# Study 228: Monitoring the Concentrations of Detected Pesticides in Wells Located in Highly Sensitive Areas (Well Network Sampling) Annual Update 2020

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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. Due to the COVID-19 pandemic in 2020, the California Department of Pesticide Regulation (DPR) had to reduce chemical analyses and alter the sampling schedule. The impact resulted in staff sampling all 59 wells for herbicides using the Triazine Screen, and only seven wells for pesticides on the Multi-Analyte Screen. Additionally, plans to sample for other pesticides that have the potential to contaminate groundwater were postponed until a future season.

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). When this study was initiated, the selected wells had already been sampled by DPR and had residues of simazine, bromacil, or diuron. The wells in this network continued to be sampled for triazine pesticides at least annually through 2020.

The Well Network is 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, this study has also served as an experimental area to sample for additional pesticides that have the potential to contaminate groundwater.

A statistical analysis of data collected from 2000–2012 is 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

Most Recent Sampling Period: 5/4/20 – 8/31/20

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## Number of Wells Sampled:

Fifty-nine wells were sampled for the Triazine Screen, and seven of those wells were also sampled for the Multi-Analyte Screen.

## Sampling and Analytical Methods:

Well sampling was conducted according to SOP FSWA001.03 (Kocis, 2020a). The California Department of Food and Agriculture, Center for Analytical Chemistry, analyzed all well samples using the Triazine Screen analytical method EM 62.9 (CDFA, 2020) and seven well samples with the Multi-Analyte Screen analytical method EMON-SM-05-032 (CDFA, 2013). Both methods are highly specific and have been determined by DPR to qualify for unequivocal detection designation (Aggarwal, 2020; 2016). The reporting limit for each analyte was 0.05 ppb (µg/L) (Tables 1, 2, and 3). The Triazine Screen includes 11 analytes by Liquid Chromatography Mass Spectrometry (LCMS) (Table 1) and the Multi-Analyte Screen includes nine analytes by Gas Chromatography Mass Spectrometry (GCMS) and 25 analytes by LCMS (Tables 2 and 3).

| Analyte     | MDL     | RL   |
|-------------|---------|------|
| ACET        | 0.00580 | 0.05 |
| Atrazine    | 0.00316 | 0.05 |
| Bromacil    | 0.00241 | 0.05 |
| DACT        | 0.00235 | 0.05 |
| DEA         | 0.00226 | 0.05 |
| Diuron      | 0.00241 | 0.05 |
| DSMN        | 0.00181 | 0.05 |
| Hexazinone  | 0.00197 | 0.05 |
| Norflurazon | 0.00252 | 0.05 |
| Prometon    | 0.00240 | 0.05 |
| Simazine    | 0.00286 | 0.05 |

**Table 1.** Triazine Screen method detection limits (MDL) and reporting limits (RL) in ppb ( $\mu$ g/L).

**Table 2.** Multi-Analyte Screen (GCMS) method detection limits (MDL) and reporting limits (RL) in ppb ( $\mu$ g/L).

| Analyte     | MDL    | RL   |
|-------------|--------|------|
| Clomazone   | 0.0168 | 0.05 |
| Dichloran   | 0.0235 | 0.05 |
| Dichlobenil | 0.4059 | 0.05 |
| Ethoprophos | 0.0178 | 0.05 |
| Malathion   | 0.0272 | 0.05 |
| Phorate     | 0.0168 | 0.05 |
| Prometryn   | 0.0204 | 0.05 |
| Propanil    | 0.0217 | 0.05 |
| Triallate   | 0.0147 | 0.05 |

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

| Analyte       | MDL    | RL   |
|---------------|--------|------|
| Atrazine      | 0.0152 | 0.05 |
| Azoxystrobin  | 0.0111 | 0.05 |
| Bensulide     | 0.0392 | 0.05 |
| Bromacil      | 0.0120 | 0.05 |
| Carbaryl      | 0.0254 | 0.05 |
| Diazinon      | 0.0493 | 0.05 |
| Dimethenamide | 0.0207 | 0.05 |
| Dimethoate    | 0.0150 | 0.05 |
| Diuron        | 0.0111 | 0.05 |
| Ethofumesate  | 0.0180 | 0.05 |
| Fludioxonil   | 0.0117 | 0.05 |
| Imidacloprid  | 0.0118 | 0.05 |
| Linuron       | 0.0134 | 0.05 |
| Mefenoxam/    | 0.0199 | 0.05 |
| Metalaxyl*    |        |      |
| Methiocarb    | 0.0146 | 0.05 |
| Metolachlor   | 0.0166 | 0.05 |
| Metribuzin    | 0.0117 | 0.05 |
| Napropamide   | 0.0174 | 0.05 |
| Norflurazon   | 0.0112 | 0.05 |
| Oryzalin      | 0.0128 | 0.05 |
| Prometon      | 0.0130 | 0.05 |
| Simazine      | 0.0141 | 0.05 |
| Tebuthiuron   | 0.0141 | 0.05 |
| Thiamethoxam  | 0.0086 | 0.05 |
| Thiobencarb   | 0.0169 | 0.05 |

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

#### **Results for Annual Triazine Screen and Multi-Analyte Screen Monitoring:**

## Sample results for 2020

The Well Network monitoring results for the Triazine Screen analytes are shown in Table 4. Table 5 includes the concentrations for all detected pesticides from the Multi-Analyte Screen and for the analytes that are on both screens. Due to the 2020 COVID-19 pandemic and the resulting reduced lab capacity, only wells with recent Multi-Analyte Screen detections were selected to be sampled for this screen. All wells that had detections above the reporting limit in 2019 on the Multi-Analyte Screen were resampled. For this screen, imidacloprid and fludioxonil were detected (Table 8). Both of these analytes are currently being investigated further by DPR (Aggarwal, 2019; Kocis, 2020b). The analytes not detected in samples analyzed with this screen are listed in the footnotes below Table 5. This year's data have been entered into DPR's Well Inventory Database (CDPR, 2021).

## Results from previous years

Summaries of previous years' results are presented in Tables 6 to 8. Tables 6 and 7 present Triazine Screen results from 1999 through 2020, including the percent of wells with positive detections above the reporting limit (RL) and the means of those detections. Table 8 presents an overview of the Multi-Analyte Screen detections from 2014 through 2020 (not including analytes reported on the Triazine Screen).

| Well                 |       |          |          |       |       |        |       |            |             |          |          | Propazine*   |
|----------------------|-------|----------|----------|-------|-------|--------|-------|------------|-------------|----------|----------|--------------|
| Number <sup>**</sup> | ACET  | Atrazine | Bromacil | DACT  | DEA   | Diuron | DSMN  | Hexazinone | Norflurazon | Prometon | Simazine | Recovery (%) |
| 1                    | Т     | nd       | nd       | Т     | Т     | Т      | Т     | Т          | Т           | Т        | Т        | 79.0         |
| 2                    | Т     | nd       | nd       | Т     | nd    | nd     | Т     | nd         | nd          | nd       | Т        | 93.5         |
| 3                    | Т     | nd       | nd       | Т     | nd    | nd     | 0.080 | nd         | nd          | nd       | 0.060    | 87.0         |
| 4                    | 0.265 | Т        | 10.30    | 1.250 | Т     | Т      | 0.296 | nd         | 0.220       | Т        | 0.066    | 85.5         |
| 5                    | 0.267 | nd       | nd       | 0.541 | nd    | nd     | 0.222 | nd         | nd          | nd       | 0.088    | 79.5         |
| 7                    | 0.102 | nd       | nd       | 0.491 | Т     | nd     | Т     | Т          | nd          | nd       | 0.059    | 90.0         |
| 8                    | 0.099 | nd       | Т        | 0.130 | Т     | Т      | Т     | nd         | nd          | nd       | 0.076    | 84.5         |
| 12                   | 0.215 | nd       | 0.271    | 0.273 | nd    | Т      | Т     | nd         | nd          | nd       | Т        | 80.0         |
| 13                   | 0.089 | nd       | 0.453    | 0.211 | nd    | Т      | 0.145 | nd         | 0.093       | nd       | Т        | 83.0         |
| 14                   | nd    | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 94.0         |
| 15                   | Т     | nd       | nd       | 0.077 | nd    | Т      | 0.109 | nd         | Т           | nd       | 0.061    | 82.5         |
| 16                   | 0.102 | nd       | nd       | 0.465 | nd    | Т      | 0.366 | nd         | 0.121       | nd       | 0.073    | 83.0         |
| 19                   | Т     | nd       | nd       | 0.091 | nd    | nd     | 0.105 | nd         | nd          | nd       | Т        | 85.5         |
| 20                   | Т     | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | Т        | 87.0         |
| 21                   | nd    | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 86.5         |
| 22                   | 0.127 | nd       | nd       | 0.392 | nd    | nd     | 0.085 | nd         | nd          | nd       | 0.067    | 76.0         |
| 23                   | 0.155 | nd       | 0.191    | 0.265 | nd    | 0.088  | 0.086 | nd         | nd          | nd       | 0.071    | 85.5         |
| 24                   | nd    | nd       | nd       | Т     | nd    | nd     | 0.235 | nd         | Т           | nd       | nd       | 83.5         |
| 25                   | 0.060 | nd       | nd       | 0.069 | nd    | nd     | Т     | nd         | nd          | nd       | Т        | 80.5         |
| 26                   | Т     | nd       | nd       | Т     | nd    | nd     | Т     | nd         | nd          | nd       | nd       | 90.5         |
| 28                   | Т     | nd       | nd       | 0.053 | nd    | nd     | nd    | nd         | nd          | nd       | Т        | 93.0         |
| 29                   | Т     | nd       | nd       | 0.095 | nd    | nd     | 0.202 | nd         | Т           | nd       | Т        | 86.0         |
| 30A                  | 0.185 | nd       | nd       | 0.288 | Т     | Т      | Т     | nd         | 0.050       | nd       | 0.108    | 94.5         |
| 32                   | 0.122 | nd       | nd       | 0.223 | nd    | nd     | 0.381 | nd         | 0.208       | nd       | 0.060    | 88.0         |
| 35                   | 0.111 | nd       | nd       | 0.174 | nd    | Т      | 0.109 | nd         | Т           | nd       | 0.085    | 87.5         |
| 36                   | Т     | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | Т        | 82.0         |
| 37                   | Т     | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 83.0         |
| 43                   | 0.141 | nd       | nd       | 0.103 | nd    | Т      | 0.071 | nd         | 0.066       | nd       | 0.087    | 89.5         |
| 44                   | 0.063 | nd       | Т        | 0.088 | nd    | Т      | Т     | nd         | nd          | nd       | Т        | 83.5         |
| 45                   | nd    | nd       | nd       | Т     | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 83.0         |
| 47                   | 0.283 | nd       | nd       | 0.692 | 0.057 | Т      | Т     | nd         | Т           | nd       | Т        | 81.5         |

**Table 4.** Triazine Screen sampling results from 2020. Concentrations in ppb ( $\mu$ g/L).

| Well<br>Number <sup>**</sup> | ACET  | Atrazine | Bromacil | DACT  | DEA   | Diuron | DSMN  | Hexazinone | Norflurazon | Prometon | Simazine | Propazine*<br>Recovery (%) |
|------------------------------|-------|----------|----------|-------|-------|--------|-------|------------|-------------|----------|----------|----------------------------|
| 49                           | 0.459 | nd       | nd       | 3.110 | nd    | nd     | 0.198 | nd         | Т           | nd       | 0.072    | 77.5                       |
| 50                           | Т     | nd       | nd       | 0.081 | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 89.5                       |
| 51                           | Т     | nd       | nd       | Т     | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 83.5                       |
| 52                           | 0.054 | nd       | nd       | nd    | nd    | nd     | 0.052 | nd         | Т           | nd       | 0.066    | 83.0                       |
| 53A                          | nd    | nd       | nd       | 0.121 | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 86.5                       |
| 54                           | Т     | nd       | nd       | Т     | nd    | nd     | nd    | nd         | nd          | Т        | 0.057    | 88.5                       |
| 56                           | 0.275 | nd       | nd       | 0.770 | nd    | nd     | nd    | nd         | nd          | nd       | 0.096    | 80.0                       |
| 57                           | 0.131 | nd       | nd       | 0.294 | nd    | nd     | Т     | nd         | nd          | nd       | Т        | 89.5                       |
| 58                           | Т     | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | Т        | 89.5                       |
| 59A                          | 0.281 | Т        | 0.855    | 0.615 | Т     | Т      | 0.967 | nd         | 0.344       | nd       | Т        | 77.5                       |
| 61                           | 0.143 | nd       | 0.528    | 1.070 | Т     | nd     | nd    | nd         | nd          | nd       | Т        | 78.0                       |
| 63A                          | nd    | nd       | nd       | Т     | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 90.5                       |
| 65                           | Т     | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 82.0                       |
| 68                           | nd    | nd       | nd       | nd    | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 82.0                       |
| 69                           | 0.468 | nd       | 0.339    | 2.240 | nd    | Т      | nd    | nd         | nd          | nd       | Т        | 75.0                       |
| 71                           | 0.369 | nd       | 1.100    | 0.916 | nd    | Т      | 0.807 | nd         | 0.236       | nd       | Т        | 73.0                       |
| 72                           | 0.618 | nd       | Т        | 1.530 | Т     | Т      | Т     | nd         | Т           | nd       | 0.067    | 79.5                       |
| 73                           | 0.122 | nd       | nd       | 1.040 | Т     | nd     | 0.061 | nd         | nd          | nd       | nd       | 78.5                       |
| 74                           | 0.618 | nd       | 0.424    | 0.993 | Т     | Т      | Т     | nd         | Т           | nd       | 0.079    | 83.0                       |
| 75A                          | 0.802 | nd       | 0.346    | 0.883 | nd    | Т      | nd    | nd         | nd          | nd       | 0.068    | 79.0                       |
| 80                           | 0.051 | nd       | Т        | 0.314 | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 84.5                       |
| 84                           | Т     | nd       | Т        | Т     | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 82.0                       |
| 86                           | 0.671 | nd       | nd       | 4.830 | Т     | nd     | nd    | nd         | nd          | nd       | Т        | 76.0                       |
| 89                           | 0.059 | nd       | Т        | 0.058 | nd    | Т      | 0.066 | nd         | nd          | nd       | Т        | 86.5                       |
| 90                           | 0.167 | 0.083    | 0.069    | 0.177 | 0.156 | 0.079  | Т     | Т          | Т           | nd       | 0.081    | 83.0                       |
| 92                           | 0.262 | nd       | nd       | 0.229 | nd    | Т      | 0.104 | nd         | 0.057       | nd       | Т        | 79.0                       |
| 94                           | 0.508 | nd       | nd       | 3.360 | nd    | nd     | 0.195 | nd         | Т           | nd       | Т        | 74.0                       |
| 95                           | nd    | nd       | nd       | Т     | nd    | nd     | nd    | nd         | nd          | nd       | nd       | 86.5                       |

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

T = Trace (positive result between the method detection limit and the reporting limit listed in Table 1)

\* = Propazine added as a surrogate for QA/QC purposes

\*\* = The well numbers DPR uses to differentiate sampling locations are not consecutive for various reasons including changes in homeowner participation and wells going dry

**Table 5.** Multi-Analyte Screen sampling results from 2020. Concentrations in ppb ( $\mu$ g/L). The table includes results for the two analytes with detections that are only included in the Multi-Analyte Screen and for the six analytes that are duplicated in the two screens.

|                | Analytes<br>Multi-Ana | s Unique to<br>Ilyte Screen* | Analytes in Both Screens (Multi-Analyte Screen/Triazine Screen) |             |             |             |          |             |  |  |  |
|----------------|-----------------------|------------------------------|---|-------------|-------------|-------------|----------|-------------|--|--|--|
| Well<br>Number | Fludioxonil           | Imidacloprid                 | Atrazine  | Bromacil    | Diuron      | Norflurazon | Prometon | Simazine    |  |  |  |
| 2              | nd                    | nd                           | nd  | nd          | nd          | nd          | nd       | Т           |  |  |  |
| 5              | nd                    | nd                           | nd  | nd          | nd          | nd          | nd       | 0.120/0.088 |  |  |  |
| 15             | nd                    | 0.106                        | nd  | nd          | Т           | Т           | nd       | 0.072/0.061 |  |  |  |
| 23             | nd                    | 0.073                        | nd  | 0.308/0.191 | 0.138/0.088 | T/nd        | nd       | 0.086/0.071 |  |  |  |
| 24             | nd                    | 0.112                        | nd  | nd          | nd          | 0.060/T     | nd       | nd          |  |  |  |
| 29             | nd                    | 0.053                        | nd  | nd          | nd/T        | Т           | nd       | nd/T        |  |  |  |
| 30A            | 0.333                 | nd                           | nd  | nd          | Т           | 0.076/0.050 | nd       | 0.121/0.108 |  |  |  |

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

T = Trace (positive result between the method detection limit and the reporting limit listed in Tables 1 to 3)

\* = the following 26 analytes are unique to the Multi-Analyte Screen but were not detected in any of the samples: azoxystrobin, bensulide, carbaryl, diazinon, dimethenamide, dimethoate, ethofumesate, linuron, mefenoxam/metalaxyl, methiocarb, metolachlor, metribuzin, napropamide, oryzalin, tebuthiuron, thiamethoxam, thiobencarb, clomazone, dichloran, dichlobenil, ethoprophos, malathion, phorate, prometryn, propanil, and triallate

| Year | ACET | Atrazine | Bromacil | DACT | DEA  | Diuron | DSMN | Hexazinone | Norflurazon | Prometon | Simazine |
|------|------|----------|----------|------|------|--------|------|------------|-------------|----------|----------|
| 1999 | 94.7 | 5.3      | 40.0     | 85.3 | 8.0  | 60.0   | NA   | 0.0        | 17.3        | 1.3      | 86.7     |
| 2000 | 89.2 | 4.1      | 37.8     | 89.2 | 4.1  | 50.0   | NA   | 1.0        | 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   | 0.0        | 15.7        | 1.4      | 92.9     |
| 2003 | 88.9 | 4.2      | 40.3     | 86.1 | 9.7  | 61.1   | NA   | 0.0        | 20.8        | 1.4      | 86.1     |
| 2004 | 86.8 | 4.4      | 33.8     | 85.3 | 8.8  | 57.4   | 44.1 | 0.0        | 25.0        | 1.5      | 80.9     |
| 2005 | 88.2 | 4.4      | 33.8     | 75.0 | 5.9  | 54.4   | 45.6 | 0.0        | 23.5        | 1.5      | 70.6     |
| 2006 | 83.3 | 4.5      | 37.9     | 83.3 | 7.6  | 51.5   | 44.0 | 0.0        | 22.7        | 1.5      | 72.7     |
| 2007 | 85.5 | 2.9      | 31.9     | 85.5 | 5.8  | 46.4   | 44.9 | 0.0        | 29.0        | 1.4      | 76.8     |
| 2008 | 85.3 | 4.4      | 33.8     | 85.3 | 5.9  | 50.0   | 44.0 | 0.0        | 20.6        | 1.5      | 69.1     |
| 2009 | 88.2 | 2.9      | 30.9     | 85.3 | 4.4  | 45.6   | 47.1 | 0.0        | 20.6        | 1.5      | 60.3     |
| 2010 | 80.9 | 2.9      | 29.4     | 85.3 | 4.4  | 38.2   | 50.0 | 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        | 0.0      | 55.9     |
| 2012 | 82.4 | 2.9      | 25.0     | 80.9 | 4.4  | 36.8   | 50.0 | 0.0        | 27.9        | 0.0      | 58.8     |
| 2013 | 76.1 | 1.5      | 26.9     | 83.6 | 6.0  | 13.4   | 41.8 | 0.0        | 20.9        | 0.0      | 58.2     |
| 2014 | 75.0 | 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 | 0.0        | 19.0        | 1.6      | 49.2     |
| 2016 | 78.7 | 1.6      | 26.2     | 82.0 | 3.3  | 16.4   | 41.0 | 0.0        | 21.3        | 1.6      | 50.8     |
| 2017 | 60.7 | 1.6      | 23.0     | 70.5 | 1.6  | 6.6    | 36.1 | 0.0        | 21.3        | 0.0      | 39.3     |
| 2018 | 57.4 | 1.6      | 23.0     | 65.6 | 4.9  | 4.9    | 36.1 | 0.0        | 21.3        | 0.0      | 36.1     |
| 2019 | 61.7 | 1.7      | 20.0     | 63.3 | 1.7  | 1.7    | 35.0 | 0.0        | 13.3        | 0.0      | 31.7     |
| 2020 | 59.3 | 1.7      | 22.0     | 67.8 | 3.4  | 6.8    | 35.6 | 0.0        | 16.9        | 0.0      | 39.0     |
| Mean | 80.2 | 3.2      | 30.9     | 80.8 | 5.7  | 35.5   | 42.8 | 0.3        | 21.6        | 1.0      | 63.8     |
| SD   | 11.5 | 1.3      | 6.5      | 7.5  | 2.7  | 21.9   | 5.7  | 0.6        | 4.1         | 0.7      | 18.1     |

Table 6. Yearly percent (%) of wells positive above the reporting limit (RL) for each analyte on the Triazine Screen.

NA = Not Analyzed - DSMN was not included in the analysis until 2004

| 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 | 0.50 | 0.10     | 1.12     | 0.97 | 0.13 | 0.33   | NA   | 0.05       | 0.11        | 0.10     | 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 | 0.50 | 0.12     | 1.12     | 0.85 | 0.15 | 0.28   | 0.22 | nd         | 0.21        | 0.09     | 0.10     |
| 2005 | 0.38 | 0.10     | 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 | 0.10 | 0.26   | 0.26 | nd         | 0.13        | 0.06     | 0.10     |
| 2008 | 0.38 | 0.07     | 0.81     | 0.68 | 0.10 | 0.21   | 0.25 | nd         | 0.24        | 0.07     | 0.09     |
| 2009 | 0.39 | 0.07     | 0.79     | 0.67 | 0.12 | 0.20   | 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 | 0.40 | 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 | 0.10   | 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        | 0.10     | 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 | 0.10 | 0.07   | 0.24 | nd         | 0.15        | nd       | 0.07     |
| Mean | 0.40 | 0.09     | 0.86     | 0.79 | 0.12 | 0.19   | 0.24 | 0.06       | 0.18        | 0.08     | 0.10     |
| SD   | 0.09 | 0.02     | 0.22     | 0.11 | 0.03 | 0.10   | 0.02 | 0.01       | 0.04        | 0.02     | 0.02     |

**Table 7.** Yearly mean concentrations in ppb ( $\mu$ g/L) for each analyte on the Triazine Screen.

NA = Not Analyzed - DSMN was not included in the analysis until 2004

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

|        |                            |                          | Sample Year |       |       |       |       |       |       |
|--------|----------------------------|--------------------------|-------------|-------|-------|-------|-------|-------|-------|
| Well # | Township/Range-<br>Section | Analyte                  | 2014        | 2015  | 2016  | 2017  | 2018  | 2019  | 2020  |
| 2      | 13S/22E-33                 | Imidacloprid             | nd          | nd    | nd    | nd    | Т     | Т     | nd    |
| 4      | 13S/23E-32                 | Imidacloprid             | nd          | nd    | nd    | Т     | nd    | nd    | NS    |
| 5      | 14S/21E-13                 | Imidacloprid             | nd          | nd    | nd    | Т     | Т     | Т     | nd    |
| 15     | 14S/22E-14                 | Imidacloprid             | nd          | nd    | nd    | 0.066 | 0.091 | 0.085 | 0.106 |
| 18     | 14S/22E-31                 | Imidacloprid             | 0.059       | 0.665 | Dry   | NLS   | NLS   | NLS   | NLS   |
| 21     | 14S/23E-33                 | Imidacloprid             | NS          | 0.065 | nd    | nd    | nd    | nd    | NS    |
| 22     | 14S/23E-34                 | Imidacloprid             | NS          | 0.120 | 0.080 | 0.090 | Т     | Т     | NS    |
| 23     | 14S/23E-35                 | Imidacloprid             | NS          | 0.218 | 0.209 | 0.534 | 0.536 | 0.470 | 0.073 |
| 24     | 15S/21E-03                 | Imidacloprid             | nd          | nd    | nd    | Т     | Т     | Т     | 0.112 |
| 26     | 15S/21E-09                 | Imidacloprid             | Т           | 0.051 | 0.072 | 0.167 | 0.053 | nd    | NS    |
| 29     | 15S/22E-03                 | Imidacloprid             | nd          | Т     | nd    | 5.970 | 0.095 | Т     | 0.053 |
| 47     | 15S/24E-14                 | Imidacloprid             | NS          | nd    | 0.644 | nd    | nd    | nd    | NS    |
| 48     | 15S/24E-36                 | Imidacloprid             | NS          | nd    | Т     | Т     | NLS   | NLS   | NLS   |
| 37     | 15S/22E-21                 | Oryzalin                 | Т           | nd    | nd    | nd    | nd    | nd    | NS    |
| 44     | 15S/23E-02                 | Oryzalin                 | NS          | Т     | nd    | nd    | nd    | nd    | NS    |
| 29     | 15S/22E-03                 | Mefenoxam/<br>Metalaxyl* | nd          | Т     | nd    | nd    | nd    | nd    | nd    |
| 74     | 19S/26E-01                 | Metolachlor              | NS          | Т     | nd    | nd    | nd    | nd    | NS    |
| 30A    | 15S/22E-05                 | Fludioxonil              | NS          | nd    | Т     | 0.066 | 0.165 | 0.380 | 0.333 |
| 4      | 13S/23E-32                 | Propanil                 | nd          | nd    | nd    | 0.060 | nd    | nd    | NS    |

**Table 8.** Summary of wells with Multi-Analyte Screen detections (other than Triazine analytes) from 2014 through 2020. Concentrations in ppb (μg/L).

nd = not detected (below the method detection limit listed in Tables 2 and 3)

T = Trace (positive results between the method detection limit and the reporting limit listed in Tables 2 and 3)

NS = Well not sampled

Dry = Well went dry

NLS = Well is no longer sampled

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

## **Results for Quality Control:**

Laboratory and field quality control were conducted according to SOP QAQC001.01 (Peoples, 2019) and the results are summarized in Table 9.

## Triazine Screen QC samples

Sixteen total matrix spikes (as duplicates) were analyzed along with eight sets of samples for the Triazine Screen. All analytes were spiked at 0.2 ppb. The average recoveries for the 11 analytes and the propazine surrogate analytes ranged from 81.3 to 86.4% (Table 10). The standard deviation of the recoveries ranged from 3.9 to 7.1%. Two analytes were beyond the upper control limits out of 176 spiked analytes in two of the 16 QC samples. The propazine surrogate recoveries were within the control limits in both the continuing QC (Table 10) and the 59 samples analyzed (Table 4).

## Multi-Analyte Screen QC samples

For the Multi-Analyte Screen, one matrix spike was extracted and split to be analyzed along with sets of samples for both the LCMS and GCMS instruments. All analytes that were analyzed with LCMS were spiked at 0.2 ppb. The recoveries for the 29 analytes ranged from 79.0 to 110% (Table 11). All 29 analytes were within the control limits. For the split QC spikes analyzed with the GCMS, all analytes were spiked at 0.1 ppb. The recoveries for the 15 analytes ranged from 83.6 to 99.1% (Table 12). All 15 analytes were within the control limits.

## **Blind spikes**

A blind spike consists of analyte-free groundwater (matrix-blank sample) fortified with the chosen analytes and is spiked by a chemist other than the chemist extracting and analyzing that screen. The EM QA Officer submitted the blind spike to the lab disguised as a field sample according to SOP QAQC008.00 (Ganapathy, 2005). Usually between five and ten percent of samples submitted for this study have been blind spikes. Due to logistical issues caused by the pandemic, one blind spike containing all 11 analytes in the Triazine Screen was submitted and included with samples extracted on June 16, 2020. All 11 analytes were within the control limits and the results are presented in Table 13.

| QC Туре                        | Triazine<br>Screen | Multi-Analyte<br>Screen | Total Number | Number Out of Control Limits                        |
|--------------------------------|--------------------|-------------------------|--------------|---|
| Continuing QC<br>matrix-spikes | 16                 | 1                       | 17           | 2 analytes out of control limits in 2 of 17 samples |
| Blind spikes                   | 1                  | 0                       | 1            | No analytes out of control                          |
| Lab matrix-blanks              | 8                  | 1                       | 9            | All non-detected                                    |
| Field blanks                   | 6                  | 1                       | 7            | All non-detected                                    |

#### Table 9. Laboratory and field quality control (QC) summary.

| Extraction                | Spike<br>#* | Spiked | ACET | Atrazine | Bromacil | DACT | DEA  | Diuron | DSMN | Hexazinone | Norflurazon | Prometon           | Simazine | Propazine |
|---------------------------|-------------|--------|------|----------|----------|------|------|--------|------|------------|-------------|--------------------|----------|-----------|
| 5/20/2020                 | 1           | 0.2    | 76.5 | 81.5     | 82.5     | 87.0 | 79.0 | 84.5   | 84.5 | 78.5       | 82.0        | 84.0               | 81.5     | 81.5      |
| 5/20/2020                 | 2           | 0.2    | 83.0 | 86.5     | 88.0     | 92.0 | 83.0 | 90.0   | 81.5 | 86.5       | 87.5        | 86.0               | 87.0     | 87.5      |
| 5/21/2020                 | 1           | 0.2    | 78.5 | 84.0     | 81.5     | 86.0 | 82.0 | 88.5   | 82.5 | 82.0       | 88.5        | 90.0               | 83.5     | 86.5      |
| 5/21/2020                 | 2           | 0.2    | 76.5 | 84.0     | 83.5     | 86.0 | 79.5 | 86.0   | 81.5 | 80.5       | 87.0        | 87.0               | 83.5     | 83.5      |
| 6/2/2020                  | 1           | 0.2    | 75.5 | 81.0     | 81.0     | 73.0 | 75.5 | 82.0   | 76.5 | 77.5       | 81.5        | 80.5               | 81.0     | 79.0      |
| 6/2/2020                  | 2           | 0.2    | 80.5 | 87.0     | 85.0     | 85.0 | 83.0 | 87.5   | 82.0 | 79.5       | 86.5        | 86.5               | 87.5     | 84.5      |
| 6/3/2020                  | 1           | 0.2    | 78.5 | 77.0     | 78.5     | 83.5 | 75.0 | 81.0   | 76.0 | 73.0       | 79.5        | 83.5               | 81.0     | 78.0      |
| 6/3/2020                  | 2           | 0.2    | 87.0 | 85.5     | 85.0     | 89.5 | 82.0 | 90.5   | 84.0 | 80.5       | 87.5        | 88.0               | 90.0     | 86.5      |
| 6/15/2020                 | 1           | 0.2    | 77.0 | 80.0     | 80.5     | 80.5 | 75.5 | 80.5   | 75.5 | 79.0       | 77.0        | 81.5               | 82.0     | 81.0      |
| 6/15/2020                 | 2           | 0.2    | 80.5 | 84.0     | 86.0     | 88.0 | 82.0 | 89.5   | 81.5 | 86.5       | 85.0        | 84.5               | 84.5     | 85.0      |
| 6/16/2020                 | 1           | 0.2    | 77.0 | 86.5     | 85.0     | 85.0 | 79.5 | 85.5   | 83.5 | 81.5       | 87.0        | 88.0               | 86.5     | 87.0      |
| 6/16/2020                 | 2           | 0.2    | 72.0 | 80.5     | 77.5     | 82.0 | 74.5 | 81.5   | 80.0 | 76.5       | 80.5        | 83.5               | 80.0     | 81.0      |
| 9/21/2020                 | 1           | 0.2    | 93.5 | 96.5     | 95.0     | 91.5 | 90.0 | 91.0   | 92.0 | 91.0       | 96.5        | 92.5               | 92.5     | 89.0      |
| 9/21/2020                 | 2           | 0.2    | 100  | 96.5     | 103**    | 99.5 | 93.5 | 94.0   | 95.0 | 99.5       | 92.5        | 95.0 <sup>**</sup> | 97.5     | 92.0      |
| 9/8/2020                  | 1           | 0.2    | 84.5 | 87.5     | 89.5     | 84.5 | 85.0 | 88.0   | 89.5 | 86.5       | 92.0        | 89.0               | 87.0     | 87.0      |
| 9/8/2020                  | 2           | 0.2    | 81.5 | 82.0     | 83.0     | 82.5 | 81.5 | 82.0   | 79.5 | 81.0       | 81.0        | 83.5               | 78.5     | 79.5      |
| Average<br>Recovery       |             |        | 81.4 | 85.0     | 85.3     | 86.0 | 81.3 | 86.4   | 82.8 | 82.5       | 85.7        | 86.4               | 85.2     | 94.3      |
| Standard<br>Deviation     |             |        | 7.1  | 5.3      | 6.4      | 5.8  | 5.2  | 4.1    | 5.5  | 6.4        | 5.3         | 3.9                | 5.0      | 16.0      |
| Upper<br>Control<br>Limit |             |        | 100  | 103      | 102      | 114  | 99.0 | 106    | 100  | 111        | 103         | 94.0               | 98.0     | 93.0      |
| Lower<br>Control<br>Limit |             |        | 51.3 | 68.7     | 57.6     | 59.7 | 58.2 | 63.0   | 64.7 | 68.6       | 64.9        | 65.4               | 58.4     | 59.8      |

**Table 10.** Triazine Screen continuing quality control (QC) percent recovery (%) results including the propazine surrogate.

\* = Spike 1 and 2 represent the duplicate spikes analyzed for each extraction set

\*\* = Beyond the upper control limit

**Table 11.** Multi-Analyte Screen (LCMS) continuing quality control (QC) percent recovery (%) results of the single extraction set.

| Factory at land | Cultured Lancel |                      | Percent  |               |               |
|-----------------|-----------------|----------------------|----------|---------------|---------------|
| Extraction      | Spiked Level    |                      | Recovery | Lower Control | Upper Control |
| Date            | (ddd)           | Pesticide            | (%)      | Limit         | Limit         |
| 6/16/2020       | 0.2             | Atrazine             | 101      | 73.1          | 115           |
| 6/16/2020       | 0.2             | Azoxystrobin         | 93.0     | 74.3          | 125           |
| 6/16/2020       | 0.2             | Bensulide            | 106      | 62.3          | 130           |
| 6/16/2020       | 0.2             | Bromacil             | 88.0     | 75.2          | 109           |
| 6/16/2020       | 0.2             | Carbaryl             | 109      | 64.1          | 143           |
| 6/16/2020       | 0.2             | Diazinon             | 96.0     | 61.7          | 115           |
| 6/16/2020       | 0.2             | Dimethenamide        | 104      | 71.0          | 118           |
| 6/16/2020       | 0.2             | Dimethoate           | 97.5     | 72.5          | 116           |
| 6/16/2020       | 0.2             | Diuron               | 100      | 76.9          | 114           |
| 6/16/2020       | 0.2             | Ethofumesate         | 97.0     | 45.9          | 132           |
| 6/16/2020       | 0.2             | Fludioxonil          | 109      | 62.1          | 122           |
| 6/16/2020       | 0.2             | Imidacloprid         | 99.5     | 70.7          | 117           |
| 6/16/2020       | 0.2             | Linuron              | 104      | 76.1          | 112           |
| 6/16/2020       | 0.2             | Mefenoxam/Metalaxyl* | 104      | 74.7          | 119           |
| 6/16/2020       | 0.2             | Methiocarb           | 106      | 67.7          | 140           |
| 6/16/2020       | 0.2             | Metolachlor          | 101      | 68.0          | 134           |
| 6/16/2020       | 0.2             | Metribuzin           | 80.5     | 75.7          | 110           |
| 6/16/2020       | 0.2             | Napropamide          | 104      | 76.7          | 115           |
| 6/16/2020       | 0.2             | Norflurazon          | 101      | 79.3          | 114           |
| 6/16/2020       | 0.2             | Oryzalin             | 103      | 79.6          | 113           |
| 6/16/2020       | 0.2             | Prometon             | 110      | 79.7          | 118           |
| 6/16/2020       | 0.2             | Simazine             | 102      | 75.3          | 111           |
| 6/16/2020       | 0.2             | Tebuthiuron          | 105      | 69.7          | 129           |
| 6/16/2020       | 0.2             | Thiamethoxam         | 79.0     | 65.5          | 107           |
| 6/16/2020       | 0.2             | Thiobencarb          | 97.5     | 75.0          | 113           |

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

**Table 12.** Multi-Analyte Screen (GCMS) continuing quality control (QC) percent recovery (%) results of the single extraction set.

| Extraction<br>Date | Spiked Level<br>(ppb) | Pesticide   | Percent<br>Recovery<br>(%) | Lower Control<br>Limit | Upper Control<br>Limit |
|--------------------|-----------------------|-------------|----------------------------|------------------------|------------------------|
| 6/16/2020          | 0.1                   | Dichlobenil | 90.7                       | 34.7                   | 149                    |
| 6/16/2020          | 0.1                   | Propanil    | 92.1                       | 58.2                   | 149                    |
| 6/16/2020          | 0.1                   | Clomazone   | 93.6                       | 42.4                   | 156                    |
| 6/16/2020          | 0.1                   | Prometryn   | 92.9                       | 46.3                   | 155                    |
| 6/16/2020          | 0.1                   | Dichloran   | 99.1                       | 51.3                   | 148                    |
| 6/16/2020          | 0.1                   | Ethoprophos | 83.6                       | 52.0                   | 144                    |
| 6/16/2020          | 0.1                   | Triallate   | 94.8                       | 52.0                   | 144                    |
| 6/16/2020          | 0.1                   | Malathion   | 97.7                       | 51.0                   | 163                    |
| 6/16/2020          | 0.1                   | Phorate     | 89.7                       | 61.5                   | 141                    |

Table 13. Blind spike levels and recoveries.

| Extraction<br>Date | Analysis           | Analyte     | Spike<br>Level<br>(ppb) | Result<br>(ppb) | Percent<br>Recovery<br>(%) | Control<br>Limit<br>Exceeded <sup>*</sup> |
|--------------------|--------------------|-------------|-------------------------|-----------------|----------------------------|---|
| 6/16/2020          | Triazine<br>Screen | ACET        | 0.10                    | 0.092           | 92.0                       | No  |
|                    |                    | Atrazine    | 0.10                    | 0.098           | 98.0                       | No  |
|                    |                    | Bromacil    | 0.10                    | 0.093           | 93.0                       | No  |
|                    |                    | DACT        | 0.10                    | 0.094           | 94.0                       | No  |
|                    |                    | DEA         | 0.10                    | 0.092           | 92.0                       | No  |
|                    |                    | Diuron      | 0.10                    | 0.100           | 100                        | No  |
|                    |                    | DSMN        | 0.10                    | 0.092           | 92.0                       | No  |
|                    |                    | Hexazinone  | 0.10                    | 0.091           | 91.0                       | No  |
|                    |                    | Norflurazon | 0.10                    | 0.106           | 106                        | No  |
|                    |                    | Prometon    | 0.10                    | 0.104           | 104                        | No  |
|                    |                    | Simazine    | 0.10                    | 0.099           | 99.0                       | No  |

\* = Control limits listed in Table 10

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Contact <u>GWPP@cdpr.ca.gov</u> for references not currently available on the web.

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