3089	4467	29168
Merced	547	526	191	430	249	118	175	31	443	129	332	453	683	1136	867	1233	1348	1198	1218	2224	4227	17758
Ventura	12	88	160	95	215	275	434	407	236	373	353	559	836	2989	1728	1811	1876	1447	1578	1132	1096	17700
Sacramento	12	2	3	9	7	6	78	133	81	122	121	299	153	692	407	1521	1557	1886	1550	2119	2678	13436
Santa Barbara			2	20	166	204	344	383	353	440	525	662	852	1288	1266	1010	937	849	1032	1202	1770	13305
San Luis Obispo			3	15	43	26	62	117	104	332	390	208	546	778	648	693	618	844	656	572	642	7297
Yolo	45	180	37	2	3	3	10	36	39	42	78	40	77	132	150	423	1053	488	862	618	1221	5539
Madera	47	129	65	140	89	3	24	28	35	27	179	409	400	539	512	329	452	234	221	354	743	4959
Napa							5	46	69	60	54	33	90	370	813	541	467	466	281	524	871	4690
Imperial	193	71	115		3			7	2	36	292	116	657	623	664	440	254	331	283	131	291	4509
Riverside	190	166	204	177	10	4	3	3	65	44	99	27	21	32	12	399	465	478	463	342	689	3893
Sonoma							3	30	62	62	165	225	166	147	172	275	189	172	234	414	686	3002
San Benito	42	59	48	29	15	9	1	20	40	45	90	232	169	171	300	295	266	274	227	333	250	2915
Santa Clara	35	47	64	52	45	38	75	54	79	62	87	214	186	168	339	263	279	207	83	205	293	2875
Stanislaus	11	46	10	3	0	0	8	2	40	77	90	174	173	314	123	191	271	102	183	371	311	2500
San Diego		0	8	16	25	44	39	23	38	79	181	194	90	116	165	153	203	268	180	108	146	2076
Colusa	163	118	380	114	21	6	162	148	93		20	16	1		2	15	132	12	52	99	308	1862
Santa Cruz			1	9	69	75	58	32	64	129	116	183	180	260	139	113	122	113	38	65	79	1845
Orange	26	26	54	46	34	31	36	36	27	23	63	25	53	33	55	50	64	54	42	10	23	811
Solano	24	1	3	4	2	1	6	5	18	2	30	21	29	27	30	25	32	45	116	103	208	732
San Bernadino					1			7		1	57	27	96	16	92	123	117	42	49	16	39	683
Contra Costa	4			10	8	23	86	51	11	38	7	42	73	57	48	94	27	9	19	4	6	617
San Mateo			6	11	8	9	22	10	7	14	23	52	44	40	55	32	40	44	27	40	44	528
Glenn	93	35	23	45	68	39	14	16	43	22	5		11	35		18	32	7				506
Los Angeles		84	89	13	3	2	5	1	9		5	2	2	22	20	7	9	19	1	13	9	315
Lake	93	44	25	18	6	4							8				18	8	11	52		287
Mendocino	14	34											19	18	8		1	49	4	4	28	179
Sutter	37	15	8		19	13	6	7	9					1			4			10	25	154
Siskiyou						5			9	11	7	31	27		18	13	4	8	2			135
Modoc										3	8	27	25		6		10				40	119
Yuba		62	9				3	3	7	4	5	3			0	5	5		4	4		114
Del Norte							5	24	12	13	4	15	10	11		7					1	102