# Monitoring Groundwater Concentrations of Pesticides in Sensitive Areas with High Agricultural Use Study 228 - Well Network Sampling - Annual Update 2022

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#### INTRODUCTION

This update summarizes the annual results of pesticide concentrations detected in a network of primarily domestic wells, with a few used partially or exclusively for irrigation, monitored for more than 20 years throughout California's San Joaquin Valley. The Well Network is located throughout Fresno and Tulare counties, in areas vulnerable to groundwater contamination and high agricultural use of pesticides based on historical monitoring (Well Inventory Database) and reported pesticide use (Pesticide Use Reporting) data. In 2022, the California Department of Pesticide Regulation's (DPR) Groundwater Protection Program (GWPP) analyzed groundwater samples from 59 wells for pesticide residues using the Triazine Screen and the Multi-Analyte Screen. Eleven wells were also analyzed for pesticides and degradates with the Metolachlor Screen in areas with higher use reported of the active ingredient.

#### Background

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. Wells in the Well Network continued to be sampled for at least some triazine pesticides annually. Due to the vulnerability of the study area, the Well Network has also served as an experimental area to monitor for additional pesticides that have the potential to contaminate groundwater.

Troiano et al. (2013) reported a statistical analysis of data collected from 2000 to 2012 in the Well Network, along with a full description of this study, including characterization of the conditions of the vulnerable areas, pesticide use, and the required mitigation measures. Annual summaries of study results have been reported since 2008. More recently, the annual summaries have included a trend analysis of changing pesticide and pesticide degradate residue concentrations since either 1999 or the first year an analyte was sampled for. The analysis in Troiano et al. (2013) and the tables included in the

annual summaries suggest that DPR's regulatory actions have resulted in measurable decreases in both detection frequencies and well water concentrations for many regulated pesticides (Davalos, 2021; Garretson, 1999; Troiano et al., 2013).

This summary of the 2022 Well Network monitoring presents the data in the following order:

- Sampling locations: **Figure 1**, Table 1, and Table 2
- Pesticides and degradates analyzed: Table 3 through Table 6
- Monitoring results: Table 7 through Table 11
- Historical data: Table 12 through Table 14
- QA/QC results: Table 15 through Table 16

*GWPP scientists would like to express their gratitude to the volunteers who have generously allowed us to sample their wells for over 20 years. Their participation has been crucial for monitoring emerging groundwater pesticide contaminants and establishing trends—work that could not have been accomplished without their participation. We would also like to acknowledge Jennifer Davalos, a former coworker who provided planning, logistics, volunteer communication and results gathering for the 2022 monitoring season.* 

#### **METHODS**

#### **Sampling Methods**

DPR's GWPP scientists conducted the study according to the protocol (Davalos, 2021) and followed the standard operating procedures (SOPs) for collecting samples (Kocis, 2022). Sampling occurred between May 16, 2022, and June 29, 2022.

#### Study Area

The Well Network's well locations are in areas susceptible to pesticide movement to groundwater within Fresno and Tulare counties (Figure 1, Table 1, and Table 2). Areas vulnerable to groundwater contamination from agricultural use of pesticides are characterized by coarse soils that are susceptible to pesticides leaching through the soil into groundwater or by hardpan soils vulnerable to pesticide runoff into sensitive areas with conduits to groundwater (www.cdpr.ca.gov/environmentalmonitoring/groundwater/). To regulate pesticide use in vulnerable soil areas of California, DPR designated certain one-square-mile sections of land that were determined to be sensitive to the movement of pesticides to groundwater as Groundwater Protection Areas (GWPAs). In GWPAs, pesticides and their degradates listed in California Code of Regulations, Title 3, Section 6800(a) are regulated to mitigate their movement to groundwater. Three types of GWPAs are designated, leaching, runoff and sections with a combined leaching and runoff. The GWPAs surrounding the Well Network are shown in Figure 1. GWPAs, sections, vulnerability and regulations are described in the 2022 annual well sampling report, <u>Sampling for Pesticide Residues in California Well Water</u>.

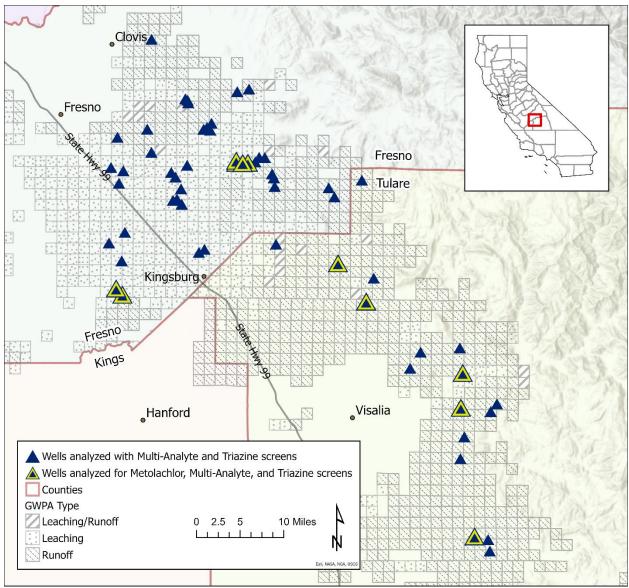


Figure 1. Location of the Well Network wells in Fresno and Tulare counties and display of GWPAs.

#### Wells Sampled

Fifty-nine wells (Table 1 and Table 2) in the Well Network were sampled in 2022. Not all wells in the Well Network are sampled every year due to changes in participation, wells going dry, and new wells being drilled to replace decommissioned wells. For this reason, well numbers used by DPR to differentiate sampling locations are not consecutive.

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-13
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
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
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

Tabl	e 1.	Well I	ocatio	ns in F	resno	o Coun	ty.	
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 Table 2. 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
96	17S/26E-29

\*Wells analyzed with the Metolachlor Screen

#### **Analytical Methods**

The CDFA Center for Analytical Chemistry analyzed samples using the Triazine Screen analytical method EM 62.9, revision 5 (CDFA, 2020), the Multi-Analyte Screen analytical method EMON-SM-05-032, revision 2 (CDFA, 2022a), and eleven well samples with the Metolachlor Screen analytical method EMON-SM-034A, revision 2 (CDFA, 2022b). These methods are highly specific and have been determined by DPR to provide unequivocal identification of the chemicals analyzed (Aggarwal, 2020; 2022a; 2022b). The reporting limit (RL) for each analyte ranged from 0.01 ppb ( $\mu$ g/L) to 0.05 ppb ( $\mu$ g/L) (Table 3 through Table 6). The Metolachlor Screen includes three analytes analyzed by Liquid Chromatography Mass Spectrometry (LC/MS) (Table 3), the Triazine Screen includes 14 analytes analyzed by LC/MS (Table 4), and the Multi-Analyte Screen includes 14 analytes by Gas Chromatography Mass Spectrometry (GC/MS) and 38 analytes by LC/MS (Table 5 and Table 6).

In 2022, groundwater samples from 59 wells were analyzed using the Triazine and Multi-Analyte Screens. A subset of eleven wells were collocated with areas of high use of metolachlor. Samples from this subset of wells were also analyzed for pesticide and pesticide degradate residues on the Metolachlor Screen.

Analyte	MDL	RL
S-Metolachlor	0.0114	0.05
Metolachlor ESA	0.0327	0.05
Metolachlor OXA	0.0321	0.05

**Table 3.** Metolachlor method detection limits (MDL) and reporting limits (RL) in ppb ( $\mu$ g/L).

Table 4. 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 5. Multi-Analyte Screen 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 6.** Multi-Analyte Screen method detection limits (MDL) and reporting limits (RL) in ppb  $(\mu g/L)$ .

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.

# RESULTS

Results in Table 7 through Table 11 will be entered into DPR's Well Inventory Database (DPR, 2024).

### **Metolachlor Screen**

The monitoring results for the eleven wells sampled for Metolachlor Screen analytes are shown in Table 7. This subset of wells was selected due to their location in high-use areas. No residues of metolachlor or the degradates were detected in the eleven wells sampled.

## **Triazine Screen**

The monitoring results for the 59 wells sampled for Triazine Screen analytes are shown in Table 8 and Table 9. The selected wells were in GWPAs, with 26 in leaching GWPAs and 33 in runoff GWPAs. Almost all wells (55 out of 59) had detections in the samples collected and analyzed of one or more pesticides or degradates on the Triazine Screen. All analytes were detected in at least one well, except metribuzin and prometryn. All detected analytes except hexazinone are 6800(a) pesticides and degradates on the groundwater protection list and regulated in GWPAs. Hexazinone was determined not to pollute at concentrations detected by DPR (Reardon, 2011).

#### **Multi-Analyte Screen**

The monitoring results for the 59 wells sampled for Multi-Analyte Screen analytes are shown in Table 10 and Table 11. Table 10 includes the quantifiable and estimated trace detections for pesticides that are unique to the Multi-Analyte Screen. Key findings include:

#### Analytes with Quantifiable Detections

The following 6 pesticides were detected at or above the RL concentrations in at least one of the wells sampled (Table 10):

- Chlorantraniliprole
- Fludioxonil
- Flutriafol
- Imidacloprid
- Mefenoxam/metalaxyl
- Methoxyfenozide

#### Analytes with Trace Detections

• Thiamethoxam was only detected at trace concentrations in one well sampled (Table 10).

#### Analytes Not Detected

The following 37 analytes were not detected in any of the samples collected:

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, thiobencarb, triallate, and uniconazole.

Previous detections of imidacloprid were provided as evidence for the formal review process required by the Pesticide Contamination Prevention Act (Davalos, 2022). As per sections 13149 and 13150 of the California Food and Agricultural Code of the Pesticide Contamination Prevention Act, in cases where a pesticide's active ingredient, specified ingredient, or degradation product is initially detected and confirmed in groundwater as a result of legal agricultural use, the law necessitates a formal review to assess whether the pesticide's usage can continue and, if so, under what condition. After formal review, imidacloprid was found not to pollute or threaten to pollute groundwater at concentrations detected in California (Henderson, 2022). DPR will continue to monitor for imidacloprid in groundwater.

Several pesticides detected in the Well Network are being evaluated through ongoing studies:

- Fludioxonil: Currently under investigation as part of a separate study (Kocis, 2020).
- Mefenoxam/metalaxyl: Under evaluation in a small-scale study.
- Methoxyfenozide, chlorantraniliprole, and flutriafol: Their detection in 2021 prompted statewide 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 Triazine and Multi-Analyte Screens**

A comparison of results from common analytes between the Triazine and Multi-Analyte Screens are shown in Table 11. The common analytes are atrazine, bromacil, diuron, norflurazon, prometon, simazine, and tebuthiuron. The results are generally similar between the two analytical methods, with minor differences, especially at lower concentrations. This indicates that the methods are consistent in detecting and quantifying the analytes. Only five detection comparisons showed variances exceeding the 30% relative percent difference. Differences arise between trace detections, where one method identifies trace concentrations while the other does not, typically because of differing detection limits. Other discrepancies could be due to differences in sensitivity of the two methods.

#### **Summary of Previous Years' Monitoring Results**

#### Metolachlor Screen

Wells in the Well Network were not previously analyzed using the Metolachlor Screen. The parent metolachlor, but not the degradates, is included in the Multi-analyte Screen, which has been used for all or some sites in the Well Network since 2014. In 2015, a trace of the parent was detected; however, all samples have been ND since that time.

#### Triazine Screen

Triazine Screen results from 1999 through 2022 are presented in Table 12 and Table 13 as the percent of wells with detections above the RL and the means of those detections. A comprehensive report similar to Troiano, et al. (2013) is currently being drafted to evaluate long-term trends.

#### Multi-Analyte Screen

An overview of the Multi-Analyte Screen detections from 2014 through 2022 is presented in Table 14, not including analytes reported on the Triazine Screen. The Multi-Analyte Screen method has been updated in recent years to add new analytes. Results vary year to year depending on the version of the method used and the number of wells analyzed using this method.

Well Number	S-Metolachlor	Metolachlor ESA	Metolachlor OXA
20	ND	ND	ND
20B	ND	ND	ND
21	ND	ND	ND
53A	ND	ND	ND
54	ND	ND	ND
59A	ND	ND	ND
63A	ND	ND	ND
68	ND	ND	ND
71	ND	ND	ND
80	ND	ND	ND
92	ND	ND	ND

Table 7. Metolachlor Screen from 2022. Concentrations in ppb ( $\mu$ g/L).

ND = not detected (below the method detection limit listed in Table 3)

Well Number	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN
1	Trace (0.0198)	ND	ND	0.0716	ND	Trace (0.00306)	ND
2	0.0419	ND	ND	Trace (0.0300)	ND	Trace (0.00625)	Trace (0.00800)
3	0.0450	ND	ND	0.0572	ND	ND	0.133
4	0.219	0.0247	1.22	0.516	0.0218	Trace (0.0168)	0.557
5	0.218	ND	ND	0.461	Trace (0.00720)	ND	0.241
7	0.0780	ND	0.0156	0.203	Trace (0.00450)	Trace (0.00649)	ND
8	0.150	Trace (0.00685)	Trace (0.0113)	0.195	0.0217	0.0279	0.0132
12	0.273	ND	0.328	0.301	Trace (0.00239)	0.0380	0.0172
13	0.101	ND	0.160	0.214	ND	0.0228	0.192
14	ND						
15	0.0434	ND	ND	0.0967	ND	Trace (0.0110)	0.0912
16	0.105	ND	ND	0.248	ND	0.0250	0.245
19	0.120	ND	ND	0.137	ND	Trace (0.00598)	0.184
20	Trace (0.0107)	ND	ND	Trace (0.00357)	ND	ND	ND
20B	ND						
21	ND	ND	ND	Trace (0.00364)	ND	ND	Trace (0.00883)
22	0.140	ND	ND	0.373	ND	ND	0.0732
23B	0.133	ND	0.0689	0.256	ND	0.0302	0.134
24	ND	ND	ND	Trace (0.00850)	ND	ND	0.113
25	0.0588	ND	ND	Trace (0.0477)	ND	ND	0.0297
26	Trace (0.00943)	ND	ND	Trace (0.0206)	ND	ND	0.0366
28	Trace (0.00787)	ND	ND	Trace (0.0146)	ND	ND	ND
30A	0.166	ND	ND	0.238	Trace (0.00746)	0.0219	0.0236
32	0.160	ND	ND	0.242	ND	ND	0.312
35	0.103	ND	ND	0.151	ND	0.0274	0.0953
36	ND	ND	ND	Trace (0.0108)	ND	ND	Trace (0.00746)
37	0.0368	ND	Trace (0.00312)	0.0516	ND	Trace (0.00557)	0.0992
43	0.138	ND	ND	0.0965	ND	Trace (0.00265)	0.0486
44	0.0837	ND	0.127	0.0979	ND	0.0241	0.0200
45	Trace (0.0226)	ND	ND	Trace (0.0456)	ND	0.0379	0.113
47	0.398	Trace (0.00816)	0.0265	0.789	0.0523	Trace (0.00979)	0.0200
49	0.663	ND	ND	3.44	Trace (0.00883)	ND	0.267
50	ND						

Table 8. Triazine Screen sampling results from 2022 (part 1). Concentrations in ppb ( $\mu$ g/L).

Well Number	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN
52	0.0476	ND	ND	0.0932	ND	ND	0.0114
53A	ND						
54	Trace (0.0218)	ND	ND	Trace (0.0420)	ND	ND	ND
56	0.274	ND	ND	0.633	ND	ND	ND
57	0.118	ND	ND	0.211	ND	ND	0.0185
58	Trace (0.00923)	ND	ND	Trace (0.00657)	ND	ND	Trace (0.00906)
59A	0.352	Trace (0.0185)	0.655	0.707	0.0411	0.0341	1.90
61	0.392	ND	1.01	1.77	Trace (0.0188)	0.0357	0.0219
63A	Trace (0.00844)	Trace (0.00887)	ND	Trace (0.0265)	Trace (0.0108)	Trace (0.00844)	ND
65	Trace (0.0266)	ND	ND	0.0515	ND	ND	ND
68	ND						
69	0.413	ND	0.289	2.01	Trace (0.00472)	0.0369	ND
71	0.364	ND	0.895	1.01	Trace (0.00606)	0.0213	1.00
72	0.639	Trace (0.00364)	Trace (0.00957)	1.74	0.0239	Trace (0.0111)	0.0358
73	0.116	Trace (0.00386)	ND	1.06	0.0394	Trace (0.00738)	0.0499
74	0.709	ND	0.479	1.26	Trace (0.0154)	0.0357	0.0289
75A	0.785	ND	0.401	0.799	Trace (0.00617)	0.0348	Trace (0.00698)
80	0.307	ND	0.129	1.03	Trace (0.00496)	0.0200	Trace (0.00401)
84	0.203	Trace (0.0105)	4.39	0.565	0.0233	0.0339	Trace (0.00243)
86	0.442	Trace (0.00512)	ND	2.88	0.0326	Trace (0.00500)	ND
89	0.0504	ND	0.0216	0.0696	ND	Trace (0.0188)	0.0708
90	0.125	0.0507	0.0242	0.163	0.111	0.0392	0.0158
92	0.270	ND	ND	0.262	Trace (0.00266)	0.0478	0.145
94	0.527	ND	Trace (0.0190)	3.35	Trace (0.00499)	Trace (0.00630)	0.553
95	ND	ND	ND	Trace (0.00767)	ND	ND	ND
96	0.479	ND	0.288	2.12	Trace (0.00567)	0.0273	0.0289

ND = not detected (below the method detection limit listed in Table 4).

Well Number**	Hexazinone	Metribuzin	Norflurazon	Prometon	Prometryn	Simazine	Tebuthiuron	Propazine %*
1	ND	ND	ND	ND	ND	ND	ND	75.6
2	ND	ND	Trace (0.00291)	ND	ND	0.0327	ND	91.9
3	ND	ND	Trace (0.00777)	ND	ND	0.0492	ND	80.1
4	ND	ND	0.562	Trace (0.0130)	ND	0.0545	ND	76.4
5	ND	ND	Trace (0.00684)	ND	ND	0.0734	ND	82.2
7	ND	ND	ND	ND	ND	Trace (0.0132)	ND	82.5
8	Trace (0.00304)	ND	Trace (0.00410)	ND	ND	0.0645	ND	78.8
12	ND	ND	ND	ND	ND	0.0218	ND	89.3
13	ND	ND	0.132	ND	ND	0.0275	ND	75.8
14	ND	ND	ND	ND	ND	ND	ND	76.7
15	ND	ND	Trace (0.0174)	ND	ND	0.0419	ND	87.4
16	ND	ND	0.0797	ND	ND	0.0606	ND	82.7
19	ND	ND	0.0251	ND	ND	0.0440	ND	70.7
20	ND	ND	ND	ND	ND	Trace (0.0131)	ND	84.0
20B	ND	ND	ND	ND	ND	Trace (0.00333)	ND	80.1
21	ND	ND	ND	ND	ND	Trace (0.00331)	ND	78.0
22	ND	ND	Trace (0.00348)	ND	ND	0.0724	ND	76.1
23B	ND	ND	Trace (0.0119)	ND	ND	0.0259	ND	79.1
24	ND	ND	Trace (0.0150)	ND	ND	Trace (0.00363)	ND	83.7
25	ND	ND	ND	ND	ND	0.0364	ND	82.0
26	ND	ND	ND	ND	ND	Trace (0.00585)	ND	75.2
28	ND	ND	ND	ND	ND	Trace (0.00964)	ND	74.1
30A	ND	ND	0.0547	ND	ND	0.0679	ND	69.8
32	ND	ND	0.153	ND	ND	0.0508	ND	80.2
35	ND	ND	0.0297	Trace (0.0101)	ND	0.0674	ND	79.1
36	ND	ND	ND	Trace (0.00290)	ND	0.0221	ND	83.7
37	ND	ND	0.0401	ND	ND	0.0243	ND	81.1
43	ND	ND	0.0281	ND	ND	0.0633	ND	77.9
44	ND	ND	Trace (0.00658)	ND	ND	0.0359	ND	79.4
45	ND	ND	0.0244	Trace (0.00390)	ND	Trace (0.00858)	ND	78.9
47	Trace (0.00243)	ND	ND	ND	ND	0.0250	ND	76.8
49	ND	ND	Trace (0.0189)	ND	ND	0.0640	ND	77.7
50	ND	ND	ND	ND	ND	ND	ND	85.1
52	ND	ND	ND	ND	ND	0.0403	ND	73.6

Table 9. Triazine Screen sampling results from 2022 (part 2). Concentrations in ppb ( $\mu$ g/L).

Well Number**	Hexazinone	Metribuzin	Norflurazon	Prometon	Prometryn	Simazine	Tebuthiuron	Propazine %*
53A	ND	ND	ND	ND	ND	ND	ND	80.9
54	ND	ND	ND	0.0297	ND	0.0351	ND	81.5
56	ND	ND	ND	ND	ND	0.0701	ND	76.7
57	ND	ND	ND	ND	ND	0.0357	ND	72.7
58	ND	ND	ND	ND	ND	Trace (0.0199)	ND	91.4
59A	ND	ND	0.553	ND	ND	0.0202	ND	77.2
61	ND	ND	Trace (0.00855)	ND	ND	0.0512	ND	82.1
63A	ND	ND	ND	ND	ND	ND	ND	76.7
65	ND	ND	ND	ND	ND	Trace (0.00988)	Trace (0.00295)	88.6
68	ND	ND	ND	ND	ND	ND	ND	85.4
69	ND	ND	ND	ND	ND	0.0343	ND	84.5
71	ND	ND	0.265	ND	ND	0.0519	ND	73.3
72	ND	ND	0.0215	ND	ND	0.0639	ND	84.2
73	ND	ND	ND	ND	ND	Trace (0.00566)	ND	80.3
74	ND	ND	0.0356	ND	ND	0.0733	ND	84.7
75A	ND	ND	Trace (0.00575)	ND	ND	0.0662	ND	79.2
80	ND	ND	ND	ND	ND	Trace (0.0179)	ND	73.5
84	ND	ND	ND	ND	ND	Trace (0.0186)	ND	85.5
86	ND	ND	ND	ND	ND	0.0358	ND	72.4
89	ND	ND	Trace (0.0108)	ND	ND	0.0349	ND	78.0
90	0.0352	ND	Trace (0.0142)	Trace (0.00307)	ND	0.0696	Trace (0.0161)	79.2
92	ND	ND	0.0569	ND	ND	0.0485	ND	79.0
94	ND	ND	0.135	ND	ND	0.0334	ND	82.3
95	ND	ND	ND	ND	ND	ND	ND	86.8
96	ND	ND	0.0331	ND	ND	0.0244	ND	92.9

ND = not detected (below the method detection limit listed in Table 4).

\*Propazine was 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.

Well		Analyte	s Unique to th	e Multi-Analyte Scree	n with Detections in at Least	One Well	
Number	Chlorantraniliprole	Fludioxonil	Flutriafol	Imidacloprid	Mefenoxam/Metalaxyl*	Methoxyfenozide	Thiamethoxam
1	ND	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	Trace (0.0137) **	ND	ND	ND
3	ND	ND	ND	Trace (0.0117)	ND	ND	ND
4	ND	ND	ND	Trace (0.00477)	Trace (0.00587)	ND	ND
5	ND	ND	ND	0.0699	ND	ND	ND
7	ND	ND	ND	ND	ND	ND	ND
8	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	Trace (0.00824)	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND
15	Trace (0.0110)	ND	ND	0.102	ND	ND	ND
16	ND	ND	ND	0.044	ND	ND	ND
19	0.220	ND	0.0754	ND	ND	0.162	ND
20	0.0445	ND	ND	Trace (0.00435)	ND	ND	ND
20B	0.0820	ND	ND	0.0388**	ND	Trace (0.0137)	Trace (0.0164)
21	Trace (0.00724)	ND	ND	0.0242	ND	ND	ND
22	0.0978**	ND	0.209	Trace (0.00950) **	ND	0.229	ND
23B	ND	ND	ND	0.0720	ND	ND	ND
24	ND	ND	ND	0.0668	ND	ND	ND
25	ND	ND	ND	Trace (0.00384)	ND	ND	ND
26	ND	ND	ND	0.0368	ND	ND	ND
28	ND	ND	ND	ND	ND	ND	ND
30A	ND	0.484	ND	ND	ND	0.122	ND
32	ND	ND	ND	ND	ND	ND	ND
35	ND	ND	ND	ND	ND	ND	ND
36	ND	ND	ND	Trace (0.00772)	Trace (0.0100)	ND	ND
37	ND	ND	ND	ND	ND	ND	ND
43	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND
45	ND	ND	ND	ND	ND	ND	ND
47	ND	ND	ND	ND	ND	ND	ND
49	ND	ND	ND	ND	ND	ND	ND

**Table 10.** Sampling results for 2022 of the seven analytes with detections in at least one well that are unique to the Multi-Analyte Screen (CDFA, 2022a). Concentrations in ppb ( $\mu$ g/L). Thirty-seven analytes were not detected in any well and are not shown in this table.

Well         Analytes Unique to the Multi-Analyte Screen with Detections in at Least One Well           Number         Chlorantraniliprole         Fludioxonil         Flutriafol         Imidacloprid         Mefenoxam/Metalaxyl*         Methoxyfenozide         Thiamethoxam												
Number	Chlorantraniliprole	Fludioxonil	Flutriafol	Imidacloprid	Mefenoxam/Metalaxyl*	Methoxyfenozide	Thiamethoxam					
50	ND	ND	ND	ND	ND	ND	ND					
52	ND	ND	ND	ND	ND	ND	ND					
53A	ND	ND	ND	ND	ND	ND	ND					
54	ND	ND	ND	0.0304	Trace (0.00371)	ND	ND					
56	ND	ND	ND	ND	ND	ND	ND					
57	ND	ND	ND	ND	ND	ND	ND					
58	ND	ND	ND	ND	ND	ND	ND					
59A	ND	ND	ND	ND	ND	ND	ND					
61	ND	ND	ND	ND	ND	ND	ND					
63A	ND	ND	ND	ND	ND	ND	ND					
65	ND	ND	ND	ND	ND	ND	ND					
68	Trace (0.00355)	ND	ND	ND	ND	ND	ND					
69	ND	ND	ND	ND	ND	ND	ND					
71	ND	ND	ND	ND	ND	ND	ND					
72	ND	ND	ND	ND	ND	ND	ND					
73	ND	ND	ND	ND	ND	ND	ND					
74	ND	ND	ND	ND	ND	ND	ND					
75A	ND	ND	ND	ND	ND	ND	ND					
80	ND	ND	ND	ND	ND	ND	ND					
84	ND	ND	ND	ND	ND	ND	ND					
86	ND	ND	ND	ND	ND	ND	ND					
89	ND	ND	ND	ND	ND	ND	ND					
90	ND	ND	ND	ND	ND	ND	ND					
92	ND	ND	ND	ND	ND	ND	ND					
94	ND	ND	ND	Trace (0.00330)	ND	ND	ND					
95	ND	ND	ND	Trace (0.00646)	ND	ND	ND					
96	ND	ND	ND	ND	0.173	ND	ND					

ND = not detected (below the method detection limit listed in Table 5 and Table 6).

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

\*\*Replicate sample is reported because it was higher.

					Analyte	s in Both th	ne Multi-Ar	alyte and 1	riazine Scr	eens*				
	Atra	zine	Broi	macil	Diur	on	Norflu	irazon	Prom	neton	Sima	zine	Tebu	thiuron
Well Number	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine
1	ND	ND	ND	ND	ND	Trace (0.00306)	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	Trace (0.00598)**	Trace (0.00625)	ND	Trace (0.00291)	ND	ND	0.0364**	0.0327	ND	ND
3	ND	ND	ND	ND	ND	ND	Trace (0.00885)	Trace (0.00777)	ND	ND	0.0571	0.0492	ND	ND
4	0.0280	0.0247	1.35	1.22	Trace (0.0190)	Trace (0.0168)	0.769	0.562	Trace (0.0152)	Trace (0.0130)	0.0698	0.0545	ND	ND
5	ND	ND	ND	ND	ND	ND	Trace (0.00812)	Trace (0.00684)	ND	ND	0.0951	0.0734	ND	ND
7	ND	ND	Trace (0.0195)	Trace (0.0156)	Trace (0.00729)	Trace (0.00649)	ND	ND	ND	ND	Trace (0.0143)**	Trace (0.0132)	ND	ND
8	Trace (0.00890)	Trace (0.00685)	Trace (0.0145)	Trace (0.0113)	0.0386	0.0279	Trace (0.00664)	Trace (0.00410)	ND	ND	0.0846	0.0645	ND	ND
12	ND	ND	0.376	0.328	0.0455	0.0380	ND	ND	ND	ND	0.0264**	0.0218	ND	ND
13	ND	ND	0.202	0.160	0.0312	0.0228	0.176	0.132	ND	ND	0.0349	0.0275	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	Trace (0.0148)	Trace (0.0110)	Trace (0.0192)	Trace (0.0174)	ND	ND	0.0532	0.0419	ND	ND
16	ND	ND	ND	ND	0.0287	0.0250	0.0942	0.0797	ND	ND	0.0704	0.0606	ND	ND
19	ND	ND	ND	ND	Trace (0.00828)	Trace (0.00598)	0.0365	0.0251	ND	ND	0.0605	0.0440	ND	ND
20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.0156)	Trace (0.0131)	ND	ND
20B	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.00507)	Trace (0.00333)	ND	ND
21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.00517)	Trace (0.00331)	ND	ND

**Table 11.** Comparison of 2022 results for replicate analyses in the Multi-Analyte and Triazine Screens. Concentrations in ppb ( $\mu$ g/L). The table includes results for the seven analytes detected out of the nine analytes analyzed in both methods.

					Analyte	s in Both th	ne Multi-Ar	alyte and 1	Triazine Scr	eens*				
	Atra	zine	Broi	macil	Diur	on	Norflu	ırazon	Prom	neton	Sima	zine	Tebu	thiuron
Well Number	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine
22	ND	ND	ND	ND	ND	ND	ND	Trace (0.00348)	ND	ND	0.0887**	0.0724	ND	ND
23B	ND	ND	0.0743	0.0689	0.0304	0.0302	Trace (0.0125)	Trace (0.0119)	ND	ND	0.0293	0.0259	ND	ND
24	ND	ND	ND	ND	ND	ND	Trace (0.0158)	Trace (0.0150)	ND	ND	Trace (0.00398)	Trace (0.00363)	ND	ND
25	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0493**	0.0364	ND	ND
26	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.00862)	Trace (0.00585)	ND	ND
28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.0126)	Trace (0.00964)	ND	ND
30A	ND	ND	ND	ND	0.0334	0.0219	0.0782	0.0547	ND	ND	0.0933	0.0679	ND	ND
32	ND	ND	ND	ND	ND	ND	0.191	0.153	ND	ND	0.0563	0.0508	ND	ND
35	ND	ND	ND	ND	0.0355	0.0274	0.0323	0.0297	Trace (0.0125)	Trace (0.0101)	0.0784	0.0674	ND	ND
36	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.00290)	0.0267	0.0221	ND	ND
37	ND	ND	ND	Trace (0.00312)	Trace (0.00515)	Trace (0.00557)	0.0404	0.0401	ND	ND	0.0259	0.0243	ND	ND
43	ND	ND	ND	ND	ND	Trace (0.00265)	0.0363	0.0281	ND	ND	0.0759	0.0633	ND	ND
44	ND	ND	0.163	0.127	0.0304	0.0241	Trace (0.00881)	Trace (0.00658)	ND	ND	0.0383	0.0359	ND	ND
45	ND	ND	ND	ND	0.0477	0.0379	0.0323	0.0244	Trace (0.00467)	Trace (0.00390)	Trace (0.01060)	Trace (0.00858)	ND	ND
47	Trace (0.0104)	Trace (0.00816)	0.0317	0.0265	Trace (0.0119)	Trace (0.00979)	ND	ND	ND	ND	0.0301	0.0250	ND	ND
49	ND	ND	ND	ND	ND	ND	0.0206	Trace (0.0189)	ND	ND	0.0733	0.0640	ND	ND
50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0590	0.0403	ND	ND

					Analyte	s in Both th	ne Multi-Ar	alyte and T	riazine Scr	eens*				
	Atra	zine	Bro	macil	Diur	on	Norflu	irazon	Prom	neton	Sima	zine	Tebu	thiuron
Well Number	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine
53A	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
54	ND	ND	ND	ND	ND	ND	ND	ND	0.0334	0.0297	0.0388	0.0351	ND	ND
56	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0850**	0.0701	ND	ND
57	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0437	0.0357	ND	ND
58	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0230	Trace (0.0199)	ND	ND
59A	0.0222**	Trace (0.0185)	0.837	0.655	0.0401**	0.0341	0.720	0.553	ND	ND	0.0277	0.0202	ND	ND
61	ND	ND	0.906	1.01	0.0346	0.0357	Trace (0.00728)	Trace (0.00855)	ND	ND	0.0496	0.0512	ND	ND
63A	Trace (0.00977)	Trace (0.00887)	ND	ND	Trace (0.0114)	Trace (0.00844)	ND	ND	ND	ND	ND	ND	ND	ND
65	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.0114)	Trace (0.00988)	ND	Trace (0.00295)
68	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
69	ND	ND	0.344	0.289	0.0442	0.0369	ND	ND	ND	ND	0.0420	0.0343	ND	ND
71	ND	ND	0.919**	0.895	0.0265	0.0213	0.303**	0.265	ND	ND	0.0642**	0.0519	ND	ND
72	Trace (0.00389)	Trace (0.00364)	Trace (0.0120)	Trace (0.00957)	Trace (0.0137)	Trace (0.0111)	0.0233	0.0215	ND	ND	0.0752	0.0639	ND	ND
73	Trace (0.00461)	Trace (0.00386)	ND	ND	Trace (0.00749)	Trace (0.00738)	ND	ND	ND	ND	Trace (0.00717)	Trace (0.00566)	ND	ND
74	ND	ND	0.532	0.479	0.0370	0.0357	0.0328	0.0356	ND	ND	0.0758	0.0733	ND	ND
75A	ND	ND	0.488	0.401	0.0420	0.0348	Trace (0.00661)	Trace (0.00575)	ND	ND	0.0823	0.0662	ND	ND
80	ND	ND	1.05	0.129	0.0250**	0.0200	0.321	ND	ND	ND	0.0598	Trace (0.0179)	ND	ND
84	Trace (0.0120)	Trace (0.0105)	4.76	4.39	0.0414	0.0339	ND	ND	ND	ND	0.0249	Trace (0.0186)	ND	ND

		Analytes in Both the Multi-Analyte and Triazine Screens*           Atrazine         Bromacil         Diuron         Norflurazon         Prometon         Simazine         Tebuthiuron												
	Atra	zine	Broi	macil	Diur	on	Norflu	irazon	Prom	neton	Sima	zine	Tebu	thiuron
Well Number	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine	Multi- Analyte	Triazine
86	Trace (0.00679)	Trace (0.00512)	ND	ND	Trace (0.00697)	Trace (0.00500)	ND	ND	ND	ND	0.0463	0.0358	ND	ND
89	ND	ND	Trace (0.0191)	0.0216	Trace (0.0171)	Trace (0.0188)	Trace (0.0104)	Trace (0.0108)	ND	ND	0.0288	0.0349	ND	ND
90	0.0588	0.0507	0.0286	0.0242	0.0472	0.0392	Trace (0.0157)	Trace (0.0142)	Trace (0.00349)	Trace (0.00307)	0.0775	0.0696	0.0219	Trace (0.0161)
92	ND	ND	ND	ND	0.0639**	0.0478	0.0742	0.0569	ND	ND	0.0623	0.0485	ND	ND
94	ND	ND	0.0221	Trace (0.0190)	Trace (0.00768)	Trace (0.00630)	0.189	0.135	ND	ND	0.0435	0.0334	ND	ND
95	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	Trace (0.00310)	ND	ND	ND
96	ND	ND	0.301**	0.288	0.0323	0.0273	0.0357	0.0331	ND	ND	0.0283	0.0244	ND	ND

ND = not detected (below the method detection limit listed in Table 4 through Table 6)

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

\*\*Replicate sample is reported because it was higher

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	39.0
2021*	61.7	1.7	23.3	65.0	8.3	28.3	60.0	3.3	26.7	1.7	63.3
2022	69.5	3.4	30.5	69.5	15.3	33.9	61.0	1.7	28.8	1.7	66.1
Mean	79.0	3.1	30.6	79.6	6.3	35.2	44.7	0.5	22.1	1.1	63.9
SD	11.8	1.3	6.4	8.2	3.3	21.0	7.7	0.9	4.3	0.7	17.3

Table 12. Yearly percent (%) of wells with detections above the reporting limit (RL) for each analyte on the Triazine Screen.

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 beginning in 2021 was due to the lower RLs for the analytical methods.

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	0.10	0.67	0.68	0.06	0.13	0.26	ND	0.20	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
2022	0.25	0.04	0.58	0.73	0.04	0.03	0.19	0.04	0.13	0.03	0.05
Mean	0.38	0.08	0.83	0.79	0.11	0.18	0.23	0.05	0.18	0.08	0.09
SD	0.099	0.018	0.224	0.104	0.034	0.108	0.028	0.016	0.045	0.020	0.023

**Table 13.** Yearly mean concentrations above the reporting limit (RL) in ppb ( $\mu$ g/L) for each analyte on the Triazine Screen.

		Lentrations in ppb (µg/L)	Sample Year									
Well #	Township/ Range- Section	Analyte	2014	2015	2016	2017	2018	2019	2020	2021**	2022	
2	13S/22E-33	Imidacloprid	ND	ND	ND	ND	Trace	Trace	ND	0.024**	Trace	
3	13S/23E-28	Imidacloprid	ND	ND	ND	ND	ND	ND	-	-	Trace	
4	13S/23E-32	Imidacloprid	ND	ND	ND	Trace	ND	ND	-	-	Trace	
5	14S/21E-13	Imidacloprid	ND	ND	ND	Trace	Trace	Trace	ND	Trace	0.0699	
13	14S/22E-12	Imidacloprid	ND	ND	ND	ND	ND	ND	-	-	Trace	
15	14S/22E-14	Imidacloprid	ND	ND	ND	0.066	0.091	0.085	0.106	0.126	0.102	
16	14S/22E-14	Imidacloprid	ND	ND	ND	ND	ND	ND	-	-	0.0440	
18	14S/22E-31	Imidacloprid	0.059	0.665	-	-	-	-	-	-	-	
20	14S/23E-32	Imidacloprid	-	ND	ND	ND	ND	ND	-	-	Trace	
20B	14S/23E-32	Imidacloprid	-	-	-	-	-	-	-	-	0.0388***	
21	14S/23E-33	Imidacloprid	-	0.065	ND	ND	ND	ND	-	-	0.0242	
22	14S/23E-34	Imidacloprid	-	0.120	0.080		Trace	Trace	-	Trace	Trace***	
23	14S/23E-35	Imidacloprid	-	0.218	0.209	0.534	0.536	0.470	0.073	-	-	
23B	14S/23E-35	Imidacloprid	-	-	-	-	-	-	-	0.0253***	0.0720	
24	15S/21E-03	Imidacloprid	ND	ND	ND		Trace		0.112	0.088	0.0668	
25	15S/21-05	Imidacloprid	ND	ND	ND	ND	ND	ND	-	-	Trace	
26	15S/21E-09	Imidacloprid	Trace	0.051	0.072	0.167	0.053	ND	-	0.0348	0.0368	
29	15S/22E-03	Imidacloprid	ND	Trace	ND	5.970	0.095	Trace	0.053	0.046**	-	
36	15S/22E-20	Imidacloprid	ND	ND	ND	ND	ND	ND	-	-	Trace	
47	15S/24E-14	Imidacloprid	-	ND	0.644	ND	ND	ND	-	ND	ND	
48	15S/24E-36	Imidacloprid	-	ND	Trace	Trace	-	-	-	-	-	
54	16S/21E-34	Imidacloprid	-	ND	ND	ND	ND	ND	-	-	0.0304	
94	15S/24E-10	Imidacloprid	-	ND	ND	ND	ND	ND	-	-	Trace	
95	14S/22E-33	Imidacloprid	ND	ND	ND	ND	ND	ND	-	-	Trace	
37	15S/22E-21	Oryzalin	Trace	ND	ND	ND	ND	ND	-	-	ND	
44	15S/23E-02	Oryzalin	-	Trace	ND	ND	ND	ND	-	-	ND	
4	13S/23E-32	Mefenoxam/Metalaxyl*	ND	ND	ND	ND	ND	ND	-	-	Trace	
29	15S/22E-03	Mefenoxam/Metalaxyl*	ND	Trace	ND	ND	ND	ND	ND	Trace	-	
36	15S/22-20	Mefenoxam/Metalaxyl*	ND	ND	ND	ND	ND	ND	-	-	Trace	
54	16S/21E-34	Mefenoxam/Metalaxyl*	-	ND	ND	ND	ND	ND	-	-	Trace	
96	27S/26E-30	Mefenoxam/Metalaxyl*	-	-	-	-	-	-	-	-	0.173	
74	19S/26E-01	Metolachlor	-	Trace	ND	ND	ND	ND	-	-	ND	
30A	15S/22E-05	Fludioxonil	-	ND	Trace	0.066	0.165	0.380	0.333	0.316***	0.484	
4	13S/23E-32	Propanil	ND	ND	ND	0.060	ND	ND	-	-	ND	
19	14S/23E-34	Methoxyfenozide	-	-	-	-	-	-	-	-	0.162	
20B	14S/23-32	Methoxyfenozide	-	-	-	-	-	-	-	-	Trace	
22	14S/23E-34	Methoxyfenozide	-	-	-	-	-	-	-	0.201	0.229	
26	15S/21E-09	Methoxyfenozide	-	-	-	-	-	-	-	Trace**	ND	
29	15S/22E-03	Methoxyfenozide	-	-	-	-	-	-	-	Trace	-	
30A	15S/22E-05	Methoxyfenozide	-	-	-	-	-	-	-	0.0872***	0.122	
15	14S/22E-14	Chlorantraniliprole	-	-	-	-	-	-	-	Trace	Trace	
19	14S/23E-34	Chlorantraniliprole	-	I	-	-	-	-	-	-	0.220	
20	14S/23E-32	Chlorantraniliprole	-	•	-	-	-	-	-	-	0.0445	
20B	14S/23-32	Chlorantraniliprole	-	-	-	-	-	-	-	-	0.0820	

**Table 14.** Summary of wells with Multi-Analyte Screen detections (other than Triazine analytes) from 2014 through 2022. Concentrations in ppb ( $\mu$ g/L).

	Township/			Sample Year										
Well #	Range- Section	Analyte	2014	2015	2016	2017	2018	2019	2020	2021**	2022			
21	14S/23-33	Chlorantraniliprole	-	-	-	-	-	-	-	-	Trace			
22	14S/23E-34	Chlorantraniliprole	-	-	-	-	-	-	-	0.266	0.0978***			
68	18S/26E-02	Chlorantraniliprole	-	-	-	-	-	-	-	-	Trace			
19	14S/23E-34	Flutriafol	-	-	-	-	-	-	-	-	0.0754			
22	14S/23E-34	Flutriafol	-	-	-	-	-	-	-	0.226	0.209			
20B	14S/23-32	Thiamethoxam	-	-	-	-	-	-	-	-	Trace			

ND = Not detected (below the method detection limit listed in Table 5 and Table 6).

Trace = result is < RL but > MDL

[-] = Not sampled because the well was not available for sampling, or not analyzed because the analyte was not part of the method. Some analytes (e.g., methoxyfenozide, chlorantraniliprole, and flutriafol) were not analyzed for until 2021.

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

\*\*RL from 2014–2020 was 0.05 ppb; from 2021–2022 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 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 15. All quality control (QC) results are available upon request.

# **Matrix Spikes**

# Metolachlor Screen

Two total matrix spikes were analyzed with two sets of samples using the Metolachlor Screen. All analytes were spiked at 0.1 ppb. The mean recoveries for the three analytes ranged from 88.1 to 97.7%. The standard deviation of the recoveries ranged from 0.4 to 3.4%. Recovery of all six analytes was within control limits.

# Triazine Screen

Twenty total matrix spikes were analyzed in duplicate 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 80.3 to 87.2%. The standard deviation of the recoveries ranged from 4.0 to 6.3%. Five out of 280 total spiked analytes were beyond the upper control limits. The propazine surrogate recoveries were within the control limits in both the continuing QC and in the 59 samples analyzed (Table 9).

#### Multi-Analyte Screen

For the Multi-Analyte Screen, matrix spikes were extracted and split to be analyzed along with sets of samples for both the LC/MS and GC/MS instruments. Eleven matrix spikes were analyzed along with the eleven sets of samples using LC/MS, with all analytes spiked at 0.2 ppb. The mean recoveries for the 38 analytes ranged from 74.2 to 103%. The standard deviation of the recoveries ranged from 9.0 to 22.2%. Out of 418 spiked analytes on the LC/MS screen, 99 were found to be outside the control limits. The CDFA Laboratory evaluates recoveries to control limits. The CDFA Laboratory and the Environmental Monitoring

Branch Quality Assurance Officer conducted a detailed review of the QC data and the associated sample results and determined that the recoveries outside of control limits in the spiked sample sets do not significantly impact the reported data.

Thirteen matrix spikes were analyzed along with sets of samples using GC/MS for the Multi-Analyte Screen. All analytes were spiked at 0.1 ppb. The mean recoveries for the 14 analytes ranged from 81.2 to 114%. The standard deviation of the recoveries ranged from 9.7 to 39.7%. Two out of the 182 spiked analytes on the GC/MS screen were beyond the upper 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 Quality Assurance Officer submitted the blind spike to the laboratory disguised as a field sample according to the SOP (Ganapathy, 2005). One metolachlor, three triazine, and three multi-analyte blind spikes were submitted throughout the study period (Table 15). Results are presented based on the blind spikes prepared by the laboratory. Of the 26 analytes spiked, recoveries of 24 analytes (92.3%) were within the control limits, while recoveries of two analytes were outside the control limits. All blind spike results are presented in Table 16.

## **Laboratory and Field Blanks**

A laboratory matrix blank and deionized water field blanks were part of the QAQC for this study as described in Davalos, 2021 and Peoples, 2019. All laboratory and field blanks had no detections (Table 15).

QC Туре	Metolachlor Screen	Triazine Screen	Multi- Analyte LC/MS Screen	Multi- Analyte GC/MS Screen	Total Number	QC Summary	
Continuing QC matrix spikes	2	20	11	13	46	Of 886 spiked analytes, 106 were outside control limits: Five on the Triazine Screen, 99 on the LC/MS Screen, and two on the GC/MS Screen	
Blind spikes	1	3	2	1	7	Two out of 26 spiked analytes were outside the control limits	
Laboratory matrix blanks	2	10	11	13	36	All non-detect	
Field blanks	1	6	36	42	85	All non-detect	

Table 15. Laboratory and field quality control (QC) summary.

Analysis Date	Analysis	Analyte	Spike Level (ppb)	Result (ppb)	% Recovery	Control limit exceeded*
6/30/2022	Triazine**	Atrazine	0.15	0.127	84.7	no
		Bromacil	0.15	0.134	89.3	no
		Diuron	0.15	0.138	92.0	no
		Hexazinone	0.15	0.128	85.3	no
		Norflurazon	0.1	0.0901	90.1	no
6/23/2022	Multi- Analyte (LC/MS)	Azoxystrobin	0.15	0.155	103	no
		Flutriafol	0.15	0.168	112	no
		Imidacloprid	0.15	0.174	116	no
		Methoxyfenozide	0.15	0.137	91.3	no
		Chlorantraniliprole	0.15	0.135	90.0	no
7/27/2022	Triazine	ACET	0.1	0.0925	92.5	no
		Bromacil	0.15	0.125	83.3	no
		Norflurazon	0.1	0.0852	85.2	no
		Simazine	0.2	0.182	91.0	no
7/29/2022	Triazine	DACT	0.15	0.138	92.0	no
		Diuron	0.1	0.108	108	YES
		Hexazinone	0.05	0.0446	89.2	no
		Prometon	0.1	0.0996	99.6	YES
8/10/2022	Multi- Analyte (LC/MS & GC/MS)	Methoxyfenozide	0.2	0.166	83.0	no
		Mefenoxam	0.1	0.098	98.0	no
		Imidacloprid	0.15	0.169	113	no
		Metolachlor	0.15	0.148	98.7	no
		Dichlobenil	0.1	0.071	71.0	no
6/29/2022	Metolachlor	Metolachlor	0.15	0.127	84.7	no
		Metolachlor ESA	0.15	0.146	97.3	no
		Metolachlor OXA	0.15	0.137	91.3	no

 Table 16. Blind spike levels and recoveries.

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

\*\*DPR requested DEA and prometon in place of bromacil and norflurazon; however, the laboratory was out of DEA and prometon standards and switched these analytes to bromacil and norflurazon.

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