RESULTS FOR STUDY GW08: GROUND WATER PROTECTION LIST MONITORING FOR TEBUTHIURON

Joy Dias
Environmental Scientist

California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street, P.O. Box 4015
Sacramento, California 95812
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ABSTRACT

Tebuthiuron is a broad-spectrum herbicide with a high potential to leach through soil to ground water based on its physical-chemical properties. It is used primarily on rights-of-way and compacted soil surfaces prior to paving (pre-paving). Use tends to be concentrated in Southern California and, from 1996 to 2005, appears to be increasing in this area. The Department of Pesticide Regulation's (DPR's) Environmental Monitoring Branch (EMB) staff sampled wells from April to June 2008 to determine whether tebuthiuron has migrated to ground water in California counties with high reported use. Tebuthiuron was detected at quantifiable levels in four of the 59 wells sampled. Concentrations ranged from 0.052 to 0.142 µg/L. Two of these detections were located in adjacent sections of Los Angeles County. The other two detections were located in Solano and San Diego Counties. Four additional wells had trace detections of tebuthiuron. The U.S. Environmental Protection Agency (U.S. EPA) has established a lifetime health advisory (HAL) of 500 µg/L for tebuthiuron in drinking water.

The two detections of tebuthiuron within a one square mile area in Los Angeles County meets the minimum criteria established by DPR to consider these detections the result of legal agricultural applications. However, the reported use of tebuthiuron confounds this assessment and does not completely support the source as agricultural. Tebuthiuron is only used as a pesticide in California; it has no other uses and is not a breakdown product of any other chemical. Although it is clear that use of this registered pesticide was reported in the counties where ground water detections were found, under the current reporting system it is not possible to determine whether rights-of-way, pre-paving applications, or both caused the detections. Pesticide applications to railroad and utility rights-of-way are considered nonproduction agricultural use whereas pre-paving applications are not considered agricultural use. The two detections in adjacent sections of Los Angeles have railroad tracks on each side within a third of a mile and there is a history of legal tebuthiuron applications to Los Angeles railroad rights-of-way, so it is possible that these detections are from legal agricultural use. In areas with both agricultural and nonagricultural use of tebuthiuron it will always be a struggle to definitively determine which use pattern contributed to the detections. The potential contributions from pre-pavement applications of persistent herbicides, including tebuthiuron, should be studied more carefully. Regardless of the source, if tebuthiuron use continues to increase, it is probable that additional tebuthiuron residues will be detected in ground water. Therefore DPR staff will continue to monitor for tebuthiuron in ground water to better assess the source of any future detections.

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DISCLAIMERS

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

INTRODUCTION

The Pesticide Contamination Prevention Act (PCPA) (Statutes of 1985, Chapter 1298, Section 1) was enacted in 1985 to prevent further pesticide pollution of California ground water that may be used for drinking water supplies. The PCPA added sections 13141–13152 to the Food and Agricultural Code (FAC) and outlines procedures for:

(1) Gathering physical and chemical data that describes the mobility, persistence, and environmental fate of agricultural use[1] pesticides proposed for registration,
(2) Establishing specific numerical values (SNVs [threshold values]) for mobility and persistence, and
(3) Placing agricultural use pesticides on the Groundwater Protection List (GWPL) (Title 3, California Code of Regulations [3 CCR] section 6800[b]) if they "exceed" the SNVs and are applied in specified ways.

The PCPA then requires DPR to monitor ground water for the GWPL pesticides to determine if these pesticides have migrated to ground water as a result of legal agricultural use. DPR's EMB selects pesticides from the GWPL for monitoring based on national detection information, mobility and persistence properties, use intensity and location, agricultural production practices, and other factors such as human health concerns and the availability of laboratory analytical methods (Troiano, 1997). Since 1990, EMB has sampled over 1200 wells for 81 pesticides and pesticide breakdown products as part of GWPL monitoring.

EMB undertook this study to assess the potential for ground water contamination in the areas of highest reported use (Dias, 2008). Tebuthiuron is a nonselective herbicide primarily labeled for noncrop weed control on rights-of-way (e.g., utility, railroad, and highway), industrial sites, rangeland, and under paved surfaces. Since it is a long-lasting nonselective herbicide, it is not labeled for use on landscaped areas or areas where future landscaping is planned. Pesticide applications to rights-of-way such as utility lines, railroad beds, highway shoulders, and roadsides are considered nonproduction agricultural uses whereas applications to industrial sites and under paved surfaces are not considered to be agricultural use (CDPR, 2009). Although overall use is low relative to other pesticides regulated as ground water contaminants, EMB selected tebuthiuron for monitoring due to:

- Environmental fate properties indicating that it is extremely mobile and persistent;
- An increase in use from 1996 to 2005; and
- Recent detections in California's ground water.

The U.S. EPA has determined that tebuthiuron is persistent, mobile, and can leach to ground water (U.S. EPA, 1994). Tebuthiuron products must contain a ground water advisory on the label indicating that the pesticide is known to leach through soil into ground water as a result of

[1] FAC section 11408 defines "agricultural use" to mean the use of any pesticide or method or device for the control of plant or animal pests, or any other pests, or the use of any pesticide for the regulation of plant growth or defoliation of plants. It excludes the sale or use of pesticides intended for home use, use in structural pest control, industrial or institutional use, the control of an animal pest under the written prescription of a veterinarian, or use of a pesticides by local districts or other public agencies for disease vector control under certain conditions.

registered uses under certain conditions (SSI Maxim, 2007; Dow AgroSciences, 2008). There are no specific use requirements or enforceable actions associated with the ground water advisory statement.

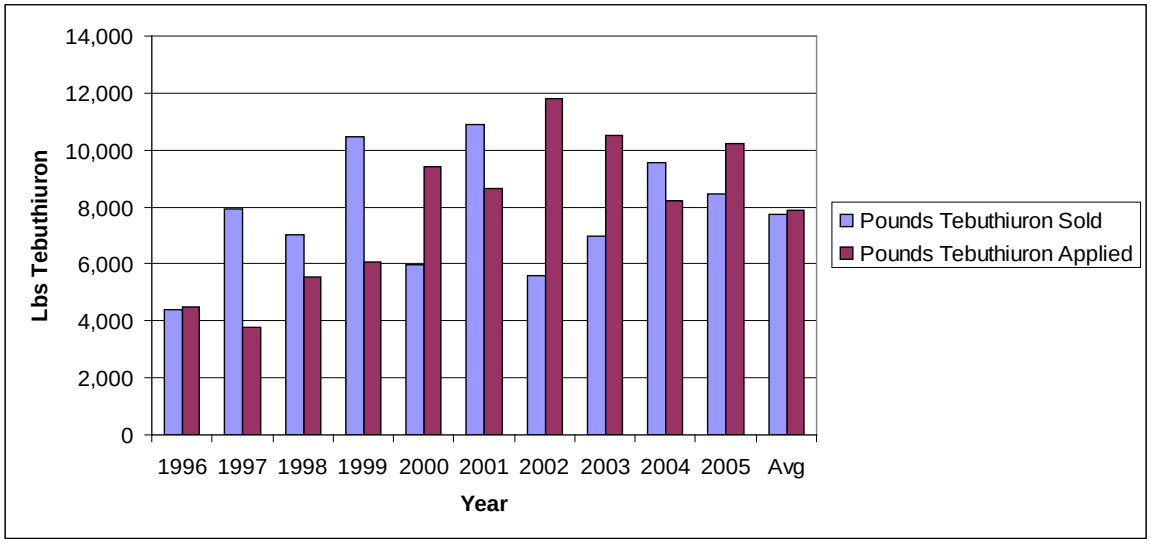
In California a pesticide must be placed on the GWPL if it has specific labeled uses and it "exceeds" one or more of the mobility SNVs and one or more of the persistence SNVs (Table 1). Tebuthiuron exceeds all of the SNVs for mobility and persistence (Table 1). Based on the LEACHM pesticide fate and transport model (Hutson and Wagenet, 1992), tebuthiuron has the highest potential to contaminate California ground water because it is the most mobile and persistent agricultural pesticide on the GWPL.

Table 1. Specific numerical value thresholds (3 CCR section 6804) and tebuthiuron physical-chemical properties (CDPR, 2008c).

	Mobility		**Persistence**		
	Water solubility (ppm)	**Koc (cm3/g)**	**Hydrolysis (days)**	**Aerobic soil metabolism (days)**	**Anaerobic soil metabolism (days)**
SNV	> 3	< 1900	> 14	> 610	> 9
Tebuthiuron	2600	80	> 64	1220	1520

Although overall use of tebuthiuron is not high compared to other pesticides EMB has monitored for in California, data obtained from DPR's Pesticide Use Report (PUR) data system indicate that tebuthiuron use throughout California has more than doubled from 1996 to 2005 (Figure 1) (CDPR, 2008a). The reported pounds of tebuthiuron sold from 1996 to 2005 were similar to the reported pounds applied during the same time (Figure 1) indicating that pest control businesses are complying with the reporting requirements (CDPR, 2008b).

Figure 1. Pounds of tebuthiuron sold and applied annually from 1996 to 2005 (CDPR, 2008a; CDPR, 2008b).



Tebuthiuron has been detected in California ground water by the SWRCB Groundwater Ambient Monitoring and Assessment (GAMA) Program. As part of the Groundwater Quality Monitoring Act of 2001 (Water Code sections 10780-10782.3) the SWRCB implemented the GAMA Program to improve statewide ambient ground water quality monitoring and assessment and to increase access to ground water quality data collected by public agencies. In collaboration with the U.S. Geological Survey (USGS) and the Lawrence Livermore National Laboratory, the SWRCB initiated the GAMA Priority Basin Project to assess ground water quality in basins that account for over 90% of all ground water used throughout the state. Prioritized basins were grouped into study units and monitored for a wide variety of constituents at very low detection limits. From 2004 through 2005, the GAMA program sampled 1340 wells in 42 counties and detected tebuthiuron in 29 wells in 10 counties (Bennett et al., 2006; Dawson et al., 2008; Kent and Belitz, 2009; Land and Belitz, 2008; Mathany et al., 2008; Montrella and Belitz, 2009; Schmitt et al., 2008; Wright et al., 2005) (Appendix VII). The samples had quantifiable concentrations of tebuthiuron ranging from and 0.02 to 0.14 µg/L with estimated concentrations ranging from E0.01 to E0.23 µg/L (Table 2 and Appendix VII). These data formed the basis for EMB's monitoring plan.

MATERIALS AND METHODS

EMB established a goal of sampling 40 to 60 wells for tebuthiuron (*N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N,N'*-dimethylurea) and four major degradation products:

- N-[5-(1,1-Dimethylethyl)-1,3,4-thiadiazol-2-yl]-N-methylurea
- 2-Dimethylethyl-5-methylamino-1,3,4-thiadiazol
- N-[5-(1,1-Dimethylethyl)-1,3,4-thiadiazol-2-yl-urea
- 2-Dimethylethyl-5-amino-1,3,4-thiadiazole

The samples were also analyzed for hexazinone, a pesticide that recently went through the detection response process at DPR, and for the following pesticides and degradation products that are regulated as ground water contaminants (3 CCR section 6800[a]): atrazine, bromacil, desethyl atrazine (DEA), desisopropyl atrazine (ACET), desmethylnorflurazon (DSMN), diamino chlorotriazine (DACT), diuron, norflurazon, prometon, and simazine. Monitoring for hexazinone provides additional data on the potential source of any detections. Monitoring for known ground water contaminants 3 CCR section 6800[a] pesticides) and degradates helps DPR assess the adequacy of our ground water protection program and to determine if new Ground Water Protection Areas (GWPAs) need to be identified. EMB has classified many sections within the state as GWPAs because they are vulnerable to ground water contamination by pesticides based on either soil conditions and the depth to ground water (less than 70 feet) or on the presence of verified pesticide residues in the ground water of the section (Troiano et al., 2000).

EMB usually selects GWPL sampling sites based on soil vulnerability and pesticide use reported at the section level. However, certain pesticide uses such as use on rights-of-way, are not reported on a section basis but as a total by county for any given month. Since tebuthiuron use is only reported at the county level, sampling sites were based on detections reported by the GAMA program and focused on the counties with the highest tebuthiuron use reported in the PUR from 1996-2005 (Table 2). As a result, even though Kern County is one of the highest use

counties, EMB did not sample wells in this county because GAMA did not detect tebuthiuron in any of the 115 wells they sampled. Also, even though GAMA detected tebuthiuron in one well each in Glenn and Yolo Counties, EMB did not sample in those counties partially due to the extremely low use relative to the other counties (Table 2).

Table 2. Total pounds of tebuthiuron applied from 1996 to 2005 and number of GAMA detections by county.

County	Total use 1996-2005 (lbs)	# of GAMA wells sampled	GAMA detections	GAMA detection range (µg/L)	GAMA references
Kern	12,709	115	0	N/A	N/A
Los Angeles	12,538	102	12	E* 0.01 – 0.14	Mathany et al., 2008; Land and Belitz, 2008
San Bernardino	11,271	45	2	E 0.01	Kent and Belitz, 2009
Riverside	8,271	101	2	E 0.01 – 0.02	Kent and Belitz, 2009
San Diego	8,261	35	4	E 0.02 – E 0.23	Wright et al., 2005
Orange	6,675	29	4	E 0.01 – 0.02	Mathany et al., 2008
Ventura	1,161	44	1	E 0.02	Montrella and Belitz, 2009
San Joaquin	676	52	1	0.03	Bennett et al., 2006
Solano	493	14	1	0.12	Dawson et al., 2008
Glenn	403	32	1	0.02	Schmitt et al., 2008
Yolo	238	23	1	0.03	Schmitt et al., 2008

*E = Estimated value

EMB staff sampled 22 of the 29 wells with tebuthiuron detections reported by GAMA. The SWRCB GAMA Program primarily focuses its sampling efforts on public supply wells with a sampling density of approximately one well per 25 km^2 (Wright et al., 2005). EMB prefers to sample domestic wells because they are generally shallower than irrigation or public supply wells which increases the likelihood of detecting pesticides that have migrated to ground water. If a well has a pesticide detection, EMB samples additional wells in the one-mile section of land of the original detection or in one or more of the three most adjacent sections (CDPR, 1996a). It was not possible to completely follow the protocol for a four-section survey in this study because many of the GAMA detections were located in urban areas with few additional wells. When possible, staff sampled additional wells within a three mile radius of the original GAMA detections.

When domestic wells were available in the sampling area, they were selected according to the well integrity procedures outlined in SOP FSWA006.00 (Marade, 1998). Where domestic wells were unavailable, public supply wells were sampled. All water samples were collected using the procedures described in SOP FSWA001.00 (Marade, 1996). CDFA's Center for Analytical Chemistry analyzed primary samples for tebuthiuron and its degradates using Method 304 (CDFA, 2007) which was determined to be unequivocal (Fattah, 2008a). Samples were also analyzed for hexazinone and the 3 CCR section 6800(a) pesticides and degradates using the unequivocal Method 303 (CDFA, 2008; Fattah, 2008b). Samples containing known amounts of pesticide disguised as actual samples (blind spikes) were prepared and analyzed in accordance with SOP QAQC001.00 (Segawa, 1995). Samples containing deionized water (field blanks) were collected at the same time as field samples and analyzed to confirm the validity of positive results (Orlando, 2007).

The reporting limit (RL) for all analytes was 0.05 µg/L, the concentration above which quantitative results can be reliably obtained. The method detection limit (MDL) for tebuthiuron was 0.014µg/L. The MDL is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (Segawa, 1995).

RESULTS

From April to June 2008, EMB staff sampled 59 wells in eight California counties for tebuthiuron, its degradates, hexazinone, and the 3 CCR section 6800(a) pesticides and degradates (Appendix I). Tebuthiuron was detected in eight wells in three counties. Four of the wells had concentrations above the RL of 0.05 µg/L and four had trace detections below the RL (Table 3). The analytical method used was unequivocal and the first four tebuthiuron detections were confirmed in the backup samples. None of the samples had detectable levels of the tebuthiuron degradates. Two wells contained detections of hexazinone. Twenty-five wells contained detections of the 3 CCR section 6800(a) pesticides and/or their degradation products (Table 3).

Table 3. Number of wells sampled by EMB in each county and number of wells with pesticide detections.

County	Number of wells sampled	Tebuthiuron detections below RL	Tebuthiuron detections above RL	Hexazinone detections	Wells with 3 CCR section 6800(a) pesticide and/ or degradate detections
Los Angeles	20	1	2	1	9
Orange	6	0	0	0	4
Riverside	3	0	0	0	3
San Bernardino	5	0	0	0	2
San Diego	12	3	1	0	2
San Joaquin	4	0	0	1	2
Solano	5	0	1	0	3
Ventura	4	0	0	0	0
TOTAL	**59**	**4**	**4**	**2**	**25**

Seven of the eight EMB-sampled wells with tebuthiuron detections had previously tested positive for tebuthiuron when sampled by USGS (Table 4). EMB detected quantifiable tebuthiuron residues in two wells in Los Angeles County and one well each in San Diego and Solano Counties. Four additional wells contained trace levels of tebuthiuron – one in Los Angeles County and three in San Diego County. All of the sampled wells appeared to be in good condition and had no obvious signs of point-source contamination. Several of the wells were located near potential use sites but use could not be confirmed because monthly PURs are not site specific. Pest control businesses are only required to report the month and county where tebuthiuron is used, but not the location, by section, where it is applied in the county.

Table 4. Wells with tebuthiuron detections when sampled by EMB or the SWRCB GAMA Program.

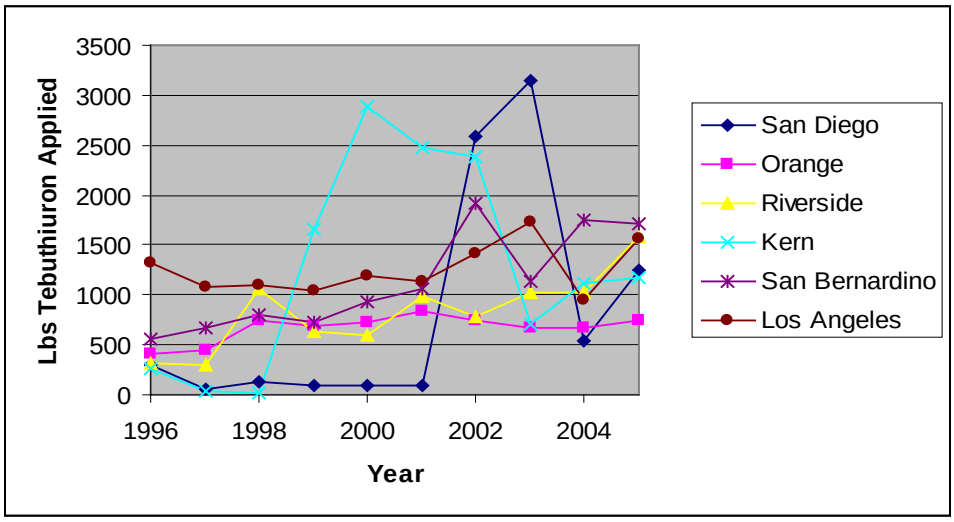
County	Location code	GWPA	DPR conc. (µg/L)	GAMA conc. (µg/L)	Well depth	Map
Los Angeles	19-02		ND	E 0.02	184	-
Los Angeles	19-07		ND	0.03	30	-
Los Angeles	*19-09*		*<RL*	*0.04*	500	*Appendix II*
Los Angeles	19-12		ND	0.03	600	-
Los Angeles	19-13		ND	E 0.01	732	-
Los Angeles	19-16		ND	0.02	210	-
Los Angeles	**19-19**	**Runoff [2]**	**0.052 [1]**	**0.14**	162	**Appendix III**
Los Angeles	**19-20**	**Runoff**	**0.055 [1]**	**NS**	183	**Appendix III**
Los Angeles	19-21	Runoff	ND	E 0.04	255	-
Orange	30-02	Leaching [3]	ND	E 0.02	1410	-
Orange	30-05	Leaching	ND	0.02	1230	-
Orange	30-06	Leaching	ND	E 0.01	465	-
Riverside	33-01	Leaching	ND	0.02	170	-
Riverside	33-04	Runoff	ND	E 0.01	252	-
San Bernardino	36-01		ND	E 0.01	160	-
San Bernardino	36-03		ND	E 0.01	450	-
San Diego	*37-01*		*<RL*	*E 0.02*	230	*Appendix IV*
San Diego	*37-02*		*<RL*	*E 0.09*		*Appendix IV*
San Diego	**37-08**		**0.116**	**E 0.23**	12.6 [4]	**Appendix V**
San Diego	*37-09*		*<RL*	*E 0.03*	906	*Appendix IV*
San Joaquin	39-01		ND	0.03		-
Solano	**48-01**		**0.142 [1]**	**0.12**		**Appendix VI**
Ventura	56-03	Leaching	ND	E 0.02		-

E = Estimated value
RL = Reporting Limit: 0.05 µg/L
ND = Not detected
NS = Not sampled
[1] Average concentration when both the primary and backup samples were analyzed. See Appendix I for individual values.
[2] Runoff GWPA = a section that is vulnerable to pesticide contamination primarily by runoff from hardpan soils to dry wells, ditches, sumps or ponds, soils with deep cracks, or coarse soil areas
[3] Leaching GWPA = a section that is vulnerable to pesticide contamination primarily by leaching through the soil to ground water
[4] Depth to water

Tebuthiuron Pesticide Use Patterns

Statewide use of tebuthiuron tends to be concentrated in the southern part of the state and appears to vary annually (Figure 2). While some of the high use counties have had an increase in use, Kern and San Diego Counties appear to have had the largest overall increase (Figure 2). Use in Los Angeles and Orange Counties have remained fairly steady with only a slight increase from 1999-2006.

Figure 2. Tebuthiuron use in six counties for reporting years 1999-2006 (CDPR, 2008a).



According to the PUR, applications to rights-of-way and for landscape maintenance account for the majority of tebuthiuron use reported by pest control businesses and other users (CDPR, 2008a) (Table 5). In Los Angeles and San Diego Counties, applicators primarily report tebuthiuron as being applied to rights-of-ways while in Solano County, applicators report using tebuthiuron mostly for landscape maintenance. The use of tebuthiuron in Solano County is extremely low compared to the other counties with detections. Since tebuthiuron is not labeled for landscape maintenance and the PUR site coding options are limited and do not distinguish the actual uses of this pesticide, it is likely that the applicators are interpreting the PUR categories differently (Table 6). In some cases, landscape maintenance reports may include rights-of-way applications and rights-of-way reports may include pre-paving applications for which there is not a designated code.

Table 5. Pounds of tebuthiuron applied from 1996 to 2005 sorted by the top three application sites as reported in the PUR (CDPR, 2008a).

County	Pounds of tebuthiuron applied 1996-2005			Total pounds applied 1996-2005
	Rights-of-way [1]	Landscape maintenance [2]	Nonagricultural areas [3]	
Kern	8,134	4,571	4	12,709
Los Angeles	12,057	430	0	12,487
San Bernardino	10,868	248	1	11,117
Riverside	2,262	5,801	0	8,063
San Diego	8,061	153	0	8,214
Orange	6,385	291	0	6,675
Ventura	921	173	0	1,094
San Joaquin	268	0	356	624
Solano	130	331	32	493
Glenn	335	69	0	403
Yolo	189	49	0	238

[1] Any pest control work performed along roadsides, power lines, railroad tracks, median strips, ditch banks, and similar sites (CDPR, 1997).

[2] Any pest control work performed on landscape plantings around residences or other buildings, golf courses, parks, cemeteries, etc. (CDPR, 1997).

[3] Uncultivated nonagricultural areas (CDPR, 1997).

Table 6. Percent of tebuthiuron applied in the six highest use counties from 1999-2005 sorted by the application type.

County	Percent of tebuthiuron applied 1999-2005 [1]			Total pounds applied 1999-2006 [4]
	Pre-paving [2]	Utility rights-of-way [2]	Undetermined [3]	
Kern [5]	0	96	4	10,745
Los Angeles	79	2	19	9,030
San Bernardino	91	3	6	9,177
Riverside	85	0	15	6,614
San Diego	7	56	37	7,751
Orange	90	2	8	5,085

[1] Business license numbers were not available prior to 1999.
[2] Categories were based on personal communication with the highest use applicators.
[3] These applicators were not contacted to determine use practices.
[4] CDPR, 2008a.
[5] Kern County only includes data from 2000-2005.

Since tebuthiuron applicators are only required to report the total number of pounds they use per county, not by individual section of land, the PUR cannot be used to determine if any applications of tebuthiuron were made to individual sections. However, the PUR was used to determine the identity of the principle pest control businesses reporting tebuthiuron use. EMB staff interviewed the pest control businesses with the highest reported use to help determine how and where they had applied tebuthiuron. Table 6 outlines the percentage of use based on personal communication with the three highest use pest control businesses in the six highest use counties. The undetermined category indicates pest control businesses who were not contacted to determine primary use. While most of the tebuthiuron was reported as being applied to rights-of-way (Table 5), talking directly with the pest control businesses allowed EMB to separate those applications into pre-paving and utility rights-of-way herbicide treatments (Table 6). Although some railroad rights-of-way use was discovered in Los Angeles County, the applications occurred prior to 1996. It also appears that in some counties, such as Riverside and Kern, a large percentage of the use was reported in the PUR as landscape maintenance, but according to the pest control businesses the use was for pre-paving and utility rights-of-way, respectively. Limited and potentially ambiguous PUR coding options are most likely the reason for these discrepancies.

Los Angeles County Tebuthiuron Detections

The majority of tebuthiuron use reported in Los Angeles County from 1999 to 2005 was applied as pre-paving herbicide treatments (Table 6). The main applicator in four of the top six counties (Los Angeles, San Bernardino, Riverside, and Orange) applies tebuthiuron to the soil before pavement is laid for roads and parking lots (California Weed Control, personal communication, 2008). Although the exact application sites are unknown, this applicator has applied 79% of the tebuthiuron reported in Los Angeles County from 1999 to 2005 (Table 6).

EMB sampled three wells in southeastern Los Angeles County (Appendix III). The wells at Location Codes 19-19 and 19-20 were located in adjacent runoff GWPAs[2], had tebuthiuron residues averaging 0.052 µg/L and 0.055 µg/L, and were 162 feet and 183 feet deep, respectively (Table 4). The third well did not have detectable levels of tebuthiuron and was located approximately 1 to 1.5 miles north of the positive wells. Both of the positive wells had railroad tracks on each side within a third of a mile. An applicator who had worked under contract for the Southern California Regional Rail Authority indicated that tebuthiuron was applied regularly to the Authority's railroad rights-of-way beginning in the late 1970's and that these applications had been discontinued in 1995 (Agrichem Services, Inc., personal communication, 2008). It is unknown what pesticides are or were applied to other railroad or utility rights-of-way in Los Angeles County.

In western Los Angeles County, one well (Location Code 19-09) contained trace levels of tebuthiuron below the RL (Table 4 and Appendix II) while another well (Location Code 19-08) sampled approximately 500 feet away did not have detectable levels of tebuthiuron. Both wells were located at a gravel mining operation and were approximately 500 feet deep. The location indicates that the soils are most likely coarse and vulnerable to leaching. DPR does not have soils data for this section to conclusively make this determination but coarse soils are associated with pesticide leaching where depth-to-ground water is shallower than 75-100 feet. A railroad track is located within a quarter mile of the well. It is unknown if tebuthiuron has been applied to this specific railroad track, but the tebuthiuron labeling does allow this use. These wells are also located in an industrial area that has the potential for non-agricultural tebuthiuron applications.

San Diego County Tebuthiuron Detections

Three wells were sampled in eastern San Diego County (Appendix V). One well contained 0.116 µg/L of tebuthiuron and had a ground water depth measured at 12.6 feet (Location Code 37-08) (Table 4). The remaining two wells, 105 feet (Location Code 37-07) and 0.9 miles (Location Code 37-10) from the positive well, respectively, did not have detectable levels of tebuthiuron. Both of these wells had a measured ground water depth of less than 50 feet. Tebuthiuron has been applied since 2002 to many miles of utility rights-of-way in the vicinity of these three wells (PROVCO, personal communication, 2008). The positive well (Location Code 37-08) and the negative well at Location Code 37-07 were within 60 feet of a utility pole with a vegetation-free circle indicating that these areas were likely treated with tebuthiuron as indicated by the applicator. The depth-to-ground water has not been systematically mapped for this area but the sampled wells had very shallow depth-to-ground water. The wells are also located in a section with coarse soils that allow for leaching.

Three wells in southwestern San Diego County contained trace detections of tebuthiuron (Table 4). The detection in El Cajon (Location Code 37-09) (Appendix IV) is approximately 1.5 miles from a utility substation that has received an annual application of tebuthiuron since 2002 (PROVCO, personal communication, 2008). The well is also located less than a quarter mile

[2] Since soils data are not available for most of Los Angeles County, current GWPAs have only been identified based on pesticide detections. Although some GWPAs have been identified in Los Angeles County, the adjacent sections with tebuthiuron detections in Los Angeles County are not GWPAs.

from railroad tracks. It is unknown if tebuthiuron has been applied to these railroad tracks, but its labeling allows this use. Although this detection was below the RL, the well is very deep at 906 feet. The other two trace detections (Location Codes 37-01 and 37-02) are located in Lakeside (Appendix IV). The main applicator in San Diego County has applied tebuthiuron to utility substations and utility poles in Lakeside since 2002 (PROVCO, personal communication, 2008). It is unknown what pesticide was used in the locations near the detections before the current applicator received the contract from the utility company. The two detections are located in coarse soil sections near sand and gravel pits. Although DPR does not have depth-to-ground water data for these sections, the well at Location Code 37-01 was 230 feet deep. Two additional wells sampled approximately one mile from each detection in Lakeside did not have detectable levels of tebuthiuron.

Solano County Tebuthiuron Detection

One well in Solano County contained an average of 0.142 µg/L of tebuthiuron (Location Code 48-01) (Table 4). The well is located approximately 75 feet from an abandoned railroad track, less than 350 feet from an active railroad track, within 100 feet of a utility pole, and approximately one mile from a utility substation (Appendix VI). Three additional wells sampled within three miles of the positive well did not have detectable residues of tebuthiuron. These wells were also located adjacent to the active railroad track. The positive well is located less than a half-mile from what appears to be a mining operation indicating the possibility that this well is located in coarse soils. DPR does not have soils or depth-to-ground water data for this section to make an accurate determination if it should be a GWPA.

Hexazinone and 3 CCR section 6800(a) Pesticide Detections

Two wells had hexazinone detections. One of the wells (Location Code 19-19) was located in a runoff GWPA in Los Angeles County that also had positive detections of tebuthiuron and DEA. The other well (Location Code 39-02) was located in San Joaquin County and no other pesticides were detected.

All of the counties except Ventura had wells that tested positive for the 3 CCR section 6800(a) pesticides or degradates. Of the twenty-five wells that contained detections of 3 CCR section 6800(a) pesticides or degradates, fifteen had detections of multiple pesticides with up to 6 pesticides in one well (Appendix I). Fourteen of the wells with detections of 3 CCR section 6800(a) pesticides or degradates were located in sections that have not been designated as GWPAs (Appendix I).

DISCUSSION

Tebuthiuron Ground Water Contamination Potential

Tebuthiuron is mobile and persistent, physical-chemical properties that make it a likely ground water contaminant. Tebuthiuron residues have also been detected in surface water runoff (CDPR, 2008d). Residue-laden runoff water could contaminate ground water if it reaches a permeable site that is vulnerable to leaching. Modeling conducted by DPR also indicates that compared to

the other pesticides on the GWPL and the 3 CCR section 6800(a) pesticides, tebuthiuron has the highest potential to move with soil water and persist in ground water.

Exposure Standards

A minimum contamination level (MCL) or public health goal (PHG) has not been determined for tebuthiuron, but the U.S. EPA has established a lifetime health advisory (HAL) of 500 µg/L for tebuthiuron in drinking water (U.S. EPA, 2009). At this concentration a chemical in drinking water is not expected to cause any adverse, noncarcinogenic health effects for a lifetime of exposure based on a 70-kg adult consuming 2 liters of water per day. The HAL is not a legally enforceable Federal standard. U.S. EPA has also set a reference dose (RfD) of 70 µg/L for tebuthiuron. An RfD is an estimate of a daily oral exposure to the human population, including sensitive subgroups, that is likely to be without appreciable risk of deleterious effects during a lifetime.

Tebuthiuron Detections

Tebuthiuron has been detected in 30 out of 1312 wells sampled throughout California. EMB confirmed tebuthiuron detections in seven of 22 wells that had previously tested positive when sampled by GAMA and EMB also found tebuthiuron residues in an additional well not sampled by GAMA (Table 4). Due to its physical-chemical properties, tebuthiuron has been detected in ground water even though it is not heavily used. Although it is not possible to determine on a section basis where tebuthiuron is used, all of the EMB detections were located close to areas with potential use sites.

The majority of tebuthiuron use in San Diego County is applied annually to utility rights-of-way. This type of application method is commonly associated with some the 3 CCR section 6800(a) pesticides detected in ground water due to legal agricultural use. The utility rights-of-way receive annual applications of tebuthiuron which could lead to a greater probability for leaching or runoff following rain events. Known ground water contaminants used on highway rights-of-way have been shown to runoff to sensitive sites and to leach into the soil, potentially transporting the herbicides to ground water by soil infiltration (Powell et al., 1996; Simmons and Leyva, 1994). Although tebuthiuron is not applied under irrigated agricultural conditions, the pesticide labels indicate that tebuthiuron is most effective in arid regions when it is applied just before the rainy season and that higher application rates can be applied in areas with higher precipitation rates (SSI Maxim, 2007; Dow AgroSciences, 2008). The timing of these applications could facilitate movement of tebuthiuron to ground water.

Tebuthiuron applications in Los Angeles County mostly consist of pre-paving treatments although there are known historical uses on railroad rights-of way. Given the reported use and discussions with licensed pest control businesses, it is unclear if the detections in Los Angeles County are from the use in pre-paving applications or from historical or current use on railroad or utility rights-of-way. Capel et al. (1999) surmised that pre-paving applications of prometon, a known ground water contaminant with properties and uses similar to tebuthiuron, may have moved to surface water and leached to ground water after becoming exposed to and moving with rainwater as the pavement became worn and cracked. This could also be the case with the

tebuthiuron detections in Los Angeles County. Tebuthiuron is extremely persistent and could possibly stay active under pavement until the pavement degrades or is disturbed. There is very little literature on the fate of pesticides under pavement so additional research is needed. Since tebuthiuron was applied to the railroad rights-of-way and the two positive wells in adjacent sections were surrounded by railroads, it is also possible that tebuthiuron could have moved with rain water after applications to railroad rights-of-way as suggested for the San Diego County detections.

EMB has added tebuthiuron to the method that DPR uses to analyze for the known ground water contaminants and hexazinone. Adding tebuthiuron to this screen will allow EMB to continue to monitor for the herbicide during future GWPL sampling studies. These samples will be especially valuable if they occur in Los Angeles County where the majority of the detections occurred although it is difficult to find wells to sample in the areas where tebuthiuron was detected.

Hexazinone and 3 CCR section 6800(a) Pesticide Detections

The two wells with positive detections for hexazinone were incorporated into Pesticide Contamination Prevention Act Review Process triggered by multiple detections of hexazinone in ground water.

The fourteen wells with detections of 3 CCR section 6800(a) pesticides or degradates located in sections that are not currently designated as GWPAs will be evaluated to determine if these sections should become GWPAs.

CONCLUSIONS

Tebuthiuron is mobile and persistent in the environment. EMB staff sampled wells in high use counties and detected tebuthiuron in 8 of 59 wells, 4 of which were above DPR's RL of 0.05 µg/L. Tebuthiuron has also been detected by other agencies in California ground water and surface water. Although tebuthiuron has not been detected in a large number of samples, modeling indicates that its low use is probably the reason for the low number of detections. Use in California has doubled from 1996 to 2005 which increases the likelihood that additional tebuthiuron residues will leach to ground water. In the areas where tebuthiuron was detected, the herbicide is primarily applied along rights-of-way and to soil before pavement is laid. EMB has not been able to definitively determine the specific application method that lead to these detections. Los Angeles County had detections in adjacent sections and the wells were located within a third of a mile of railroad tracks. There have also been historical applications to railroad rights-of-way in Los Angeles County. EMB will continue to analyze wells sampled for tebuthiuron because it has been included in the DPR analytical screen for known ground water contaminants that is often used when wells are sampled for pesticides. Since tebuthiuron is also part of the pesticide analytical screen that the GAMA Program uses, we will continue to monitor their results for additional tebuthiuron detections.

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APPENDIX I

Sampling results for GW08 in µg/L. Tebuthiuron detections over the reporting limit are in **bold** type. Trace tebuthiuron detections are in *italics*.

								6800(a) pesticides						6800(a) degradates					
County	Township/ Range-Section	Location Code	GWPA	GAMA	Tebuthiuron	Tebuthiuron Back-up	Hexazinone	Atrizine	Simazine	Diuron	Prometon	Bromacil	Norflurazon	dsmn	dea	acet	dact	# of Pesticides Detected	Well Depth (ft)
Los Angeles	01N/13W-10	19-01	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		184
Los Angeles	01N/13W-10	19-02	-	E 0.02	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		184
Los Angeles	02N/13W-33	19-03	-		ND		ND	0.057	ND	ND	ND	ND	ND	ND	0.050	ND	ND	2	180
Los Angeles	01N/13W-03	19-04	-		ND		ND	ND	0.050	ND	ND	ND	ND	ND	ND	ND	ND	1	210
Los Angeles	02N/13W-33	19-05	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		180
Los Angeles	02N/13W-33	19-06	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		165
Los Angeles	02N/13W-29	19-07	-	0.03	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		30
Los Angeles	02N/14W-30	19-08	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		500
Los Angeles	02N/14W-30	19-09	-	0.04	*(0.035)*	*(0.039)*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	(1)	500
Los Angeles	02S/12W-25	19-11	R		ND		ND	ND	0.066	0.112	ND	ND	ND	ND	ND	ND	ND	2	512
Los Angeles	02S/12W-23	19-12	-	0.03	ND		ND	ND	0.081	ND	ND	ND	ND	ND	ND	ND	ND	1	600
Los Angeles	02S/11W-05	19-13	-	E 0.01	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		732
Los Angeles	03S/12W-14	19-14	R		ND		ND	0.158	0.155	ND	ND	ND	ND	ND	0.066	0.062	ND	4	175
Los Angeles	03S/12W-14	19-15	R		ND		ND	0.180	0.259	ND	ND	ND	ND	ND	0.066	0.075	ND	4	180
Los Angeles	03S/12W-11	19-16	-	0.02	ND		ND	0.103	0.262	ND	ND	ND	0.050	ND	ND	ND	ND	3	210
Los Angeles	03S/12W-16	19-17	-		ND		ND	0.101	0.053	ND	ND	ND	ND	ND	ND	ND	ND	2	250
Los Angeles	01S/09W-26	19-18	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		280
Los Angeles	01S/09W-27	19-19	R	0.14	**0.049**	**0.054**	0.069	ND	ND	ND	ND	ND	ND	ND	0.050	ND	ND	3	162
Los Angeles	01S/09W-34	19-20	R		**0.048**	**0.061**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	183
Los Angeles	01S/13W-04	19-21	R	E 0.04	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		255
Orange	04S/10W-14	30-01	L		ND		ND	ND	0.063	ND	ND	ND	ND	ND	ND	ND	ND	1	1550
Orange	04S/10W-24	30-02	L	E 0.02	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		1410
Orange	04S/10W-22	30-03	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		1340
Orange	04S/10W-09	30-04	L		ND		ND	ND	0.076	ND	ND	ND	ND	ND	ND	ND	ND	1	941
Orange	03S/09W-32	30-05	L	0.02	ND		ND	ND	0.163	ND	ND	ND	ND	ND	ND	ND	ND	1	1230

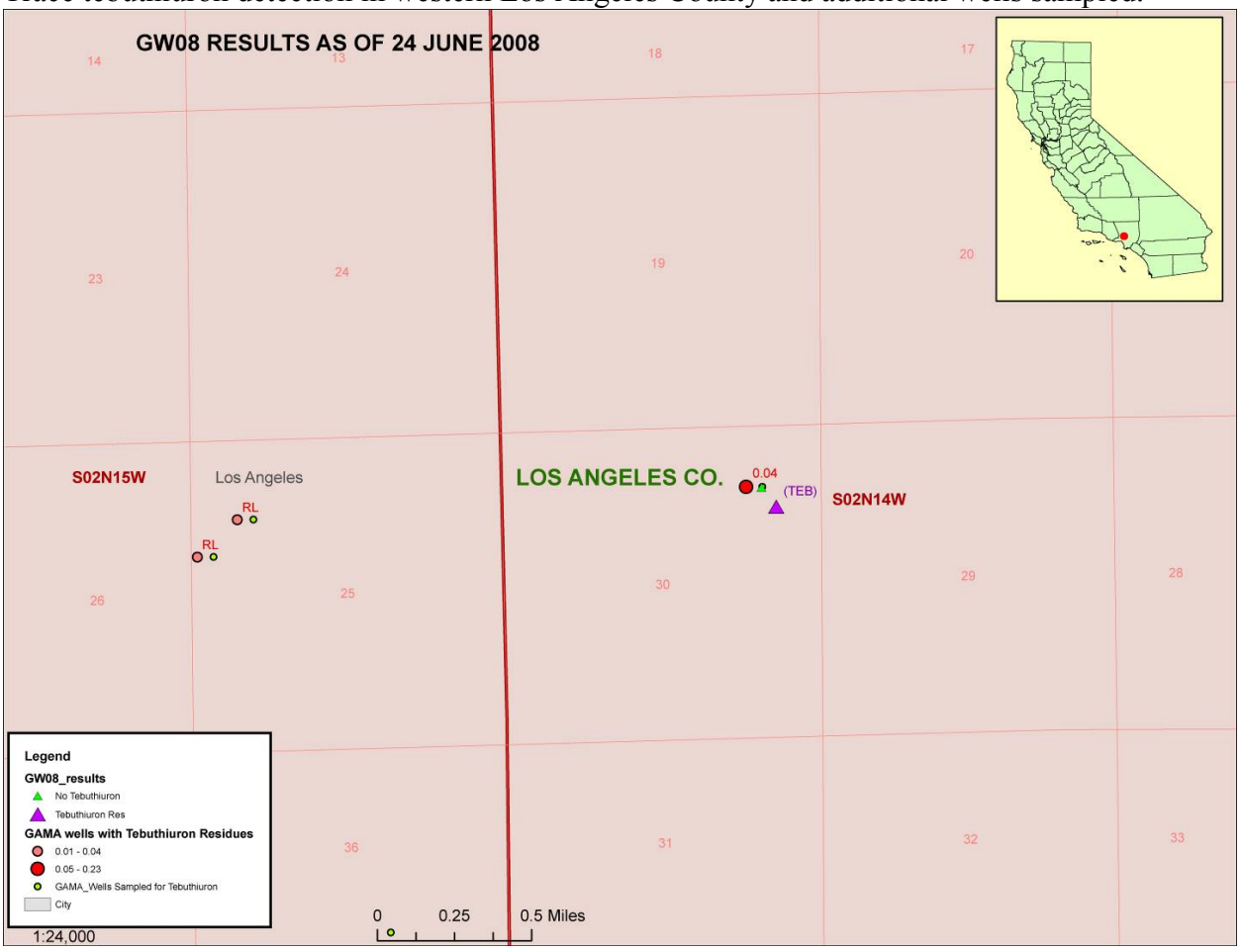
County	Township/ Range-Section	Location Code	GWPA	GAMA	Tebuthiuron	Tebuthiuron Back-up	Hexazinone	6800(a) pesticides						6800(a) degradates				# of Pesticides Detected	Well Depth (ft)
								Atrizine	Simazine	Diuron	Prometon	Bromacil	Norflurazon	dsmn	dea	acet	dact		
Orange	03S/09W-33	30-06	L	E 0.01	ND		ND	ND	0.213	ND	ND	ND	ND	ND	ND	ND	ND	1	465
Riverside	03S/06W-23	33-01	L	0.02	ND		ND	ND	0.077	0.091	ND	0.375	ND	ND	ND	0.722	1.190	5	170
Riverside	03S/06W-14	33-02	R		ND		ND	ND	0.071	0.063	ND	0.285	ND	ND	ND	0.698	1.380	5	150
Riverside	02S/05W-11	33-04	R	E 0.01	ND		ND	0.079	ND	ND	ND	ND	ND	ND	0.089	ND	ND	2	252
San Bernardino	01S/02W-19	36-01	-	E 0.01	ND		ND	ND	0.134	0.070	ND	0.092	ND	ND	ND	0.135	0.154	5	160
San Bernardino	01S/02W-19	36-02	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		180
San Bernardino	01N/04W-07	36-03	-	E 0.01	ND		ND	ND	ND	ND	ND	0.278	ND	ND	ND	ND	ND	1	450
San Bernardino	01N/04W-08	36-04	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		424
San Bernardino	01N/04W-08	36-05	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		285
San Diego	15S/01E-18	37-01	-	E 0.02	*(0.020)*		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	(1)	230
San Diego	15S/01W-24	37-02	-	E 0.09	*(0.020)*		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	(1)	
San Diego	15S/01W-24	37-03	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		20.2*
San Diego	15S/01E-19	37-04	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		38.4*
San Diego	15S/02E-26	37-05	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		26.5*
San Diego	15S/03E-30	37-06	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		30
San Diego	16S/05E-32	37-07	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		15.6*
San Diego	16S/05E-32	37-08	-	E 0.23	**0.116**		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	12.6*
San Diego	16S/01W-04	37-09	-	E 0.03	*(0.019)*		ND	0.052	ND	ND	ND	ND	ND	ND	ND	ND	ND	1 (1)	906
San Diego	17S/05E-06	37-10	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		46.2*
San Diego	17S/05E-20	37-11	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
San Diego	17S/05E-19	37-12	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	0.050	ND	ND	1	525
San Joaquin	01N/05E-16	39-01	-	0.03	ND		ND	ND	ND	0.116	ND	ND	ND	ND	ND	ND	ND	1	
San Joaquin	01N/05E-16	39-02	-		ND		0.092	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	
San Joaquin	01N/05E-15	39-03	-		ND		ND	ND	ND	0.116	ND	ND	ND	ND	ND	ND	ND	1	80
San Joaquin	01N/05E-15	39-04	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Solano	05N/01W-10	48-01	-	0.12	**0.130**	**0.154**	ND	ND	ND	ND	ND	ND	ND	ND	0.081	ND	ND	2	
Solano	06N/01W-36	48-02	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		1000
Solano	05N/01W-02	48-03	-		ND		ND	0.100	ND	ND	ND	ND	0.068	0.078	0.414	0.112	0.105	6	45
Solano	05N/01W-02	48-04	-		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		140

County	Township/ Range-Section	Location Code	GWPA	GAMA	Tebuthiuron	Tebuthiuron Back-up	Hexazinone	6800(a) pesticides						6800(a) degradates				# of Pesticides Detected	Well Depth (ft)
								Atrizine	Simazine	Diuron	Prometon	Bromacil	Norflurazon	dsmn	dea	acet	dact		
Solano	05N/01W-15	48-05	-		ND		ND	0.054	ND	ND	ND	ND	ND	ND	0.429	0.058	0.084	4	48
Ventura	04N/18W-29	56-01	L		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Ventura	04N/18W-29	56-02	L		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Ventura	04N/18W-29	56-03	L	E 0.02	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Ventura	04N/18W-30	56-04	L		ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
# of Wells with Detections					**4 (4)**		**2**	**9**	**14**	**6**	**0**	**4**	**2**	**1**	**9**	**7**	**5**		

LOC = Location code established during sampling
GWPA = Ground Water Protection Area
GAMA = Groundwater Ambient Monitoring and Assessment Program
dsmn = Desmethylnorflurazon
dea = Deethyl Atrazine
acet = Deisopropyl Atrazine
dact = Diamino Chlorotriazine
E = Estimated
* = depth to water
NS = Not sampled
R = Runoff GWPA
L = Leaching GWPA

APPENDIX II

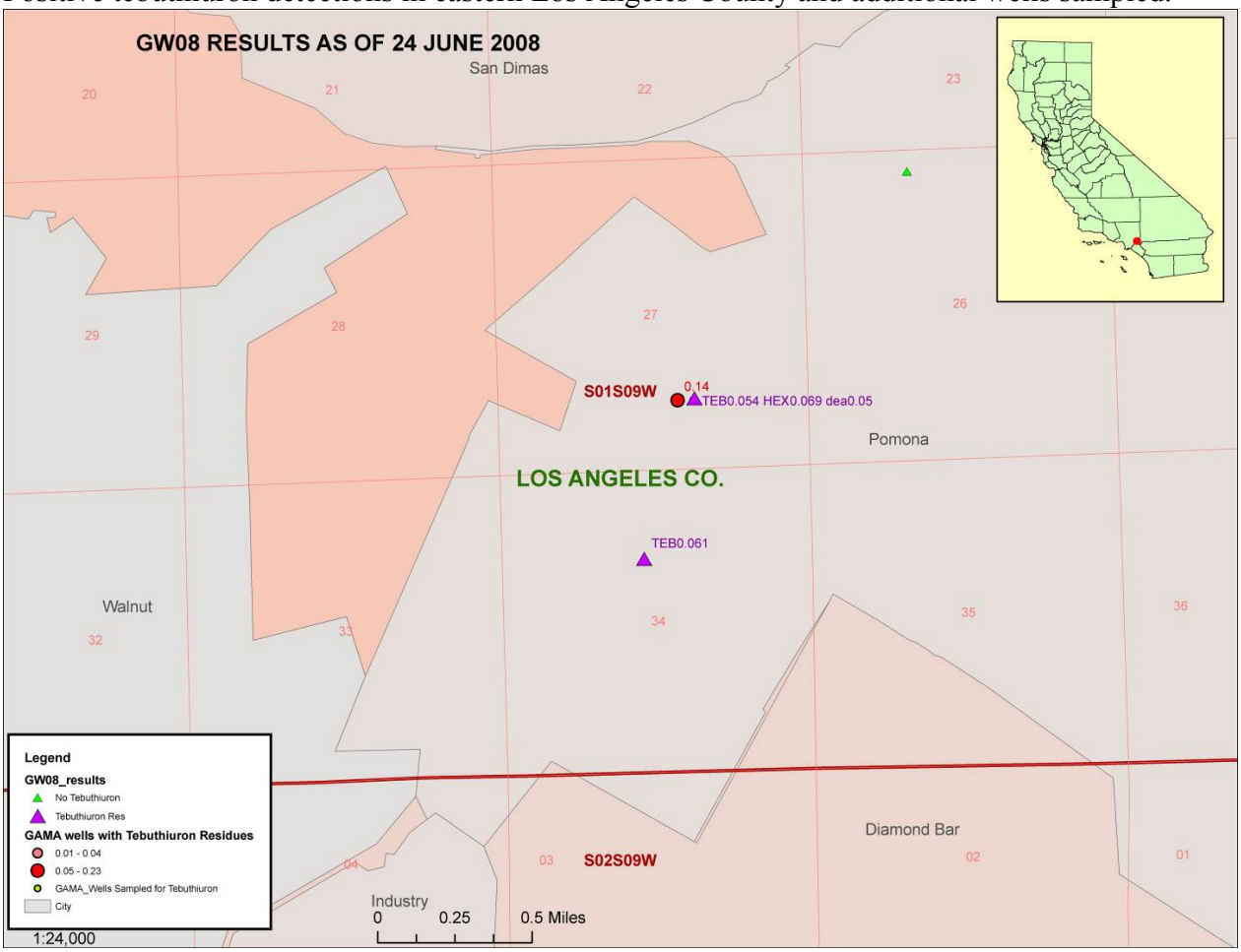
Trace tebuthiuron detection in western Los Angeles County and additional wells sampled.



RL = below the reporting limit
(TEB) = trace tebuthiuron detection

APPENDIX III

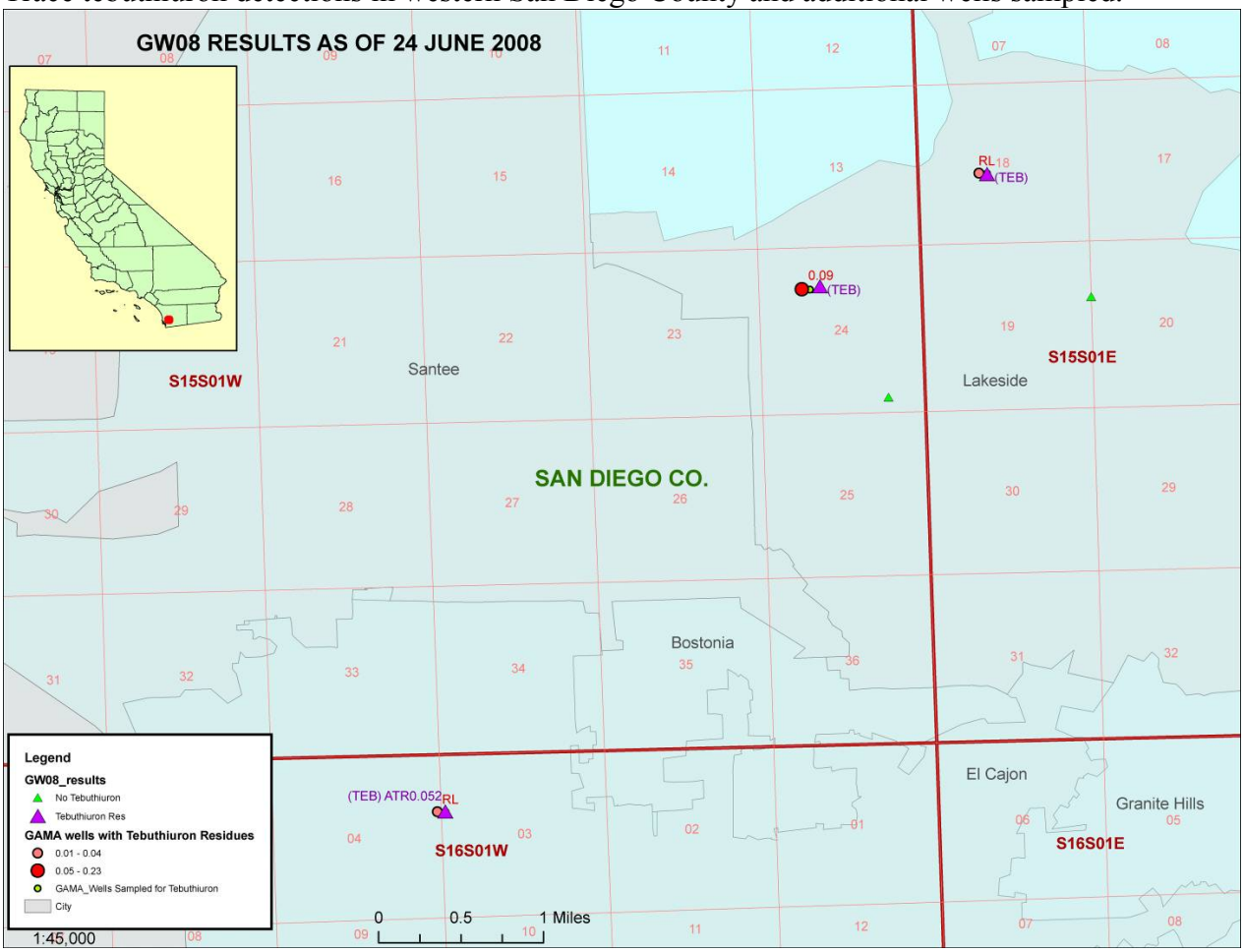
Positive tebuthiuron detections in eastern Los Angeles County and additional wells sampled.



RL = below the reporting limit

APPENDIX IV

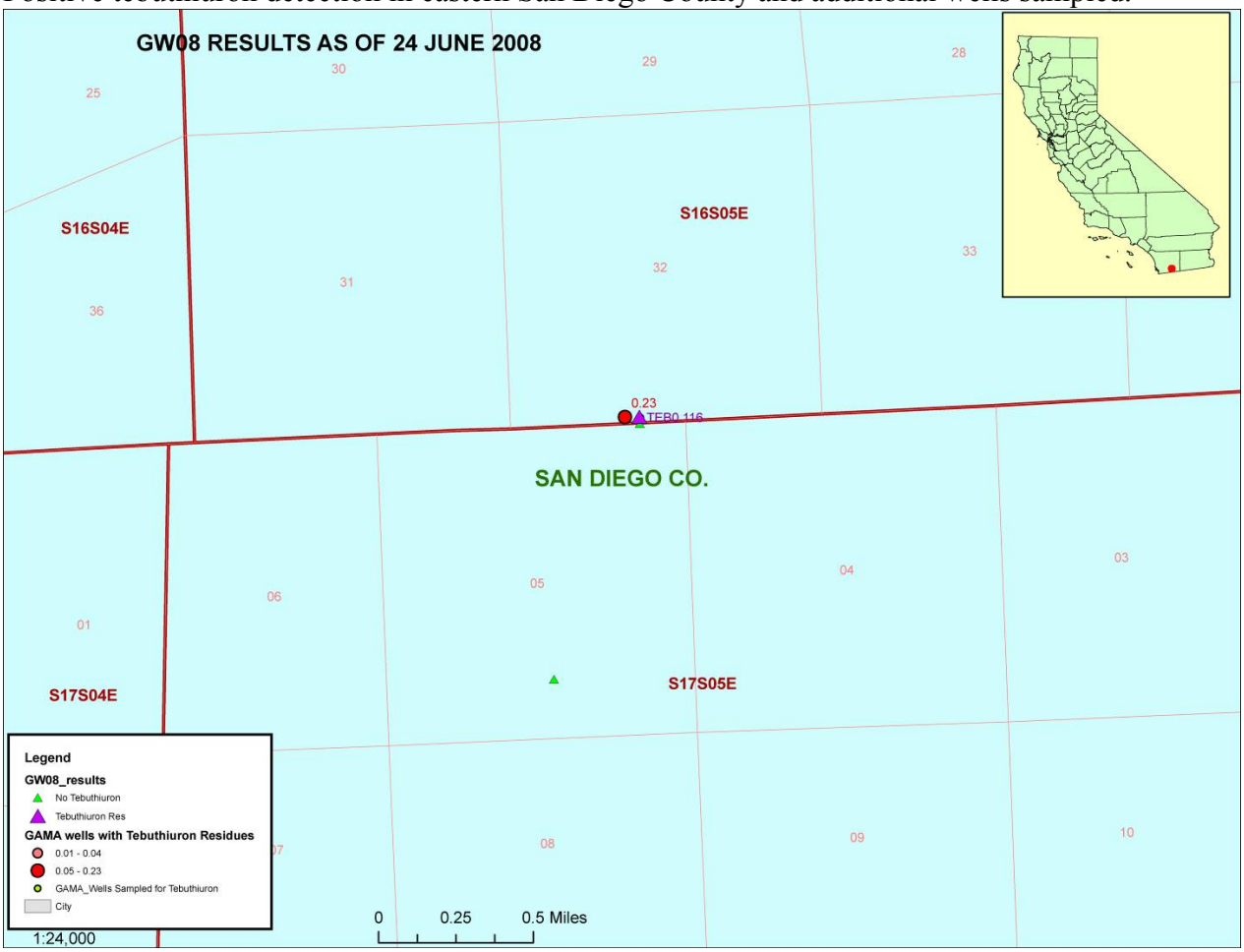
Trace tebuthiuron detections in western San Diego County and additional wells sampled.



RL = below the reporting limit
(TEB) = trace tebuthiuron detection

APPENDIX V

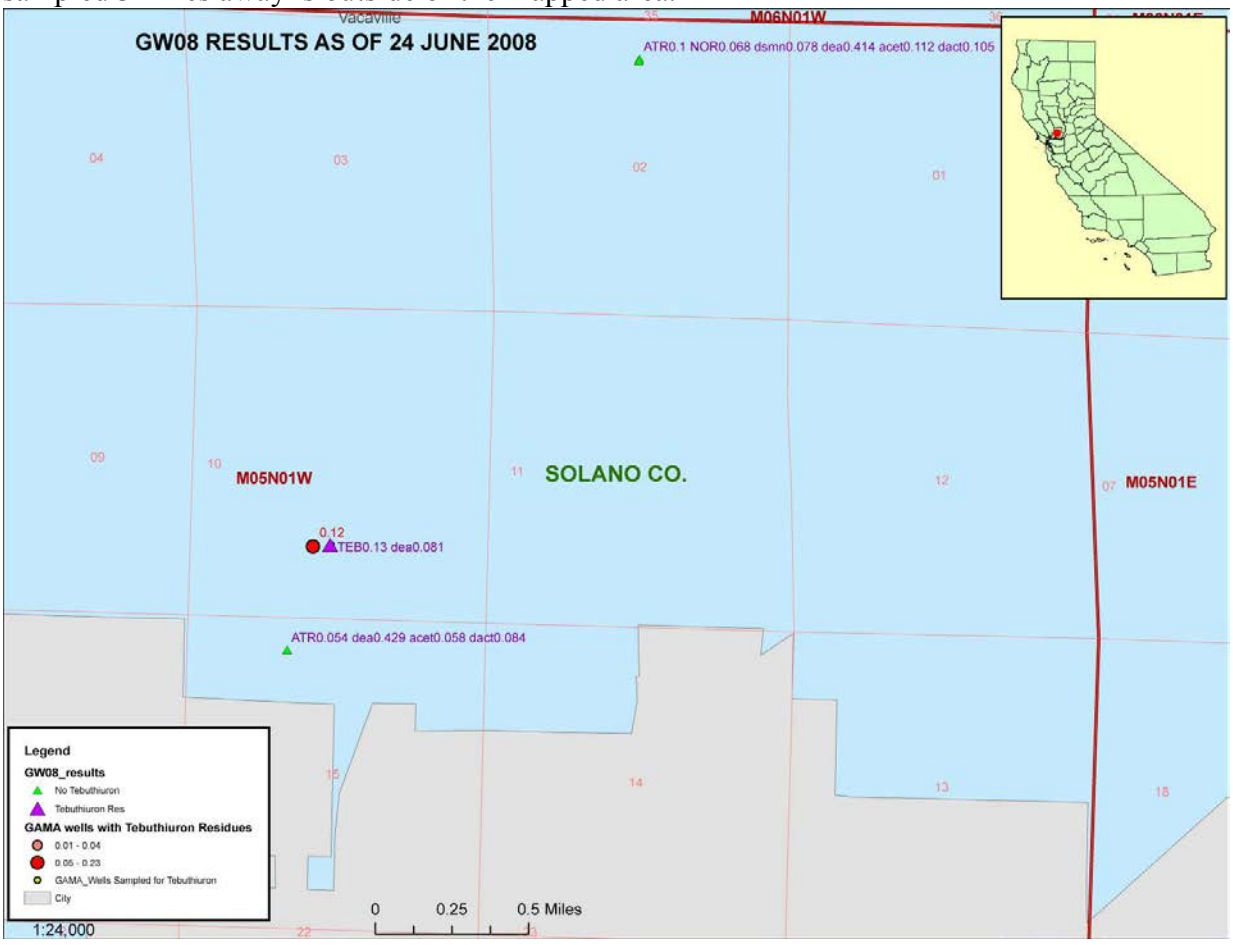
Positive tebuthiuron detection in eastern San Diego County and additional wells sampled.



RL = below the reporting limit

APPENDIX VI

Positive tebuthiuron detection in Solano County and additional wells sampled. A third well sampled 3 miles away is outside of the mapped area.



RL = below the reporting limit

Appendix VII. Tebuthiuron detections and non-detects in wells sampled by the GAMA Program in 2004 and 2005.

County	# Non-detects	# Detections	Detection range (µg/L)	Reference
Alameda	26	0		
Amador	2	0		
Butte	24	0		
Calaveras	1	0		
Colusa	22	0		
Contra Costa	4	0		
El Dorado	23	0		
Fresno	50	0		
Glenn	31	1	0.02	Schmitt et al., 2008
Inyo	48	0		
Kern	115	0		
Kings	11	0		
Los Angeles	90	12	E0.01 – 0.14	Mathany et al., 2008; Land and Belitz, 2008
Madera	29	0		
Marin	2	0		
Merced	42	0		
Mono	2	0		
Monterey	69	0		
Napa	22	0		
Nevada	15	0		
Orange	25	4	E0.01 – E0.02	Mathany et al., 2008
Placer	19	0		
Riverside	99	2	E0.01 – 0.02	Kent and Belitz, 2009
Sacramento	49	0		
San Bernardino	43	2	E0.01	Kent and Belitz, 2009
San Diego	31	4	E0.02 – E0.23	Wright et al., 2005
San Francisco	6	0		
San Joaquin	51	1	0.03	Bennett et al., 2006
San Luis Obispo	9	0		
San Mateo	9	0		
Santa Clara	38	0		
Santa Cruz	22	0		
Shasta	11	0		
Solano	13	1	0.12	Dawson et al., 2008
Sonoma	63	0		
Stanislaus	38	0		
Sutter	15	0		
Tehama	28	0		
Tulare	42	0		
Ventura	43	1	E0.02	Montrella and Belitz, 2009
Yolo	22	1	0.03	Schmitt et al., 2008
Yuba	7	0		
TOTAL	**1311**	**29**	**E0.01 – E0.23**	