

Study 228: Monitoring the Concentrations of Detected Pesticides in Wells Located in Highly Sensitive Areas (Well Network Sampling)

Annual Update 2014

- **Introduction:**

This report summarizes the annual results of a monitoring project that documents pesticide concentrations in domestic wells located in the San Joaquin Valley of California. This study was initiated to monitor levels of herbicides in wells located in areas that are highly vulnerable to pesticide movement to ground water in order to determine efficacy of ground water protection regulations implemented in those areas. The wells were sampled annually from 1999 through 2014 (Garretson, 1999). Included here are the results of the 2014 sampling. A statistical analysis of data collected from 1999-2012 is reported in Troiano et al., 2013. This study is ongoing and updates of results are posted annually.

- **Study Area:** Fresno and Tulare Counties

- **Most Recent Sampling Period:** 3/17/14 – 5/19/14

- **Number of Wells Sampled:** 64

- **Pesticides, Pesticide Degradates, and Chemicals Monitored:**

1. Annual triazine screen – 11 analytes including: atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, simazine, ACET, DACT, DEA, and DMN.
2. Multi Residue screen – 29 analytes by Liquid Chromatography Mass Spectrometry (LC/MS) including: atrazine, azinphos-methyl, azoxystrobin, bensulide, bromacil, carbaryl, carbofuran, diazinon, dimethenamide, dimethoate, diuron, ethofumesate, fenamiphos, fludioxonil, imidacloprid, linuron, mefenoxam/metalaxyl, methiocarb, metolachlor, metribuzin, napropamide, norflurazon, oryzalin, prometon, simazine, tebuthiuron, thiamethoxam, thiobencarb, and uniconazole.

- **Results for Annual Triazine Screen Monitoring and for Multi Residue Screen:**

Results for each well are included in Tables 1-2 and in the California Department of Pesticide Regulation well inventory database (CDPR, 2013). The California Department of Food and Agriculture, Center for Analytical Chemistry analyzed all samples according to analytical method EM 62.9 (CDFA, 2009) and Multi Residue Screen analytical method EMON-SM-05-032 (CDFA, 2013). The reporting limit for each analyte is 0.05 ug/L. Chemistry results and quality control data are presented in Tables 3-5.

Of the 64 wells, 27 were analyzed using the LC/MS portion of the Multi Residue screen. Results are shown in Table 2.

Positive finds (other than triazine screen analytes) from Multi Residue screen:

1. Imidacloprid
 - (a) 0.059 ug/L Well #18
 - (b) Trace Well #26

2. Oryzalin
 - (a) Trace Well #37

REFERENCES

CDFA, 2009. EM 62.9 Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotraizine (DACT), Tebuthiuron and the metabolites Tebuthiuron-104, Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 in Well Water and River Water By Liquid Chromatography- Atmospheric Pressure Chemical Ionization Mass Spectrometry (Revised 2009) Available at:

<http://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/emon-sm-62_9.pdf> (Verified May 15, 2017).

CDFA, 2013. EMON-SM-05-032 Determination of 44 Pesticides in Well Water by Liquid Chromatography Coupled to Linear Ion Trap Quadrupole and Gas Chromatography Coupled to Triple Quadrupole Mass Spectrometer. Available at:

<http://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/emon-sm-05-032.pdf>(Verified October 6, 2017).

CDPR. 2014. Well inventory data base. California Department of Pesticide Regulation, Sacramento, California. Available at:

<http://www.cdpr.ca.gov/docs/emon/grndwtr/well_inventory_database/index.htm>(verified July 12, 2017).

Garretson, C. 1999. Protocol for Monitoring the Concentration of Detected Pesticides in Wells Located in Highly Sensitive Areas. Study 182. Environmental Monitoring Branch, Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, California. Available at: <<http://www.cdpr.ca.gov/docs/emon/pubs/protocol/prot182.pdf>> (verified May 15, 2017).

Troiano, J., C. Garretson, A. Dasilva, J. Marade, and T. Barry. 2013. Pesticide and Nitrate Trends in Domestic Wells where Pesticide Use Is Regulated in Fresno and Tulare Counties, California. J. Environ. Qual. doi:10.2134/jeq2013.06.0219 Available at:

<http://www.cdpr.ca.gov/docs/emon/pubs/ehapref/pesticide_well_trends.pdf> (verified May 15, 2017).

Table 1. Spring 2014 Triazine Screen Sampling Results in ug/L (ppb)

Sample Number	Well Number	Date Sampled	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DMN	Hexazinone	Norflurazon	Prometon	Simeazine	Propazine	RL in ug/l
2525	1	5/19/14	0.087	ND	ND	0.103	ND	T	ND	ND	ND	ND	ND	78.5	0.05
2463	2	5/19/14	0.119	ND	ND	0.081	ND	T	T	ND	ND	ND	0.063	72.0	0.05
2444	3	5/12/14	0.096	ND	T	0.098	ND	ND	0.208	ND	T	ND	0.061	77.0	0.05
2452	4	5/12/14	0.415	0.097	2.430	0.717	0.058	0.062	0.197	ND	0.239	T	0.079	83.0	0.05
2503	5	5/19/14	0.474	ND	0.060	0.752	T	T	0.260	ND	ND	ND	0.102	85.0	0.05
2449	6	5/12/14	0.644	ND	T	0.937	ND	T	T	ND	ND	ND	0.090	80.5	0.05
2417	7	5/12/14	0.066	ND	T	0.186	ND	ND	ND	ND	ND	ND	T	76.0	0.05
2615	8	5/19/14	0.273	ND	T	0.322	T	0.056	ND	ND	ND	ND	0.078	77.5	0.05
2437	12	5/19/14	0.319	ND	0.283	0.222	ND	T	ND	ND	ND	ND	T	67.5	0.05
2470	13	5/12/14	0.169	ND	0.428	0.274	ND	T	0.086	ND	0.070	ND	T	81.0	0.05
2556	14	5/19/14	T	ND	ND	ND	ND	ND	ND	ND	ND	ND	T	74.5	0.05
2555	15	5/19/14	0.124	ND	ND	0.348		T	0.330	ND	0.198	ND	0.068	73.0	0.05
2489	16	5/19/14	0.233	ND	0.072	0.571	ND	0.101	0.566	ND	0.351	ND	0.080	82.5	0.05
2512	18	5/5/14	0.060	ND	T	0.180	ND	ND	ND	ND	ND	ND	T	82.5	0.05
2568	19	3/24/14	0.198	ND	ND	0.291	ND	T	0.233	ND	T	ND	0.071	105.0	0.05
2618	20	4/7/14	0.099	ND	ND	T	ND	ND	ND	ND	ND	ND	0.051	95.0	0.05
2614	21	3/24/14	T	ND	ND	0.108	ND	ND	0.166	ND	ND	ND	ND	87.0	0.05
2598	22	4/1/14	0.196	ND	0.062	0.835	ND	ND	ND	ND	ND	ND	0.068	75.5	0.05
2600	23	4/1/14	0.143	ND	0.069	0.190	ND	T	0.123	ND	ND	ND	T	80.0	0.05
2506	24	5/13/14	T	ND	0.096	T	T	ND	0.111	ND	ND	ND	ND	92.5	0.05
2505	25	5/12/14	0.101	ND	T	0.062	ND	ND	ND	ND	ND	ND	0.058	78.0	0.05
2450	26	5/13/14	0.070	ND	T	0.073	ND	ND	0.097	ND	ND	ND	T	89.0	0.05
2562	28	4/8/14	T	ND	ND	T	ND	ND	ND	ND	ND	ND	T	70.0	0.05
2554	29	5/6/14	0.074	ND	ND	0.166	ND	ND	0.175	ND	T	ND	T	84.5	0.05
2544	30	5/6/14	0.209	ND	ND	0.526	T	ND	0.757	ND	T	ND	0.065	88.5	0.05
2536	32	5/6/14	0.243	ND	ND	0.244	ND	ND	0.462	ND	0.290	ND	0.088	77.0	0.05
2472	34	5/6/14	T	ND	T	T	ND	ND	0.050	ND	ND	ND	T	82.0	0.05
2518	35	5/5/14	0.121	ND	0.127	0.128	ND	T	T	ND	T	T	0.082	80.5	0.05
2454	36	5/5/14	T	ND	ND	0.064	ND	ND	ND	ND	ND	ND	T	81.5	0.05
2504	37	5/5/14	0.217	ND	ND	0.189	ND	0.058	0.329	ND	0.207	ND	0.095	85.0	0.05
2608	43	3/24/14	0.286	ND	ND	0.178	ND	0.137	0.112	ND	0.161	ND	0.127	95.5	0.05
2612	44	3/24/14	0.115	ND	0.241	0.151	ND	0.068	T	ND	ND	ND	T	103.0	0.05
2606	45	4/1/14	T	ND	ND	0.063	T	T	ND	ND	ND	ND	ND	90.5	0.05
2588	47	3/24/14	0.695	T	ND	1.220	0.082	T	0.056	ND	ND	ND	0.057	104.0	0.05
2610	48	3/24/14	0.814	ND	0.834	1.320	ND	T	0.050	ND	T	ND	0.063	89.0	0.05
2566	49	3/24/14	0.923	ND	ND	1.960	T	ND	0.319	ND	0.078	ND	0.103	87.0	0.05
2546	50	4/8/14	T	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.066	73.5	0.05
2558	51	4/8/14	T	ND	ND	T	ND	ND	ND	ND	ND	ND	T	72.5	0.05
2616	52	4/8/14	0.146	ND	ND	0.187	ND	ND	0.067	ND	ND	ND	0.094	76.5	0.05
2550	53	4/8/14	T	ND	ND	0.092	ND	T	ND	ND	ND	ND	T	72.5	0.05
2622	54	4/7/14	T	ND	ND	0.056	ND	ND	ND	ND	ND	0.099	0.051	75.5	0.05
2624	56	4/7/14	0.371	ND	ND	0.865	ND	ND	ND	ND	ND	ND	0.105	71.5	0.05
2626	57	4/7/14	0.175	ND	ND	0.377	ND	ND	T	ND	ND	ND	T	82.5	0.05
2604	58	4/1/14	T	ND	ND	T	ND	ND	T	ND	ND	ND	0.085	101.0	0.05
2602	59	4/1/14	0.364	0.102	ND	0.302	0.062	T	0.843	ND	0.286	ND	0.059	89.0	0.05

ND = None Detected (<0.05ug/L)

T = Trace (found below detection limit at a level too low to be reliably quantified)

Table 1. cont'd. Spring 2014 Triazine Screen Sampling Results in ug/L (ppb)

Sample Number	Well Number	Date Sampled	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DMN	Hexazinone	Norflurazon	Prometon	Simazine	Propazine	RL in ug/l
2596	61	4/1/14	0.389	ND	0.742	0.992	T	T	T	ND	ND	ND	0.107	104.0	0.05
2564	63	3/25/14	0.152	ND	ND	0.193	ND	T	0.209	ND	0.096	ND	0.082	86.0	0.05
2570	65	3/25/14	0.068	ND	ND	0.060	ND	ND	ND	ND	ND	ND	T	111.0	0.05
2592	68	3/18/14	ND	ND	ND	T	ND	ND	ND	ND	ND	ND	T	92.0	0.05
2572	69	3/25/14	0.956	ND	1.810	2.290	ND	T	ND	ND	ND	ND	T	103.0	0.05
2586	71	3/17/14	0.677	ND	2.440	1.090	ND	T	1.000	ND	0.456	ND	0.054	91.5	0.05
2630	72	3/18/14	0.656	ND	ND	1.140	T	T	ND	ND	ND	ND	0.091	96.0	0.05
2632	73	3/18/14	0.238	ND	ND	1.280	T	ND	0.067	ND	ND	ND	T	104.0	0.05
2590	74	3/17/14	0.761	ND	0.484	0.857	T	T	T	ND	0.103	ND	0.113	97.5	0.05
2584	75	3/17/14	0.884	ND	0.476	0.653	ND	T	ND	ND	ND	ND	0.072	86.5	0.05
2580	79	3/17/14	0.113	ND	0.064	T	ND	0.577	T	ND	T	ND	0.274	87.5	0.05
2582	80	3/17/14	0.803	ND	2.380	3.260	ND	0.061	0.052	ND	T	ND	T	103.0	0.05
2578	84	3/17/14	T	ND	T	T	ND	ND	ND	ND	ND	ND	ND	89.5	0.05
2594	86	3/17/14	1.200	ND	0.073	5.070	T	ND	0.064	ND	ND	ND	0.083	103.0	0.05
2540	89	5/12/14	ND	ND	ND	T	ND	ND	ND	ND	ND	ND	ND	83.0	0.05
2560	90	5/6/14	0.077	T	T	0.098	0.057	T	ND	ND	ND	ND	0.068	77.0	0.05
2620	92	4/7/14	0.287	ND	ND	0.277	ND	0.128	0.137	ND	0.084	ND	0.056	75.5	0.05
2574	94	3/24/14	0.892	ND	0.275	2.960	ND	0.050	0.491	ND	0.170	ND	0.062	103.0	0.05
2542	95	5/6/14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	T	73.5	0.05

ND = None Detected (<0.05ug/L)

T = Trace (found below detection limit at a level too low to be reliably quantified)

Table 2. Results for 2014 Triazine Screen vs Multi Residue Screen in ug/L (ppb). The table includes the six analytes that are duplicated in the two screens plus any positive or trace finds for analytes that are only included in the multi residue screen.

Screen	Well Number	Date Sampled	Atrazine	Bromacil	Diuron	Norflurazon	Prometon	Simazine	Imidacloprid	Oryzalin
M	1	5/19/14								
Tr	1				T					
M	2	5/19/14						0.071		
Tr	2				T			0.063		
M	3	5/12/14						0.067		
Tr	3			T		T		0.061		
M	4	5/12/14	0.093	2.650	0.061	0.261		0.078		
Tr	4		0.097	2.430	0.062	0.239		0.079		
M	5	5/19/14						0.100		
Tr	5			0.060	T			0.102		
M	6	5/12/14						0.086		
Tr	6			T	T			0.090		
M	7	5/12/14								
Tr	7			T				T		
M	8	5/19/14			0.064			0.096		
Tr	8			T	0.056			0.078		
M	12	5/19/14		0.327						
Tr	12			0.283	T			T		
M	13	5/12/14		0.468		0.074				
Tr	13			0.428	T	0.070		T		
M	14	5/19/14								
Tr	14							T		
M	15	5/19/14				0.197		0.066		
Tr	15				T	0.198		0.068		
M	16	5/19/14			0.112	0.373		0.083		
Tr	16			0.072	0.101	0.351		0.080		
M	18	5/5/14							0.059	
Tr	18			T				T		
M	24	5/13/14								
Tr	24			0.096						

Blank spaces = None Detected

Detection Limit = 0.05ug/L

T = Trace (positive results below the detection limit, too low to reliably quantify)

M = Multi residue screen

Tr = Triazine screen

Table 2. cont'd. Results for 2014 Triazine Screen vs Multi Residue Screen in ug/L (ppb). The table includes the six analytes that are duplicated in the two screens plus any positive or trace finds for analytes that are only included in the multi residue screen.

Screen	Well Number	Date Sampled	Atrazine	Bromacil	Diuron	Norflurazon	Prometon	Simazine	Imidacloprid	Oryzalin
M	25	5/12/14						0.060		
Tr	25			T				0.058		
M	26	5/13/14							T	
Tr	26			T				T		
M	29	5/6/14								
Tr	29					T		T		
M	30	5/6/14				0.325		0.082		
Tr	30					T		0.065		
M	32	5/6/14				0.050		0.061		
Tr	32					0.290		0.088		
M	34	5/6/14								
Tr	34			T				T		
M	35	5/5/14			0.054			0.082		
Tr	35			0.127	T	T	T	0.082		
M	36	5/5/14								
Tr	36							T		
M	37	5/5/14			0.060	0.217		0.086		T
Tr	37				0.058	0.207		0.095		
M	89	5/12/14								
Tr	89									
M	90	5/6/14	0.053					0.076		
Tr	90		0.077	T	T	T		0.068		
M	95	5/6/14								
Tr	95							T		

Blank spaces = None Detected

Detection Limit = 0.05ug/L

T = Trace (positive results below the detection limit, too low to reliably quantify)

M = Multi residue screen

Tr = Triazine screen

Table 3. Quality Control – Triazine Screen Matrix Spike Percent Recoveries

Analytes: Triazine Screen
 Reporting Limit: 0.05ug/L
 Lab: CDFA

QC Matrix: CDPR Ground water
 Method: EM 62.9
 Spike Level: 0.200ug/L

Extraction Date	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DMN	Hexazinone	Norflurazon	Prometon	Simazine	Propazine
3/21/2014	106	98.0	113	94.0	102	109	102	97.0	100	92.0	106	96.5
	101	101	111	90.0	102	120	95.5	93.0	95.0	90.5	99.5	90.5
4/1/14	96.0	93.0	98.0	86.0	90.5	107	98.5	93.0	103	95.5	90.5	88.0
	91.5	87.5	95.5	81.0	86.5	106	92.0	90.0	95.5	89.0	86.5	83.0
4/7/2014	108	100	99.0	102	101	110	101	108	106	103	106	99.0
	98.0	92.5	94.5	92.5	93.5	100	96.0	95.5	100	94.5	96.5	91.0
4/11/2014	94.5	89.0	93.0	91.5	88.0	98.0	91.0	90.5	91.0	88.0	91.5	84.0
	85.5	80.5	85.5	83.0	81.0	81.5	82.5	81.5	81.0	79.5	83.0	78.0
5/9/2014	87.0	82.0	83.0	95.0	86.0	80.5	81.0	82.0	84.0	81.5	82.5	75.0
	84.0	78.0	92.0	83.5	82.5	76.5	78.5	81.0	80.0	78.0	80.0	76.0
5/16/2014	87.0	83.0	91.5	88.5	86.0	85.5	84.0	85.0	87.5	84.5	84.0	84.5
	82.0	76.5	99.0	82.0	84.5	83.0	84.0	79.0	81.0	78.5	79.0	76.5
5/28/2014	91.0	84.5	78.0	89.5	86.0	84.5	73.5	102.0	85.0	77.5	80.0	77.5
	88.5	77.5	91.0	94.5	82.5	87.0	79.5	82.5	86.5	81.5	79.0	84.5
Mean	92.9	87.4	94.6	89.5	89.4	94.9	88.5	90.0	91.1	86.7	88.9	84.6
SD	8.1	8.4	9.5	6.0	7.4	13.8	9.2	8.7	8.8	7.8	9.7	7.7
Observed Minimum	82.0	76.5	78.0	81.0	81.0	76.5	73.5	79.0	80.0	77.5	79.0	75.0
LCL	74.5	68.7	68.6	70.3	74.7	51.9	53.2	68.5	52.6	73.5	69.6	46.3
UCL	109	103	117	116	105	146	139	111	151	106	108	142
Observed Maximum	108	101	113	102	102	120	102	108	106	103	106	99

LCL = Lower Control Limit : Method Validation Mean minus 3 X SD

UCL = Upper Control Limit : Method Validation Mean plus 3 X SD

One matrix blank was run with each extraction set, no detections were found.

Table 4. Quality Control – Triazine Screen Blind Spike Percent Recoveries

CDFA Sample #	Extraction Date	Analyte	Spike Level (ppb)	Result (ppb)	% Recovery	Control limit exceeded
2593	4/14/2014	Diuron	0.2	0.185	92.5%	No
		Norflurazon	0.1	0.085	85.0%	No
2595	5/20/2014	Atrazine	0.15	0.119	79.3%	No
		DACT	0.1	0.098	98.0%	No
		DMN	0.2	0.184	92.0%	No

Table 5. Quality Control – Multi Residue LC/MS Screen Matrix Spike Percent Recoveries

Analytes: Multi Residue LC/MS Screen
 Lab: CDFA

Reporting Limit: 0.05ug/L
 Method: EMON-SM-05-032

Extraction Date	Spiked Level (ppb)	Percent Recovery (%)																												
		Atrazine	Axirphos-methyl	Azoxystrobin	Bensulfide	Bromacil	Carbaryl	Carbofuran	Diazinon	Dimethenamide	Dimethoate	Diuron	Ethofumesate	Fenamiphos	Fludioxonil	Imidacloprid	Linuron	Mefenoxam/Metalaxy	Methiocarb	Metolachlor	Metribuzin	Napropamide	Noflurazon	Oryzalin	Prometon	Simazine	Tebuthiuron	Thiamethoxam	Thiobencarb	Uniconazole
5/12/14	0.05	104	107	101	108	85	85	88	93	102	85	100	96	92	103	90	95	100	100	97	82	104	97	94	99	88	102	96	103	101
5/19/14	0.1	93.1	98.1	98.4	109	77.0	90.8	89.0	94.1	97.3	87.1	95.7	94.4	102	104	90.8	97.0	103	97.0	95.1	85.7	99.0	97.4	95.0	101	91.3	99.1	94.4	99.0	98.4
5/23/14	0.2	92.5	97.0	98.0	105	70.0	93.0	86.0	95.0	96.5	80.5	93.5	92.0	93.0	81.0	87.5	95.5	92.0	92.5	95.5	79.0	96.5	96.0	93.5	95.5	86.5	95.0	92.5	98.5	97.0
5/23/14	0.2	95.0	97.0	101	105	69.5	111	85.0	95.0	98.0	83.0	94.5	92.5	92.0	83.5	88.5	96.0	92.5	93.0	95.5	77.5	97.5	95.5	92.0	97.0	85.0	94.0	92.5	101	97.0
Mean		96.2	99.8	99.6	107	75.4	95.0	86.9	94.4	98.5	83.8	95.9	93.8	94.8	92.9	89.2	95.8	96.8	95.6	95.9	81.0	99.3	96.6	93.6	98.1	87.7	97.5	93.8	100	98.4
SD		5.3	4.8	1.6	2.1	7.3	11.2	1.8	.8	2.4	2.8	2.9	1.9	4.8	12.3	1.5	.9	5.4	3.5	1.0	3.6	3.3	1.0	1.3	2.4	2.7	3.7	1.5	2.1	1.9
Observed Minimum		92.5	97.0	98.0	105	69.5	85.0	85.0	93.4	96.5	80.5	93.5	92.0	92.0	81.0	87.5	94.8	92.0	92.5	95.1	77.5	96.5	95.5	92.0	95.5	85.0	94.0	92.5	98.5	97.0
LCL		73.1	50.9	74.3	62.3	75.2	64.1	75.7	61.7	71.0	72.5	76.9	45.9	73.5	62.1	70.7	76.1	74.7	67.7	68.0	75.7	76.7	79.3	79.6	79.7	75.3	69.7	65.5	75.0	79.4
UCL		115	151	126	130	109	144	115	116	118	116	115	133	118	123	118	113	120	140	134	111	116	114	113	118	111	130	107	114	117
Observed Maximum		104	107	101	109	85	111	89	95	102	87	100	96	102	104	91	97	103	100	97	86	104	97	95	101	91	102	96	103	101

LCL = Lower Control Limit : Method Validation Mean minus 3 X SD

UCL = Upper Control Limit : Method Validation Mean plus 3 X SD

One matrix blank was run with each extraction set, no detections were found.