DETECTION OF ATRAZINE, SIMAZINE, AND THEIR BREAKDOWN PRODUCTS IN PUBLIC WATER SUPPLY WELLS

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ABSTRACT

Atrazine and simazine are pre-emergence herbicides that are known to contaminate ground water from normal agricultural use. According to a recent U.S. Environmental Protection Agency (EPA) re-registration eligibility decision for atrazine, the breakdown products of atrazine and simazine were determined to be as toxic as the parent chemical. Consequently, EPA concluded that the concentrations of parent and breakdown triazine residues in a well sample should be summed and that value compared to established health standards. Atrazine, simazine, and their breakdown products have been frequently detected in wells sampled by the Environmental Monitoring Branch, Department of Pesticide Regulation (DPR), California EPA. Most wells sampled by DPR staff were domestic, single family wells but some small public water supply (PWS) wells have also been sampled and found to contain triazine residues. The California Department of Public Health (CDPH) requires public water agencies to include atrazine and simazine in their sampling schedule because they are state and federally regulated potential contaminants. Public water agencies are not required to sample for the triazine breakdown products because they have not yet been included in established health standards. DPR conducted this study to compare the presence of parent atrazine and simazine residues to breakdown product residues in PWS wells. DPR sampled PWS wells that had previous detections of dibromochloropropane (DBCP) in areas of high simazine use. DBCP is a banned agricultural soil fumigant that was widely detected in drinking water wells beginning in 1977. Residues of atrazine, simazine, or their breakdown products deethyl-atrazine (DEA), deethyl-simazine (ACET), or diamino chlorotriazine (DACT) were detected in 15 of 49 PWS wells sampled in eastern Fresno and Tulare Counties. Parent residues were present in 3 of the 15 wells whereas the breakdown products were detected in all of the 15 wells. When compared to previous results from domestic wells, the breakdown products occurred more frequently in the absence of parent chemical in the PWS wells. The higher detection frequency is likely due to the deeper depth of PWS wells in comparison to domestic wells. The greater travel time for residues to reach these water supply wells facilitates conversion of the parent to breakdown products. With respect to established health standards for triazine herbicides, the total residue detected in each well was below California's current atrazine maximum contaminant level (MCL) of one microgram per liter (μg/L). Although this study surveyed only a small sample of the PWS wells in the Fresno and Tulare county area, factors that contributed to a greater chance of detecting residues in a well were location in areas with greater reported use of simazine, previous detection of DBCP at relatively high concentrations, and sampling of PWS wells that were shallower in total borehole depth. Sampling over time will be required to establish potential temporal trends in concentrations, especially with respect to the concentration of the breakdown products.

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DISCLAIMER

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INTRODUCTION

The U.S. EPA completed an intermediate registration eligibility decision for atrazine in 2003 (U.S. EPA, 2003a and b). Atrazine is a widely used pre-emergence herbicide. In that decision, U.S. EPA determined that toxicity of the chlorinated breakdown products was equivalent to the parent chemicals. Owing to the similarity in toxicity, the U.S. EPA recommended summing the concentrations of all detected triazine residues in a water sample and comparing the summed value to established health standards. Federal and state drinking water standards only apply to individual triazine herbicide parent compounds. To regulate triazine residues collectively, including breakdown products, requires formal rulemaking by either the U. S. EPA or the CDPH. Inclusion of pesticide breakdown products in a health level is not unprecedented. For example, aldicarb and its breakdown products, aldicarb sulfoxide and aldicarb sulfone, each have an MCL of three, four, and two μg/L, respectively. When detected in any combination in a water sample, the MCL is 7 μg/L because of similar modes of action (U.S. EPA, 2006). Troiano and Nordmark (2002) analyzed the concentration distribution of total triazine residues detected in previous California well water samples and compared the results to California MCLs for atrazine and simazine. Total triazine residues include the parent compounds and their degradation products: deethyl-atrazine (DEA), deethyl-simazine (ACET), and diamino chlorotriazine (DACT). The degradation of atrazine and simazine produces common breakdown products (Figure 1). ACET is the first product formed upon degradation of either atrazine or simazine parent products. Further degradation of ACET produces DACT. DACT can also be produced through the degradation of DEA, which is another breakdown product of atrazine. Well data analyzed by Troiano and Nordmark were mostly derived from sampling of shallow domestic wells where 131 wells had detections of triazine residues. Although the concentrations of atrazine and simazine did not exceed their respective MCLs of one μg/L and four μg/L, respectively, the total triazine residues exceeded the MCL for atrazine, 1 μg/L, in approximately 31% of the wells and the MCL for simazine, 4 μg/L, in 5% of the wells.

DPR samples drinking water wells to monitor the spatial distribution and the concentration of pesticide residues in California's ground water (Schuette et al., 2005). These studies are targeted to areas of high pesticide use or to areas where pesticide residues had previously been reported in well water samples. DPR's monitoring program focuses on domestic wells because they draw water from shallow ground water aquifers where the probability of contamination is greatest. In contrast, data reported to DPR by CDPH are from samples taken from PWS wells. Since these wells require a higher yield of water to supply a larger population, they are drilled deeper than domestic wells to draw water from deeper aquifers. Screened areas within PWS wells can also be larger so water is also collected throughout the screened distance. Since deeper aquifer water is older than water in shallow aquifers, contamination is assumed to be less likely in PWS wells than in domestic wells. Thus, data obtained from domestic wells that draw water from shallower aquifers and from a narrower range of aquifers may not be representative of the potential detection frequency and concentration in PWS wells. Since July 1996, data submitted to DPR by CDPH contained no atrazine detections and only two wells were reported with simazine residues. In addition, reporting limits (lowest detectable concentrations) for chemical analyses required by CDPH are higher than for DPR well sampling studies. For example, CDPH reporting limits are 0.5 μg/L for atrazine and 1.0 μg/L for simazine whereas the DPR reporting limit is lower at 0.05 μg/L for both chemicals. Lastly, the triazine breakdown products are not included in the standard chemical analysis required by CDPH for PWS wells.

Pre-emergence herbicide residues, such as atrazine and simazine, have been detected in wells sampled throughout a large contiguous area in Fresno and Tulare Counties (Troiano et. al., 2001). DPR well sampling has occasionally included PWS wells, but usually only when shallow, domestic wells were not available to accomplish the required monitoring, or in response to a reported detection of pesticide residues in a PWS well. Prior to this study, data in DPR's well inventory data base indicated that DPR well sampling resulted in the detection of triazine parent and breakdown products in 7 of 19 PWS wells sampled in Fresno, Tulare, and Kern counties. Three PWS wells sampled by DPR in the Sanger area contained simazine and DEA or ACET residues. DACT was not reported because the samples were taken prior to its inclusion on the chemical analytical screen in 1996. Two of these three wells were also reported by CDPH to contain dibromochloropropane (DBCP) residues as recently as 2003. CDPH continues to detect DBCP in numerous wells throughout the state even though DBCP use was banned in California in the late 1970's. California growers used DBCP as a soil fumigant for nematode control in vineyards, orchards, and annual crops and its use resulted in widespread contamination of ground water in both domestic and PWS wells.

The primary objectives of this study were to sample for the parent and breakdown products of atrazine and simazine residues in PWS systems that draw from deeper ground water aquifers, and to compare to the PWS detection frequency and concentrations to historical results for domestic wells. PWS wells were selected that had a recent history of DBCP contamination because presence of DBCP residues indicated impacts from agricultural sources. In addition, the candidate PWS wells were located in areas where simazine had been used and where triazine residues had been previously detected in nearby wells. Another study objective was to correlate detections in the PWS wells with the factors used to identify sampling locations.

MATERIALS AND METHODS

Study Area

The study area encompassed central Fresno County through northern Kern County (Figure 2). The study area is underlain with a shallow ground water aquifer that is vulnerable to contamination (Troiano et al., 2000; Marade and Troiano, 2003). Previous DBCP sampling indicated its presence in both domestic and PWS wells throughout the study area (Figure 2). Simazine is used on many crops (Table 1) and has been found, in addition to its breakdown products, in numerous domestic wells in the study area (Figure 3).

Well Selection

PWS wells were chosen for sampling based on three criteria:

1. Previous report of DBCP detection by CDPH since 2000.
2. Proximity to wells with previous detections of triazine residues.
3. Amount of cumulative simazine use, 1993─2002, in surrounding sections of land.

The presence of DBCP was chosen as an indicator that the well could be impacted by the application of agricultural chemicals. Total simazine use was determined for the period 1993─2003 for each section of land in which a PWS well was located and for the eight surrounding sections. A section of land is approximately a 1-mile square area as defined by the Public Land Survey coordinate system (Davis and Foote, 1966). Pesticide use is reported to DPR by section location.

Based on cumulative simazine reports from 1993─2002, use occurred throughout the study area with heaviest applications located along the eastern boundary (Figure 2). Atrazine is used primarily on corn and soybeans. Since these crops are not predominant in the study area, atrazine use for the same period was low. Even though reported use was low, several wells with atrazine residue have been reported in the study area. Since 1985, DPR has detected triazine residues in over 500 wells in this area. Since 2000, CDPH has reported detections of DBCP residues in 200 PWS wells in this same area.

DPR contacted well operators to seek permission to sample from targeted wells. If a selected well was unavailable, another well, situated nearby, was substituted. In a few cases, the substituted well did not have a reported detection of DBCP. Information for each sampled well was recorded from documents provided by the well operator when possible or from verbal statements from the owner or representative providing access to the well. We sought the depth-to-water, borehole depth, pumping depth, casing perforations, and screened intervals for each well. Some information was obtained for all wells. However, not all wells provided the full set of information. We were able to obtain the borehole depth for all but one of the wells (L08). Depth for well L08 was estimated based on the depths of nearby municipal wells with similar levels of water pumping. Additional information was taken from sampling staff observations and measurements including casing size and the condition of the well pad and seal.

Well Sampling

Wells were sampled according to the standard DPR well sampling protocols (Marade, 1996; Marade, 1998). Most of the wells were operational and had been running prior to the time of sampling. However, some wells were not operational (L06, L12, L34, L21, L22) due to known water contamination. These wells were kept in reserve by water purveyors for emergencies or until a suitable source of mixing water was operational, such as another well with no DBCP contamination. Most wells had a faucet on the discharge pipe for collecting samples prior to any water treatment. One primary sample, two backup samples and one field blank were collected from each well in one-liter amber bottles. Samples were stored on wet ice for transport and were refrigerated until analysis.

This study was conducted in two phases. The initial phase began in early October 2004 when 12 wells were sampled. Wells for this first phase were selected from a graphical overlay of sectional use for simazine and location of PWS wells with previous DBCP detections. Well sampling sites were visually selected from areas of overlap of the greatest magnitude for each variable. Results from these 12 wells had a high number of detections so a second phase of sampling (Phase II) was conducted. The sites chosen for sampling were not restricted to the overlap of the greatest magnitude of each variable. Phase II was conducted from November through December 2004.

Chemical Analysis and Quality Control

The Center for Analytical Chemistry, Environmental Monitoring Section, California Department of Food and Agriculture (CDFA) (Sacramento, CA) performed the laboratory analyses. The laboratory method was originally developed by ALTA Analytical Laboratory (El Dorado Hills, CA) in 1993 to provide simultaneous measurement for selective triazine parent and breakdown products but it also included analysis of other herbicide residues. CDFA's method utilized liquid chromatography for separation that was coupled to an atmospheric pressure chemical ionization, ion trap tandem mass spectrometer (APCI/MS/MS) for detection. The method is CDPR reference number 245 and it is available upon request. The method measures concentrations in well water for atrazine, simazine and their breakdown products DEA, ACET, and DACT. Additional pesticides included in the method were diuron, prometon, bromacil, hexazinone, norflurazon, and the norflurazon breakdown product, desmethyl norflurazon. The reporting limit was 0.05 μg/L for all analytes.

Quality control (QC) was conducted according to the standard operating procedure for chemistry laboratory quality control (Segawa, 1995). When pesticide residue was detected in a primary sample, the corresponding field blank was submitted for analysis. None of the field blank samples submitted contained detectable residues. Samples containing known amounts of pesticides were disguised as field samples (blind spiked samples) and they were randomly submitted to the laboratory. Except for the DEA blind spike sample on November 8, all recoveries were within their respective control limits (Table 2). The DEA result exceeded the upper warning limit (UWL).

Continuing QC was based on a set of duplicate laboratory-spiked samples included with each extraction set (Table 3). All analytes in these samples were spiked at 0.2 μg/L and subjected to the extraction procedure. Some of the analyses exceeded the UWL with a few sporadic exceedances of the upper control limit. When these values are exceeded the laboratory is to evaluate the accuracy of the results and the need for adjusting the procedure.

Data Analysis

The data analysis for this report was generated using SAS/STAT® software, Version 9.1 of the SAS System for Windows 5.0. Copyright (c) 2002-2003 by SAS Institute Inc. SAS and all other SAS Institute Inc. product or service names are registered trademarks or trademarks of SAS Institute Inc., Cary, NC.

Since simazine applications and detections dominated the data, statistical analysis focused on the relationship between explanatory variables and the detection of simazine or its breakdown products ACET or DACT. The explanatory variables were the two used to select sampling sites, which were cumulative simazine use in the sampled section and eight surrounding sections and the maximum concentration of DBCP previously reported in a PWS well. Two additional potential explanatory variables were derived after sampling. One was the borehole depth of the PWS well that was obtained during sampling and the other was the average depth to ground water in the section in which the well was sampled. The depth to ground water is a variable that was derived for the determination of vulnerable areas in California (Spurlock, 2000; Troiano et. al, 2000).

All variables were tested for conformity to assumptions of normality using PROC CAPABILITY. For each variable, this procedure reports simple statistics, histograms of the distribution, and four tests of fit for normality assumption, which are Shapiro-Wilk W statistic, Kolmogorov-Smirnov D statistic, Cramer-von Mises W-sq statistic, and Anderson-Darling A-sq statistic. All statistics indicated the distributions were not normally distributed, which was due to numerous values at or below the reporting limit coupled with the presence of tailing caused by sporadic high values. Due to the lack of normality, nonparametric analysis was conducted. Analyses for detections of simazine and its breakdown products were conducted with the detections derived as a binary variable where wells were assigned a value of one when a well sample contained detections of simazine, ACET, or DACT, otherwise they were assigned a 0 value. For the binary categorical analysis, the PROC LOGISTIC procedure was used with the model selection option of score. This option uses the branch and bound algorithm of Furnival and Wilson (1974) to find a specified number of models with the highest likelihood score (Chi-square) statistic for all possible model sizes, from 1, 2, and 3 effect models, and so on, up to the single model containing all of the explanatory effects.

RESULTS

Residues in PWS Wells

In the initial sampling conducted in October 2004, 12 PWS wells were sampled that were located in the areas of highest simazine use and where DBCP was measured in the PWS well (Figure 2). These wells are labeled as L01 through L12 in the Tables. Ten of the wells contained pesticide residues: Simazine was detected in two wells; DACT was detected in ten wells; ACET was detected in eight wells; bromacil was detected in five wells; and diuron was detected in four wells (Table 4). Atrazine and DEA residues were detected in one well (L4) that had previously been sampled by DPR in 1994 and found to contain atrazine and DEA residues. Eight of the ten wells had three or more residues of various combinations of parent and breakdown products.

The high pesticide detection rate during the first phase of this study at 83% of sampled wells prompted a second phase in which an additional 37 PWS wells were sampled during November and December 2004. These wells are identified as L13 through L49 in the tables. Triazine residues were detected in five of these wells. DACT was found in four wells and ACET in three wells (Table 4). Diuron residues were found in two wells and bromacil in one well. Three well samples had two pesticide residues present. The rate of detection in this second phase was lower than in the initial sampling and may be due to targeting of wells in areas with lower pesticide use and lower maximum DBCP concentrations.

Overall, 17 (35%) of the 49 wells sampled contained pesticide residues. With respect to triazine residues, parent residues were detected in 3 (6%) of the 49 wells, whereas, the breakdown products were detected in 15 (31%) wells. With respect to the pattern of detection of breakdown products in relation to parent chemical, DEA is a major breakdown product that is associated with atrazine and not simazine (Figure 1). DEA was only found in the well where atrazine was detected. ACET and DACT are also breakdown products of atrazine and they were detected in that well. ACET and DACT were detected in both wells that contained the parent simazine with no associated detection of DEA. Since the remaining wells that contained ACET, DACT or both had no DEA residues, this pattern indicated that the source was from application of simazine, the predominant triazine herbicide applied in this geographical area.

The relationship between raw ACET and DACT concentrations in well water is illustrated in Figure 4A. There were three wells that contained only DACT residues and two wells that contained only ACET residue. In the ten remaining wells where both residues were measured, the concentrations were highly correlated but with a slight bias towards higher DACT concentrations. Since DACT is a further breakdown product of ACET, its molecular weight is lower at 145.7 g/mol as compared ACET at 173.7 g/mol. When DACT concentrations were corrected to represent a molar comparison, the comparative values fall more closely to the 1:1 line (Figure 4B). Comparisons based on the molecular relationships could be important when attempting to derive specific travel times to ground water and when deriving hypothesis to explain differences in concentration.

With respect to comparisons to current health levels, all individual atrazine and simazine concentrations and the summed values for all triazine residues in each well sample were below California's MCL of 1.0 μg/L for atrazine.

Relationship of Detections to Explanatory Variables

DPR selected PWS wells for sampling based on the total cumulative reported simazine use for the section containing the PWS well and the eight surrounding sections, and on previous detection of DBCP in the wells. During sampling, the borehole depth of the PWS well sampled was obtained from the well operators and the average sectional depth to ground water was obtained from previous determination of vulnerable areas of California. Scatter plots of each explanatory variable against the total simazine residue (TSR) in a well are illustrated in Figure 5. TSR was determined as the addition of simazine, ACET, and DACT residues in each well sample. For each of the plots, there are low to nondetections throughout the range of each explanatory variable. Logistic regression analysis was conducted to determine the relative contribution of each variable to occurrence of detections. The data set used in the SAS procedures to relate the explanatory variables to the TSR detections is given in Table 5 where for computing purposes non-detected values were assigned a 0 value.

Table 6 gives the chi-square values sorted by magnitude for each model at 1 through 4 variable combinations. Table 7 contains the solution for the model with the highest chi-square value at each of the 1 through 4 variable combinations. The chi-square value for each of the best models was significant. The two-variable combination of borehole depth of the PWS well and cumulative simazine use increased the chi-square value by nearly two-fold when compared to the best single-variable model, with shallower borehole depth and higher simazine use correlated with more frequent detections. The 3-variable model added the term for the maximum DBCP concentration in a PWS well. Addition of DBCP concentration increased the significance level for simazine application from $p=0.07$ to $p=0.02$, with higher DBCP concentrations correlated with more frequent detections (Table 7). For the 1-variable model with PWS borehole depth, the rate of concordant predictions, which measures the agreement between the model estimate and observed data, was relatively high at 71%. This value increased to 79% for the 2-variable model and to 83% for the 3-variable model (Table 8). The full 4-variable model provided no further increase in concordant percentage, indicating that depth to ground water did not correlate with detections. Criteria that judged the performance of the model fit in relation to the number of variables are provided in Table 8, where AIC is the Akaike Information Criterion, SC is the Schwarz Criterion, and –2 Log L is the –2 Log Likelihood criterion. The AIC and SC provide two methods to adjust the –2 Log L for the number of terms in the model and the number of observations used. Lower values of each statistic indicate a more desirable model. The 3-variable model provided the lowest AIC and SC criterion values.

DISCUSSION

The first objective was to determine the presence and concentration of triazine residues in PWS systems that typically draw from deep ground water aquifers. Triazine residues were detected in 15 of 49 PWS wells sampled. Three wells contained residues for the parent atrazine and simazine chemicals, whereas, all 15 of the wells contained residues of the breakdown products. In a previous analysis of the distribution of triazine residues in wells with samples taken from predominantly shallow, domestic wells, Troiano and Nordmark (2002) reported detection of parent simazine in 77% (75 of 98) of wells that contained residues for simazine, ACET, and/or DACT. Although the sample size for positive wells was lower for the deeper PWS wells, the frequency for detection of parent was lower at only 20% (3 of 15) of wells with detections. This comparison indicates a lower probability for detecting parent residues in relation to breakdown products in PWS wells. Spurlock et al. (2000) used a chlorofluorocarbon technique to provide an estimate of the travel time for residues to reach domestic wells after pesticide application to the surface. The estimated median travel time was 7 to 9 years for wells drawing water from shallow aquifer depths that were located from 15 to 80 feet below the surface. The screened intervals for PWS wells in this survey were deeper than the wells reported by Spurlock et al. (2000). Thus, the longer travel time for recharge water to reach the well facilitates the complete conversion of parent chemical into breakdown products.

The current California MCL for atrazine is 1 μg/L. When all triazine residue concentrations were added together for each well sample, none exceeded MCL. This study only provided a snapshot of potential concentrations; it did not provide any indication of decreasing or increasing trends in concentration. PWS wells tap water from a broad distance mixing water from a number of aquifers so concentrations could remain below MCL due to mixing of water from many aquifers. On the other hand, water migrating from the shallower contaminated aquifers could be a source of contamination to the deeper aquifers and result in increased concentrations in PWS wells. Monitoring of these wells over time will determine if the potential for contamination is increasing over time.

A second objective was to affirm the usefulness of spatial information in identifying sampling sites with a higher probability for detection of residues. Identifying the areas of highest overlap between simazine applications and a history of DBCP detections in a PWS well resulted in a high rate of detection for the first 12 wells sampled: residues were detected in 83% (10 of 12) of the wells sampled in this first cut. In the second phase, the sampling sites included more variability in the amount of simazine applied and the historical DBCP concentrations detected which resulted in a much lower rate of detection with residues detected in 14% (5 of 37) of these additional wells. This result qualitatively indicated that the frequency of detection was affected as lower values of simazine use and DBCP concentration were included in order to provide for a greater number of sampling sites in Phase II.

In addition to the two variables used to locate sampling sites, logistic regression analysis also identified borehole depth of the PWS well as another significant explanatory factor. The coefficients for the 3-variable model logically agreed with known processes whereby detections increased as simazine use and DBCP concentration increased, and detections decreased as borehole depths became deeper. The model was additive in nature but low values of one of the explanatory variables did not preclude a determination of non-detection. For example, even though well L11 had a relatively low maximum value for DBCP concentration at 0.04 µg/L, the borehole depth was shallow and the cumulative application of simazine was moderate (Table 6). Well L11 was predicted in the detection category and it did contain residues. Well L02, on the other hand, had a high maximum DBCP concentration at 3.3 µg/L and a relatively shallow borehole, but the total cumulative application of simazine was low. This combination again predicted detection in that well and the well did contain residues. With respect to the practical application of these results, data for pesticide use and previous information on pesticide detections are available for pre-diagnosis of areas to sample. In contrast, data for the borehole depth of the well may not be known prior to sampling. However, this data, when available, would be an important addition to locating potential sampling sites with a high probability for detection.

Six wells sampled for this study had previously been sampled in 1992 or 1994 by DPR (L04, L09, L11, L19, L20, and L24) and they provide a comparison to the results of this survey. Data are comparable because the reporting limits were the same at 0.05 µg/L for each chemical. For three of the wells, L19, L20, and L24, none had detections at the previous sampling and, similarly, residues were not detected in this study. Based on the results of this study, these wells were located in areas where detection probability was low due to deeper boreholes and relatively low cumulative simazine use.

In contrast, the location of Wells L04, L09, and L11 were projected to be in areas of higher probability for detection. Residues were not previously detected in wells L09 and L11, but in this study, well L09 contained bromacil at 0.05 µg/L, ACET at 0.09 µg/L, and DACT at 0.16 µg/L. The bromacil detection is at the previous reporting limit. Neither ACET nor DACT were included in the analysis screen in the previous sampling in 1994 so this data is ambiguous regarding changes over time. For well L11, diuron was detected at 0.10 µg/L and simazine at 0.12 µg/L, indicating appearance of residues over time. Lastly, the previous sampling of Well L04 indicated atrazine at 0.12 µg/L, DEA at 0.11 µg/L, and simazine below the detection limit. Fourteen years later in this current study, the levels were similar with atrazine at 0.1 µg/L, DEA higher at 0.2 µg/L, and simazine still undetected. The consistency in detection of the atrazine residues over the 14-year period indicates the potential longevity of residues once they contaminate ground water. Data for well L11 could indicate a trend for increasing concentrations, but more monitoring data would be required to provide an adequate basis for determining long-term trends in pesticide concentrations.

CONCLUSIONS

1. Atrazine, simazine, and their breakdown products DEA, ACET, and DACT were detected in public water supply wells sampled in Fresno and Tulare counties.
2. Breakdown products were detected more frequently and in higher concentration than the parent residues, indicating that the greater travel time to ground water allowed for conversion from parent chemicals. In light of the similar toxicity of the breakdown products, they should be included in the normal sampling procedures associated with PWS wells.
3. When compared to concentrations measured in shallower domestic wells, the concentration of total triazine residues in these PWS samples was below the established California atrazine MCL at 1 μg/L. This sampling provided only a snapshot of the concentrations in wells so additional sampling over time will determine whether or not there is a tendency for the concentrations to increase over time as the shallower contaminated ground water eventually recharges the deeper aquifers.
4. Spatial data on the magnitude of pesticide use and on the concentration of previous DBCP detections in a well proved to be effective explanatory variables for selecting sampling locations that resulted in a higher frequency of pesticide detections. The observed depth of the PWS well, which was obtained after the sampling, was also shown to provide additional information. If known, well depth could be added as another factor to maximize the probability of detecting residues.

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TABLES

Table 1. Summary of the total use of simazine summed from 1993 to 2002 for the top five counties in California, the number of PWS wells containing DBCP residues, and the number of wells sampled by DPR with residues of simazine or its breakdown products ACET or DACT.

County	Cumulative Simazine Use for 1993-2002	Public Water Wells with Reported DBCP Levels Since 1990.	DPR Sampled Wells with Simazine or Breakdown Produce Residues Since 1990
	---------lbs a.i------	---------------------#	-----------------------
Tulare	1,856,705	95	226
Fresno	1,398,145	252	179
Kern	788,285	65	8
San Joaquin	529,548	51	32
Madera	517,840	8	7

Table 2. Analytical results for upper control limit (UCL), upper warning limit (UWL), lower warning limit (LWL), and lower control limit (LCL) and selected blind spiked samples submitted to the laboratory. Blind samples were randomly submitted during the study at varied spike levels.

Chemical	UCL	UWL	LWL	LCL	Spike Level	Analysis Date	Percent Recovery
	--------------------%---------------------				--µg/L--		---%---
Atrazine	101	93.7	66	58.5	0.15	11/10/2004	98.7
Simazine	111	101	64.5	55.3	0.20	11/8/2004	102.0
Diuron	117	108	69.2	59.6	0.35	11/8/2004	92.0
Prometon	107	98.4	62.8	53.9			
Bromacil	126	117	79.5	70.2	0.25	11/10/2004	86.4
Hexazinone	112	106	84	78.5			
Norflurazon	111	104	76.3	69.3			
DEA	112	104	71	62.9	0.40	11/8/2004	109.0
ACET	120	111	73.5	64.2	0.20	11/10/2004	107.0
DACT	130	117	64.7	51.6	0.25	11/8/2004	99.6
DMN	118	111	84.7	78	0.15	11/8/2004	99.3
Propazine Surrogate	104	97.4	69.4	62.4			

Table 3. Results for continuing duplicate spiked samples added with each extraction set. Each analyte was spiked at 0.2 µg/L.

		% Recovery For:											
Date Extracted	Spike #	ATRAZINE	SIMAZINE	DIURON	PROMETON	BROMACIL	HEXAZINONE	NORFLURAZON	DEA (DEETHYL)	ACET (DEISO)	DACT	Desmethyl Norflurazon	Propazine Surrogate
8/27/2004	1	84.5	85	79	83.5	88	100	93.5	98	87.5	85	83.5	79
	2	82.5	82.5	85	84.5	86.5	98.5	96	102	84.5	82.5	78	79.5
8/27/2004	1	94.5	92.5	105	93.5	97	103	104	103	95.5	86	94.5	84.5
	2	89.5	90.5	95	92	97.5	101	104	102	93	86	101	87
9/9/2005	1	99	103	101	102	106	107	101	106	96.5	89.5	100	102
	2	92.5	98.5	96	93.5	103	101	109	100	99	89	109	96
9/10/2005	1	77.5	78.5	81	78	83.5	94	91	85	86.5	84	81	77.5
	2	82.5	79.5	89.5	83.5	87	95	95	85	86	88	93	78.5
10/12/2004	1	102	106	106	100	110	100	110	105	104	97.5	107	96
	2	95.5	99.5	98.5	95.5	100	100	103	101	97	98	102	96
10/12/2004	1	98	103	98	98.5	114	103	108	106	113	97	107	99.5
	2	93.5	96.5	96.5	99	102	94.5	106	94	96	82.5	99	93.5
11/1/2004	1	98.5	97.5	98.5	101	110	102	106	101	102	98.5	103	95
	2	96	102	99.5	100	107	107	107	101	103	100	109	94
11/5/2004	1	91.5	96	99	91.5	102	97.5	107	112	115	91	103	103
	2	95.5	114	116	105	116	103	114	112	104	98	117	104
11/8/2004	1	90.5	109	101	101	119	105	76.5	96.5	110	101	115	101
	2	104	93	90	103	108	105	109	103	106	97	105	95
11/9/2004	1	95.5	96	97	89.5	99	104	97.5	98	102	98.5	106	96.5
	2	104	102	97	99	108	103	109	111	113	105	110	102
11/29/2004	1	92.5	94	103	90.5	104	107	105	92	94.5	90.5	108	93.5
	2	89.5	90.5	92	87.5	92	95	93.5	85.5	95	86.5	98	88
12/2/2004	1	92.2	91.5	97.5	101	100	66.5	85.5	86.5	78.5	101	117	93
	2	73	75.5	101	91.5	97	106	73	107	115	101	104	67
12/10/2004	1	94	95.5	94	93	95.5	94	101	95.5	95.5	92	109	91.5
	2	82	90.5	87	89.5	95	93.5	92.5	93	87	87	93.5	86
12/13/2004	1	88	84.5	92	83.5	91	100	96	90	82	84.5	86.5	82
	2	98.5	98.5	99	101	100	102	108	112	99	95	93.5	96.5
1/18/2005	1	89.5	94.5	97	65	98	95.5	104	98	105	92.5	98	88.5
	2	83.5	104	93.5	88	94	100	95.6	89	91.5	84	98	88.5
Average Recovery		91.7	95	96	92.8	92	99.4	100	99	97.9	92.3	101	91.1
Standard Deviation		7.5	8.4	7.4	8.8	9.6	7.5	9.7	8.2	9.9	6.7	9.9	8.9
CV		8.2	8.87	7.75	9.4	10.4	7.56	9.71	8.31	10.1	7.24	9.83	9.76

Table 4. Analytical results for sampled PWS wells where ND means nondetected at a reporting limit of 0.05 μg/L.

Well Number	Sample Date	Chemical Analyte and Concentration (ug/L)						
		Atrazine	DEA	Simazine	ACET	DACT	Diuron	Bromacil
L01	10/4/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L02	10/4/2004	*ND*	*ND*	*ND*	0.23	0.26	0.11	0.08
L03	10/4/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L04	10/4/2004	0.1	0.2	*ND*	0.1	0.1	*ND*	*ND*
L05	10/6/2004	*ND*	*ND*	0.05	0.44	0.37	0.17	0.13
L06	10/5/2004	*ND*	*ND*	*ND*	0.16	0.29	*ND*	0.24
L07	10/5/2004	*ND*	*ND*	*ND*	0.22	0.26	*ND*	0.06
L08	10/5/2004	*ND*	*ND*	*ND*	0.15	0.15	0.07	*ND*
L09	10/5/2004	*ND*	*ND*	*ND*	0.09	0.16	*ND*	0.05
L10	10/5/2004	*ND*	*ND*	*ND*	*ND*	0.08	*ND*	*ND*
L11	10/5/2004	*ND*	*ND*	0.12	0.17	0.21	0.1	*ND*
L12	10/5/2004	*ND*	*ND*	*ND*	*ND*	0.08	*ND*	*ND*
L13	11/2/2004	*ND*	*ND*	*ND*	0.09	0.13	*ND*	*ND*
L14	11/2/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L15	11/2/2004	*ND*	*ND*	*ND*	0.17	0.24	*ND*	*ND*
L16	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L17	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L18	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L19	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L20	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L21	11/3/2004	*ND*	*ND*	*ND*	*ND*	0.07	*ND*	*ND*
L22	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L23	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L24	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L25	11/3/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L26	11/4/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L27	11/4/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L28	11/4/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L29	11/16/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L30	11/16/2004	*ND*	*ND*	*ND*	*ND*	0.06	*ND*	*ND*
L31	11/16/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L32	11/16/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L33	11/17/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L34	11/17/2004	*ND*	*ND*	*ND*	0.05	*ND*	0.09	*ND*
L35	11/17/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L36	11/17/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L37	11/17/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L38	11/18/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	0.1
L39	11/18/2004	*ND*	*ND*	*ND*	*ND*	*ND*	0.06	*ND*
L40	11/18/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L41	12/7/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L42	12/7/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L43	12/7/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L44	12/7/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L45	12/8/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L46	12/8/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L47	12/8/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L48	12/8/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*
L49	12/8/2004	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*	*ND*

Table 5. Data used for the statistical analyses relating explanatory variables to detections of simazine, ACET, and/or DACT in a PWS well.

Well Identifier	Concentration			Depth of		Cumulative Amount of Simazine Applied	Highest DBCP Concentration
	Simazine	ACET	DACT	PWS well	DGW		
	-------------------µg/L--------------------			------------feet-------------		----lbs----	----µg/L----
L01	0.00	0.00	0.00	379	31	5947	0.08
L02	0.00	0.23	0.26	216	31	6177	3.30
L03	0.00	0.00	0.00	192	33	8388	0.63
L04	0.00	0.10	0.10	198	31	8232	0.40
L05	0.05	0.44	0.37	425	49	18843	0.50
L06	0.00	0.16	0.29	300	49	18843	0.42
L07	0.00	0.22	0.26	296	42	21099	0.21
L08	0.00	0.15	0.15	300	37	10153	0.12
L09	0.00	0.09	0.16	234	62	41741	0.15
L10	0.00	0.00	0.08	537	62	41741	0.25
L11	0.12	0.17	0.21	273	58	24689	0.04
L12	0.00	0.00	0.08	276	62	41741	0.11
L13	0.00	0.09	0.13	250	60	1865	2.50
L14	0.00	0.00	0.00	700	59	4224	0.87
L15	0.00	0.17	0.24	260	61	5414	0.13
L16	0.00	0.00	0.00	270	62	8665	1.00
L17	0.00	0.00	0.00	700	54	7731	0.04
L18	0.00	0.00	0.00	374	41	8395	0.22
L19	0.00	0.00	0.00	616	54	7731	Not Available
L20	0.00	0.00	0.00	500	54	7731	0.25
L21	0.00	0.00	0.07	400	50	5375	0.84
L22	0.00	0.00	0.00	392	48	11165	1.00
L23	0.00	0.00	0.00	615	24	16588	0.03
L24	0.00	0.00	0.00	560	39	9131	0.00
L25	0.00	0.00	0.00	502	35	8131	0.29
L26	0.00	0.00	0.00	500	43	21328	0.19
L27	0.00	0.00	0.00	540	43	21328	0.21
L28	0.00	0.00	0.00	400	43	15266	0.03
L29	0.00	0.00	0.00	390	37	5954	0.67
L30	0.00	0.00	0.06	640	39	5633	1.09
L31	0.00	0.00	0.00	651	40	3951	0.04
L32	0.00	0.00	0.00	572	40	3951	0.16
L33	0.00	0.00	0.00	715	61	2072	0.05
L34	0.00	0.05	0.00	430	58	1409	0.02
L35	0.00	0.00	0.00	200	76	961	0.40
L36	0.00	0.00	0.00	265	79	717	0.22
L37	0.00	0.00	0.00	345	90	5037	0.00
L38	0.00	0.00	0.00	720	111	30887	0.08
L39	0.00	0.00	0.00	735	81	3600	2.10
L40	0.00	0.00	0.00	240	81	3600	0.03
L41	0.00	0.00	0.00	582	31	10833	0.07
L42	0.00	0.00	0.00	299	30	6533	0.87
L43	0.00	0.00	0.00	560	30	6533	0.03
L44	0.00	0.00	0.00	300	30	4484	0.06
L45	0.00	0.00	0.00	552	46	34252	0.16
L46	0.00	0.00	0.00	1000	275	11303	0.60
L47	0.00	0.00	0.00	1000	66	676	0.08
L48	0.00	0.00	0.00	200	111	21482	0.06
L49	0.00	0.00	0.00	120	111	21482	Not Available

Table 6. Logistic regression analysis using the score option to test the relationship between frequency of detection in wells and explanatory variables. For explanatory variables, Pwsdepth is the borehole depth of the PWS well, simapp is the cumulative lbs of simazine applied in the sampled section and eight surrounding sections, dbcphigh is the highest DBCP concentration reported in the PWS well, and gwdepth is the sectional averaged depth to ground water. The top four scores for the 2-variable and 3-variable models are shown?

Regression Models Selected by Score Criterion

Number of Variables	*Score Chi-Square*	*Variables Included in Model*
1	6.6879	pwsdepth
1	4.3221	simapp
1	2.7627	dbcphigh
1	0.7226	gwdepth
2	10.1943	pwsdepth simapp
2	9.2438	dbcphigh simapp
2	8.5531	pwsdepth dbcphigh
2	6.6909	pwsdepth gwdepth
3	13.7769	pwsdepth dbcphigh simapp
3	10.3148	gwdepth dbcphigh simapp
3	10.2158	pwsdepth gwdepth simapp
3	8.5531	pwsdepth gwdepth dbcphigh
4	13.8565	pwsdepth gwdepth dbcphigh simapp

Table 7. Logistic model solution for the best 1 through 4 variable models as indicated in Table 6.

	Analysis of Maximum Likelihood Estimates				
Parameter	DF	Estimate	Standard Error	WaldChi-Square	Pr>ChiSq
Best 1-variable model					
Intercept	1	1.1667	0.8527	1.8723	0.1712
pwsdepth	1	-0.00491	0.00212	5.3589	0.0206
Best 2-variable model					
Intercept	1	0.5059	0.9501	0.2836	0.5944
pwsdepth	1	-0.00516	0.00229	5.0699	0.0243
simapp	1	0.000058	0.000032	3.2996	0.0693
Best 3-variable model					
Intercept	1	-0.0974	1.1266	0.0075	0.9311
pwsdepth	1	-0.00594	0.0026	5.2261	0.0223
dbcphigh	1	1.3028	0.7717	2.8501	0.0914
simapp	1	0.000089	0.000038	5.4255	0.0198
Full 4-variable model					
Intercept	1	0.9479	1.6538	0.3286	0.5665
pwsdepth	1	-0.00624	0.00285	4.8119	0.0283
dbcphigh	1	1.3399	0.8183	2.6814	0.1015
simapp	1	0.000096	0.00004	5.7509	0.0165
gwdepth	1	-0.0202	0.0206	0.9607	0.327

Table 8. Association of predicted probabilities and observed responses and model fit statistics presented for the best models containing 1 through 4 variables in Table 6. AIC is the Akaike Information Criterion, SC is the Schwarz Criterion, and –2 Log L is the –2 Log Likelihood criterion. Higher concordant values indicate better agreement between model predicted and observed values.

Number of Variables in Model[a]	Classification Results			Model Fit Statistics		
	Percent Concordant	Percent Discordant	Percent Ties	AIC	SC	-2 Log L
1	71.0	28.4	0.6	57.328	61.112	53.328
2	79.0	20.8	0.2	55.714	61.389	49.714
3	83.3	16.3	0.4	50.325	57.725	42.325
4	83.3	16.7	0.0	51.246	60.497	41.246

[a] From Table 6, specific variables in each model are: 1-pwsdepth; 2-pwsdepth, simapp; 3-pwsdepth, simapp, dbcphigh; 4-pwsdepth, simapp, dbcphigh, gwdepth.

FIGURES

Figure 1. Breakdown products for atrazine and simazine.

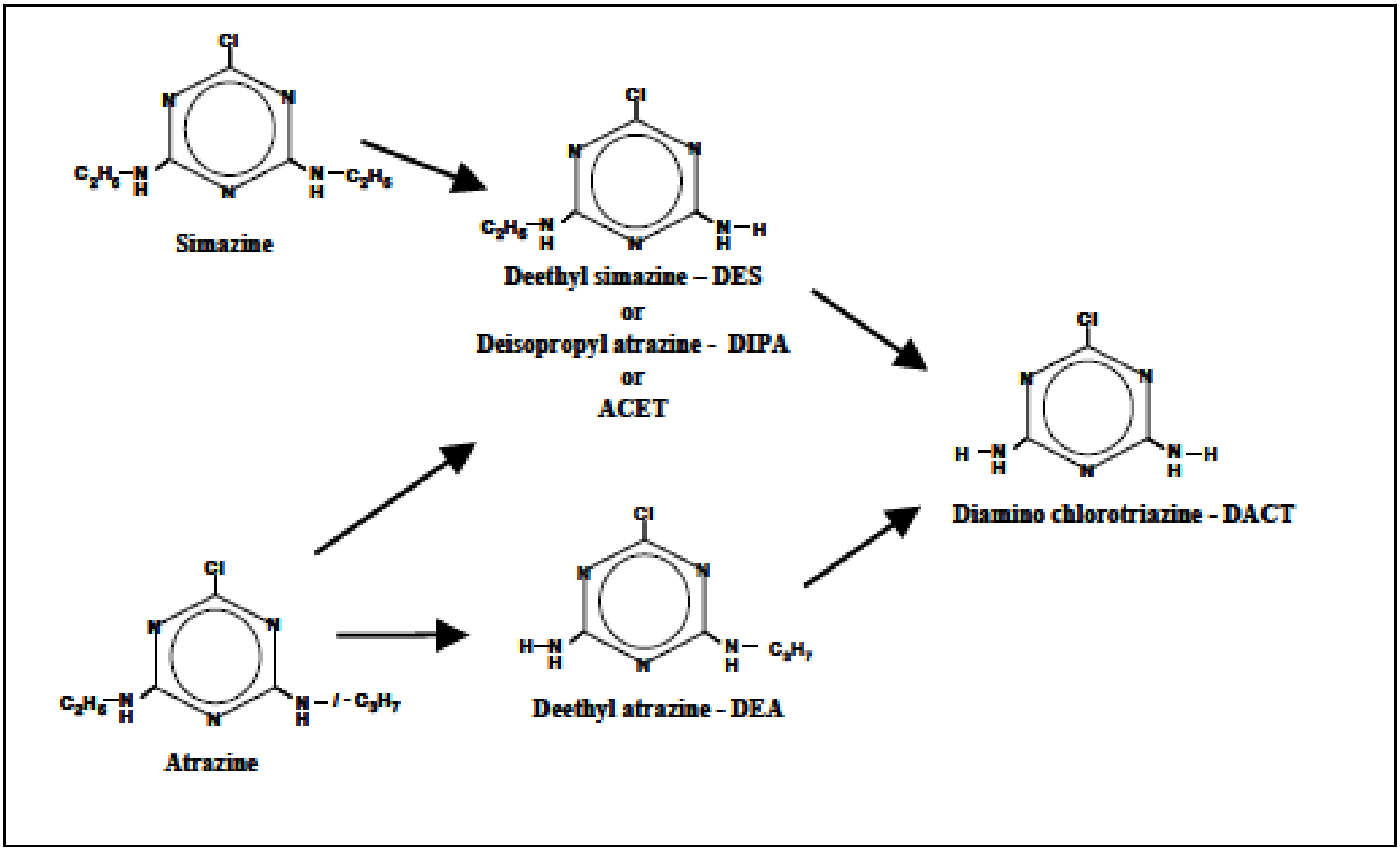

Figure 2. Spatial relationship between areas of simazine use (colored squares) and previous DBCP detections in PWS wells (circles) in the Fresno, Tulare, and Kern county areas.

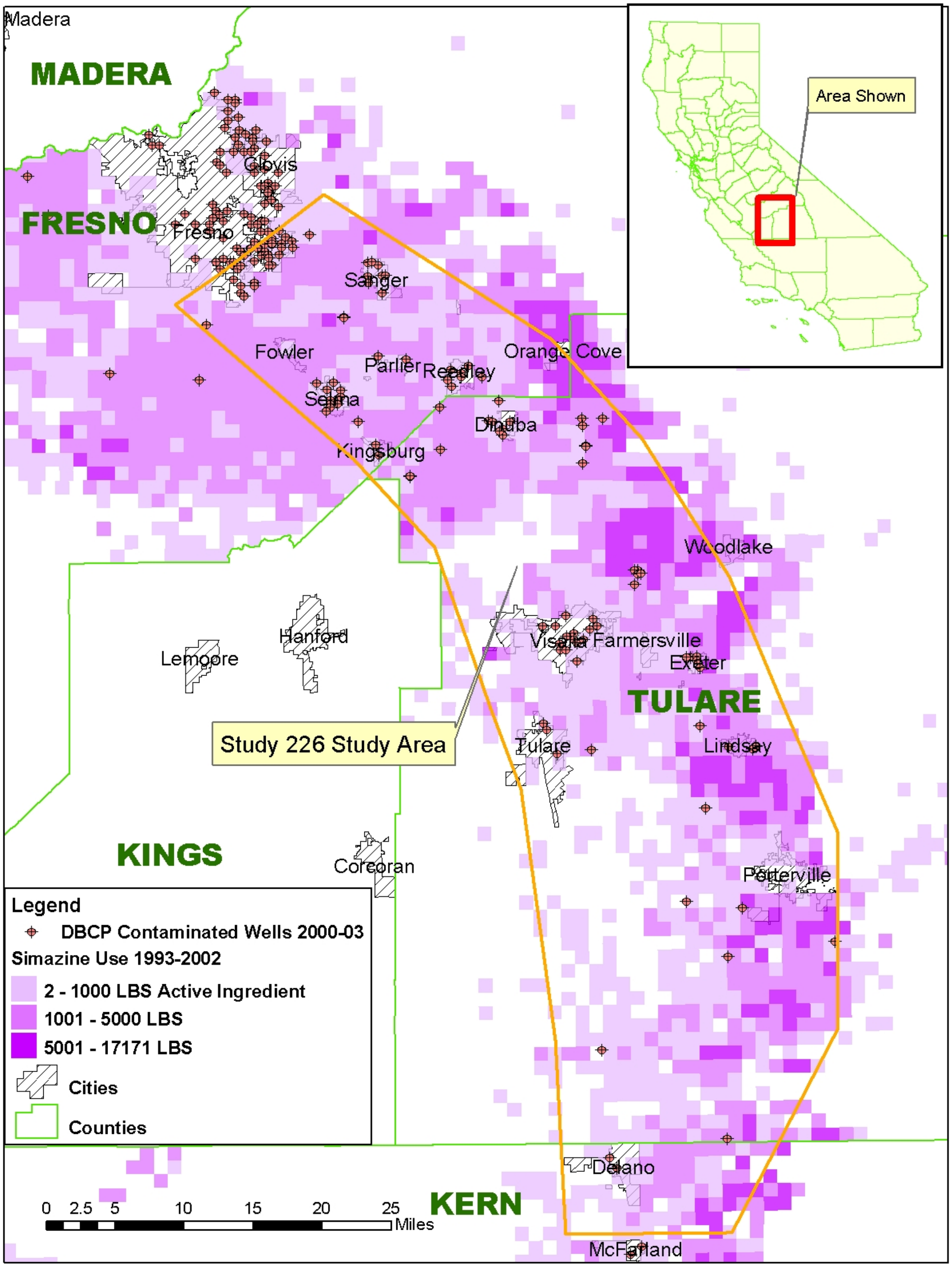

Figure 3. Spatial relationship between results of PWS wells sampled in this study (triangles) to simazine use (colored squares) and to wells with previous reported detections of simazine and or breakdown products (circles).

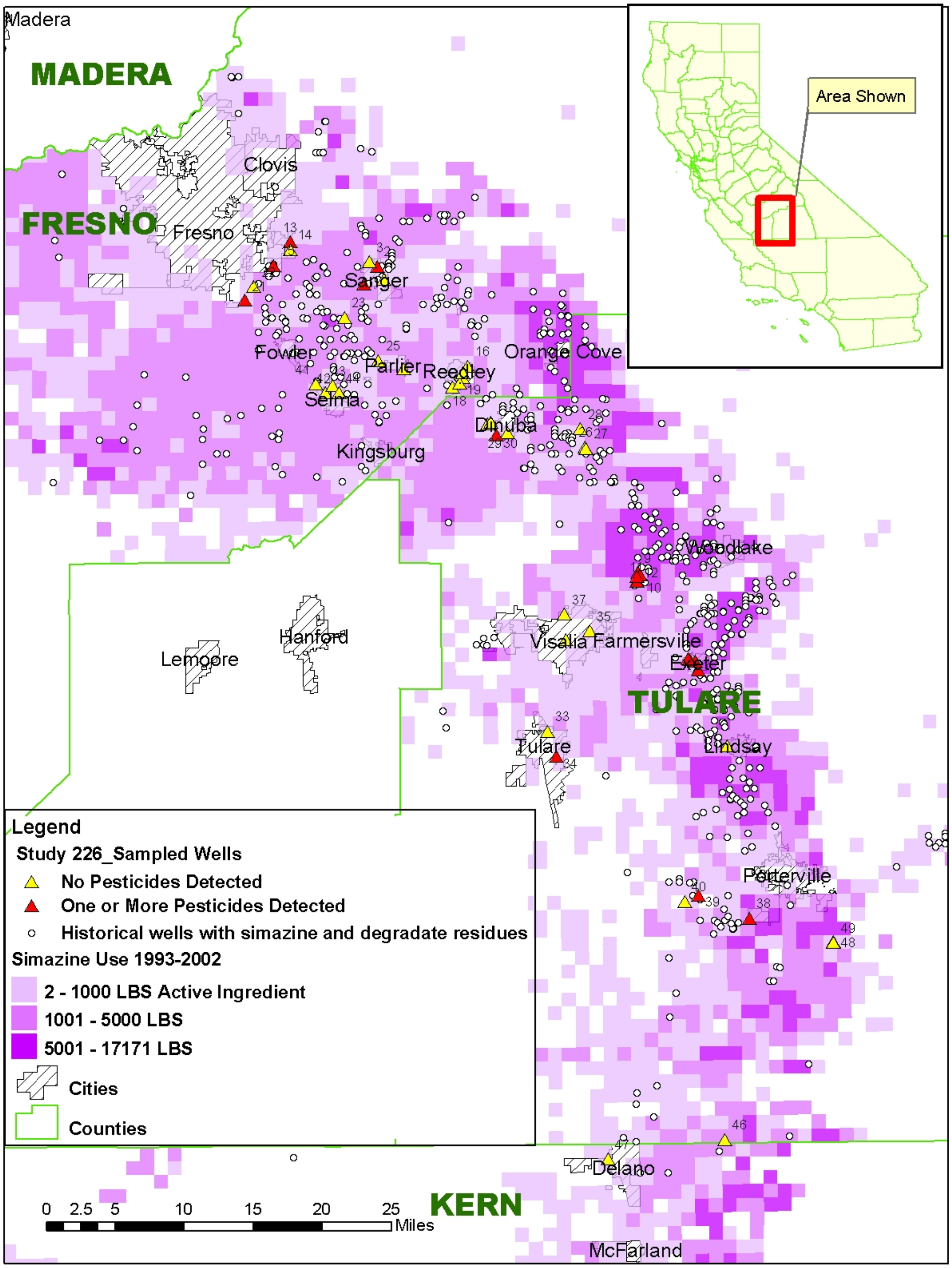

Figure 4. Relationship of ACET and DACT concentrations measured in wells where graph A is the relationship of the raw data and graph B is DACT concentration expressed in equivalent ACET units.

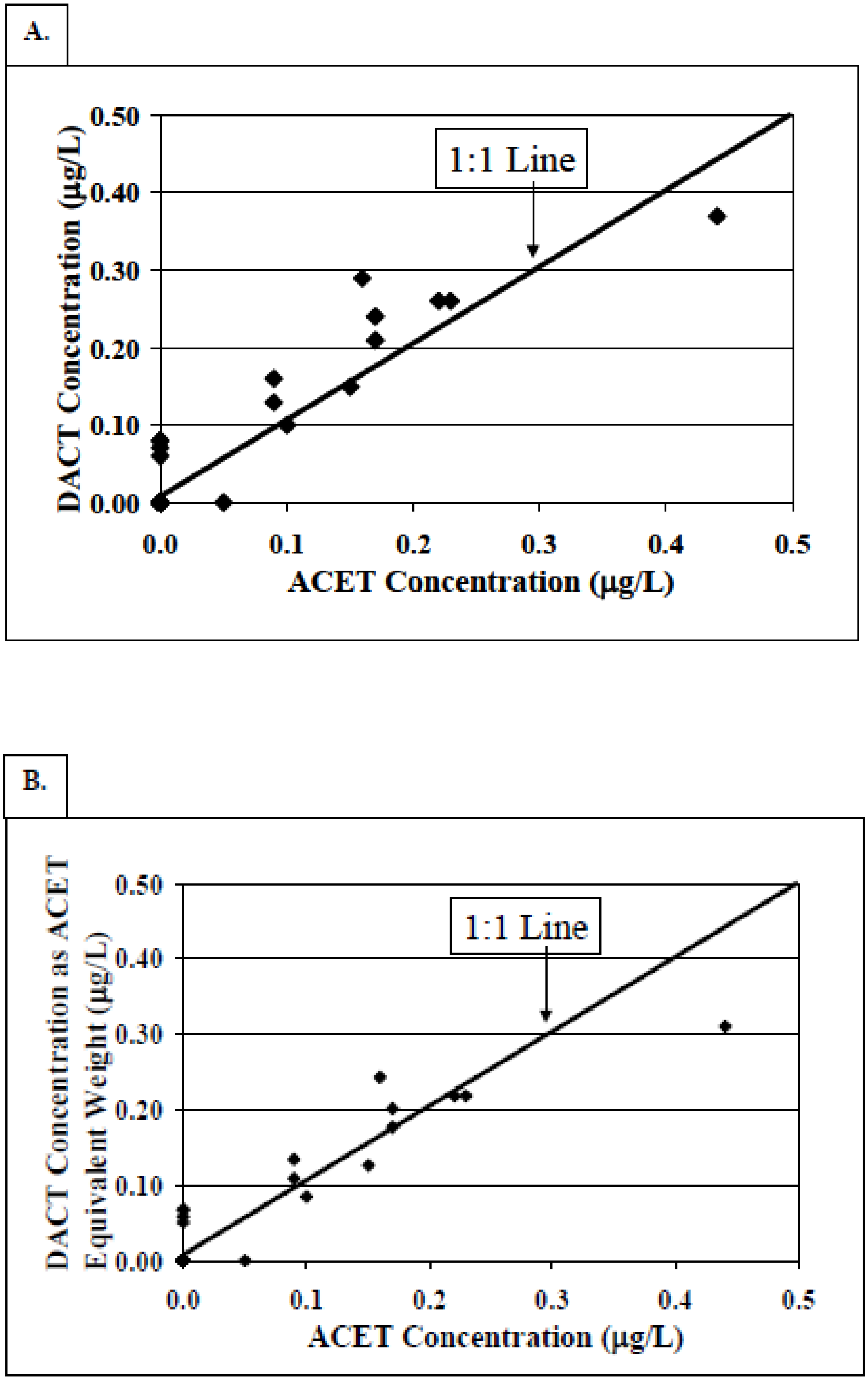

Figure 5. Scatter plot of the relationship between total simazine concentration in a well and the A) average sectional depth to ground water; B) reported depth of the PWS well; C) cumulative simazine use in the sampled section and eight surrounding sections; and D) maximum DBCP concentration reported in PWS well.