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Pesticide and Nitrate Trends in Domestic Wells where Pesticide Use Is Regulated in Fresno and Tulare Counties, California

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The California Department of Pesticide Regulation initiated regulations on pesticide use in 1989 to mitigate groundwater contamination by atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and subsequently for simazine (6-chloro-*N*,*N*′-diethyl-1,3,5-triazine-2,4-diamine), diuron [*N*′-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea], bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1*H*,3*H*)-pyrimidinedione], and norflurazon [4-chloro-5-(methylamino)-2-[3-(trifluoromethyl) phenyl]-3(2*H*)-pyridazinone]. Annual water samples from 2000 to 2012 were obtained from domestic wells in Fresno and Tulare counties in regulated areas designated either as leaching groundwater protection areas (GWPAs), where residues move downward in percolating water, or runoff GWPAs, where residues move offsite in rain or irrigation runoff water to sensitive sites such drainage wells. Concentrations decreased below the reporting limit, so maximum likelihood estimation methodology for left-censored data was used. Decreasing trends in concentration were measured in both GWPA designations for simazine, its breakdown products desisopropyl atrazine (ACET, 2-amino-4-chloro-6-ethylamino-*s*-triazine) and diamino chlorotriazine (DACT, 2,4-diamino-6-chloro-*s*-triazine), and diuron. Bromacil crop use was predominant in runoff GWPAs, where decreases over time were also measured. In contrast, increased trends were observed for norflurazon and its breakdown product desmethyl norflurazon [DMN, 4-chloro-5(amino)-2-(α,α,α trifluorometa-tolyl] in runoff GWPAs. Use of simazine, diuron, and bromacil was regulated before norflurazon, so patterns of detection represent a shift to use of unregulated products. For NO_3, 22 of 67 wells indicated linear decreases in concentration coinciding with decreases in pesticide residues in those wells. Concentration of ACET, DACT, diuron, and NO_3 in well water was two to five times greater when located in runoff GWPAs. Greater amounts of herbicide were applied to crops grown in runoff GWPAs, but high concentrations in runoff water entering ponds or drainage wells could also be a factor for increased well water concentration. Initial regulatory measures appear to have been effective in reducing groundwater concentrations, but continued monitoring is needed to evaluate changes made to the regulatory approach in 2004.

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Detection of pesticide residues in water sampled from drinking water wells in the 1970s and 1980s resulted in regulatory responses at the state and federal levels in the United States (Holden, 1986; USEPA, 1991). Compared with point source contamination, identification of groundwater contamination from agricultural sources is difficult because multiple agricultural applications are made across large contiguous land areas. Owing to uncertainties in specific sources, regulatory responses to detections in the United States have ranged from banning use in subareas of a state, such as aldicarb [(*EZ*)-2-methyl-2-(methylthio)propionaldehyde *O*-methylcarbamoyloxime] in Suffolk County of Long Island, New York, to cessation of all sales of DBCP (1,2-dibromo-3-chloropropane) in the conterminous United States by the USEPA (Zaki et al., 1982; USEPA, 1995).

Many states conduct well sampling surveys to identify areas where pesticide residues have contaminated groundwater. In Wisconsin, for example, well sampling results are used to identify areas where use of the pre-emergent herbicide atrazine is regulated (http://datcp.wi.gov/Environment/Water_Quality/Atrazine/index.aspx). Further repeat sampling of wells has been suggested as a method to modify the original regulatory decision that prohibited use in detected areas in Wisconsin (Rheineck, 2007). A well monitoring program designed to measure potential changes in groundwater with time requires a long-term commitment because there is a lag time for changes made in management practices to be reflected in respective groundwater aquifers (Broers et al., 2001). Residues must move from the root zone, through the vadose zone, mix with aquifers, and eventually become available for extraction by a well. The exact length of time required varies depending on the depth to groundwater and on vadose zone and aquifer stratigraphy, but in general deeper aquifers require longer times for changes to be detected. Strategies to measure changes with time vary from comparison of sampling between two points in time located decades apart to attempting to account for seasonal influences within a year (Belitz et al., 2003; Goss et al., 1994: Paschke et al., 2008). Forecasts of trends with time have been developed

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Abbreviations: ACET, desisopropyl atrazine; DACT, diamino chlorotriazine; DMN, desmethyl norflurazon; DPR, Department of Pesticide Regulation; GWPA, groundwater protection area; MCL, maximum contaminant level; PMZ, pesticide management zone; RL, reporting limit.

from combining measurements of solute concentrations in municipal, domestic, and/or monitoring wells with estimates of groundwater ages (Burow et al., 1999, 2008).

Similar to pesticides, NO_3 has been detected in groundwater, with a major source of detection in rural areas from use as a fertilizer in agricultural applications (Spalding and Exner, 1993). Due to potential health concerns, the USEPA has established a long-term health level in drinking water, denoted the maximum contaminant level (MCL), of 10 mg/L N, equivalent to 45 mg/L NO_3 (http://www.epa.gov/safewater/contaminants/index.html#inorganic). Pesticide and NO_3 residues follow the same pathway with water as it recharges groundwater so it is logical to monitor and regulate them simultaneously (Burow et al., 1998). Separate regulatory actions, however, have been taken because of statutory constraints and/or the results from well monitoring studies. In Nebraska for example, well sampling studies in the 1980s provided detections of NO_3 and atrazine, but the number of wells containing NO_3 above the MCL spurred development of a regulatory program focused on reducing NO_3 contamination (Exner et al., 2010). The opposite action has been taken in California, where the Department of Pesticide Regulation (DPR) only regulates pesticides: regulation enacted in 1986 specified well monitoring and regulatory activities (Troiano et al., 2001). California regulatory programs are now being developed to minimize NO_3 contamination of groundwater.

A brief explanation of the regulatory actions and time lines taken in California provides a context for discussion of results from the trend analysis. In California, the DPR has regulated pesticides found in groundwater since 1989. Agricultural use of pesticides is regulated in 1-mile^2 (2.6-km^2) increments of land identified as sections, as defined by the Public Lands Survey Coordinate System (Davis et al., 1966, p. 597–629). A vulnerable section of land was identified as a pesticide management zone (PMZ) if a drinking water well was sampled and found to contain residue of a pesticide active ingredient that had been identified as moving to groundwater as a result of agricultural nonpoint source applications. Most of the detections and sampling activities were focused on domestic wells rather than municipal drinking water wells because domestic wells are situated in rural, agricultural settings and they draw water from shallow, vulnerable groundwater aquifers. At first, 62 PMZs were enacted in 1989 for atrazine, but additional sections and active ingredients were regulated and, by 2001, 489 distinct sections of land were regulated (Table 1). At the time, the regulatory approach was specific to the pesticide active ingredient detected, so a section of land could be listed multiple times as a PMZ based on specific pesticide sampling results and as reflected by the difference between columns for all sections and distinct sections in Table 1.

The burden to identify additional vulnerable areas increased with time as residues were detected in more sections of land. In 1990, a statistically based project was initiated to determine if geographic characteristics could aid in identifying vulnerable areas of land and if this approach could be used to ease the well sampling burden. Soil and depth-to-groundwater (DGW) data layers were developed and eventually provided geographic delineation of vulnerable areas. Two pathways to groundwater were identified and geographically located based on soils data. Leaching of residues downward from surface applications was identified as the major pathway to groundwater in areas where coarse-textured soils were predominant (Troiano et al., 1999). However, groundwater contamination was also shown to occur in areas where soils had low water infiltration rates: runoff water generated from either rainfall or irrigation and containing dissolved pesticide residue was identified as flowing into sensitive sites located near a field, such as to a drywell or pond. Drywells, in particular, were unique to the areas with hardpan soils because they provided drainage and relief from flooding for newly planted citrus crops through channeling of runoff water to boreholes that were drilled through the surface layers of the soil and backfilled with gravel or rock (DeMartinis and Royce, 1990). These sensitive sites provided a direct route for water to enter the subsurface soil and accelerate groundwater recharge (Braun and Hawkins, 1991; Prichard et al., 2005). Data for DGW were obtained from monitoring wells maintained by the California Department of Water Resources. Comparison of the frequency of detection of pesticide residues vs. estimated 10-yr average DGW for a section of land indicated that a value of 21 m

Table 1. Regulatory time line for the number of and year in which pesticide management zones (PMZs) were enacted into regulation for each active ingredient in California.

Year regulated	Sections designated as PMZs						Total sections	
	Atrazine	Bromacil	Diuron	Prometon	Simazine	Norflurazon	All	Distinct
	no.							
	All sampled sections							
1989	62	0	0	0	0	–	62	62
1990	1	11	20	7	66	–	105	41
1992	14	13	18	0	48	–	93	55
1999	100	114	201	18	269	–	702	330
2001	0	0	0	0	0	11	11	1
Total	177	138	239	25	383	11	973	489
	Sections in the Department of Pesticide Regulation's Domestic Well Network							
1989	0	0	0	0	0	–	0	0
1990	0	0	0	0	0	–	0	0
1992	0	4	3	0	9	–	16	8
1999	17	25	42	3	50	–	137	50
2001	0	0	0	0	0	6	6	1
Total	17	29	45	3	59	6	159	59

or less potentially defined a vulnerable section of land (Spurlock, 2000; Troiano et al., 1999). These results were incorporated into a revision of the groundwater regulations in May of 2004 when, in addition to detection in a well water sample, vulnerable sections of land were identified through layering the soil and DGW databases. Vulnerable areas were renamed and identified either as leaching or runoff GWPAs. The regulated area increased from 489 sections of land identified only by detection to approximately 4000 sections of land. An in-depth description of the statistical methods used and the final model for combination of soil and DGW is available at http://www.cdpr.ca.gov/docs/emon/grndwtr/vasmnt.htm.

Documentation of decreases in pesticide residues in contaminated wells is the ultimate measure of success with respect to enactment of regulations to protect the groundwater. The DPR established a monitoring network of domestic wells in fall 1999 to measure potential trends in previously contaminated single-family drinking water wells. The network was initiated 5 yr before the revision of the regulatory approach in 2004. Although participation in the program is voluntary, the number of wells sampled each year has been consistent, with only a few yearly changes. This current analysis includes 13 yr of data collected from 2000 to 2012. Because the pathway to groundwater and the appropriate agricultural management practices that minimize offsite movement differ between leaching and runoff GWPA designations, the design included a comparison for potential differences in concentration and trends between the GWPA designations. Well owners requested inclusion of NO_3 in the chemical analysis and it was included in 2001. Growers in California are required to report annual pesticide use within each section of land. Patterns of pesticide use obtained for land sections containing the monitored wells were investigated as a potential explanatory variable for the measured trends in well water concentrations with time.

Materials and Methods

Study Area

Fresno and Tulare counties are located in California's southern San Joaquin Valley (Fig. 1). These two counties lead the nation in agricultural production, with vineyard and citrus crops among the largest commodities (http://www.motherjones.com/files/2agovstat10_web-1.pdf). These counties have the greatest reported use of three common pre-emergent herbicides, simazine, diuron, and norflurazon, and they are among the top five counties for total pounds applied for bromacil. Simazine,

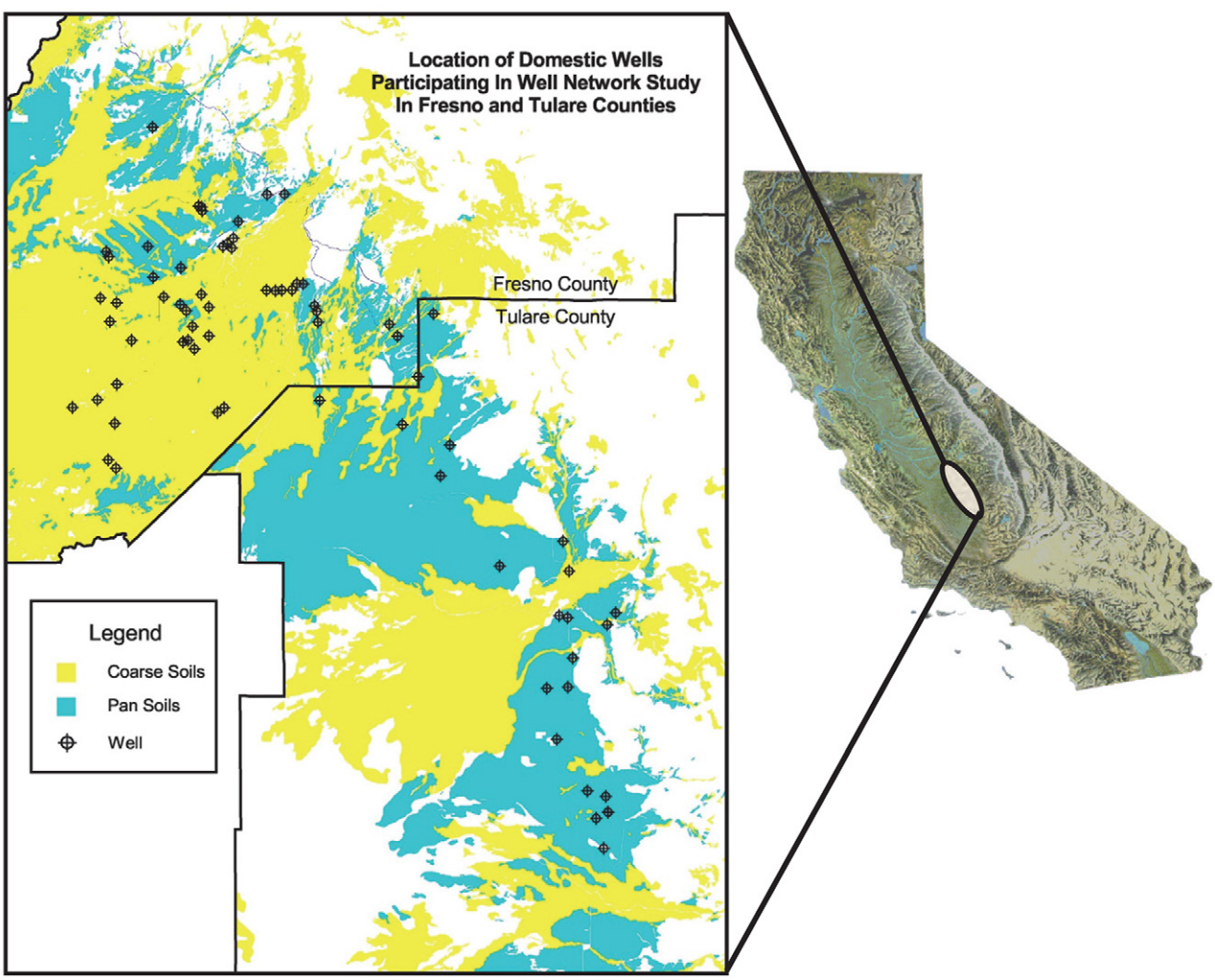

Fig. 1. Location of the eastern San Joaquin study area in relation to the state of California and the spatial distribution of domestic wells participating in the Department of Pesticide Regulation's long-term monitoring for the presence of pesticide residues. Sampled domestic wells are located with respect to soil types that typify either leaching or runoff groundwater protection area (GWPA) designation in Fresno and Tulare counties.

diuron, norflurazon, and bromacil have been detected in well water samples; they have been listed in regulation as known groundwater contaminants, and their use is regulated in vulnerable areas.

Wells chosen for this study were located in GWPAs where in 1999 the major uses of these herbicides were for weed control in vineyard and citrus crops but with substantial use also reported on deciduous tree fruit and nut crops and on field crops. Data for crop use were obtained from the DPR's Pesticide Use Reporting database, which was initiated in 1990 and accumulates data from growers (http://www.cdpr.ca.gov/docs/pur/purmain.htm). Grape (*Vitis vinifera* L.) is the predominant crop grown in leaching GWPAs. Although grape is grown in a wide range of soils, it is concentrated on the valley floor in soils that are coarse textured, where leaching is the predominant pathway to groundwater. Citrus (*Citrus* spp.) is the predominant crop grown in runoff GWPAs located along the eastern side of the San Joaquin Valley near the foothills. The area near the foothills is preferred because winter freezing temperatures are less frequent at these elevations than toward the center of the valley floor (Kallsen, 2005). The soils adjacent to the foothills contain a shallow hardpan layer such as the San Joaquin (fine, mixed, active, thermic Abruptic Durixeralfs) and Exeter (fine-loamy, mixed, superactive, thermic Typic Durixeralfs) soil series. The hardpan soil layer has been associated with the runoff pathway to groundwater (Troiano et al., 1999). These pre-emergence herbicides are also used for applications to rights-of-way such as for control of roadside vegetation. This use, however, is not reported on a section basis so the portion potentially used for rights-of-way in each section cannot be identified.

Study Design

The monitoring well study was initiated in the fall of 1999 in anticipation of revisions to the existing groundwater regulations, which were enacted in May 2004. The design included a comparison of well water concentrations and trends between leaching and runoff GWPA designations in Fresno and Tulare counties. A previous study conducted to age-date water in domestic drinking water wells located in this study area indicated a median total travel time of 7 to 9 yr for groundwater recharge water to be extracted by wells (Spurlock et al., 2000). Based on this estimate, we chose to sample at least annually because the effects could potentially be measured within a decade. Samples taken in the spring from 2000 to 2012 were included in this analysis.

Domestic wells included in the selection process had a previous detection of one or more residues of simazine, bromacil, or norflurazon or one of simazine's breakdown products ACET or DACT. Owners of randomly chosen wells were invited to participate in the study, granting permission for staff to periodically sample the well. If an owner declined participation, another well was randomly selected for replacement. Initially, 31 owners in leaching GWPAs and 41 owners in runoff GWPAs agreed to participate. The locations of the wells in Fresno and Tulare counties are given in Fig. 1 with respect to their distribution between the two GWPA designations. Total well depth was available for 49 wells and ranged from 11 to 76 m, with a median depth of 40 m. Well logs were available for 32 wells. Sanitary seals were reported on 20 of the logs, typically extending 6 m down from the surface. Perforations were reported for 22 of the wells, ranging from 4 to 42 m in length with a median of 7 m. Gravel pack was reported for 15 wells, ranging from 11 to 50 m in length with a median of 34 m.

Sampling Method

Well water samples were taken according to standard operating procedures developed by staff from the Environmental Monitoring Branch, DPR (Nordmark and Herrig, 2011). Water was sampled from a port located between the wellhead and the holding tank. If the sampling port was a Schrader valve, water flowed from a small-diameter Teflon tube into 1-L amber glass jars with Teflon-lined lids. Water sampled from faucets flowed directly into the amber jar. Water samples were taken after the water pump was run for 10 min, which assured sampling of fresh water from the local aquifer and not just water standing in the borehole. The jars were rinsed with the well water before collection. Sample bottles were stored and transported to the laboratory on wet ice at 4°C. The handling, location, and disposition of each sample was tracked with an accompanying chain-of-custody form that was filled out each time the sample was relinquished, starting from when the sample was first collected until it was returned from the chemical analytical laboratory with the results of the chemical analysis. Analyses were typically conducted within 7 to 14 d after collection. Data from previous storage studies indicated no degradation for 30 d under these sampling and handling conditions.

Chemical Analysis

Analysis for pesticide residues in the water samples was conducted by the Environmental Monitoring Laboratory, Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento. In addition to the parent active ingredients and degradation products targeted for inclusion in this study, the method was modified in 2004 to include analysis for DMN, norflurazon's primary degradation product. Chemicals were extracted from water samples with methanol and the extracts analyzed using liquid chromatography coupled to a thermospray triple-stage quadrupole mass spectrometer (California Department of Food and Agriculture, 1999). A Waters SymmetryShield C18 column was used to provide separation of the chemicals. The following quality control procedures were used: (i) each extraction set included two replicate standard spikes containing all chemicals at 0.2 mg/L in a groundwater matrix; (ii) an extraction standard was included where propazine [6-chloro-*N*,*N*′-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine] was added at 0.2 mg/L to each sample before extraction; (iii) blind spike samples were prepared in the field and transported to the laboratory; (iv) blank samples of deionized water were prepared for 10% of the sampled wells; and (v) duplicate well samples were included in the spring 2002 sampling interval. Quality control data indicated that the method was stable with time. Extraction procedures resulted in some low bias in results that over the long term ranged from 86 to 94% as measured from the ongoing 0.2 μg/L spiked standards. Analytical results have not been corrected for the lower bias. Coefficients of variation for spiked standards were low, ranging from 9.6 to 16%. Residues were never detected in the blank samples. The variation measured in the blind spike samples and

duplicate well samples was within the range measured for the ongoing spiked standards (Segawa, 1995). The reporting limit (RL) for all analytes was set at 0.05 μg/L.

Nitrate was included in the water analysis starting in 2001, with analysis conducted by different laboratories. Nitrate analysis for 2001 and 2002 was conducted by Agriculture and Priority Pollutants Laboratory located in Clovis, CA, using ion chromatography. For 2003 and 2004, analyses were conducted by California State University, Fresno, using selective ion electrode methodology. In 2005 and 2009, analyses were conducted by Dellavalle Laboratory, Fresno, CA, using ion chromatography, denoted as Dellavalle Method W-17.00. In 2010, analysis was conducted in-house using a reflectometer-based method (Phillips et al., 1995). This analysis system consists of reading reflectoquant NO_3 test strips (EMD 16971-1) with an RQflex2 reflectometer (EMD 16950-1). For all methods, NO_3 quality control samples specified for each set of 10 samples were: (i) a deionized water reagent blank; (ii) a fortified blank where deionized water was spiked with a known concentration of NO_3; (iii) a fortified sample matrix where a sample was spiked with a known concentration; and (iv) an instrument performance check standard using a mid-range calibration standard and a calibration blank. An additional comparison was conducted for the reflectoquant method because it was a relatively new methodology. Samples taken in 2009 were split and the results compared between the Dellavalle ion chromatography method and the reflectoquant analysis. Sample concentrations for the comparison ranged from <10 mg/L to >100 mg/L. In an initial comparison of 11 split samples, the slope between methods was 1.0. For a second sampling of 32 split samples, the slope was 0.96 with the value of 1.0 included within the 95% confidence limits. Both tests indicated excellent agreement between these methods, which was in agreement with the results of an earlier comparison reported by Phillips et al. (1995). The reporting limit was set at 1 mg/L NO_3.

Statistical Analyses

Statistical analyses were conducted using SAS software (SAS Institute, 2008). Comparisons for the frequency of residue detection were conducted using a chi-square contingency table analysis as implemented in PROC FREQUENCY. Tests were conducted comparing data from the first and last year sampled to measure changes in the overall frequency of detection and potential differences between GWPA designations.

Trends in concentration with time were compared between two levels of tests. One level, denoted *overall trend analysis* tested for the presence of trends in the pooled data. The design was a mixed model where GWPA designation was a fixed effect, and random effects for the parameters of time and subunit of the well were included. Concentrations in wells decreased below the RL with time, producing a left-censored data set. Likelihood-based statistical methods have been used to analyze left-censored longitudinal data (Thiebaut and Jacqmin-Gadda, 2004). The syntax for the SAS programs was used as suggested by Jin et al. (2011). A maximum likelihood analysis was implemented through PROC NLMIXED where the full model was designated as

$$Y = a + a\,\mathrm{var} + b_1 X + b_1\,\mathrm{var}\,X + b_2 X^2 + b_2\,\mathrm{var}\,X^2 + cZ + dXZ + eX^2 Z$$

where a is the intercept and $a$var is the corresponding random effect, b_1X is the linear effect of time and $b_1$var$X$ is the corresponding random effect, b_2X^2 is the quadratic effect of time and $b_2$varX^2 is the corresponding random effect, cZ is the effect for GWPA designation, and dXZ and eX^2Z are the interaction terms for linear and quadratic effects of time with GWPA designation. Individual wells were identified as the subject i.d. in a "Random" statement. The syntax suggested by Jin et al. (2011) is for repeated measures of lognormally distributed data. Tests of the residuals for data in this current study indicated that the data were lognormally distributed, which is commonly observed for environmental concentrations (Blackwood, 1992).

Analyses of the full model comparing concentrations between GWPA designation were possible for simazine, ACET, DACT, and NO_3 because residues were detected in nearly all wells. If the results from the full model indicated no significant interaction between regression terms and GWPA designation, then the model was sequentially reduced testing linear, quadratic, and GWPA main effects. Model selection comparing full to reduced models for fixed and random terms was based on comparison of fit statistics. The difference between values for the −2 log likelihood statistic was compared with chi-square values at $P = 0.01$, with the degrees of freedom for the test calculated as the difference between the numbers of parameters in the models (Williams et al., 2003; Littell et al., 2006). Optimal models with significant effects included the random term for intercept and linear effects and a term to describe the covariance between them (UCLA Statistical Computing Group, 2013). When an interaction term between regression coefficients and GWPA designation was significant, separate analyses were conducted within each GWPA designation. The number of wells with detections of diuron, bromacil, and norflurazon was greater in runoff GWPAs so, owing to this imbalance, separate regression analyses were conducted within each GWPA designation for these chemicals. Predicted lines determined from the means of the antilogarithms of the predicted regression values were compared with the means of the observed values that included imputed values for observations below the RL.

The second level of analysis, denoted *trends measured within each well*, was regression analysis conducted for each chemical within each well. Analyses were conducted within each well because local agronomic practices and the geologic setting influence the occurrence of residues in an individual well, an effect that may not be represented by the overall analysis. The model and programming for individual wells was similar to the pooled analysis, but a simpler model was used testing the linear and quadratic effects of time. Results from these regressions are presented as counts for the number of wells within each GWPA designation with decreasing, increasing, or no trend. A model with only the linear term was sufficient for the majority of significant regressions. Only a few regressions were improved by the addition of the quadratic term, typically for patterns where most of data were below the RL, with two or three detections above the RL occurring at the beginning or end of the 13-yr sampling interval. These situations were indicated as a decreased or increased trend, respectively.

Table 2. Number of wells with detections of residues of simazine, its breakdown products ACET and DACT, total simazine residues, diuron, bromacil, norflurazon, its breakdown product DMN, total norflurazon residues, and NO_3 for water samples obtained from a domestic well monitoring network in leaching and runoff groundwater protection area (GWPA) designations. Data are compared between the initial year of sampling for that chemical at 2000, 2001, or 2004 and the last date sampled in spring 2012.

GWPA classification	Wells sampled	Wells with detections									
		2000							2004		2001
		Simazine	ACET	DACT	Total simazine	Diuron	Bromacil	Norflurazon	DMN	Total norflurazon	NO_3
		no.									
Leaching GWPA	31	27	30	26	30	9	2	4	13	13	31
Runoff GWPA	36	28	34	34	34	25	21	7	16	16	36
		2012									
Leaching GWPA	31	14	22	22	25	5	1	4	15	15	31
Runoff GWPA	36	25	34	33	34	18	15	12	18	19	36

Results

Occurrence in Wells

The frequency of detection of simazine and its breakdown products was high in both leaching and runoff GWPAs (Table 2). A previous analysis of the co-occurrence of parent and degradation products for triazines in well water sampled in this area of Fresno and Tulare counties indicated a high rate of detection for simazine and co-occurrence of the breakdown products ACET and DACT and a low detection rate for atrazine and related breakdown products (Troiano and Nordmark, 2002). This pattern reflected historically high annual use of simazine for a wide range of crops grown in this area of California. Contingency table analysis comparing the frequency of detection between GWPA classifications indicated more frequent detections for diuron, bromacil, (chi-square < 0.01, analysis not shown), and/or norflurazon (chi-square < 0.05) in runoff GWPAs, an effect that was consistent for separate analyses conducted for 2000 and 2012 data (Table 2). Bromacil is registered for use only on citrus, which is the predominant crop grown in runoff GWPAs, indicating a close relationship between crop use and detection in wells.

Contingency table analyses comparing the frequency of detection between 2000 and 2012 indicated a lower detection frequency in 2012, especially noticeable for simazine, ACET, and diuron in the leaching GWPA designation (chi-square < 0.01, analysis not shown) (Table 2). In contrast, frequency of detection tended to increase for norflurazon and its degradate DMN but the increases were not significant.

Chemical analyses for NO_3 residues were added in spring 2001 with residues detected in all wells. Frequency of wells above the MCL of 45 mg NO_3/L was much greater in runoff GWPAs, averaging 58% of wells compared to 27% of wells in leaching GWPAs: The overall mean value was above the MCL in runoff GWPAs (Table 3). The overall average frequency of wells above the MCL was 42%. For monitored pesticides, simazine has an established MCL at 4.0 μg/L. The highest detection of simazine was below the MCL at 0.52 μg/L, however, total simazine residues, the sum of parent and ACET and DACT residues, could be above the MCL with the highest recorded at 8.84 μg/L.

Overall Trend Analysis

An overall linear decrease in concentration over time was measured for simazine, ACET, DACT, and total simazine residues (simazine + ACET + DACT) (Table 4; Fig. 2). A subtle difference in response was indicated for DACT; in the full model, a significant interaction term for the quadratic effect and GWPA classification indicated a different response in each GWPA classification (Table 4). Analyses conducted within each GWPA indicated a linear decrease in leaching GWPAs but a curvilinear response in runoff GWPAs, where concentrations initially decreased with time but then leveled off in later years (Table 5; Fig. 3). Regression interaction terms with GWPA classification were not significant for simazine, ACET, or total simazine, so the slopes for linear decreases were similar in both runoff and leaching GWPA designations. For ACET and total simazine, however, the significant term for GWPA indicated greater concentrations in runoff GWPAs by threefold and fourfold, respectively, compared with the leaching GWPAs (Tables 3 and 4). The term for GWPA was also significant for DACT, with a nearly fivefold greater concentration in runoff GWPAs.

Significant linear decreases in concentration with time were also indicated in the separate analyses conducted for diuron and bromacil (Table 5). A subtle difference was again noted for diuron, where the response in runoff GWPAs was curvilinear with concentrations dramatically decreasing with time after an initial lag period (Fig. 2). Concentrations were again greater in runoff GWPAs for diuron, but the differences were smaller in later years because concentrations in many wells fell below the RL, causing the observed convergence in concentrations measured at the last sampling interval in 2012. For bromacil, there were only three wells with detections in leaching GWPAs, but their average concentration was much less than in runoff GWPAs (Fig. 2). Results for norflurazon provided a contrast because although there was no significant trend in leaching GWPAs, increases in concentration with time were indicated in runoff GWPAs (Fig. 3). The magnitude of concentrations was similar between the GWPA designations. Results for the breakdown product DMN mimic the parent, but there was only a trend ($P \leq 0.10$) indicated for increasing concentration in runoff GWPAs.

Analysis for NO_3 concentration indicated a significant regression, but only the quadratic term was significant (Table 4). The predicted curve for this response increased

in average concentration, followed by decreases back to near the initial measurement (Fig. 3). The interaction terms were not significant so the curves were similar in both leaching and runoff GWPAs, but average concentrations were significantly greater in runoff than in leaching GWPAs by approximately twofold (Table 3). The pattern for trends measured in individual wells provides a basis for explanation of the curvilinear response, discussed below.

Trends Measured within Each Well

Although both linear and quadratic terms were tested, linear trends were dominant. Table 6 contains a count of wells with respect to whether significant increases or decreases or no significant trend was measured for regressions conducted for each chemical within each well. Decreasing trends in concentration with time was the predominant response for simazine, ACET, diuron, and bromacil. For example, decreases in simazine concentration with time were measured in 40 of 59 wells, with only one well indicating an increasing trend. As indicated in the pooled analysis, an opposite effect was observed for norflurazon and its breakdown product DMN, where a greater number of wells indicated increases rather than decreases in concentration with time. For norflurazon, concentrations were initially below the RL in seven of the nine wells with significant increases.

The response from the individual trend analyses conducted for NO_3 provided a contrast to the overall pooled curvilinear response. Decreasing trends were measured in 22 wells and increasing trends in nine wells, with all modeled by a linear effect (Table 6). A response similar to the curved response in the pooled data in Fig. 4 was observed in only 10 of the wells. Thus the overall effect was due to the pooling of these mixtures of responses. This contrast in results between the pooled and individual analyses illustrates the wider range in trends that can be measured at the local level, illustrating the importance of understanding the local factors that influence the movement of solutes to aquifers.

Pesticide Use in Relation to Observed Trends in Concentration

Most of the sections of land in this study were regulated as PMZs in 1999 when 42 and 39 sections of land were designated for simazine and diuron, respectively. Comparison of the annual use of simazine, diuron, and norflurazon from 1990 to 2009 provides a clear pattern for preferential use when sections of land were designated PMZs (Fig. 4). Two aspects of the graphs in Fig. 4 are of interest. First, the total amounts of simazine and diuron used are greater in runoff than in leaching GWPAs. This pattern may be associated with the combination of soils and major crops associated within each classification. To avoid potential crop injury, per-acre use rates for the pre-emergent herbicides are lower on coarse-textured soils, typical in leaching GWPAs. Soils in runoff GWPAs are dominated by medium-textured, loamy soils, where a higher rate is permitted. Also, the method of application to grapevines, which is the predominant crop in leaching GWPAs, has evolved from application across an entire furrow bottom and berm to application to the berm

Table 3. Summary statistics for the raw data collected for simazine, its breakdown products ACET and DACT, total simazine residues, diuron, bromacil, norflurazon, its breakdown product DMN, total norflurazon residues, and NO_3 within each groundwater protection area (GWPA) designation. For this initial comparison, data below the reporting limits were assigned a zero value.

GWPA designation	Simazine			ACET			DACT			Total simazine residue			NO_3			Diuron			Bromacil			Norflurazon			DMN			Total norflurazon residue		
	n	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD
	μg/L												mg/L			μg/L														
Leaching GWPA	361	0.08	0.05	400	0.18	0.17	361	0.24	0.21	399	0.48	0.40	369	36.0	31.6	182	0.10	0.13	39	0.09	0.12	117	0.08	0.11	171	0.18	0.21	162	0.23	0.27
Runoff GWPA	402	0.09	0.06	439	0.60	0.43	439	1.13	1.23	452	1.77	1.60	429	61.1	37.2	375	0.24	0.23	322	0.85	1.30	194	0.15	0.24	187	0.22	0.23	196	0.32	0.38

Table 4. Results of PROC NLMIXED statistical analysis using maximum likelihood analysis to measure trends in concentrations of simazine, its breakdown products ACET and DACT, total simazine residue, and NO_3 with time conducted on data pooled from both groundwater protection area (GWPA) designations. In the presence of a significant interaction for DACT, analyses were conducted within each GWPA designation. Otherwise, in addition to the full model, the result from the optimal reduced model excluding interaction terms is also presented for each chemical.

Model specification	Probability Level for Effects				
	Simazine	ACET	DACT	Total simazine	NO_3
Full model testing significance of interaction terms					
GWPA classification	0.91	0.001	0.001	0.001	0.005
Linear	0.52	0.15	0.3	0.3	0.24
Quadratic	0.05	0.69	0.03	0.44	0.04
Linear × GWPA	0.79	0.7	0.09	0.08	0.6
Quadratic × GWPA	0.14	0.55	0.01	0.37	0.3
Reduced model testing significance of main effects					
GWPA classification	–	0.001	–	0.001	0.001
Linear	0.001	0.001	–	0.001	0.03
Quadratic	–	–	–	–	0.001

only. This change was due to the adoption of pressurized drip irrigation systems, where water application is directed onto a smaller area of soil on the berm that supports plant growth.

Second, the pattern of use indicates a sizable reduction in simazine and diuron use between 1998 and 1999 and further reductions between 1999 and 2000, coinciding with the designation of these sections of land as PMZs. In comparison, the use of norflurazon within the same sections of land increased from 1998 to 1999, but after a few years its use also decreased after norflurazon PMZs were designated in 2001. Norflurazon is a substitute for simazine and diuron, so there was an apparent switch in products used from 1999 until regulation of norflurazon in 2001. Only a relatively small number of sections were designated as norflurazon PMZs, but the process of listing the active ingredient as a regulated entity produced a rather large effect on use throughout all regulated areas.

Discussion

The areas where pesticide use is regulated in Fresno and Tulare counties are highly vulnerable to contamination of groundwater by agriculturally applied chemicals. Vulnerability is due to the specific combination of soil characteristics, depth to groundwater, irrigation management practices, and anthropogenic changes in the routes for surface water to recharge the groundwater. Results from the overall trend analysis of pooled data indicated that well water concentrations in the regulated sections of land are trending downward for simazine, diuron, and bromacil. Analysis conducted on data for individual wells confirmed that large proportions of the wells exhibited downward trends, with 68, 66, and 57% of wells reflecting linear decreases in simazine, diuron, and bromacil concentrations, respectively, with time. The downward trends were apparent by the time the regulatory structure was revised in May 2004 (Fig. 2 and 3). Consequently, decreases noted in well water are probably associated with the first regulatory approach when vulnerable areas were denoted as PMZs. The revised regulations require a permit for use issued by the local county agricultural commissioner. The permit contains conditions of pesticide use where, in leaching GWPAs, efficient irrigation management practices are required when irrigation water contacts applied pesticide residues. In runoff GWPAs, management practices focus either on eliminating residues from the runoff water by incorporation into the soil matrix or on managing collection and/or retention of runoff water to prevent contact with sensitive sites that enhance percolation of water into the subsurface soil. Continued monitoring is required to determine if the observed decreases in pesticide concentrations are sustained following implementation of the revised regulatory structure.

Differences in well water concentrations observed between GWPA designations coincided with the reported patterns of agricultural use. Greater amounts of simazine and diuron were used in sections of land located in runoff GWPAs, where concentrations of residues in well water were also greater. Although simazine parent concentrations were equal between GWPA designations, concentrations of both breakdown products were much higher in runoff GWPAs, resulting in greater total simazine residues. The breakdown proceeds from simazine to ACET to DACT (Gunasekara et al., 2007). Averaged concentrations appeared to follow this progression, where stable DACT residues were highest.

In addition to the total amount applied, changes in pesticide use patterns were reflected in the detection pattern for specific herbicide residues in well water. The initial regulatory approach that established PMZs was specific to the pesticide active ingredient detected in that section of land. Simazine- and diuron-specific PMZs were established before the detection of norflurazon residues in well water and its listing as a regulated active ingredient (Table 1). Anecdotal information obtained from training sessions for the implementation of PMZs indicated that one grower response was to use an unregulated product rather than one that was listed with suggested management practices, a pattern confirmed by observations of reported pesticide use data. Norflurazon is a broad-spectrum, pre-emergence herbicide with similar crop uses as simazine and diuron and with the potential to move to the groundwater (Troiano et al., 1999). Regulation of simazine and diuron resulted in enhanced detection of norflurazon and its breakdown product in wells due to the shift in use from regulated to unregulated products.

Trends noted for NO_3 may implicate the adoption of management practices as another factor that results in decreasing trends. Decreases in NO_3 concentrations were observed in

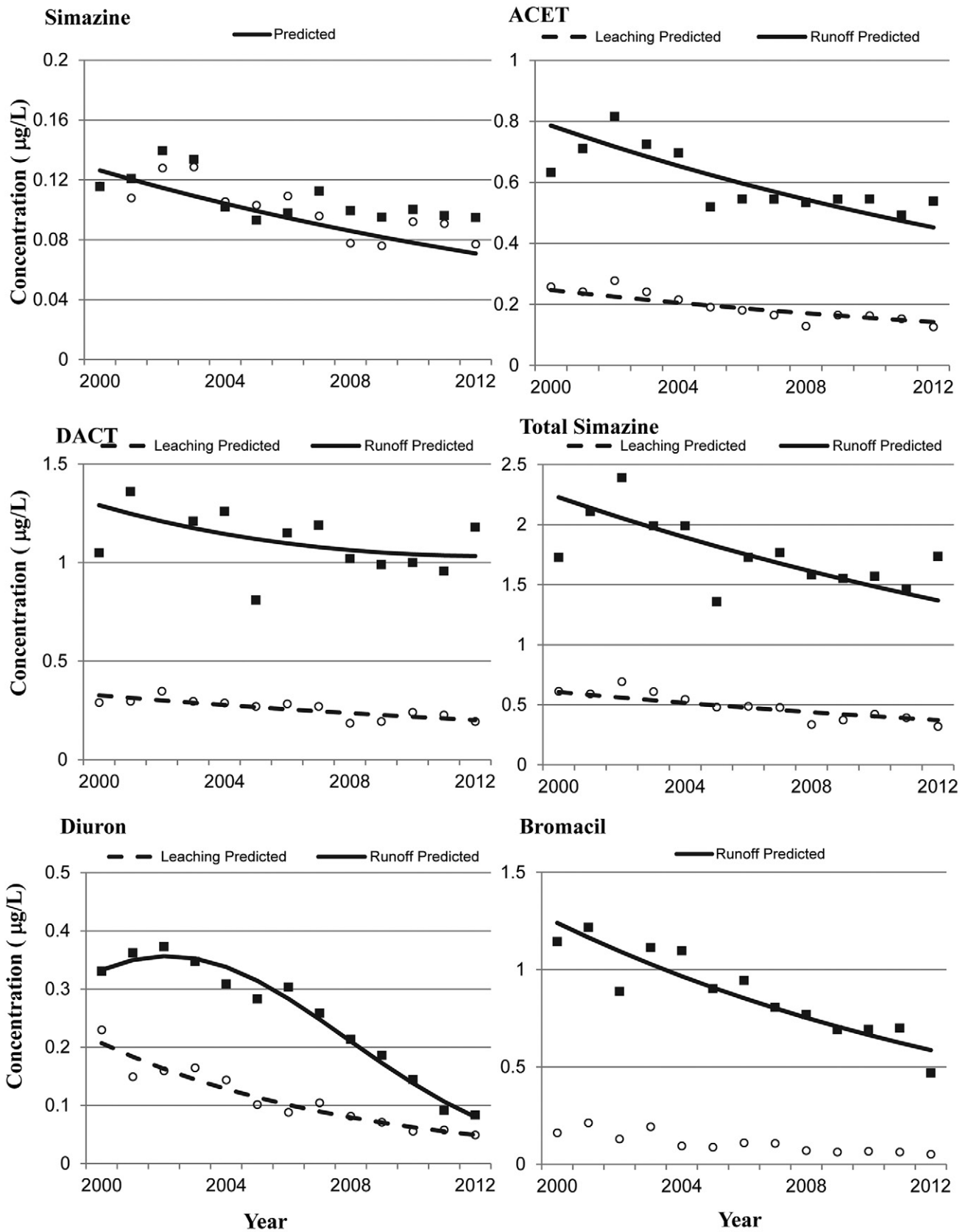

Fig. 2. Comparison of the predicted line to observed mean values for simazine, its breakdown products ACET and DACT, total simazine residue, diuron, and bromacil. The line for simazine is from pooled regression, otherwise open circles and dashed lines represent data for wells located in leaching groundwater protection areas (GWPAs), and filled squares and solid lines represent data for wells located in runoff GWPAs.

Table 5. Results of PROC NLMIXED statistical analysis using maximum likelihood analysis to measure trends in concentration with time for the simazine breakdown product DACT, diuron, bromacil, norflurazon, and its breakdown product DMN. A separate analysis was conducted within each groundwater protection area (GWPA) designation.

GWPA designation and regression term	Probability level for effect				
	DACT	Diuron	Bromacil	Norflurazon	DMN
Leaching GWPAs					
Linear	0.007	0.02	–	0.51	0.88
Quadratic	–	–	–	–	–
Runoff GWPAs					
Linear	0.13	0.001	0.03	0.03	0.1
Quadratic	0.04	0.001	–	–	–

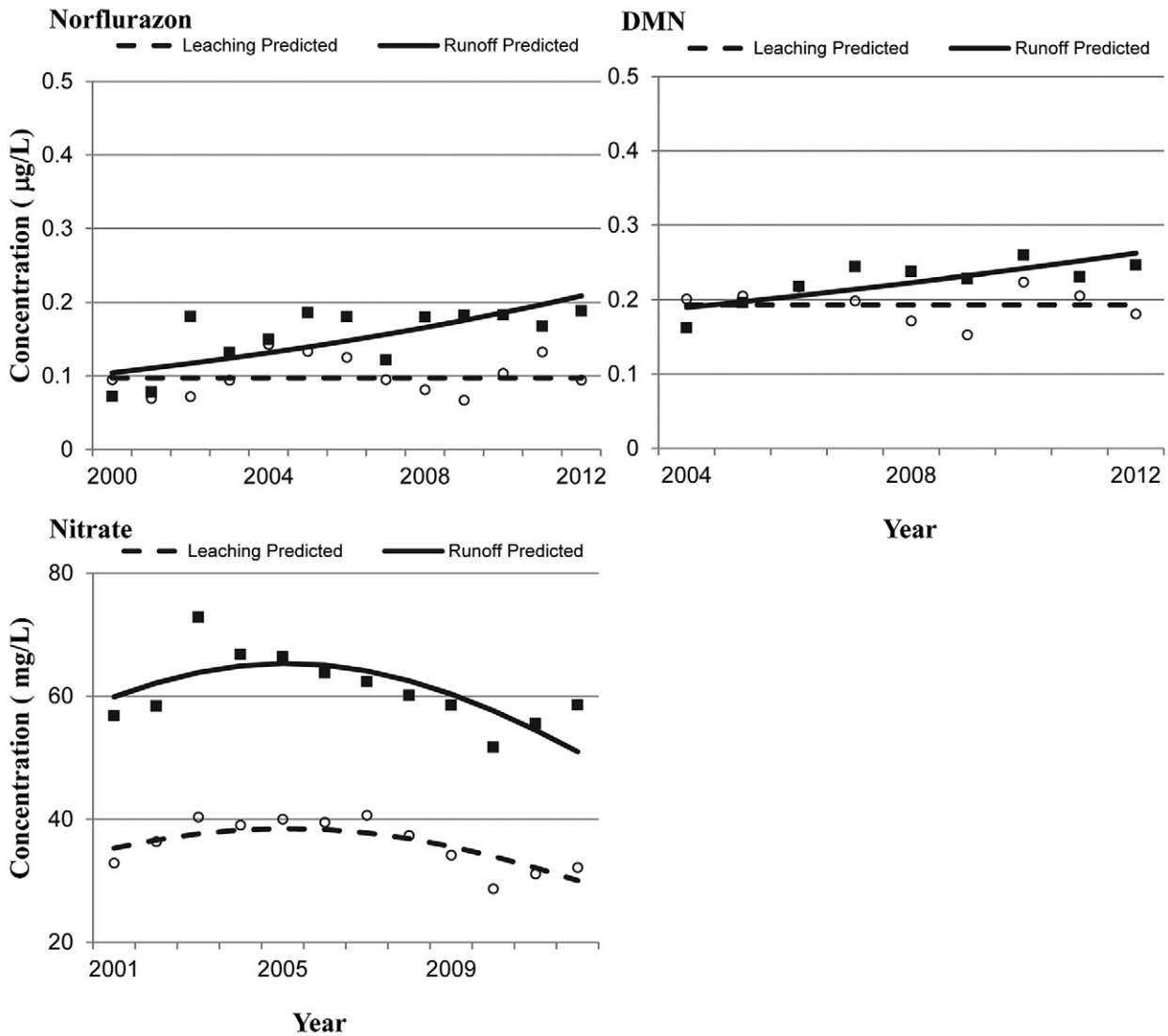

Fig. 3. Comparison of the predicted line to observed mean values for norflurazon, its breakdown product DMN, and NO_3 residues. Open circles and dashed lines represent data for wells located in leaching groundwater protection areas (GWPAs), and filled squares and solid lines represent data for wells located in runoff GWPAs.

approximately 33% of the wells, which coincided with decreases in simazine residues, parent or breakdown products, in all but three of those wells. A previous analysis of N and O isotope ratios for NO_3 residue sampled from these same wells indicated that the source was agricultural-based fertilizers (Suen, 2008). The use of NO_3 is not regulated so there was no impetus for growers to change NO_3 use practices. To continue pesticide use in PMZs, growers were advised to make changes in their management practices, such as implementing more efficient irrigation practices in coarse-textured soils where leaching was predominant or adopting alternative management practices for runoff water that might recharge groundwater if their soils contained a hardpan layer. Pesticide and NO_3 residues follow the same pathway with water as it recharges the groundwater aquifer so their movement should be similarly influenced by changes in grower practices (Burow et al., 1998). The specific response of the growers located near these wells with respect to implementing best management practices or switching use from

Table 6. Count of regression results conducted for residues of simazine, its breakdown products ACET and DACT, total simazine residues, diuron, bromacil, norflurazon, its breakdown product DMN, total norflurazon residues, and NO_3 in each well with respect to measuring significant decreasing or increasing trends or no significant change in concentration with time.

GWPA† designation and trend	Wells with indicated regression result									
	Simazine	ACET	DACT	Total simazine	Diuron	Bromacil	Norflurazon	DMN	Total norflurazon	NO_3
	no.									
Leaching GWPA										
Decrease	21	16	11	18	7	1	0	5	5	13
No change	6	12	13	9	5	1	7	10	10	13
Increase	1	3	4	4	2	1	2	3	3	5
Total	28	31	28	31	14	3	9	18	18	31
Runoff GWPA										
Decrease	19	21	9	15	22	15	2	1	1	9
No change	12	11	23	19	6	7	6	12	9	23
Increase	0	2	2	1	2	3	7	8	14	4
Total	31	34	34	35	30	25	15	21	24	36
All wells										
Decrease	40	37	20	33	29	16	2	6	6	22
No change	18	23	36	28	11	8	13	22	19	36
Increase	1	5	6	5	4	4	9	11	17	9
Total	59	65	62	66	44	28	24	39	42	67

† GWPA, groundwater protection area.

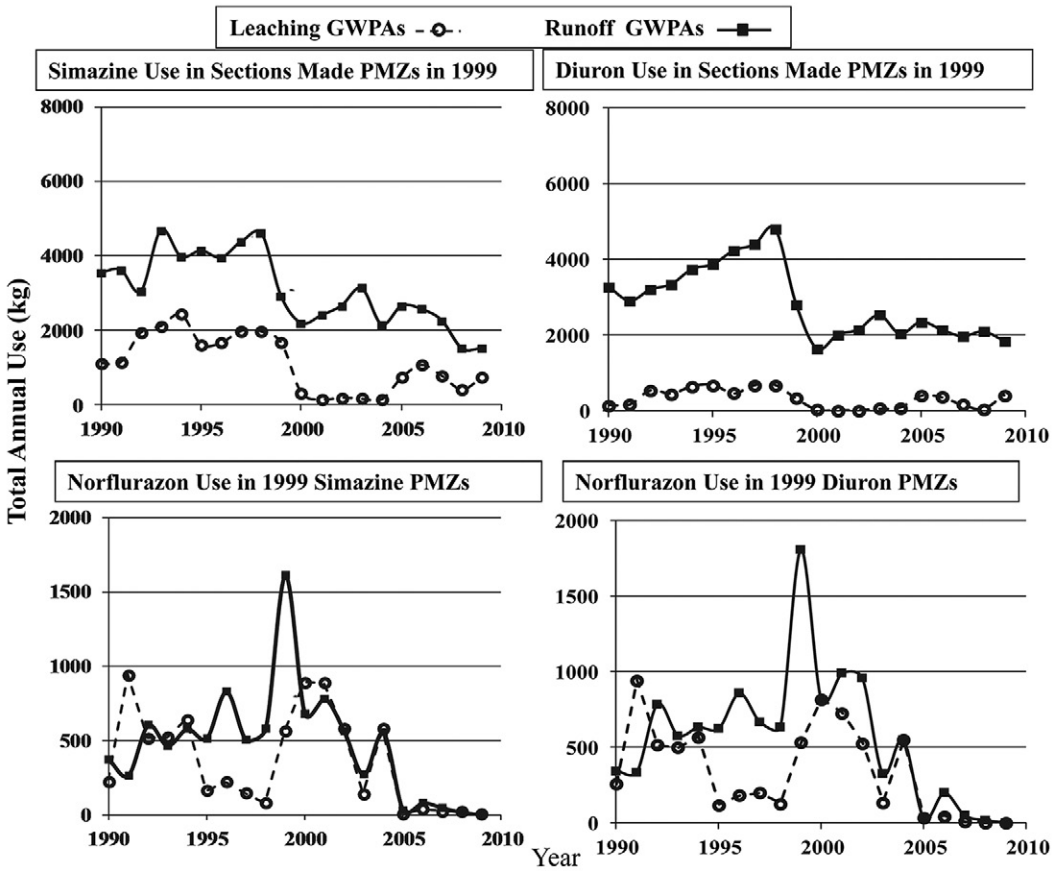

Fig. 4. Total annual crop use for applications of simazine and diuron summed from 1990 through 2009 for sections of land in the domestic well network that were denoted pesticide management zones (PMZs) in 1999. The pattern of norflurazon use is compared in the corresponding sections. Open circles and dashed lines represent data for leaching groundwater protection areas (GWPAs) and filled squares and solid lines represent data for runoff GWPAs.

regulated to unregulated products has not yet been investigated. Observed decreases in concentration are probably due to a mix in responses because the pesticide use data implicate changes in the pattern of products used but anecdotal information on irrigation practices indicates adoption of more efficient water management methods. Understanding the exact relationship between changes

in surface management practices and loading of solutes to these groundwater aquifers requires further investigation on specific grower practices and pesticide use patterns around these domestic wells.

The relation of the temporal changes in pesticide use and trends in pesticide concentration in well water infers a relatively short period of time for changes in surface activity to be measured in well water concentrations. The range of values measured in the age-dating study by Spurlock et al. (2000) also indicated short time intervals for the movement of surface-applied residues to appear in domestic drinking water wells. Studies by the USGS have determined the age of water sampled from dedicated monitoring wells installed in these and other vulnerable areas of the San Joaquin Valley (Burow et al., 1999; Domagalski et al., 2008; Jurgens et al., 2008). As expected, the estimated age of the sampled water increased with well depth. In one study area, the age of recharge water was >10 yr when the groundwater depth was >30 m; in a second study area, the age of recharge water was >10 yr when the groundwater depth was >20 m. The median depth of the domestic wells in our study was 40 m, so based on the results from dedicated monitoring wells, recharge would be expected to be >10 yr. Construction details of domestic wells could explain the faster than expected response time. The length of the perforated interval was >10 m in 10 of the 39 wells with well logs. Large perforation lengths would enhance vertical mixing of water. Another feature that could enhance mixing is the presence of a conductive gravel pack around the well. The length of the gravel pack was much greater than the perforation length, with a median length at 34 m. The gravel pack extended the entire length of the well in six of the wells. Based on mathematical modeling, Horn and Harter (2009) concluded that gravel packing around domestic wells facilitates some mixing of water between shallow and deeper aquifers, resulting in an increased risk for contamination. The opposite then would also be possible, where the adoption of mitigation measures, as reflected in cleaner recharge water, would appear faster than expected. If these construction characteristics play a role in accelerating changes in solute concentration at the well, then their effects need to be included when modeling the transport of surface-applied solutes to domestic drinking water wells. We are currently investigating site-specific aspects of water movement for a subset of these wells through a cooperative study with the USGS to apply updated age-dating methodology to estimate the distribution of water ages in a subset of the wells in this network.

Conclusions

Annual monitoring of domestic wells commenced in Fresno and Tulare counties in California in 1999, with the goal of linking potential trends in pesticide well water concentrations to regulations enacted by the DPR to mitigate pesticide movement to the groundwater. Downward trends in concentrations with time were measured for wells that initially contained residues of simazine, ACET, diuron, and bromacil, indicating an effect of the initial regulatory approach. The regulatory approach used by the DPR was modified in 2004, so continued monitoring is needed to determine if the measured trends are sustained by the new approach. One potential cause for the downward trends was a change in pesticide use patterns, where growers switched use from a regulated to an unregulated product. However, growers have been adopting better management practices, such as improving irrigation efficiencies that minimize the percolation of water. Additional studies will be conducted to investigate links between actual implementation of management practices as specified in the regulations and results from individual wells.

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