Study 228: Monitoring the Concentrations of Detected Pesticides in Wells Located in Highly Sensitive Areas (Well Network Sampling) Annual Update 2021

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Introduction:

This update summarizes the annual results of pesticide concentrations detected in a network of domestic wells monitored for more than 20 years in California's San Joaquin Valley. In 2021, the California Department of Pesticide Regulation's (DPR) Groundwater Protection Program (GWPP) analyzed groundwater samples from 60 wells for herbicides using the Triazine Screen and the Glyphosate Screen. Based on previous detections, samples from 10 of those wells were also analyzed for pesticides on the Multi-Analyte Screen. The Triazine and Multi-Analyte screen results are reported in this summary. The Glyphosate Screen results will be reported in 2023. Beginning with this year's monitoring at the GWPP's request, the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry laboratory reduced the reporting limits (RL) for the pesticides and degradates analyzed from 0.05 ppb (µg/L) to a range of RLs from 0.01 to 0.05 ppb (Tables 1-3).

In 1999, DPR initiated the Well Network Study to monitor potential changes in groundwater pesticide concentrations due to new regulations with enforceable management practices designed to minimize pesticide movement to groundwater (Garretson, 1999; Davalos, 2021). When this study was initiated, the selected wells had been previously sampled by DPR and had residues of simazine, bromacil, or diuron. The wells in the network continued to be sampled for triazine pesticides at least annually through 2021. The total number of wells sampled each year can fluctuate due to changes in participation, wells going dry, and new wells being drilled to replace low-yield wells.

The wells in the network are located in areas susceptible to pesticide movement to groundwater within Fresno and Tulare counties. Areas vulnerable to groundwater contamination from the agricultural use of pesticides are typified by either sections with coarse soils that are vulnerable to pesticides leaching through the soil into groundwater, or by sections containing hardpan soils vulnerable to pesticide runoff into sensitive areas with conduits to groundwater. Due to the vulnerability of the study area, the Well Network also served as an

experimental area to monitor for additional pesticides that have the potential to contaminate groundwater.

A statistical analysis of data collected from 2000-2012 was reported in Troiano et al. (2013), along with a full description of this study, including characterization of the conditions of the vulnerable areas, pesticide use, and the required mitigation measures. Updates of the study results have been reported annually since 2008.

Study Area:
Fresno and Tulare counties

Sampling Period:
May 17 - August 31, 2021

Number of Wells Sampled:
Sixty wells (Tables 4 and 5) were sampled for the Triazine Screen and ten of those wells were also sampled for the Multi-Analyte Screen. For reasons including changes in participation and wells going dry, well numbers used by DPR to differentiate sampling locations are not consecutive.

Sampling and Analytical Methods:
DPR's GWPP scientists conducted the study according to the protocol (Davalos, 2021) and well sampling according to the Obtaining and Preserving Well Water Samples standard operating procedure (SOP) (Kocis, 2020a). The CDFA Center for Analytical Chemistry analyzed samples from all wells using the Triazine Screen analytical method EM 62.9, revision 5 (CDFA, 2020), and samples from 10 wells with the Multi-Analyte Screen analytical method EMON-SM-05-032, revision 2 (CDFA, 2022)[1]. Both methods are highly specific and have been determined by DPR to provide unequivocal identification of the chemicals analyzed (Aggarwal, 2020; 2022). The RL for each analyte ranged from 0.01 ppb (µg/L) to 0.05 ppb (µg/L) (Tables 1-3). The Triazine Screen includes 14 analytes by Liquid Chromatography Mass Spectrometry (LCMS) (Table 1), and the Multi-Analyte Screen includes nine analytes by Gas Chromatography Mass Spectrometry (GCMS) and 38 analytes by LCMS (Tables 2 and 3).

[1] CDFA updated the analytical method before DPR sampled in 2021. The written revision was approved in 2022.

Table 1. Triazine Screen method detection limits (MDL) and reporting limits (RL) in ppb (µg/L).

Analyte	MDL	RL
ACET*	0.00580	0.03
Atrazine	0.00316	0.02
Bromacil	0.00241	0.02
DACT*	0.00235	0.05
DEA*	0.00226	0.02
Diuron	0.00241	0.02
DSMN*	0.00181	0.01
Hexazinone	0.00197	0.01
Metribuzin	0.00238	0.05
Norflurazon	0.00252	0.02
Prometon	0.00240	0.02
Prometryn	0.00265	0.05
Simazine	0.00286	0.02
Tebuthiuron	0.00236	0.05

*Acronyms are ACET = Deethyl-simazine or Deisopropyl-atrazine (degradate of atrazine and simazine), DACT = Diaminochlorotriazine (degradate of simazine), DEA = Deethyl-atrazine (degradate of atrazine), DSMN = Desmethylnorflurazon (degradate of norflurazon)

Table 2. Multi-Analyte Screen (GCMS) method detection limits (MDL) and reporting limits (RL) in ppb (µg/L).

Analyte	MDL	RL
Clomazone	0.00799	0.05
Dichloran	0.01103	0.05
Dichlobenil	0.00678	0.03
Disulfoton	0.01040	0.05
Ethoprophos	0.00506	0.03
Fonofos	0.00616	0.03
Malathion	0.00691	0.03
Parathion ethyl	0.00646	0.03
Parathion methyl	0.00655	0.03
Phorate	0.00521	0.03
Piperonyl butoxide	0.00785	0.03
Prometryn	0.00738	0.03
Propanil	0.00836	0.05
Triallate	0.00638	0.03

Table 3. Multi-Analyte Screen (LCMS) method detection limits (MDL) and reporting limits (RL) in ppb (µg/L).

Analyte	MDL	RL
Alachlor	0.00920	0.03
Atrazine	0.00286	0.02
Azinphos-methyl	0.01440	0.05
Azoxystrobin	0.00584	0.02
Bensulide	0.00571	0.02
Bromacil	0.00393	0.02
Carbaryl	0.00323	0.02
Carbofuran	0.00393	0.02
Chlorantraniliprole	0.00345	0.02
Cyprodinil	0.00427	0.02
Diazinon	0.01050	0.03
Dimethenamid	0.00490	0.02
Dimethoate	0.00330	0.02
Diuron	0.00484	0.02
Ethofumesate	0.00845	0.03
Fenamiphos	0.01070	0.03
Fludioxonil	0.00892	0.03
Flutriafol	0.00298	0.02
Imidacloprid	0.00323	0.02
Isoxaben	0.00493	0.02
Linuron	0.00697	0.02
Mefenoxam/metalaxyl*	0.00295	0.02
Methiocarb	0.00710	0.02
Metolachlor	0.01660	0.02
Methomyl	0.00301	0.02
Methoxyfenozide	0.00628	0.03
Metribuzin	0.00414	0.02
Napropamide	0.00462	0.02
Norflurazon	0.00550	0.02
Oryzalin	0.01140	0.05
Prometon	0.00245	0.02
Propiconazole	0.00424	0.02
Pyraclostrobin	0.00210	0.02
Simazine	0.00279	0.02
Tebuthiuron	0.00524	0.02
Thiamethoxam	0.00386	0.02
Thiobencarb	0.00245	0.02
Uniconazole	0.01370	0.05

*Mefenoxam and metalaxyl are stereoisomers and cannot be analytically distinguished

2021 Monitoring Results:

Triazine Screen

The monitoring results for the 60 wells sampled for Triazine Screen analytes are shown in Tables 6 and 7.

Multi-Analyte Screen

Ten wells with Multi-Analyte Screen detections in the past five years were selected to be sampled for this screen. Table 8 includes the concentrations for all detected pesticides that are unique to the Multi-Analyte Screen. Imidacloprid, fludioxonil, methoxyfenozide, chlorantraniliprole, and flutriafol were detected (Table 8). The analytes not detected in samples analyzed with this screen are listed in the footnotes below Table 8. The imidacloprid detections were reported as evidence for the formal review process required by the Pesticide Contamination Prevention Act (Davalos, 2022). The fludioxonil detection is being explored further as part of a separate study (Kocis, 2020b). The detections of methoxyfenozide, chlorantraniliprole, and flutriafol in the Well Network prompted sampling for the three analytes in high use areas (Afyuni and Nordmark, 2022), as well as the decision to analyze all wells in the Well Network with the Multi-Analyte Screen in 2022.

Replicate Analyses in Both Screens

Table 9 includes the analytes that are included on both the Triazine and Multi-Analyte screens.

Results that are presented in Tables 6 to 9 will be entered into DPR's Well Inventory Database (CDPR, 2022).

Summary of Previous Years' Monitoring Results:

Triazine Screen

Tables 10 and 11 present Triazine Screen results from 1999 through 2021, including the percent of wells with detections above the RL and the means of those detections.

Multi-Analyte Screen

Table 12 presents an overview of the Multi-Analyte Screen detections from 2014 through 2021 and does not include analytes reported on the Triazine Screen.

Table 4. Well locations in Fresno County.

Well Number	Township/Range-Section
1	13S/21E-01
2*	13S/22E-33
3	13S/23E-28
4	13S/23E-32
5*	14S/21E-13
7	14S/21E-21
8	14S/21E-25
12	14S/22E-03
13	14S/22E-12
14	14S/22E-13
15*	14S/22E-14
16	14S/22E-14
19	14S/23E-34
20	14S/23E-32
20B	14S/23E-32
21	14S/23E-33
22*	14S/23E-34
23B*	14S/23E-35
24*	15S/21E-03
25	15S/21E-05
26*	15S/21E-09
28	15S/21E-34
29*	15S/22E-03
30A*	15S/22E-05
32	15S/22E-09
35	15S/22E-16
36	15S/22E-20
37	15S/22E-21
43	15S/23E-02
44	15S/23E-02
45	15S/23E-12
47*	15S/24E-14
50	16S/21E-05
51	16S/21E-07
52	16S/21E-16
53A	16S/21E-33
54	16S/21E-34
56	16S/22E-11
57	16S/22E-11
89	13S/22E-33
90	15S/22E-05
92	14S/23E-33
94	15S/24E-10
95	14S/22E-33

Table 5. Well locations in Tulare County.

Well Number	Township/Range-Section
49	15S/25E-05
58	16S/23E-01
59A	16S/24E-14
61	16S/25E-21
63A	17S/25E-05
65	17S/26E-26
68	18S/26E-02
69	18S/26E-06
71	18S/26E-23
72	18S/27E-21
73	18S/27E-29
74	19S/26E-01
75A	19S/26E-14
80	20S/26E-24
84	20S/27E-20
86	20S/27E-32

*Wells analyzed with the Multi-Analyte Screen

Table 6. Triazine Screen sampling results from 2021 part 1. Concentrations in ppb (µg/L).

Well Number	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN
1	trace (0.0174)	nd	nd	0.0626	nd	trace (0.0029)	nd
2	0.0371	nd	nd	trace (0.0284)	nd	trace (0.0055)	trace (0.0079)
3	0.0414	nd	nd	0.0542	nd	nd	0.0969
4 primary	0.201	trace (0.0121)	0.824	0.337	trace (0.00907)	trace (0.0168)	0.546
4 replicate	0.206	trace (0.0119)	0.899	0.356	trace (0.00874)	trace (0.0171)	0.560
5	0.290	nd	nd	0.522	trace (0.0083)	trace (0.0031)	0.263
7	0.0754	trace (0.00562)	nd	0.264	trace (0.0176)	trace (0.00363)	trace (0.00839)
8	0.0959	trace (0.00468)	trace (0.0163)	0.122	trace (0.0129)	0.0297	0.0142
12	0.271	nd	0.242	0.260	nd	0.0372	0.0147
13	0.0946	nd	0.354	0.242	nd	0.0201	0.212
14	trace (0.00744)	nd	nd	nd	nd	nd	nd
15	0.0453	nd	nd	0.0847	nd	trace (0.0133)	0.107
16	0.111	nd	trace (0.00288)	0.365	nd	0.0270	0.336
19	trace (0.0290)	nd	nd	0.0521	nd	nd	0.127
20	trace (0.0130)	nd	nd	trace (0.00406)	nd	nd	trace (0.00221)
20b	nd	nd	nd	nd	nd	nd	trace (0.00187)
21	nd	nd	nd	nd	nd	nd	trace (0.00734)
22	0.121	nd	nd	0.385	trace (0.0027)	nd	0.0799
23b	0.0864	nd	0.0567	0.196	nd	0.029	0.131
24	trace (0.0059)	nd	nd	trace (0.0090)	nd	nd	0.152
25	0.0699	nd	nd	0.0726	nd	trace (0.00405)	0.0252
26	trace (0.0125)	nd	nd	trace (0.0203)	nd	nd	0.0443
28	trace (0.00819)	nd	nd	trace (0.0162)	nd	nd	nd
29	trace (0.0243)	nd	nd	0.0832	nd	trace (0.0056)	0.176
30a	0.171	nd	trace (0.00310)	0.242	trace (0.00837)	0.0258	0.0287
32	0.142	nd	nd	0.237	nd	nd	0.444
35	0.0898	nd	nd	0.115	nd	0.0275	0.0825
36	trace (0.00702)	nd	nd	trace (0.0159)	nd	nd	trace (0.00412)
37	trace (0.00702)	nd	nd	trace (0.0148)	nd	nd	0.0137
43	0.0985	nd	nd	0.0630	nd	trace (0.00807)	0.0649
44	0.0584	nd	0.133	0.0884	nd	0.0254	0.0177

Well Number	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN
45	trace (0.0260)	nd	nd	trace (0.0411)	nd	trace (0.00427)	trace (0.00511)
47	0.319	trace (0.0106)	trace (0.0186)	0.799	0.0581	trace (0.0079)	0.0402
49	0.557	nd	nd	3.31	trace (0.00687)	nd	0.270
50	nd	nd	nd	nd	nd	nd	nd
51	trace (0.0202)	nd	nd	trace (0.0463)	nd	nd	0.0229
52	0.0637	nd	nd	0.113	nd	nd	0.0222
53a	nd	nd	nd	nd	nd	nd	nd
54	trace (0.0291)	nd	nd	trace (0.0440)	nd	nd	trace (0.00195)
56	0.285	nd	nd	0.992	nd	nd	nd
57	0.125	nd	nd	0.227	nd	nd	0.0306
58	trace (0.00664)	nd	nd	trace (0.0464)	nd	nd	trace (0.00533)
59a	0.210	nd	0.926	0.808	trace (0.0131)	0.0357	0.850
61	0.279	nd	0.933	1.32	trace (0.0166)	0.0309	0.0140
63a	nd	trace (0.00814)	nd	trace (0.0177)	trace (0.0103)	trace (0.00596)	nd
65	trace (0.0238)	nd	nd	trace (0.0437)	nd	nd	nd
68	nd	nd	nd	nd	nd	trace (0.0110)	nd
69	0.407	nd	0.300	1.88	trace (0.00470)	0.0374	nd
71	0.382	nd	1.46	1.21	trace (0.00662)	0.0259	1.27
72	0.657	trace (0.00386)	nd	1.42	0.0267	trace (0.00796)	0.0380
73	0.119	trace (0.00362)	nd	1.06	0.0354	trace (0.00607)	0.0707
74	0.555	nd	0.433	0.984	trace (0.0121)	0.0340	0.0187
75a	0.672	nd	0.364	1.00	trace (0.00609)	0.0310	trace (0.00585)
80	0.392	nd	0.304	1.40	trace (0.00494)	0.0277	trace (0.00782)
84	0.0721	trace (0.00386)	1.04	0.199	trace (0.00746)	trace (0.0139)	nd
86	0.776	nd	nd	5.94	0.0228	trace (0.00262)	trace (0.00288)
89	trace (0.0292)	nd	trace (0.0112)	nd	nd	trace (0.0132)	0.0817
90	0.124	0.0635	0.0410	0.173	0.105	0.0558	0.0174
92	0.222	nd	nd	0.266	trace (0.00257)	0.0438	0.131
94	0.406	nd	trace (0.00811)	2.58	trace (0.00353)	trace (0.00385)	0.570
95	trace (0.0152)	nd	nd	trace (0.0222)	nd	trace (0.00345)	trace (0.00829)

nd = not detected (below the method detection limit listed in Table 1)

Table 7. Triazine Screen sampling results from 2021 part 2. Concentrations in ppb (µg/L).

Well Number**	Hexazinone	Metribuzin	Norflurazon	Prometon	Prometryn	Simazine	Propazine %*
1	nd	nd	nd	nd	nd	nd	74.3
2	nd	nd	trace (0.0033)	nd	nd	0.0298	69.1
3	nd	nd	trace (0.00398)	nd	nd	0.0489	65.6
4 primary	nd	nd	0.656	trace (0.00977)	nd	0.0731	70.3
4 replicate	nd	nd	0.679	trace (0.0101)	nd	0.0763	72.4
5	nd	nd	trace (0.0057)	nd	nd	0.0709	68.5
7	0.0149	nd	nd	nd	nd	0.0273	66.4
8	nd	nd	trace (0.00491)	nd	nd	0.0616	72.2
12	nd	nd	trace (0.00277)	nd	nd	0.0310	70.4
13	nd	nd	0.113	nd	nd	0.0303	75.0
14	nd	nd	nd	nd	nd	nd	65.5
15	nd	nd	trace (0.0173)	nd	nd	0.0425	72.5
16	nd	nd	0.106	nd	nd	0.0583	70.5
19	nd	nd	trace (0.00766)	nd	nd	0.0424	68.8
20	nd	nd	nd	nd	nd	trace (0.0136)	67.5
20b	nd	nd	nd	nd	nd	nd	68.5
21	nd	nd	nd	nd	nd	trace (0.00397)	72.5
22	nd	nd	trace (0.0031)	nd	nd	0.0603	67.6
23b	nd	nd	trace (0.0101)	nd	nd	0.0260	74.6
24	nd	nd	0.0226	nd	nd	trace (0.0032)	60.6
25	nd	nd	nd	nd	nd	0.0423	72.5
26	nd	nd	trace (0.00405)	nd	nd	trace (0.00789)	76.0
28	nd	nd	nd	nd	nd	trace (0.0115)	70.2
29	nd	nd	0.0202	nd	nd	trace (0.0075)	67.8
30a	nd	nd	0.0673	trace (0.00270)	nd	0.0808	73.9
32	nd	nd	0.232	nd	nd	0.0552	78.0
35	nd	nd	0.0246	trace (0.0112)	nd	0.0595	70.6
36	nd	nd	nd	trace (0.00241)	nd	0.0229	72.2
37	nd	nd	trace (0.00816)	nd	nd	trace (0.0104)	72.8
43	nd	nd	0.0478	nd	nd	0.0572	68.2
44	nd	nd	trace (0.0054)	nd	nd	0.0287	67.5

Well Number**	Hexazinone	Metribuzin	Norflurazon	Prometon	Prometryn	Simazine	Propazine %*
45	nd	nd	nd	nd	nd	trace (0.00743)	69.9
47	trace (0.0029)	nd	trace (0.0055)	nd	nd	0.0242	69.0
49	nd	nd	0.0206	nd	nd	0.0597	68.7
50	nd	nd	nd	nd	nd	nd	72.7
51	nd	nd	nd	nd	nd	trace (0.0150)	65.3
52	nd	nd	trace (0.00285)	nd	nd	0.0502	67.3
53a	nd	nd	nd	nd	nd	nd	73.2
54	nd	nd	nd	0.0749	nd	0.0485	76.7
56	nd	nd	nd	nd	nd	0.0722	72.5
57	nd	nd	nd	nd	nd	0.0367	79.4
58	nd	nd	nd	nd	nd	trace (0.0174)	73.3
59a	nd	nd	0.221	nd	nd	trace (0.00584)	68.2
61	nd	nd	trace (0.00520)	nd	nd	0.0368	67.5
63a	nd	nd	nd	nd	nd	nd	70.2
65	nd	nd	nd	nd	nd	trace (0.00828)	70.2
68	nd	nd	nd	nd	nd	nd	74.9
69	nd	nd	nd	nd	nd	0.0310	76.8
71	nd	nd	0.374	nd	nd	0.0483	71.3
72	nd	nd	0.0201	nd	nd	0.0652	73.6
73	nd	nd	trace (0.00330)	nd	nd	trace (0.00608)	72.1
74	nd	nd	0.0257	nd	nd	0.0638	65.1
75a	nd	nd	trace (0.00412)	nd	nd	0.0600	67.2
80	nd	nd	nd	nd	nd	0.0236	75.7
84	nd	nd	nd	nd	nd	trace (0.00536)	73.0
86	nd	nd	nd	nd	nd	0.0414	70.4
89	nd	nd	trace (0.0124)	nd	nd	0.0290	62.0
90	0.0433	nd	trace (0.0147)	trace (0.00315)	nd	0.0625	71.5
92	nd	nd	0.0573	nd	nd	0.0463	65.7
94	nd	nd	0.136	nd	nd	0.0289	69.7
95	nd	nd	nd	nd	nd	trace (0.01228)	88.0

nd = not detected (below the method detection limit listed in Table 1)

*Propazine added as a surrogate for QA/QC purposes

**Well numbers used by DPR to differentiate sampling locations are not consecutive for reasons including changes in participation and wells going dry

Table 8. 2021 sampling results of the analytes that are unique to the Multi-Analyte Screen. Concentrations in ppb (µg/L). The table includes results for the six analytes detected.

Well Number	Analytes Unique to the Multi-Analyte Screen*					
	Fludioxonil	**Imidacloprid**	**Mefenoxam/Metalaxyl****	**Methoxyfenozide**	**Chlorantraniliprole**	**Flutriafol**
2	nd	0.024***	nd	nd	nd	nd
5	nd	trace (0.011)	nd	nd	nd	nd
15	nd	0.126	nd	nd	trace (0.008)	nd
22	nd	trace (0.01)***	nd	0.201	0.266	0.226
23b	nd	0.0253***	nd	nd	nd	nd
24	nd	0.088	nd	nd	nd	nd
26	nd	0.0348	nd	nd	nd	nd
29	nd	0.046***	trace (0.004)	trace (0.008)	nd	nd
30a	0.316***	nd	nd	0.0872***	nd	nd
47	nd	nd	nd	nd	nd	nd

nd = not detected (below the method detection limit listed in Tables 1 to 3)

*38 analytes were not detected in any of the samples: alachlor, azinphos-methyl, azoxystrobin, bensulide, carbaryl, carbofuran, clomazone, cyprodinil, diazinon, dichlobenil, dichloran, dimethenamid, dimethoate, disulfoton, ethofumesate, ethoprophos, fenamiphos, fonofos, isoxaben, linuron, malathion, methiocarb, methomyl, metolachlor, napropamide, oryzalin, parathion ethyl, parathion methyl, phorate, piperonyl butoxide, prometryn, propanil, propiconazole, pyraclostrobin, thiamethoxam, thiobencarb, triallate, uniconazole

**Mefenoxam and metalaxyl are stereoisomers and cannot be analytically distinguished

***Replicate sample is reported because it was higher

Table 9. 2021 sampling results of the analytes that are duplicated in the Multi-Analyte Screen and Triazine Screen. Concentrations in ppb (µg/L). The table includes results for the six analytes detected.

	Analytes in Both the Multi-Analyte and Triazine Screens*											
	Atrazine		Bromacil		Diuron		Norflurazon		Prometon		Simazine	
Well Number	Multi-Analyte	Triazine	Multi-Analyte	Triazine	Multi-Analyte	Triazine	Multi-Analyte	Triazine	Multi-Analyte	Triazine	Multi-Analyte	Triazine
2	nd	nd	nd	nd	trace (0.008)**	trace (0.0055)	nd	trace (0.0033)	nd	nd	0.037**	0.0298
5	trace (0.004)	nd	nd	nd	trace (0.006)	trace (0.0031)	nd	trace (0.0057)	nd	nd	0.097	0.0709
15	nd	nd	nd	nd	0.022	trace (0.0133)	0.028	trace (0.0173)	nd	nd	0.056	0.0425
22	nd	nd	nd	nd	nd	nd	nd	trace (0.0031)	nd	nd	0.083	0.0603
23b	nd	nd	0.0719**	0.0567	0.0369**	0.0290	trace (0.0117)**	trace (0.0101)	nd	nd	0.0295**	0.0260
24	nd	nd	nd	nd	nd	nd	0.035	0.0226	nd	nd	trace (0.006)	trace (0.0032)
26	nd	nd	nd	nd	nd	nd	nd	trace (0.00405)	nd	nd	trace (0.00970)**	trace (0.00789)
29	nd	nd	nd	nd	trace (0.01)**	trace (0.0056)	0.026	0.0202	trace (0.003)	nd	trace (0.011)**	trace (0.0075)
30a	nd	nd	nd	trace (0.00310)	0.0298**	0.0257	0.0655**	0.0673	nd	trace (0.00270)	0.0838	0.0808
47	trace (0.013)	trace (0.0106)	0.026	trace (0.0186)	trace (0.014)	trace (0.0079)	nd	trace (0.0055)	nd	nd	0.032	0.0242

nd = not detected (below the method detection limit listed in Tables 1 to 3)

*The following 3 analytes were duplicated in both screens but were not detected in any of the samples: metribuzin, prometryn, tebuthiuron

**Replicate sample is reported because it was higher

Table 10. Yearly percent (%) of wells with detections above the reporting limit (RL) for each analyte on the Triazine Screen.

Year	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN	Hexazinone	Norflurazon	Prometon	Simazine
1999	94.7	5.3	40	85.3	8	60	NA	0	17.3	1.3	86.7
2000	89.2	4.1	37.8	89.2	4.1	50	NA	1	17.6	1.4	82.4
2001	94.4	4.2	39.4	85.9	8.5	59.2	NA	1.4	22.5	1.4	85.9
2002	94.3	4.3	38.6	88.6	12.9	64.3	NA	0	15.7	1.4	92.9
2003	88.9	4.2	40.3	86.1	9.7	61.1	NA	0	20.8	1.4	86.1
2004	86.8	4.4	33.8	85.3	8.8	57.4	44.1	0	25	1.5	80.9
2005	88.2	4.4	33.8	75	5.9	54.4	45.6	0	23.5	1.5	70.6
2006	83.3	4.5	37.9	83.3	7.6	51.5	44	0	22.7	1.5	72.7
2007	85.5	2.9	31.9	85.5	5.8	46.4	44.9	0	29	1.4	76.8
2008	85.3	4.4	33.8	85.3	5.9	50	44	0	20.6	1.5	69.1
2009	88.2	2.9	30.9	85.3	4.4	45.6	47.1	0	20.6	1.5	60.3
2010	80.9	2.9	29.4	85.3	4.4	38.2	50	1.5	27.9	1.5	63.2
2011	76.5	4.4	30.9	79.4	5.9	32.4	52.9	1.5	27.9	0	55.9
2012	82.4	2.9	25	80.9	4.4	36.8	50	0	27.9	0	58.8
2013	76.1	1.5	26.9	83.6	6	13.4	41.8	0	20.9	0	58.2
2014	75	3.1	31.3	79.7	6.3	15.6	45.3	1.6	21.9	1.6	57.8
2015	76.2	1.6	23.8	84.1	3.2	9.5	34.9	0	19	1.6	49.2
2016	78.7	1.6	26.2	82	3.3	16.4	41	0	21.3	1.6	50.8
2017	60.7	1.6	23	70.5	1.6	6.6	36.1	0	21.3	0	39.3
2018	57.4	1.6	23	65.6	4.9	4.9	36.1	0	21.3	0	36.1
2019	61.7	1.7	20	63.3	1.7	1.7	35	0	13.3	0	31.7
2020	59.3	1.7	22	67.8	3.4	6.8	35.6	0	16.9	0	39
2021*	61.7	1.7	23.3	65.0	8.3	28.3	60.0	3.3	26.7	1.7	63.3
Mean	79.4	3.1	30.6	80.1	5.9	35.2	43.8	0.4	21.8	1.0	63.8
SD	11.9	1.3	6.5	8.0	2.7	21.4	6.8	0.9	4.2	0.7	17.7

NA = Not analyzed - DSMN was not included in the analysis until 2004. Metribuzin and prometryn were included in 2021, but were not detected

*Higher number of detections during 2021 was due to the lower RLs for the analytical methods

Table 11. Yearly mean concentrations above the reporting limit (RL) in ppb (µg/L) for each analyte on the Triazine Screen.

Year	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN	Hexazinone	Norflurazon	Prometon	Simazine
1999	0.48	0.08	0.96	0.82	0.11	0.35	NA	nd	0.16	0.07	0.13
2000	0.47	0.08	1.31	0.75	0.13	0.35	NA	0.07	0.14	0.06	0.11
2001	0.5	0.1	1.12	0.97	0.13	0.33	NA	0.05	0.11	0.1	0.12
2002	0.58	0.08	0.85	1.08	0.09	0.31	NA	nd	0.28	0.09	0.13
2003	0.55	0.11	0.99	0.89	0.12	0.31	NA	nd	0.18	0.08	0.14
2004	0.5	0.12	1.12	0.85	0.15	0.28	0.22	nd	0.21	0.09	0.10
2005	0.38	0.1	0.95	0.66	0.17	0.25	0.25	nd	0.24	0.09	0.10
2006	0.42	0.09	0.88	0.82	0.13	0.28	0.27	nd	0.23	0.06	0.10
2007	0.40	0.07	0.85	0.80	0.1	0.26	0.26	nd	0.13	0.06	0.10
2008	0.38	0.07	0.81	0.68	0.1	0.21	0.25	nd	0.24	0.07	0.09
2009	0.39	0.07	0.79	0.67	0.12	0.2	0.23	nd	0.21	0.06	0.09
2010	0.41	0.11	0.83	0.70	0.15	0.17	0.27	0.05	0.19	0.09	0.10
2011	0.4	0.09	0.82	0.71	0.15	0.12	0.23	0.07	0.19	nd	0.09
2012	0.39	0.09	0.65	0.82	0.12	0.1	0.24	nd	0.19	nd	0.09
2013	0.39	0.08	0.82	0.75	0.08	0.13	0.25	nd	0.19	nd	0.09
2014	0.35	0.1	0.67	0.68	0.06	0.13	0.26	nd	0.2	0.1	0.08
2015	0.32	0.06	0.64	0.69	0.12	0.13	0.22	nd	0.19	0.11	0.08
2016	0.36	0.08	0.71	0.90	0.14	0.07	0.24	nd	0.18	0.09	0.08
2017	0.24	0.07	0.83	0.85	0.12	0.06	0.19	nd	0.11	nd	0.07
2018	0.28	0.08	0.59	0.87	0.09	0.08	0.24	nd	0.13	nd	0.07
2019	0.25	0.08	0.38	0.72	0.16	0.08	0.19	nd	0.13	nd	0.07
2020	0.24	0.09	1.24	0.77	0.1	0.07	0.24	nd	0.15	nd	0.07
2021	0.24	0.06	0.53	0.76	0.05	0.03	0.18	0.03	0.13	0.07	0.05
Mean	0.39	0.09	0.84	0.79	0.12	0.19	0.23	0.05	0.18	0.08	0.09
SD	0.098	0.016	0.222	0.105	0.031	0.105	0.027	0.0171	0.045	0.016	0.022

Table 12. Summary of wells with Multi-Analyte Screen detections (other than Triazine analytes) from 2014 through 2021. Concentrations in ppb (µg/L).

Well #	Township/ Range-Section	Analyte	Sample Year							
			2014	2015	2016	2017	2018	2019	2020	2021**
2	13S/22E-33	Imidacloprid	nd	nd	nd	nd	T	T	nd	0.024**
4	13S/23E-32	Imidacloprid	nd	nd	nd	T	nd	nd	NS	NS
5	14S/21E-13	Imidacloprid	nd	nd	nd	T	T	T	nd	T
15	14S/22E-14	Imidacloprid	nd	nd	nd	0.066	0.091	0.085	0.106	0.126
18	14S/22E-31	Imidacloprid	0.059	0.665	dry	NLS	NLS	NLS	NLS	NLS
21	14S/23E-33	Imidacloprid	NS	0.065	nd	nd	nd	nd	NS	NS
22	14S/23E-34	Imidacloprid	NS	0.120	0.080	0.090	T	T	NS	T
23	14S/23E-35	Imidacloprid	NS	0.218	0.209	0.534	0.536	0.470	0.073	NS
23B	14S/23E-35	Imidacloprid	NS	NS	NS	NS	NS	NS	NS	0.0253***
24	15S/21E-03	Imidacloprid	nd	nd	nd	T	T	T	0.112	0.088
26	15S/21E-09	Imidacloprid	T	0.051	0.072	0.167	0.053	nd	NS	0.0348
29	15S/22E-03	Imidacloprid	nd	T	nd	5.970	0.095	T	0.053	0.046**
47	15S/24E-14	Imidacloprid	NS	nd	0.644	nd	nd	nd	NS	nd
48	15S/24E-36	Imidacloprid	NS	nd	T	T	NLS	NLS	NLS	NLS
37	15S/22E-21	Oryzalin	T	nd	nd	nd	nd	nd	NS	NS
44	15S/23E-02	Oryzalin	NS	T	nd	nd	nd	nd	NS	NS
29	15S/22E-03	Mefenoxam/ Metalaxyl*	nd	T	nd	nd	nd	nd	nd	T
74	19S/26E-01	Metolachlor	NS	T	nd	nd	nd	nd	NS	NS
30A	15S/22E-05	Fludioxonil	NS	nd	T	0.066	0.165	0.380	0.333	0.316***
4	13S/23E-32	Propanil	nd	nd	nd	0.060	nd	nd	NS	NS
22	14S/23E-34	Methoxyfenozide	NA	NA	NA	NA	NA	NA	NA	0.201
26	15S/21E-09	Methoxyfenozide	nd	nd	nd	nd	nd	nd	NS	T**
29	15S/22E-03	Methoxyfenozide	NA	NA	NA	NA	NA	NA	NA	T
30A	15S/22E-05	Methoxyfenozide	NA	NA	NA	NA	NA	NA	NA	0.0872***
15	14S/22E-14	Chlorantraniliprole	NA	NA	NA	NA	NA	NA	NA	T
22	14S/23E-34	Chlorantraniliprole	NA	NA	NA	NA	NA	NA	NA	0.266
22	14S/23E-34	Flutriafol	NA	NA	NA	NA	NA	NA	NA	0.226

nd = not detected (below the method detection limit listed in Tables 2 and 3)
NS = Well not sampled
Dry = Well went dry
NLS = Well is no longer sampled
NA = methoxyfenozide, chlorantraniliprole, and flutriafol were not analyzed until 2021
*Mefenoxam and metalaxyl are stereoisomers and cannot be analytically distinguished
**RL from 2014-2020 was 0.05 ppb; in 2021 the RL was 0.02 ppb for chlorantraniliprole, imidacloprid, flutriafol, and mefenoxam, and 0.03 ppb for fludioxonil and methoxyfenozide
***Replicate sample is reported because it was higher

Quality Control (QC) Results:

Laboratory and field quality control were conducted according to the Chemistry Laboratory Quality Control SOP (Peoples, 2019) and the results are summarized in Table 13. All quality control results are available upon request.

Triazine Screen QC Samples

Fourteen total matrix spikes were analyzed for the Triazine Screen. All analytes were spiked at 0.2 ppb. The mean recoveries for the 14 analytes and the propazine surrogate analyte ranged from 74.5 to 88.6%. The standard deviation of the recoveries ranged from 3.8 to 8.3%. Two out of 196 total spiked analytes were beyond the upper control limits. The propazine surrogate recoveries were within the control limits in both the continuing QC and the 60 samples analyzed (Table 7).

Multi-Analyte Screen QC Samples

For the Multi-Analyte Screen, matrix spikes were extracted and split to be analyzed along with sets of samples for both the LCMS and GCMS instruments. Two matrix spikes were analyzed along with the two sets of samples using LCMS for the Multi-Analyte Screen. All analytes were spiked at 0.2 ppb. The mean recoveries for the 38 analytes ranged from 62.0 to 104%. Twenty-four out of the 76 spiked analytes were beyond the lower control limits. These were the first few extraction and analysis sets with the updated method.

Two matrix spikes were analyzed along with sets of samples using GCMS for the Multi-Analyte Screen. All analytes were spiked at 0.1 ppb. The mean recoveries for the 14 analytes ranged from 72.9 to 87.2%. One out of the 28 spiked analytes was beyond the lower control limits.

Blind Spikes

A blind spike consists of analyte-free groundwater (matrix-blank sample) fortified with the chosen analytes and spiked by a chemist other than the chemist extracting and analyzing that screen. The Environmental Monitoring Branch (EM) Quality Assurance (QA) Officer submitted the blind spike to the laboratory disguised as a field sample according Ganapathy (2005). Three triazine, and two multi-analyte blind spikes were submitted throughout the study period (Table 14). The EM QA Officer requested blind spikes fortified with four triazines; however, the laboratory prepared the blind spike with all the analytes on the Triazine Screen. Results are presented based on the blind spikes prepared by the laboratory, i.e., using all the analytes on the Triazine Screen. Of the 53 analytes spiked, recoveries of 47 analytes (88.0%) were within the control limits, while recovery of six analytes were outside the control limits. All blind spike results are presented in Table 14.

Table 13. Laboratory and field quality control (QC) summary.

QC Type	Triazine Screen	Multi-Analyte Screen	Total Number	Number Out of Control Limits
Continuing QC matrix-spikes	14	4	18	27 out of 272 analytes were beyond the control limits: Two Triazine spikes and 25 Multi-Analyte spikes
Blind spikes	3	2	5	Six out of 53 analytes were beyond the control limits
Laboratory matrix-blanks	6	4	10	All non-detected
Field blanks	6	1	7	All non-detected

Table 14. Blind spike levels and recoveries.

Analysis Date	Analysis	Analyte	Spike Level (ppb)	Result (ppb)	% Recovery	Control limit exceeded*
6/9/2021	Triazine**	ACET	0.15	0.124	82.3	NO
		Atrazine		0.124	82.7	NO
		Bromacil		0.131	87.0	NO
		DACT		0.134	89.6	NO
		DEA		0.119	79.3	NO
		Diuron		0.135	90.0	NO
		DSMN		0.138	92.0	NO
		Hexazinone		0.129	85.7	NO
		Metribuzin		0.120	80.0	NO
		Norflurazon		0.140	93.6	NO
		Prometon		0.128	85.2	NO
		Prometryn		0.135	90.2	NO
		Simazine		0.124	82.5	NO
		Tebuthiuron		0.127	84.9	NO
		Propazine	0.20	0.277	139	YES

Analysis Date	Analysis	Analyte	Spike Level (ppb)	Result (ppb)	% Recovery	Control limit exceeded*
7/2/2021	Triazine**	ACET	0.10	0.0978	97.8	NO
		Atrazine		0.0886	88.6	NO
		Bromacil		0.0957	95.7	NO
		DACT		0.0994	99.4	NO
		DEA		0.0862	86.2	NO
		Diuron		0.101	100.8	NO
		DSMN		0.0979	97.9	NO
		Hexazinone		0.0877	87.7	NO
		Metribuzin		0.0874	87.4	NO
		Norflurazon		0.0986	98.6	NO
		Prometon		0.0917	91.7	NO
		Prometryn		0.0953	95.3	YES
		Simazine		0.0877	87.7	NO
		Tebuthiuron		0.0884	88.4	NO
		Propazine	0.20	0.245	123	YES
7/20/2021	Multi-Analyte	Methoxyfenozide	0.15	0.109	72.7	NO
		Diazinon		0.114	76.0	NO
		Metolachlor		0.115	76.7	YES
		Dichlobenil		0.161	107	NO
7/2/2021	Triazine**	ACET	0.10	0.0930	93.0	NO
		Atrazine		0.0915	91.5	NO
		Bromacil		0.100	100	NO
		DACT		0.110	110	NO
		DEA		0.0886	88.6	NO
		Diuron		0.0990	99.0	NO
		DSMN		0.100	100	NO
		Hexazinone		0.0871	87.1	NO
		Metribuzin		0.0910	91.0	NO
		Norflurazon		0.0977	97.7	NO
		Prometon		0.0926	92.6	NO
		Prometryn		0.0955	95.5	NO
		Simazine		0.0911	91.1	NO
		Tebuthiuron		0.0884	88.4	NO
		Propazine	0.20	0.251	126	YES
7/20/2021	Multi-Analyte	Methoxyfenozide	0.15	0.087	58.0	YES
		Fludioxonil		0.124	82.7	NO
		Metribuzin		0.174	116	NO
		Fonofos	0.15	0.105	70.0	NO

*Control limits are available in the analytical methods (CDFA, 2020; 2022)

**DPR requested blind spikes fortified with four triazines; however, the laboratory spiked with the entire working standard. Results presented are based on the working standard.

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Contact GWPP@cdpr.ca.gov for references not currently available on the web.

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