MEMORANDUM

May 24, 2011

To: Dr. Aldos C. Barefoot

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Title: Summary of Hexazinone California Use and Groundwater Concentrations (Monitoring and Modeling) – May 24th Update based on May 9th Hearing Questions

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This memorandum is submitted to E.I. du Pont de Nemours & Company in support of their response to a November 1, 2010 Notice of Hexazinone Residue Detections in California Groundwater and Registrant Opportunity to Request a Hearing ("Notice") issued by the Department of Pesticide Regulation ("DPR" or "Department") pursuant to the Pesticide Contamination and Prevention Act ("PCPA"), Cal. Food & Agric. Code § 13149. This memorandum includes information to address questions raised during the May 9th hearing of DPR's Pesticide Registration and Evaluation Committee. The memorandum also includes additional spatial modeling results (additional use areas and environmental fate representation).

This memorandum is an addition to, not a revision of the April 11, 2011 (revised May 6th, 2011) memorandum included as "Attachment 5" of DuPont's response.

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SUMMARY OF HEXAZINONE CALIFORNIA USE AND GROUNDWATER CONCENTRATIONS (MONITORING AND MODELING)

1.0 INTRODUCTION

California Department of Pesticide Regulation (DPR) published a memorandum outlining the history and current status of hexazinone detections in groundwater monitoring in California which were used to make a Legal Agricultural Use (LAU) determination. Additionally, they summarized detections in monitoring programs attributed to point sources, runoff collection ponds, and many that were isolated from any other detection. Waterborne Environmental Inc. (WEI) prepared a memorandum for DuPont on April 11, 2011 (revised May 6, 2011) to provide additional context to the existing monitoring data, analysis through modeling to assess a broader exposure estimate than is feasible with monitoring, and a framework to place the limited detections into a broader context. This memorandum expands on the previous work to include additional information based on questions raised at the May 9th hearing of DPR's Pesticide Registration and Evaluation Committee (PREC) including:

- Clarification of the extent of monitoring in areas where hexazinone is used.
- Trends in acreage planted to alfalfa.
- Expanded spatial modeling to include additional use areas and average environmental fate parameters.

2.0 RESPONSE TO QUESTIONS AND DISCUSSIONS FROM MAY 9TH HEARING OF DPR'S PREC

2.1 Monitoring and Use

In the previous memorandum, WEI prepared a detailed review of the CDPR groundwater monitoring program. As part of the program, hexazinone was included in the analysis of 3,866 samples from 2344 wells, and detected in concentrations ranging from 0.05 (the reporting limit) to 0.27 parts per billion (ppb) in 27 wells (Quagliaroli, 2011). The summary presented in the CDPR memorandum (Nordmark and Quagliaroli, 2010) highlights the conditions surrounding 26 wells (2010 sampling identified single additional detection) with detections including follow-up sampling used to make a determination of Legal Agricultural Use (LAU) and existence of documented hexazinone applications. The previous memorandum from WEI provided general maps of locations and use and a grand summary that the detections were limited to 1.2% of sampled wells. For ease of reference, the classification of sample detections is included as Table 1. Additional details on detection frequency were requested at the May 9th, 2011 CDPR PREC hearing.

Following the analysis by CDPR, three use history ranges were selected and an analysis conducted at the section resolution of use data. The samples and total use for three time intervals are included as Figure 1, Figure 2, and Figure 3 (use is displayed as a total in the township, 36 sections, for a more clear visual representation) for sampling during and before 1995, between 1996 and 2000, and 2001 through 2009, respectively. The detection types and township use are presented in Figure 4. Monitoring and use were analyzed by intersecting the sampling location and section use for the three time periods (example image as Figure 5). Summaries are presented for the entire sampling record of sections with sampling meeting one of three criteria.

Sections with sampling starting 1995 or earlier: A total of 2274 samples were collected from 1330 wells. Use was reported in the sections that included 300 samples (13%) from 200 (15%) of the wells. Hexazinone was detected in 5 wells sampled during this time period, including four detections attributed to point sources. Excluding the four detections that were attributed to point sources, the detection frequency was 0.5%, for hexazinone in wells located in sections with documented use.

Sampling started or continued between 1996 and 2000: A total of 1936 samples were collected from 737 wells. Use was reported in the sections that included 305 samples (16%) from 207 (28%) of the wells. Hexazinone was detected in 6 wells sampled during this time period. Excluding the two detections attributed to leakage from ponds and 2 detections in sections with no documented use, the detection frequency was 1% for hexazinone in wells located in sections with documented use.

Sampling started or continued after 2000: A total of 2170 samples were collected from 982 wells. Use was reported in the sections that included 471 samples (22%) from 365 (37%) of the wells. Hexazinone was detected in 16 wells sampled during this time period. Excluding the five detections in sections with no reported use, the detection frequency was 3.0% for hexazinone in wells located in sections with documented use.

Finally, sampling and use data was reviewed in the larger township area (36 sections) as shown in the example (Figure 6) with use summarized for the entire period. Of the 3866 samples from 2344 wells, it was found that 2599 (67%) samples from 1621 (69%) wells were in townships with use during the period of 1990 to 2009.

2.2 Monitoring Study Summary

In addition to the summary of use, the sampling database was reviewed and summarized by study focus. The CDPR groundwater monitoring database includes samples from a variety of sources. The study identification and sampling frequency and detection frequency are summarized in Table 2.

2.3 Alfalfa Acreage Trends

The previous WEI memorandum highlighted hexazinone use trends in California and highlighted the relatively stable use patterns in California. Additional details on alfalfa acreage were requested at the May 9th, 2011 CDPR PREC hearing.

Total alfalfa production in California has been in the range 900,000-1,000,000 acres over the past 20+ years (USDA-NASS, 2011). As shown in the table below, there was a 25% increase in total acreage in 2002 compared to 1997 followed by a 15% decline in 2007 compared to 2002.

Year	Alfalfa Hay (harvested acres)
1987	948,719
1992	939,097
1997	944,056
2002	1,176,021
2007	986,982

3.0 MODELING OF GROUNDWATER EXPOSURE – SPATIAL MODELING

A recently developed PRZM based tool was also used to evaluate the spatial distribution of potential hexazinone leaching associated with actual applications. All applications for the period of 2000 to 2008 in the Bay-Delta Estuary, Sacramento and San Joaquin Watersheds and the Tulare Basin (the primary use area) were evaluated using spatially assigned soils data, weather files, and the WinPRZM Pesticide Root Zone Model (PRZM-4.51) to simulate the pesticide leaching. Additional soil, use, and weather files (for the Tulare Basin) were added to the simulations after the memorandum presented on April 11 (and updated May 6th). The PRZM model is a dynamic, compartmental model developed by the U.S. Environmental Protection Agency for use in simulating water and chemical movement in unsaturated soil systems within and below the plant root zone (Carsel et al., 1998, Focus 2000a, FOCUS 2000b). The model simulates time-varying hydrologic behavior on a daily time step, including physical processes of runoff, infiltration, erosion, and evapotranspiration. The chemical transport component of PRZM calculates pesticide uptake by plants, surface runoff, erosion, decay, vertical movement, foliar loss, dispersion and retardation. PRZM includes the ability to simulate pesticide metabolites and irrigation. Unlike the CDPR Monte Carlo methodology of variable degradation rates and sorption parameters, the simulations are deterministic and were conducted with a conservative set of inputs using the maximum field dissipation half-life (154 days) in the soil and the minimum sorption parameter (K_{oc} = 38 mL/g). A set of simulations (added after the previous memorandum) were conducted using mean parameters (field dissipation half-life of 139 days and K_{oc} of 57.5 mL/g). Additionally, errors in the soils database resulting from missing soil parameters were corrected which altered the final results. Simulations were conducted for two-year periods that include the year of application and a following year of weather and irrigation with results being presented for the combined water and mass amounts for the two-year period associated with each simulated application year.

Irrigation was enabled in the model using USEPA standard scenario irrigation rates. In comparing simulated irrigation plus rainfall in relation to evapotranspiration, it is clear the adequate water was available for leaching with over 39% of the simulations having a greater than 125% of modeled evapotranspiration and over 2% having a greater than 160% of the modeled evapotranspiration. The total evaporation was exceeded by rainfall and irrigation in all scenarios. The irrigation routines of PRZM are driven by the simulated field capacity and irrigation events are automatically added based on the set threshold and irrigation rate parameters.

The maximum total leached below the soil core (315 cm) for each soil within each PLSS cell receiving a hexazinone application according to the PUR database was used as an input to the CDPR groundwater assessment methodology and used to determine estimated groundwater concentrations. As discussed previously, travel times of 13, 10, 5, 4, and 3 years were evaluated using the equation:

*Well water concentration (µg/L) = (M L *0.5 N) / D*

Table 3 provides a summary of well concentration for different travel times and percentiles relevant to the CDPR methodology (50^{th}, 90^{th} and 95^{th} percentile). Similar to CDPR modeling, a very low percentage of simulated areas were shown to have detectable levels of hexazinone and only when short travel times were considered. For travel times of 10 and 13 years, no detectable residues are expected. For shorter travel times, minimal residues are predicted at the 90^{th} and 95^{th} percentile of simulations. It is important to note that the simulation results used conservative assumptions for both soil degradation (the longest observed field half-life) and sorption (lowest K_{oc}). When considering mean environmental fate parameters (while maintaining the longest field half-life for aging), the predicted results drop significantly. Maps of the maximum predicted concentrations (from any year) in each simulated section for different travel times (3 and 10 years) are presented for the more conservative (Figure 7 and Figure 8) and average environmental fate scenarios (Figure 9 and Figure 10). There is a slight reduction in areas with measurable predicted concentrations when comparing the 3-year travel time results between the more conservative and average environmental fate parameters. With a 10-year travel time, the maximum concentrations are below 0.05 ppb in all sections and years.

4.0 REFERENCES

Carsel, R.F., J.C. Imhoff, P.R. Hummel, J.M. Cheplick, and A.S. Donigian, Jr., 1998. PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.0, National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia. Available at http://www.epa.gov/ceampubl/gwater/przm3/przm3122.htm.

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Quagliaroli, Lisa. 2011. Groundwater Monitoring Data for Hexazinone. April 22, 2011 Email from Lisa Quagliaroli (CDPR EMB) to Aldos Barefoot (DuPont Crop Protection) transmitting monitoring data query and results as MS Excel™ data file (req_ABarefoot_hexazinone wells.xls)

Nordmark, C. and L. Quagliaroli. 2010. Hexazinone Residues in California Ground Water-Monitoring Data Provide Evidence That Detections Result From Legal Agricultural Use. May 27, 2010 Memorandum from Nordmark and Quagliaroli to Lisa Ross, Ph.D. Environmental Program Manager I, CDPR Environmental Monitoring Branch.

TABLE 1 SUMMARY OF HEXAZINONE DETECTIONS

County	Location[1]	Wells Sampled For Hexazinone	Hexazinone Positive Wells: Unique Positive Wells	Highest conc. (ppb)	First Year Detected	Last Year Sampled	Hexazinone Use (LBS)[2]: Single Section	Nine Sections[3]
Section Used for Legal Agricultural Use (LAU) Determination by CDPR								
Fresno	10M17S19E36	4	3	0.247	2007	2008	320	2,155
San Joaquin	39M02S06E19	3	1	0.072	2009	2009	171	3,214
San Joaquin	39M02S06E30	1	1	0.093	2009	2009	178	3,615
Sections with Reported Use								
Merced	24M09S14E23	3	1	0.11	1997	1997	347	826
San Joaquin	39M01N05E16	2	1	0.092	2008	2008	541	4,937
San Joaquin	39M02S04E22	5	1	0.096	2002	2002	625	2,288
Solano	48M06N01E23	2	1	0.126	2007	2007	1198	7,644
Solano	48M06N01W36	4	1	0.092	1995	1995	788	1,763
Stanislaus	50M04S09E19	5	1	0.27	1996	1996	7	484
Stanislaus	50M04S11E31	5	1	0.263	2004	2004	152	1,422
Stanislaus	50M06S08E26	2	1	0.062	2007	2007	80	720
Stanislaus	50M07S09E06	2	1	0.094	2007	2007	102	1,088
Section with No Reported Use, 9 Section Block had Some Use								
Fresno	10M14S21E21	3	1	0.063	2001	2006	0	14
Solano	48M06N01E05	4	1	0.094	2002	2002	0	2,650
Stanislaus	50M07S08E14	1	1	0.073	2001	2002	0	125
Fresno[4]	10M15S22E05	3	1	0.054	2010	2010	0	25.31
Section with No Reported Use, 9 Section Block had no reported Use								
Colusa	6M15N03W36	2	1	0.056	1998	1998	0	0
Fresno	10M14S22E13	3	1	0.07	2000	2006	0	0
Los Angeles	19S01S09W27	1	1	0.069	2008	2008	0	0
Detections resulted from point source contamination.								
Tulare	54M22S27E07	1	1	0.22	1994	1995	0	0
Tulare	54M22S27E18	6	3	0.24	1994	1995	0	0
Detections were determined to be transitory (Gosselin, 1997) and later due to agricultural drainage ponds (Prichard, et al., 2005)								
San Joaquin	39M02S05E23	2	1	0.11	1996	2002	216	1,130
San Joaquin	39M02S05E24	6	1	0.07	1996	2002	435	2,642

[1]County, Township, range and section of the well(s). A section is approximately one square mile.

[2]Hexazinone use totals are given for one of three periods, 1990-95, 1990-2000 and 1990-2005, based on the year of the first detection in the section. The period used was selected to represent the hexazinone use prior to the first reported hexazinone detection. Since full pesticide user reporting began in 1990, the 1990-95 bracket was used for detections prior to 1996. Rights-of-way use is reported at the county level and is not included here.

[3]Total hexazinone use in the section where the positive well is located and the surrounding 8 sections.

[4]Single detection occurred in 2010 and was added to the database provided by CDPR but not included in the May, 2010 CDPR memorandum

TABLE 2 SUMMARY OF CDPR STUDIES INCLUDING HEXAZINONE MONITORING

Study Identifier	Number of Samples	Minimum Detection	Maximum Detection	Number of Duplicates	Number of Detections	Title/Description
130	260	0	0	84	0	Identifying Areas of Groundwater Contamination by Pesticides in California
182	1047	0.05	0.07	1	5	Pesticide Concentration Monitoring in Domestic Wells in the San Joaquin Valley 1999-2009
226	49	0	0	0	0	Detection of Atrazine, Simazine, and their Breakdown Products in Public Water Supply Wells
240	176	0.062	0.247	0	5	Monitoring Groundwater in Sections with Reported Detection Outside Existing Ground Water Protection Areas
BE	61	0	0	0	0	Bentazon Monitoring
AS	403	0	0	0	0	Annual Monitoring Studies
GW	977	0.05	0.27	87	14	Yearly Groundwater Monitoring Studies
Z279	49	0.16	0.24	24	7	Special Initiatied CDPR Study Looking for Hexazinone
Z289	8	0.064	0.092	2	2	Special Initiatied CDPR Study Looking for Aldicarb and Carbaryl
Z385	23	0.063	0.11	0	4	Special Initiated CDPR Study Looking for Atrazine and Bromacil
Z448	5	0.073	0.073	0	1	Special CDPR Study mentioned in Yearly Update
Z455	5	0.094	0.094	0	1	Special CDPR Study mentioned in Yearly Update
Z558	6	0.263	0.263	0	1	Special Iniatiead CDPR Study Looking for Metolachlor
Z573	10	0.127	0.127	0	1	Special Initiatied CDPR Study Looking for Hexazinone
Z404	5	0	0	0	0	Special Initiatied CDPR Study Looking for Hexazinone
Z414	4	0	0	0	0	Special Initiatied CDPR Study Looking for Hexazinone
Z398	5	0	0	0	0	Special Initiatied CDPR Study Looking for Hexazinone
Z410	5	0	0	0	0	Special Initiatied CDPR Study Looking for Diuron and Hexazinone
Other Special CDPR Studies	768	0	0	91	0	All other Special Studies Iniated by CDPR

Note: CDPR webpage includes reports and protocols for most of these studies

TABLE 3 RESULTS OF PRZM SPATIAL MODELING ASSESSMENT

Environmental Fate (Most Vulnerable): K_{oc} = 38, Half-life = 154d				
Aging time (years)	**Longest half-life (days)**	**Cumulative percentile (µg/L) of all Simulations**		
		50th	**90th**	**95th**
13	154	0.0000	0.0000	0.0000
10	154	0.0000	0.0000	0.0000
5	154	0.0000	0.0000	0.0008
4	154	0.0000	0.0001	0.0043
3	154	0.0000	0.0003	0.0223
Environmental Fate (mean) K_{oc} = 57.5, Half-life 139d				
Aging time (years)	**Longest half-life (days)**	**Cumulative percentile (µg/L) of all Simulations**		
		50th	**90th**	**95th**
13	154	0.0000	0.0000	0.0000
10	154	0.0000	0.0000	0.0000
5	154	0.0000	0.0000	0.0000
4	154	0.0000	0.0000	0.0002
3	154	0.0000	0.0000	0.0008

FIGURE 1 HEXAZINONE USE AND MONITORING (FIRST SAMPLE BEFORE 1995)

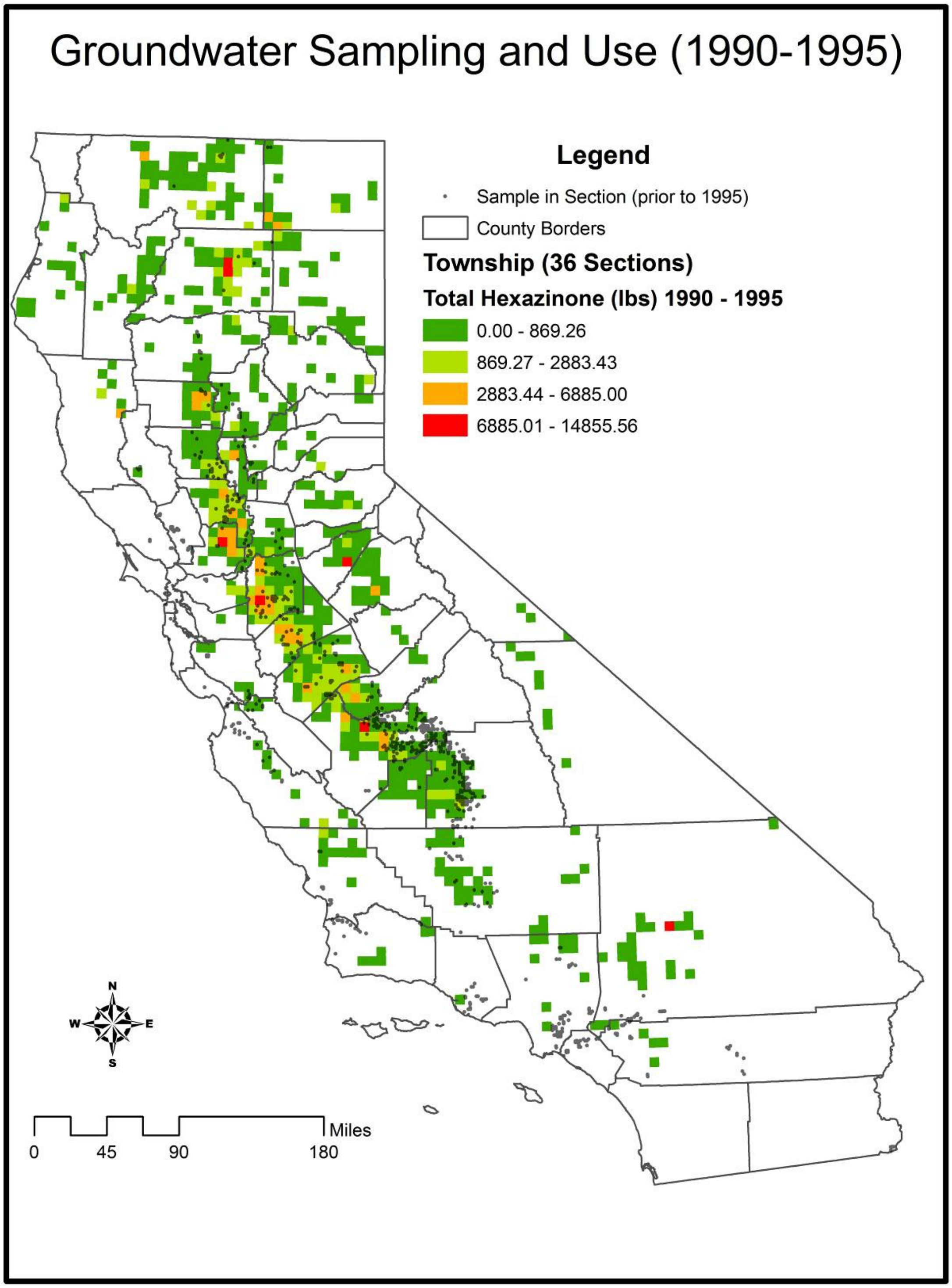

FIGURE 2 HEXAZINONE USE AND MONITORING (FIRST SAMPLE OR CONTINUED SAMPLING BETWEEN 1996 AND 2000)

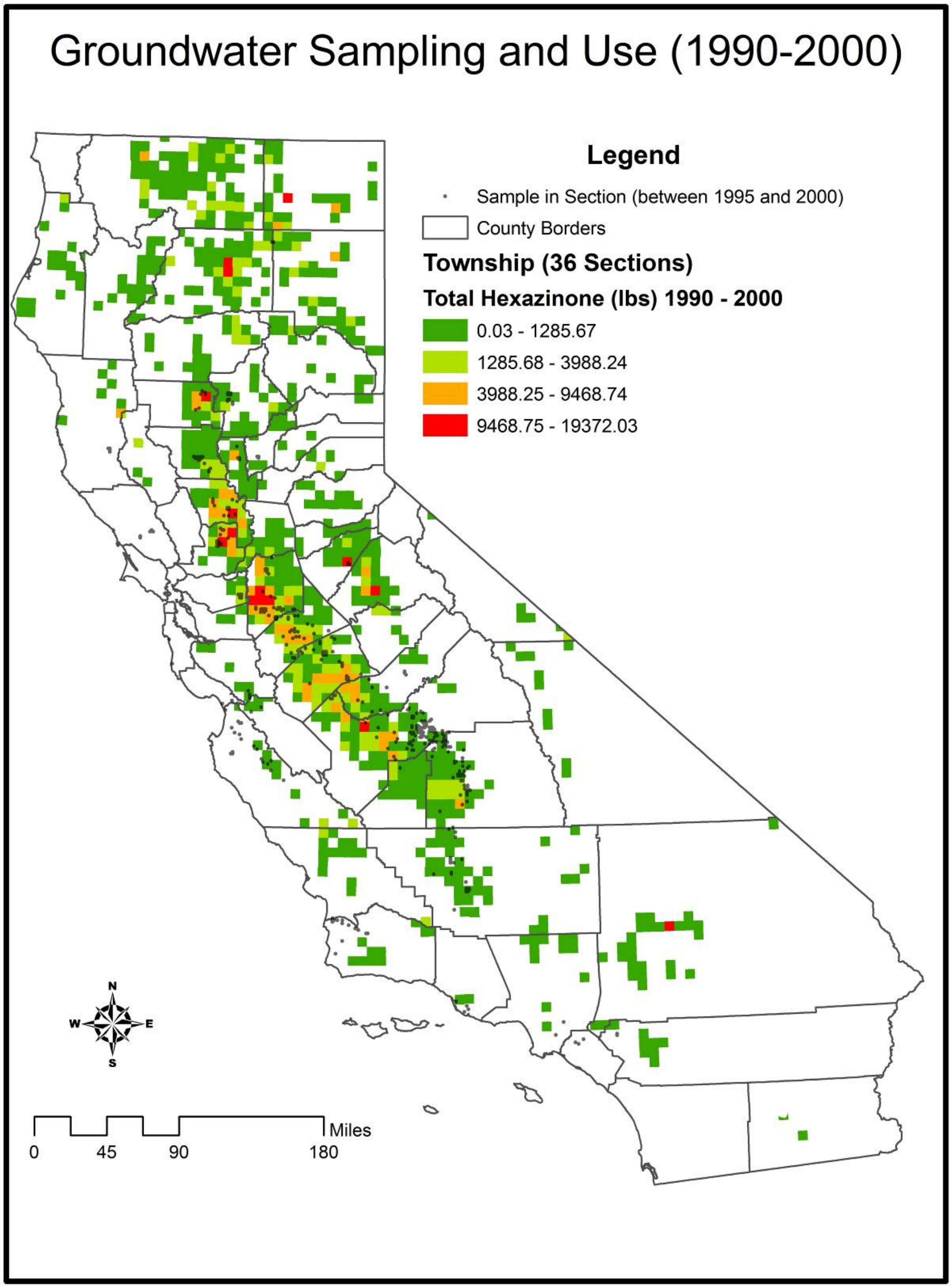

FIGURE 3 HEXAZINONE USE AND MONITORING (FIRST SAMPLE OR CONTINUED SAMPLING AFTER 2000)

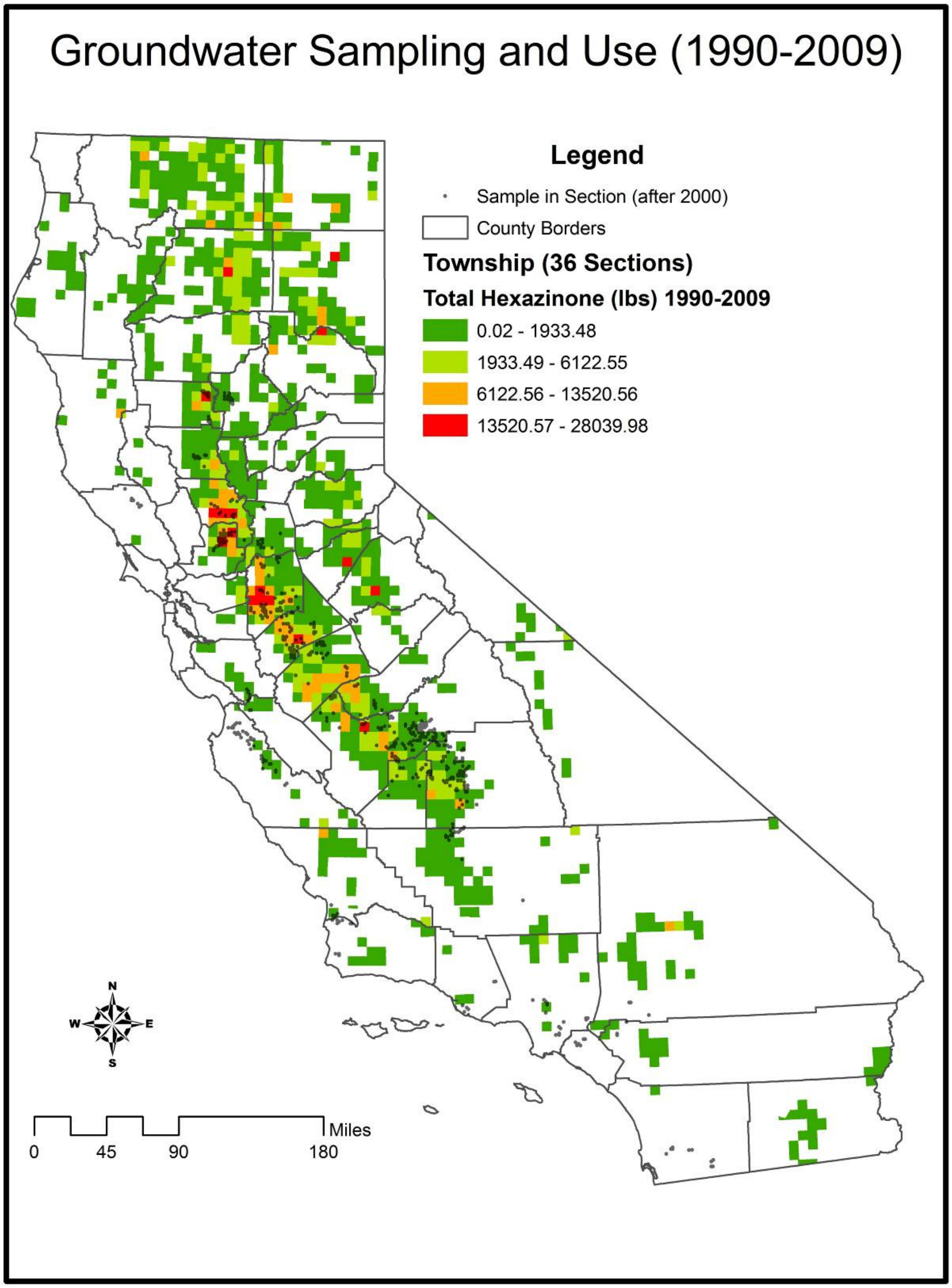

FIGURE 4 HEXAZINONE GROUNDWATER SAMPLE DETECTIONS AND REPORTED USAGE

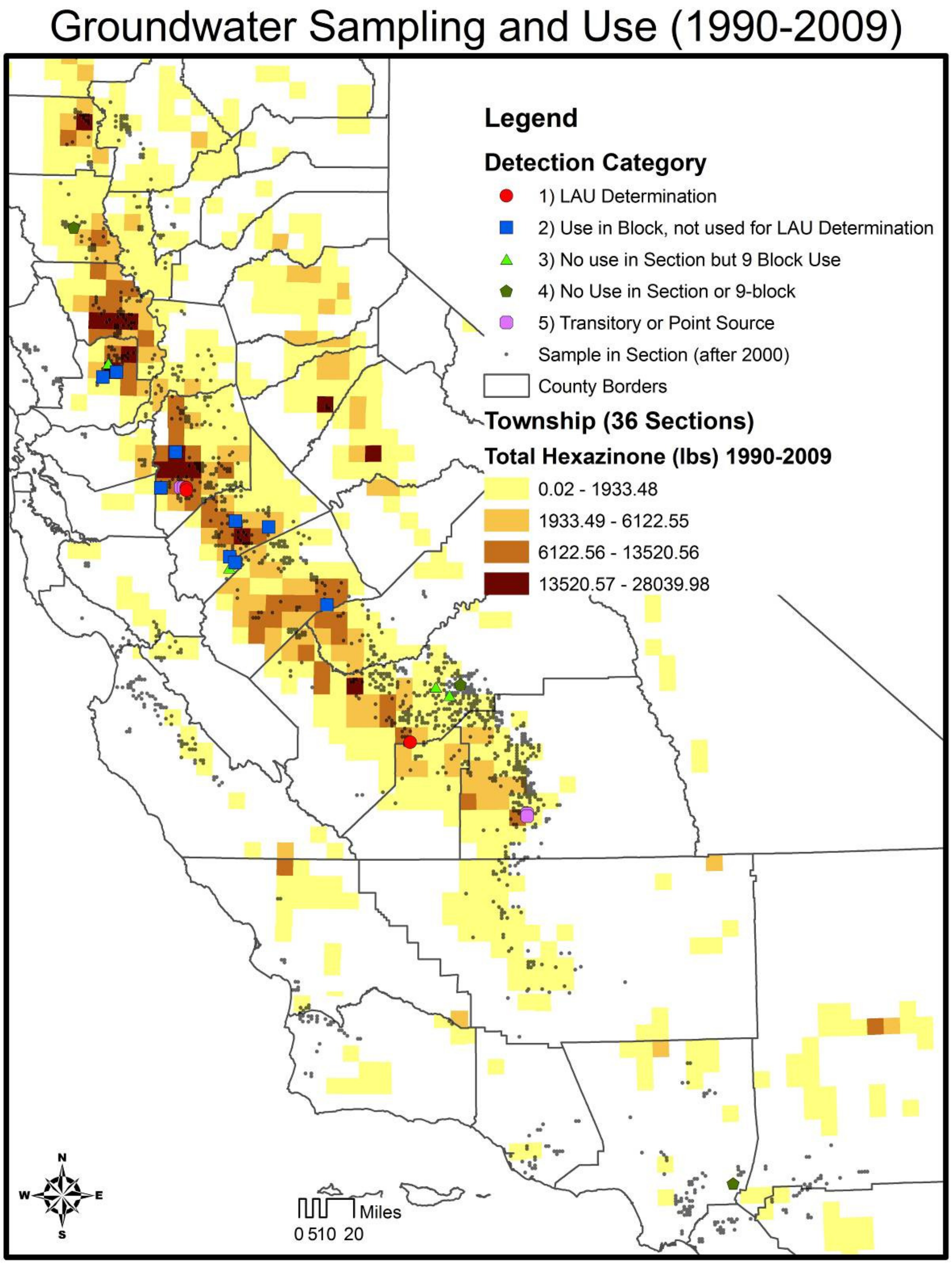

FIGURE 5 EXAMPLE USE (SECTION RESOLUTION) AND SAMPLING

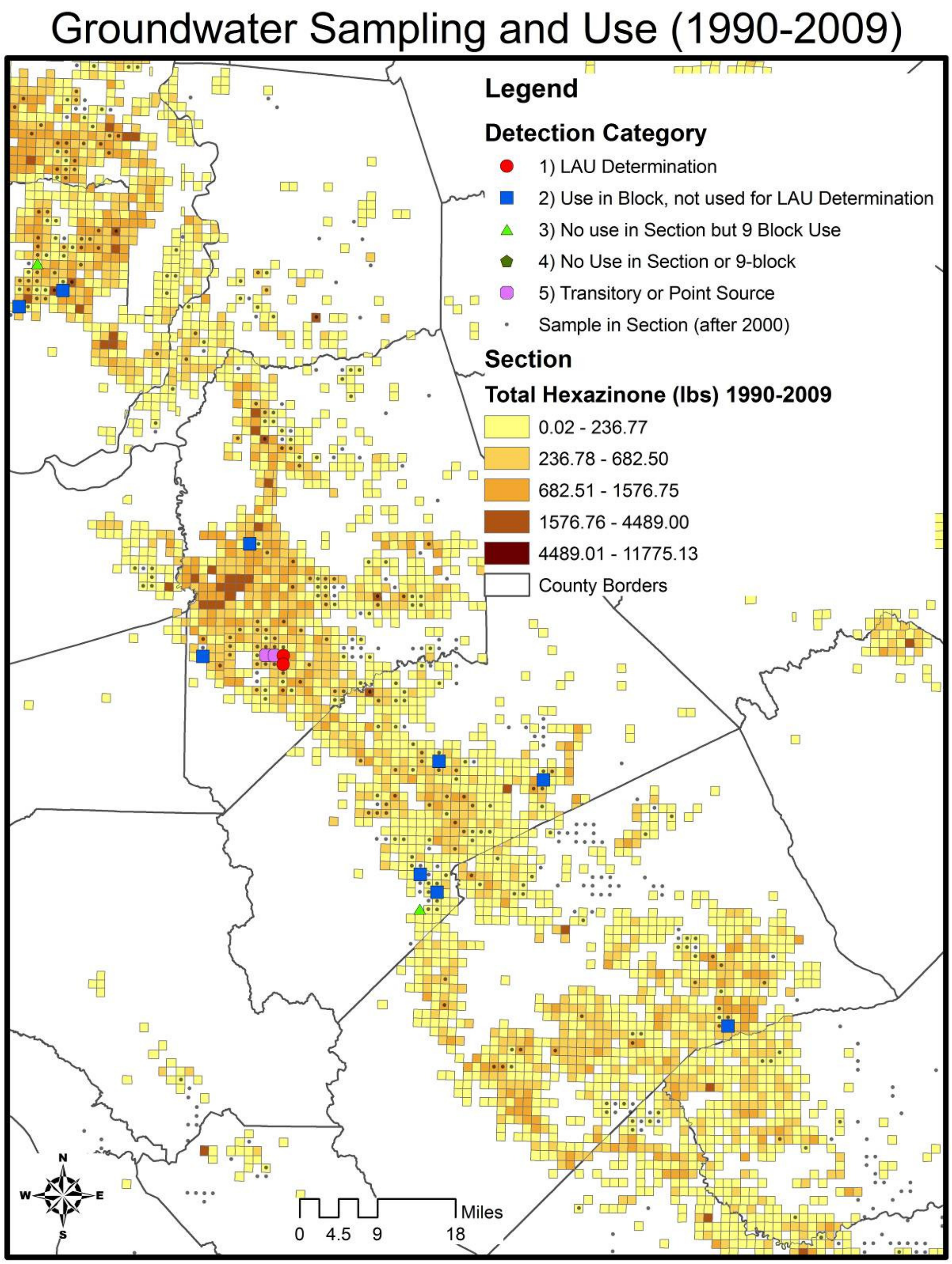

FIGURE 6 EXAMPLE USE (TOWNSHIP RESOLUTION) AND SAMPLING

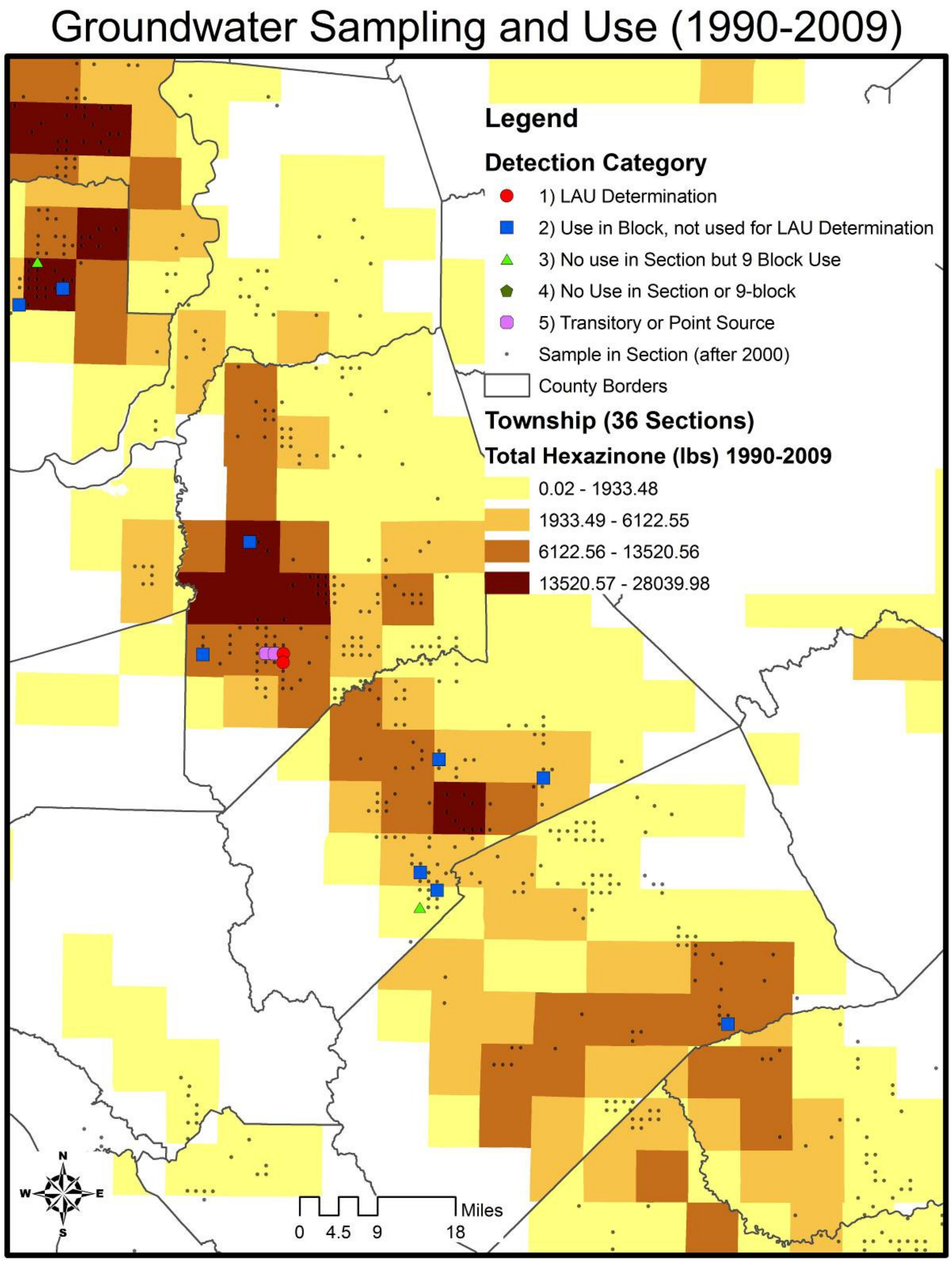

FIGURE 7 MAXIMUM PREDICTED WELL CONCENTRATION (3-YEAR TRAVEL TIME) – MAXIMUM HALF-LIFE, MINIMUM K_{OC}

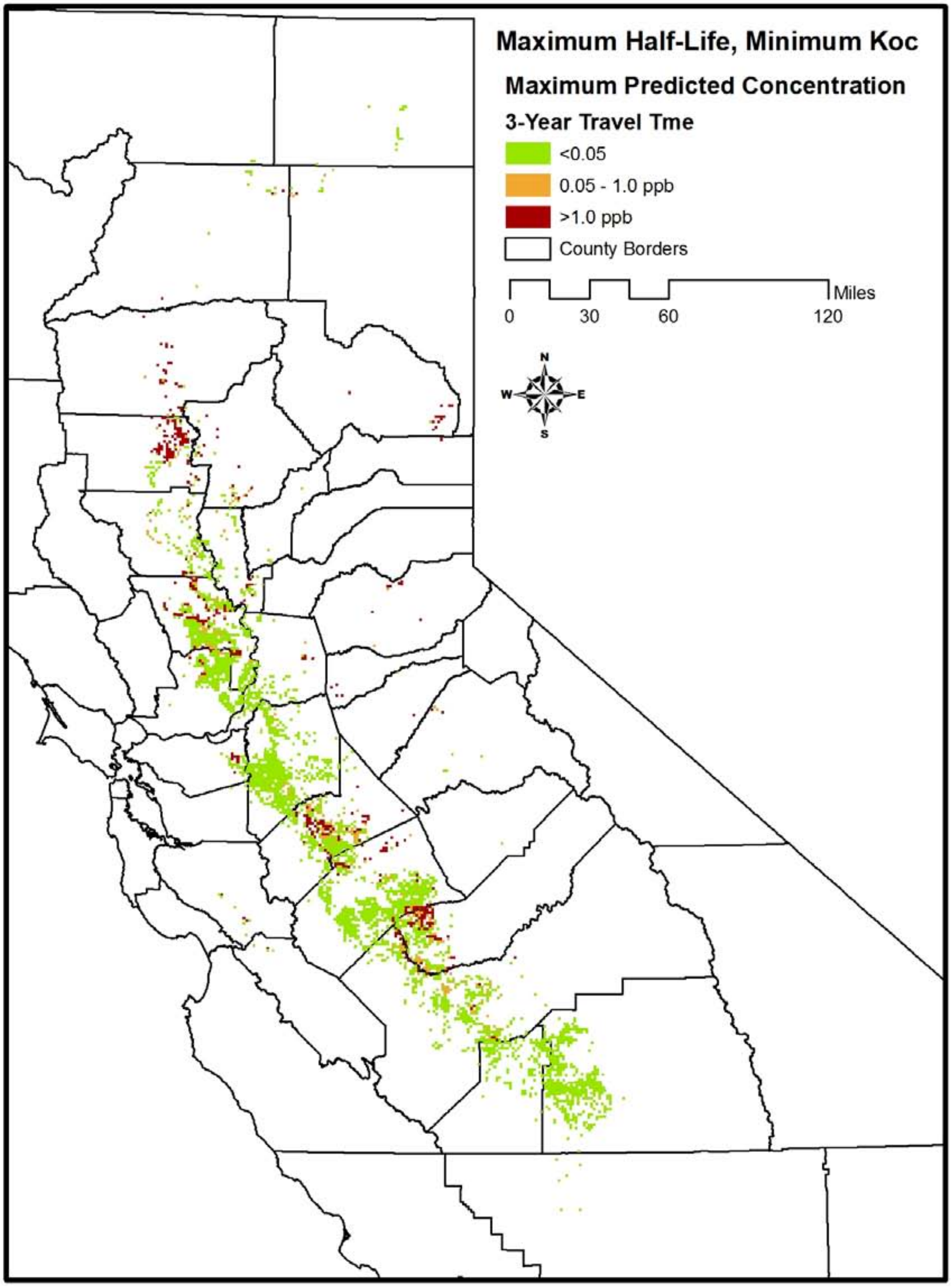

FIGURE 8 MAXIMUM PREDICTED WELL CONCENTRATION (10-YEAR TRAVEL TIME) – MAXIMUM HALF-LIFE, MINIMUM K_{OC}

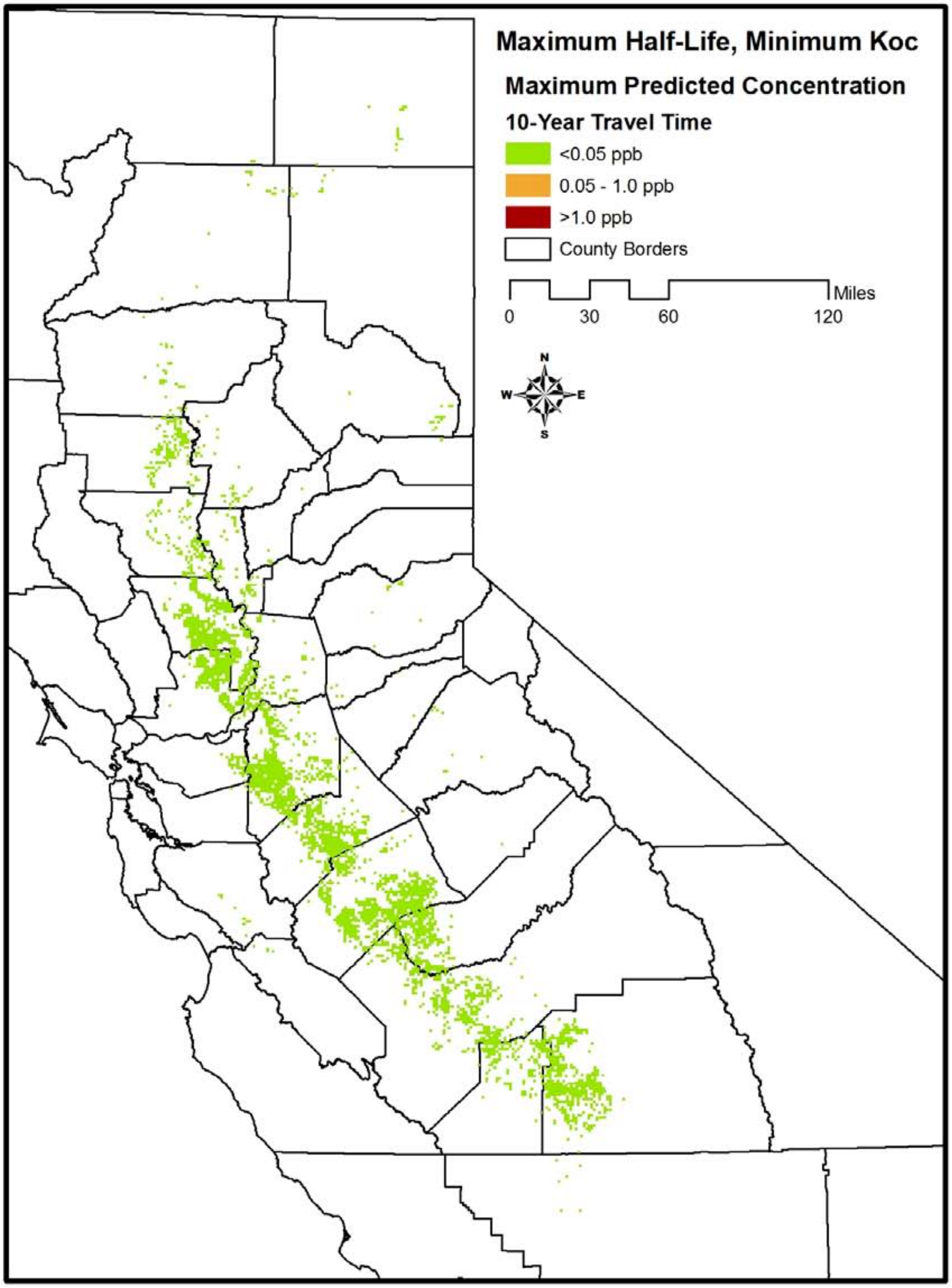

FIGURE 9 MAXIMUM PREDICTED WELL CONCENTRATION (3-YEAR TRAVEL TIME) – AVERAGE HALF-LIFE AND K_{OC}

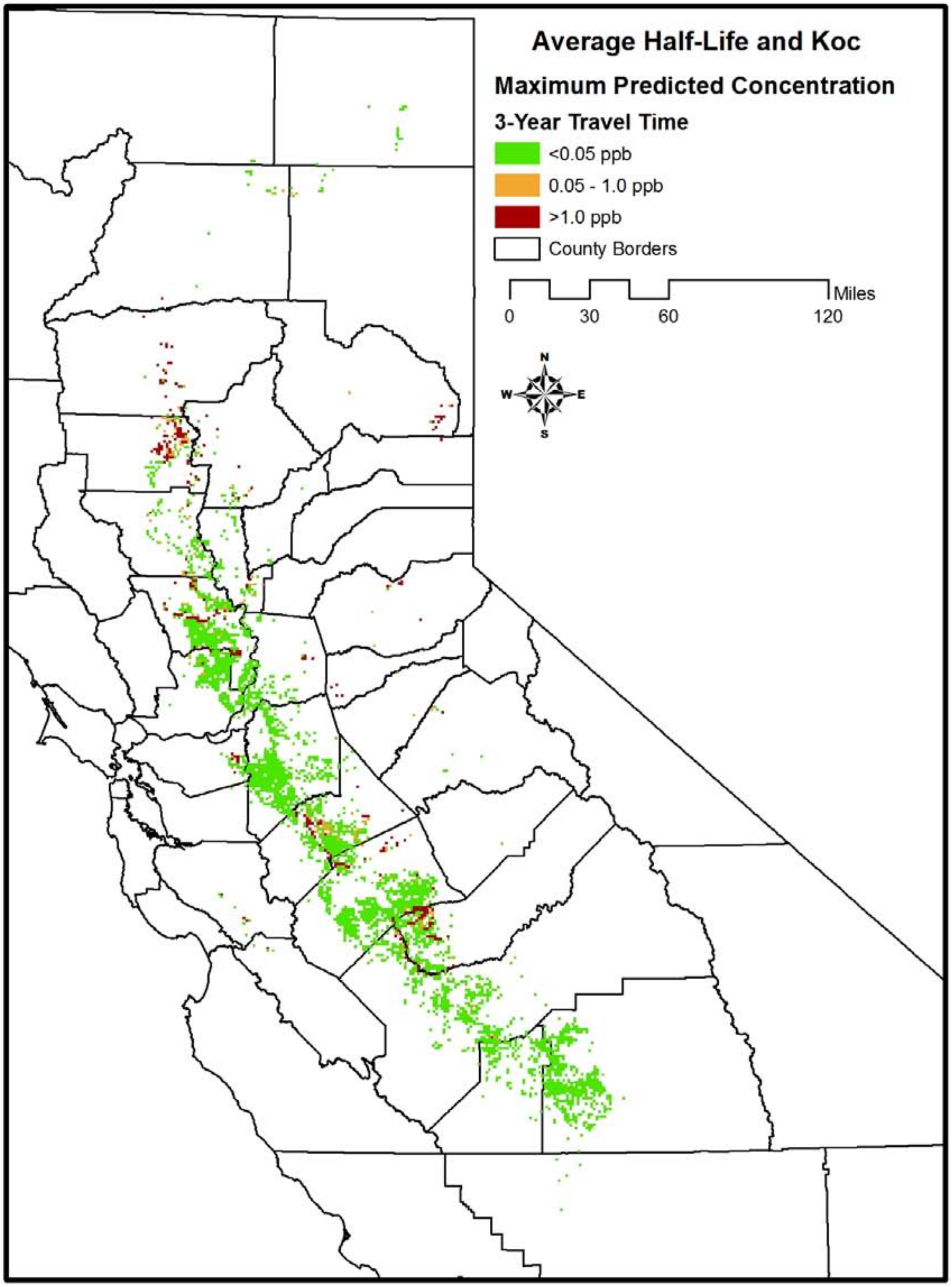

FIGURE 10 MAXIMUM PREDICTED WELL CONCENTRATION (10-YEAR TRAVEL TIME) – AVERAGE HALF-LIFE AND K_{OC}