

Empirical Modeling of Spatial Vulnerability Applied to a Norflurazon Retrospective Well Study in California

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ABSTRACT

One goal of mandated well monitoring in California, U.S.A, is to search for residues of active ingredients previously undetected in the state's groundwater. The realization that pesticide residues move into groundwater via a number of different pathways has lead us to develop an empirical approach to delineate vulnerable areas; major climatic and edaphic features of areas where pesticides residues have been detected in well water have been identified on a geographic basis. The objective of this study was to evaluate the use of our empirical model in a retrospective well sampling study for norflurazon, a pre-emergence herbicide with physical-chemical properties that indicated potential to move offsite with water. In our modeling approach, sections of land, which are 2.59 km² areas, were identified as having a greater potential for contamination based on soil and depth-to-groundwater data. Wells were sampled from a subset of these sections where use of norflurazon was historically the greatest. Norflurazon residue was detected in 8 of 43 wells sampled in Fresno County, CA., and in concentrations ranging from 0.07 to 0.69 µg L⁻¹. This result was considered highly successful because residues had not been detected in 18 previous California groundwater studies for other active ingredients, some of which had been detected in other state and federal sampling programs. Location of sampling sites in these previous 18 California studies was based only on pesticide use data. The detections of norflurazon in this study indicated that, even though using an empirical modeling approach appeared to be unorthodox, it enabled us to effectively identify vulnerable areas.

Abbreviations: CALVUL, California vulnerability modeling approach; DGW, Depth-to-groundwater; DPR, California Department of Pesticide Regulation; DEA, deethylatrazine; ACET, deethylsimazine; KC, known contaminated; MDL, minimum detection limit.

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Most methods for identifying areas vulnerable to pesticide movement into groundwater focus on delineating land areas where pesticides would leach to groundwater as a result of simple percolation of water from the land surface (National Research Council, 1993). Well sampling studies have been conducted to test the application of vulnerability indices, but all have reported detections of pesticide residues in areas identified as relatively invulnerable (U.S. Environmental Protection Agency, 1992; Balu and Paulsen, 1991; Holden *et al.*, 1992, Kalinski *et al.*, 1994; Roux *et al.*, 1991). These results indicate that it is inappropriate to base a modeling approach on a single pathway of contamination. Other potential pathways include: movement of surface water into agricultural drainage wells (Braun and Hawkins, 1991; Roux *et al.*, 1991); movement of water into Karst formations (Hallberg, 1989); or movement of water through cracks in clay soils (Graham *et al.*, 1992). Measurement and modeling the movement of residues in macropore flow has recently gained more attention (Bergstrom *et al.*, 1991; Chen *et al.*, 1993).

An example of an alternative pathway to groundwater in California was uncovered when residues of bromacil (5-bromo-3-sec-butyl-6-methyluracil), diuron [$N^-(3,4\text{-dichlorophenyl})\text{-}N,N\text{-dimethylurea}$], and simazine [2-chloro-4,6-bis(ethylamino)-s-triazine], all pre-emergence herbicides, were detected in several hundred wells located in a citrus growing region of Fresno and Tulare Counties, counties located in the southeastern portion of the Central Valley of California (Roux *et al.*, 1991; Troiano and Segawa, 1987). Predominant soils in this area contain a shallow hardpan layer, and during the rainy winter months, flooding is a common problem. One method that is used to alleviate flooding is to dispose runoff water into shallow drainage wells. These drainage wells penetrate the hardpan layer, allowing water to move into deeper, more permeable soil. Concentrations of bromacil, diuron, and simazine ranging from 0.2 to 1 mg L⁻¹ were measured in rain runoff water that was sampled prior to entering drainage wells in Tulare County (Braun and Hawkins, 1991). The runoff samples were taken 1 to 2 months after the herbicides had been applied. Based on these data and in conjunction with other studies, we have concluded that movement in winter rain runoff followed by entry into drainage wells is a principal mechanism for herbicide movement into groundwater in this area.

A spatial assessment of vulnerability to groundwater should enable decisions on pesticide use to be based on local climatic and geographic conditions. Owing to a large body of historical monitoring data from areas where pesticide residues had been found in ground water in California, we were able to develop an empirical approach to determining vulnerability by relating geographic data to the pattern of detections. The first of two previous publications explained the development of a multivariate statistical approach to identify groups of vulnerable sections with similar climatic and soil properties (Troiano *et al.*, 1994). In the second publication, a well sampling study was conducted to test the statistical model (Troiano *et al.*, 1997).

The objective of this current study was to apply the model in a retrospective study for presence of norflurazon in well water. Norflurazon residues had not yet been detected in well water sampled in California. Prior to discussing the norflurazon study, we will summarize the philosophy and methodology on which our modeling approach was based and its initial evaluation.

Background on CALifornia VULnerability Modeling Approach

The empirical CALVUL model was developed in order to accommodate the reality of multiple pathways for pesticide movement to groundwater, such as movement in surface runoff to drainage wells. Our objective was to identify similar climatic and geographic features of sections of land where residues of currently registered pesticides had been found in groundwater (Troiano et al., 1994). A section of land is defined by the U.S. Geological Survey's Public Lands Survey Coordinate System as a 2.59 km² area of land and a Township is a square composed of 36 sections (Davis and Foote, 1966). At the time the model was developed, 254 sections of land had been identified where pesticide residues had been detected in well samples and determined to result from non-point source pesticide applications. These sections were denoted as Known Contaminated sections (KC sections) and formed the basis for the statistical investigation. Clustering methodology was used to group KC sections according to climatic and soil variables. For soil data, five groups of KC sections were identified using two soil variables. One variable, the number 200 sieve size (0.074-mm mesh sieve), reflected soil texture with groups ranging from coarse to fine-textured conditions (Table 1). The second variable indicated the prevalence of a hardpan layer in soils within a section, and it provided further differentiation within the groups formed by the texture variable.

The results from the clustering procedure were used to develop an algorithm to classify sections that lacked pesticide detections or well sampling data into one of the five KC soil clusters or, alternatively, into a not-classified category (Troiano et al., 1997). A well sampling study was conducted in Fresno and Tulare Counties to test the ability of the CALVUL model to identify areas of potential contamination. Wells were sampled in sections of land that were previously unsampled but that were identified as a member of one of the prevalent vulnerable soil clusters. A detection frequency of 42% (59 of 142 sections) was measured which was considered high for this type of study.

Modification of CALVUL Model

The CALVUL model approach is intended to be dynamic and flexible, allowing incorporation of new geographical information that provides further discrimination between land areas. For example, statewide data for depth-to-groundwater (DGW) were not available when the project was initiated, but data were available to provide estimates for average sectional DGW in the Fresno and Tulare County areas. When data from the well study conducted to evaluate the model were stratified according to DGW, a much larger probability for detections in both coarse and hardpan soil clusters was observed when average DGW in a section was 15 m or less (Troiano et al., 1994). DGW is now being developed statewide and has been included as a geographical data layer to indicate areas with a greater potential for contamination.

Implementation of CALVUL Model Approach

One goal of the California Department of Pesticide Regulation's (DPR) well monitoring program is to characterize the occurrence of pesticides in California's groundwater. Pesticides and significant breakdown products that have not yet been detected in groundwater were chosen for retrospective well sampling studies based on physical-chemical properties. Previous studies had been conducted for 18 other active ingredients, but no residues had been detected, even though some had been reported in other state or federal surveys, e.g. cyanazine and hexazinone. In these previous 18 well

Table 1. Description of vulnerable soil clusters based on variables that reflect the presence of hardpan and percentage of soil particles passing a No. 200 soil sieve (0.074 mm) in each of 5 clusters of sections with groundwater contaminated by pesticides.

| Cluster Description | # of KC Sections ^H | Cluster Variables ^I | | Distribution of Pesticide AIs in each cluster ^J | | | | | | |
|------------------------------------|-------------------------------|--------------------------------|---------------|------------------------------------------------------------|-----|-----|-----|-----|-----|-----|
| | | Hardpan | No. 200 Sieve | Atra | Ben | Bro | Diu | Pro | Sim | TPA |
| | | | -----%----- | -----# of Sections----- | | | | | | |
| No Hardpan and Coarse Textured | 72 | 0.08± 0.11 | 35.5± 5.9 | 5 | 3 | 10 | 23 | 2 | 63 | 4 |
| Hardpan and Coarse-Medium Textured | 82 | 0.50± 0.14 | 49.3± 7.7 | 4 | 6 | 36 | 56 | 3 | 67 | 1 |
| No Hardpan and Medium Textured | 26 | 0.01± 0.03 | 59.6± 6.4 | 6 | 9 | 1 | 2 | 0 | 6 | 9 |
| Hardpan and Medium Textured | 26 | 0.94± 0.13 | 61.9± 10.1 | 2 | 4 | 12 | 16 | 3 | 20 | 0 |
| No Hardpan and Fine Textured | 48 | 0.03± 0.10 | 81.7± 4.3 | 17 | 25 | 0 | 0 | 4 | 7 | 0 |

^H Sections of land where pesticide residues had been detected in well water designated as Known Contaminated sections.

^I Hardpan variable generated from a scale where 0 indicates no soils in section with hardpan and 1 indicates all soils in a section with hardpan. No. 200 sieve indicates the percentage by weight of soil particles that pass a No. 200 soil sieve and the smaller the percentage, the more coarse textured the soil. Values are estimated section average±standard deviation.

^J Atra = Atrazine; Ben = Bentazon; Bro = Bromacil; Diu = Diuron; Pro = Prometon; Sim = Simazine; TPA = 2,3,5,6-tetrachloroterephthalic acid, a breakdown product of Dacthal.

surveys, sampling sites were primarily located based on pesticide use data.

For the norflurazon well study, our hypothesis was that a greater probability of detection would be achieved by adding geographic stratification to the prioritization of sampling sites. In this paper we describe how data from the CALVUL model approach and pesticide use were combined to target sections for a retrospective well sampling study to detect norflurazon [4-chloro-5-methylamino-2-(α , α , α -trifluoro-m-tolyl)pyridazin-3(2H)-one]. Norflurazon was selected for sampling because residues had been found in well water sampled in Florida, U.S.A., its agricultural use has increased in part because of its use as a substitute for other pre-emergence herbicides that had already been detected in California well water, and its physical-chemical properties indicated a potential to move offsite with water (Johnson, 1991).

MATERIALS AND METHODS

Norflurazon GIS Study Design

In 1990, the DPR initiated mandatory reporting of all agricultural pesticide use in California. Using these data, the greatest use of norflurazon was determined on a countywide and on a section basis. Fresno County was chosen as the location for the norflurazon well sampling because it was the county with the greatest norflurazon use. Sections in Fresno County were identified for sampling based on the soil classification algorithm, DGW data, and on the amount of norflurazon used in a section.

The soil index for each section was derived as the mean value for the number 200 sieve size and hardpan indicator variables for all soil series within a section. For example, the list of soil series occurring in just one of the sections was: Exeter, Madera, and San Joaquin series which are all Typic Durixeralfs (Alfisols); Roma and Greenfield series which are both Typic Haploxeralfs (Alfisols); and the Cometa series which is a Typic Palexeralfs (Alfisols). Based on the mean number 200 sieve size and hardpan indicator variables for these soils, the profiling algorithm classified this section into a cluster which was described as having an average soil condition that was medium-to-coarse in texture and with a hardpan. Candidate sections were chosen from two of the five KC soil groups that were prevalent in Fresno County which were those in the coarse-textured or hardpan soil clusters (Fig. 1).

Estimates for DGW were determined as the average DGW during the months of February through May. The average DGW was calculated from approximately 31 000 measurements taken in the San Joaquin Valley between 1985 and 1996 by the California Department of Water Resources, representing measurements on 5 700 wells over approximately 7 500 km². The values for each well were averaged, and these averages ordinarily kriged to obtain the average DGW for each section centroid (Surfer v. 6, Golden Software Inc., Golden, CO) (Fig. 2). A linear variogram model was used for kriging after calculating sample variograms from the data using GEOEAS v. 1.2 (England and Sparks, 1988). The high density of data points allowed use of a small search radius of approximately 6.4 km in the 3.2 km x 4.0 km gridding. DGW had been previously identified as an important variable in the identification of spatial vulnerability (Troiano et al., 1997). In that limited

Fig. 1. Classification of sections in Fresno County, California, U.S.A., into soil vulnerability clusters based on an empirical model developed by Troiano et al. (1997).

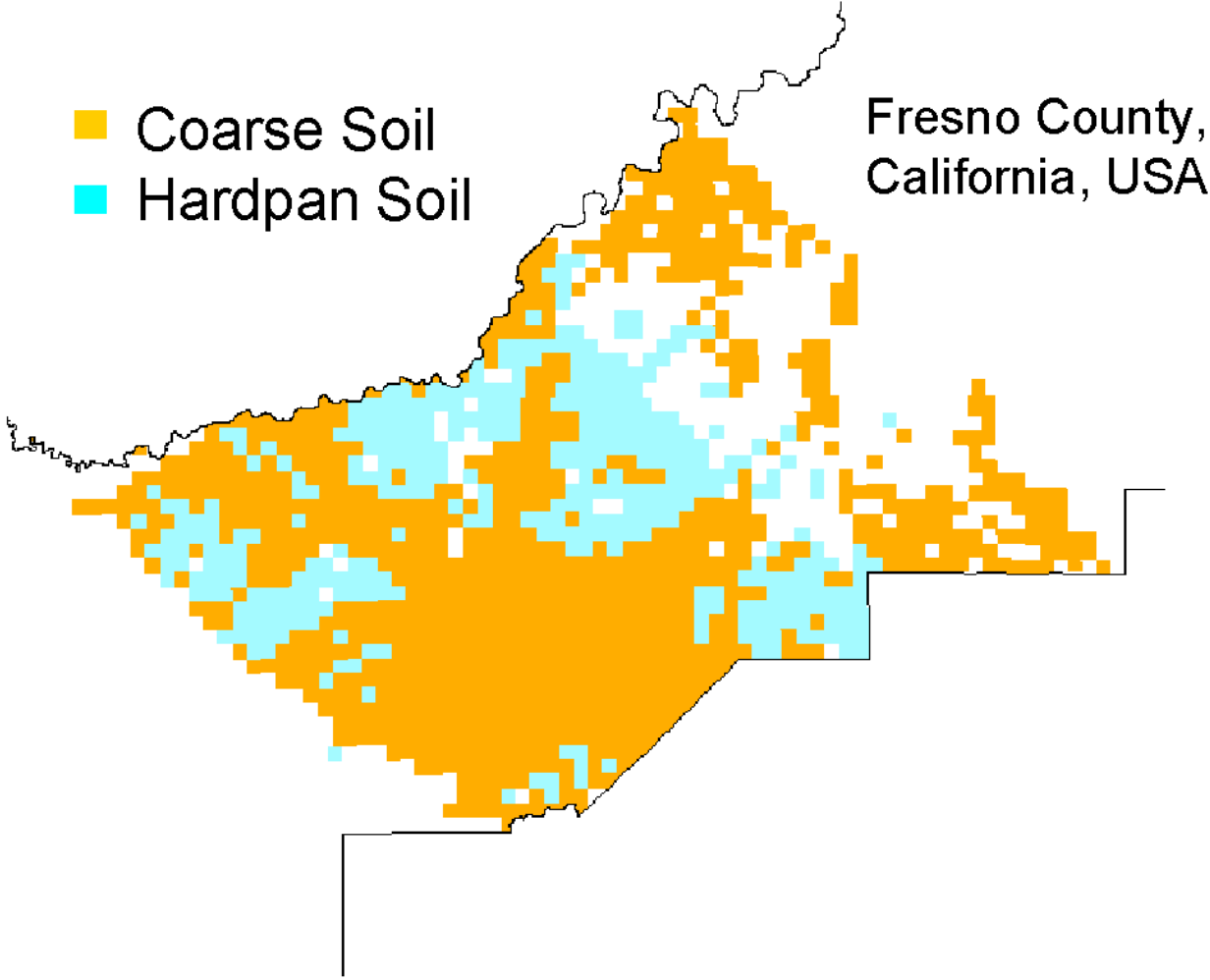
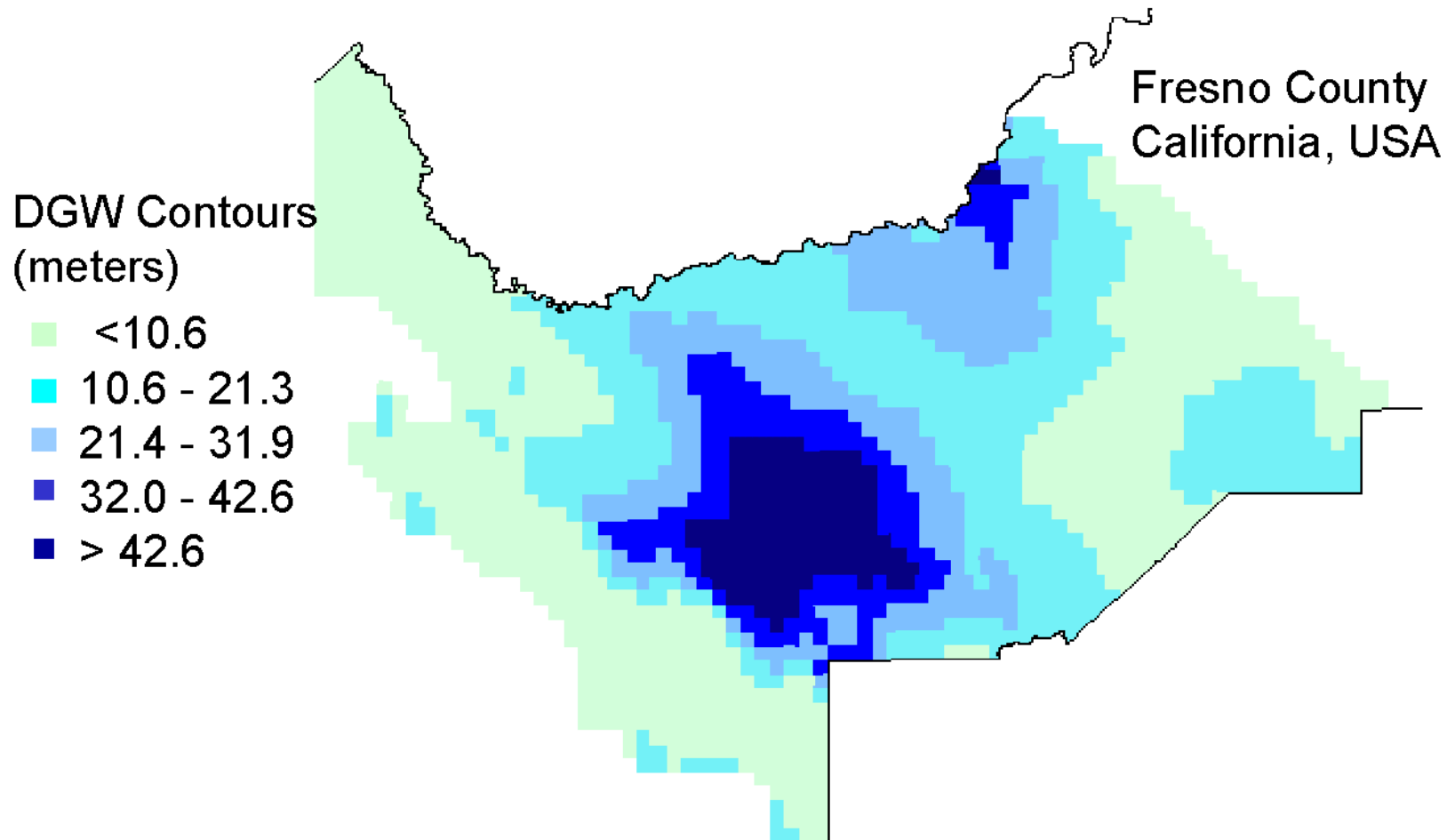


Fig. 2. Contours for sectional estimates of depth-to-groundwater (DGW) in Fresno county, California.



study, 15 m was arbitrarily chosen as a cut-off. Further analysis of a larger data set was conducted to provide a better estimate. The frequency of pesticide detections was calculated from the DPR's Well Inventory Database (Maes et al., 1992) and they were plotted against average sectional DGW in Fresno and Tulare Counties (Fig. 3). Fresno and Tulare Counties were chosen because this area had been the target for numerous well sampling studies, contained the greatest number of pesticide detections, and had data from well sampling conducted in groundwater depths that ranged from less than 9 m to greater than 52 m (Troiano et al., 1994). A value of 22 m was chosen from a visual inspection of Fig. 3.

An overlay of soil classification (Fig. 1) and DGW (Fig. 2) produced sections of land with the greatest potential for contamination which were sections that were either in the coarse-textured or hardpan soil cluster **and** that had an average DGW of 22 m or less (Fig. 4). The final pool of sections for potential sampling in the norflurazon study was determined from a final overlay of norflurazon use data (Fig 5). Norflurazon use data for the years 1991-1994 were included.

Well Sampling

Surveys for potential sampling sites were conducted by visually searching for wells, residences, or occupied buildings in targeted sections. Upon permission to sample, the well was inspected for the following criteria:

1. The well was sampled only if it was sealed, and when the pad and cap were in good condition. This ensured that the well was not a point source for entry of residues into groundwater;
2. The well was remotely located from pesticide sprayer filling stations, wash down areas, or pesticide storage facilities;
3. A sample port, faucet, valve or stand pipe, was located between the well and an above-ground water storage tank.

Well water samples were collected in one-liter amber glass bottles with Teflon⁷-lined caps. One bottle was analyzed for norflurazon and a second bottle was analyzed for a multi-herbicide screen. Two additional field blanks, one for each chemical analysis, was prepared at the sampling site. Prior to sampling, the pump was run for at least 10 min to clear the casing of standing water and bring in fresh water from the aquifer. The sample bottles were rinsed and then filled with the well water and the field blank was rinsed and filled with de-ionized water. Bottles were transported on wet ice and stored in a refrigerator at 4° C until analysis.

Chemical Analysis

Norflurazon analysis was conducted by Quanterra Environmental Services, West Sacramento, CA. The analyte was extracted from water using a C-18 Solid Phase Extraction (SPE) and the extract analyzed by liquid chromatography coupled to a thermospray triple-stage quadrupole mass spectrometer (TSP-LC/MS/MS). In order to attain a 0.05 µg L⁻¹ minimum detection limit, 100 µL of a 0.25 µg mL⁻¹ fortification standard was added to 500 mL of sample prior to extraction. The first mass spectrometer was set to reject all mass/charge values that did not correspond to the norflurazon molecular ion. The transmitted ion was then fragmented in the next state and the final mass spectrometer quantified norflurazon based on a single, characteristic fragment. Minimum detection limits were 0.05 µg L⁻¹. A storage stability study was conducted where buffered solutions of

Fig. 3. Frequency of pesticide detections in well water in relation to average sections spring, depth- to-groundwater for Fresno and Tulare Counties. Numbers of wells sampled in each category are indicated in parentheses.

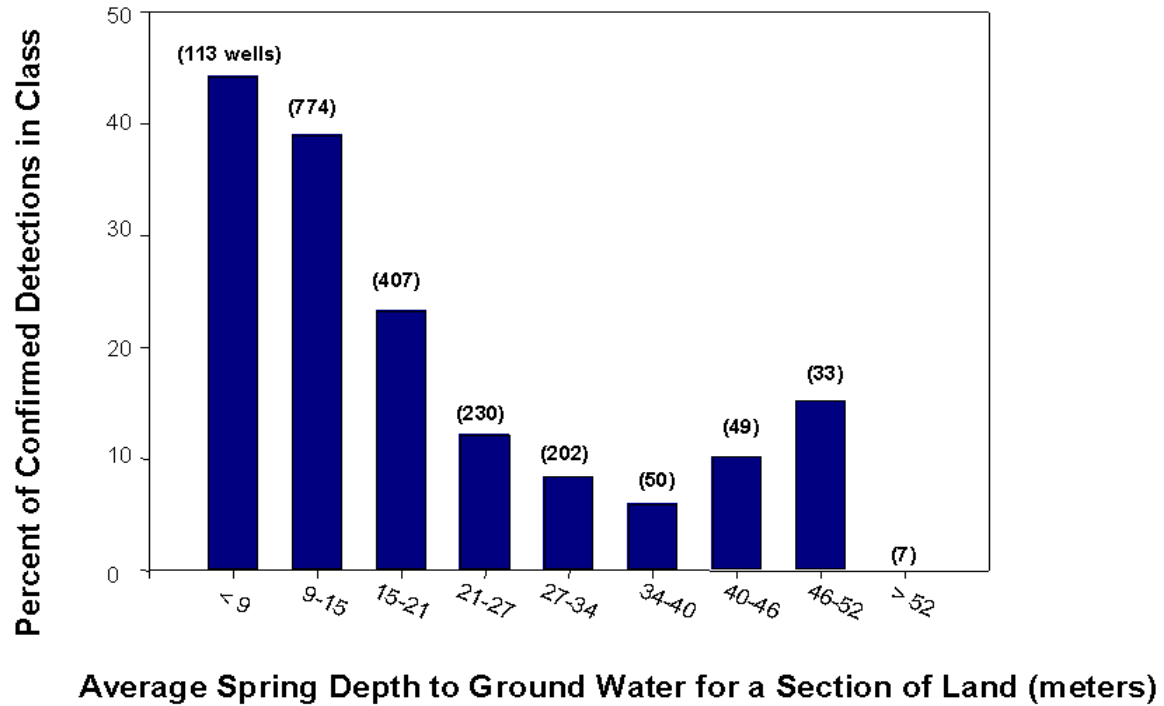


Fig. 4. Sections with greater vulnerability for pesticide contamination indicated by the overlay of soils vulnerability (Fig. 1) and DGW (Fig. 2).

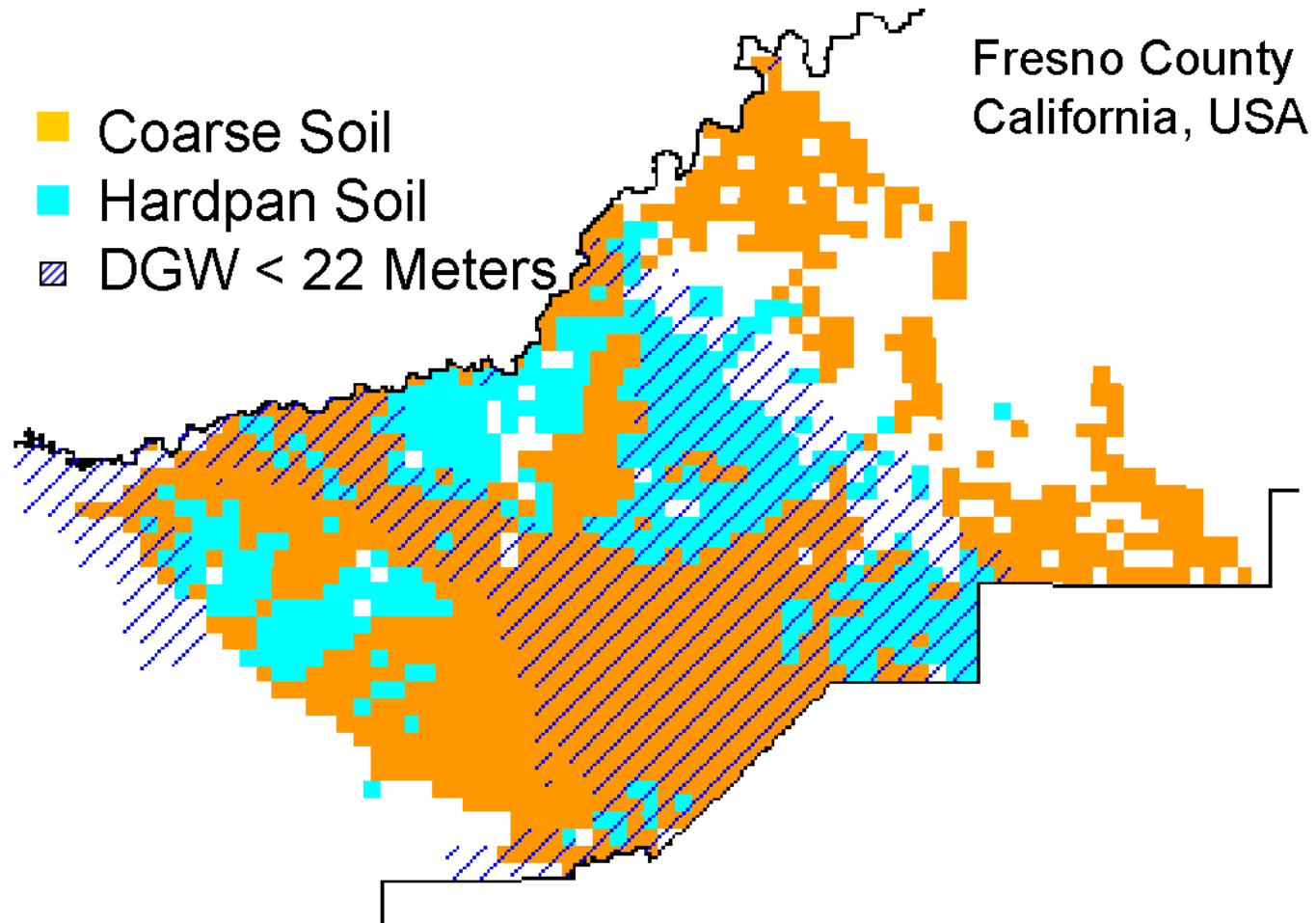
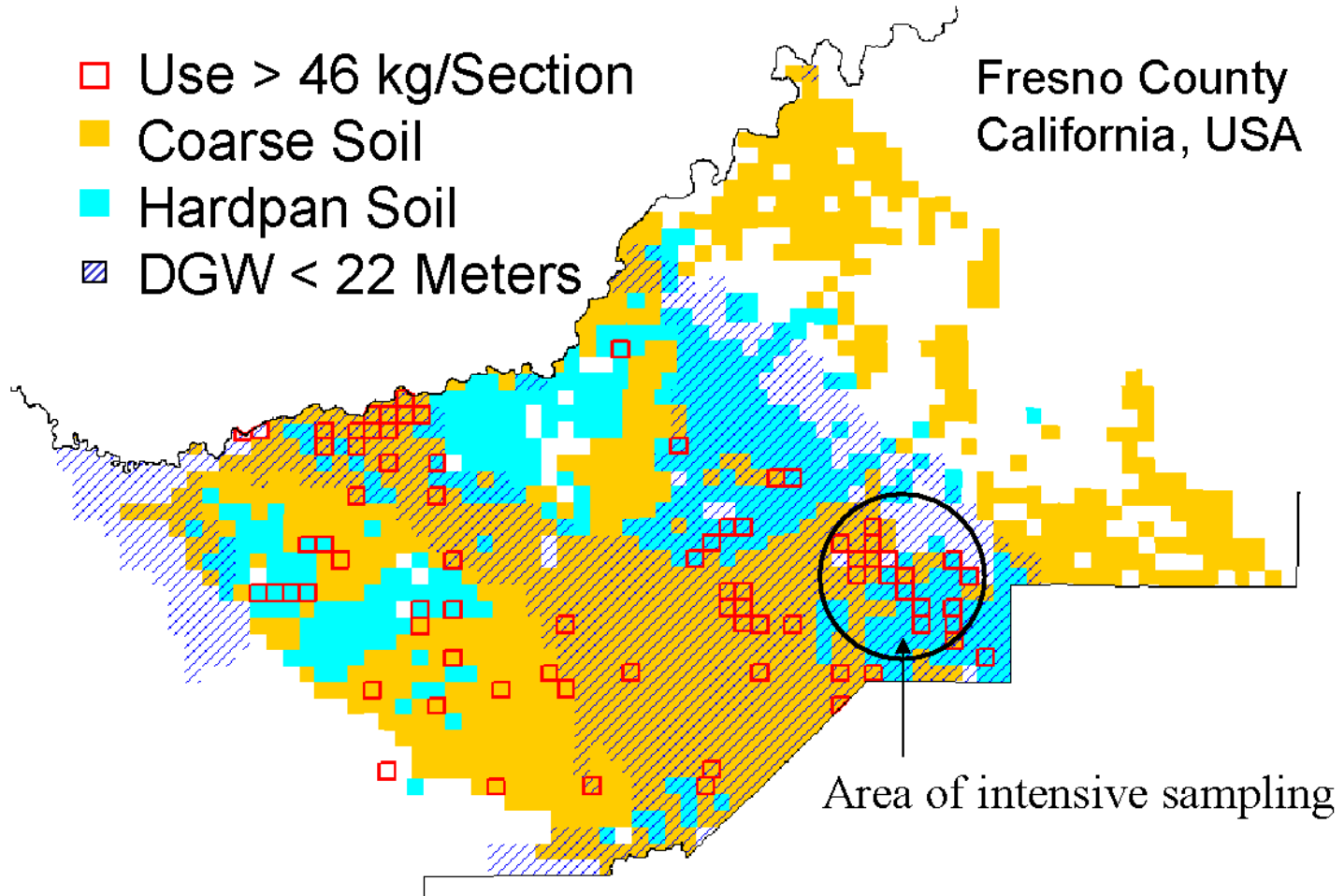


Fig. 5. Potential sections for well sampling determined from an overlay of sections with high norflurazon use and those with high vulnerability (Fig. 4). Sections within the circle were subject to more intensive sampling.



norflurazon at pH 5, 7, and 9 maintained at 25° C were found to be stable during a 30-day storage period. The recovery for four blind spike samples at 0.5 µg L⁻¹ averaged 98.5%. Residue was not detected in field blank samples indicating that there was no contamination resulting from either field sampling procedures or laboratory analytical methodology.

Analyses for confirmation of norflurazon and an additional multi-herbicide screen was conducted by ALTA Analytical Laboratories, El Dorado Hills. Multi-herbicide screen analytes were atrazine (6-chloro-N²-ethyl-N⁴-isopropyl-1,3,5-triazine-2,4-diamine), bromacil, simazine, and the triazine breakdown products deethyl simazine (ACET) (2-amino-4-chloro-6-ethylamino-s-triazine), deethylatrazine (DEA) (2-amino-4-chloro-6-isopropylamino-s-triazine) and prometon ([2,4-bis(isopropylamino)-6-methoxy-s-triazine]. These were chemicals that had previously been detected in well water studies in California and determined to result from non-point source agricultural applications. The analytes were extracted from water using C18 SPE and the extract analyzed by reversed phase LC coupled to a triple stage mass spectrometer using an atmospheric pressure chemical ionization nebulizer (APCI-MS/MS). The MDL for all analytes was 0.05 µg L⁻¹.

RESULTS AND DISCUSSION

Well sampling was conducted in two phases. In the first phase, well sampling sites were chosen from throughout Fresno County with wells sampled from vulnerable sections that had the greatest norflurazon use (Fig. 5). Residues for one or more of all herbicide analytes were detected in 9 of 12 wells sampled but, most importantly, norflurazon was detected at 0.25 µg L⁻¹ in one well located in the southeastern portion of Fresno.

In the second phase, a more intensive sampling was conducted in the area of the initial detection (Fig. 5). Potential sampling areas again were determined using GIS overlays of the soil data, DGW data, and norflurazon-use data. The area targeted for sampling consisted of 56 sections, encompassing 145 km². Norflurazon was detected in 7 of 31 additional wells sampled, which were located in 7 of 19 sections sampled. Norflurazon concentrations in all 8 positive wells ranged from 0.07 to 0.69 µg L⁻¹ (Table 2).

In addition, residues of other pre-emergence herbicides were detected in 22 of the 31 wells sampled, which were located in 12 of the 19 sections sampled in the second phase (Table 2). Summary results for each herbicide active ingredient and breakdown product detected in the 31 wells were: atrazine detected in one well at 0.31 µg L⁻¹; simazine detected in 15 wells ranging between 0.08 and 0.93 µg L⁻¹; DEA in two wells at 0.06 and 2.0 µg L⁻¹; ACET in 15 wells ranging between 0.05 and 0.7 µg L⁻¹; prometon in one well at 0.27 µg L⁻¹; bromacil in three wells at 0.18, 0.19, and 0.31 µg L⁻¹; and diuron in 15 wells ranging between 0.09 and 0.87 µg L⁻¹. Including the well with the original norflurazon detection, residues for two or more different analytes were detected in 19 of 32 wells, and in all 8 wells where norflurazon was detected.

Table 2. Analytical results for wells with detections of herbicide residues during the second intensive well sampling phase. Sections are coded from S1-S12.

| Section -Well | CALVUL Attribute | | Herbicide Active Ingredient or Breakdown Product | | | | | | | |
|------------------|------------------|------------------|--------------------------------------------------|-----------------|----------|------|------|--------|----------|----------|
| | Soil Cluster | DGW ^H | Norflurazon | Atrazine | Simazine | ACET | DEA | Diuron | Bromacil | Prometon |
| | | --m-- | ----- $\mu\text{g L}^{-1}$ ----- | | | | | | | |
| S1-01 | Coarse | 11.6 | 0.24 | ND ^H | 0.21 | 0.66 | ND | 0.15 | ND | ND |
| S1-02 | Coarse | 11.6 | 0.69 | ND | 0.32 | ND | ND | 0.21 | ND | ND |
| S2-01 | Coarse | 14.3 | ND | ND | 0.15 | ND | ND | ND | ND | ND |
| S2-02 | Coarse | 14.3 | ND | ND | 0.31 | ND | ND | 0.20 | ND | ND |
| S3-01 | Coarse | 13.1 | ND | ND | ND | ND | ND | 0.10 | ND | ND |
| S3-02 | Coarse | 13.1 | 0.16 | ND | 0.23 | ND | ND | 0.13 | ND | ND |
| S4-01 | Hardpan | 7.9 | ND | ND | 0.13 | 0.30 | 0.06 | 0.54 | 0.31 | ND |
| S4-02 | Hardpan | 7.9 | ND | ND | ND | 0.43 | ND | 0.27 | 0.19 | ND |
| S5-01 | Hardpan | 8.8 | ND | ND | 0.16 | 0.70 | ND | 0.52 | 0.18 | ND |
| S5-02 | Hardpan | 8.8 | 0.09 | ND | ND | 0.07 | ND | ND | ND | ND |
| S6-01 | Coarse | 11.9 | ND | ND | 0.23 | 0.29 | ND | 0.24 | ND | ND |
| S6-02 | Coarse | 11.9 | 0.20 | ND | 0.19 | 0.40 | ND | 0.14 | ND | ND |
| S7-01 | NC ^I | 14.3 | 0.09 | ND | ND | 0.25 | 0.19 | ND | ND | ND |
| S8-01 | Coarse | 11.9 | ND | ND | 0.11 | 0.11 | ND | ND | ND | ND |
| S8-02 | Coarse | 11.9 | ND | ND | 0.12 | 0.16 | ND | 0.14 | ND | ND |
| S9-01 | Hardpan | 16.1 | ND | ND | ND | 0.17 | ND | 0.87 | ND | ND |
| S9-02 | Hardpan | 16.1 | ND | ND | ND | 0.07 | ND | ND | ND | ND |
| S10-01 | Hardpan | 19.2 | ND | 0.31 | 0.93 | nd | 2.00 | ND | ND | ND |
| S10-02 | Hardpan | 19.2 | ND | ND | ND | 0.05 | ND | 0.27 | ND | ND |
| S11-01 | Hardpan | 17.6 | ND | ND | 0.08 | 0.09 | ND | 0.09 | ND | ND |
| S11-02 | Hardpan | 17.6 | 0.07 | ND | 0.22 | 0.40 | ND | 0.10 | ND | ND |
| S12-01 | Hardpan | 19.8 | 0.10 | ND | 0.12 | 0.14 | ND | 0.36 | ND | 0.27 |

^H DGW = Average depth to ground water for a section of land; ND=Not detected at an MDL of 0.05 $\mu\text{g L}^{-1}$.

^I Section not classified into either coarse or hardpan vulnerable soil cluster designated as NC.

A comparison between norflurazon and simazine use in the intensively sampled area provided an additional perspective for the detections. Total norflurazon use on agricultural crops in this area was much less than simazine, with norflurazon use ranging from 14 to 23% of simazine use over the 1991-1994 period (Table 3). Although both herbicides are registered for use on similar crops, norflurazon is a relatively new pesticide that was initially registered in California in 1977 when compared with 1958 for simazine. Norflurazon is registered for use on rights-of-way but the reported use in the intensively sampled area was exclusively on agricultural crops, primarily citrus, grapes, olives, and stone fruit and nut trees.

The measurement of multiple residues for pre-emergence herbicides in well water samples is most likely the result of their similar physical-chemical properties. Pre-emergence herbicides are applied before weed seeds germinate and in order to be effective during the period of weed growth, they must be available for uptake by roots from the soil solution. Consequently, most pre-emergence herbicides demonstrate low sorption to soils, and they have relatively long soil half-lives which allows residues to be present during weed growth. Koc is a relative measure of the attraction of pesticides to soil with greater values indicating greater attraction. Estimated Koc and aerobic half-lives values for pre-emergence herbicides detected in California indicate Koc values less than $1\ 000\ \text{L Kg}^{-1}$ and a half-life of 60 days or greater (Table 4) (Wauchope and Hornsby, 1992). Two contact herbicides are included for comparison and they exhibit somewhat shorter half-lives but much greater Koc values. To date, there have been no reports for the presence of these contact herbicides in California's groundwater. Since the detection of multiple pre-emergence herbicide residues in well samples indicates that chemicals are moving to groundwater by a similar pathway, substitution among pre-emergence herbicide active ingredients will not be an effective approach for mitigating groundwater contamination. Instead, mechanisms of movement into groundwater need to be identified, and management practices developed that are based on agronomic practices as they relate to identified mechanisms. For example, we are pursuing greater control of percolating water in vulnerable sections with coarse-textured soils because chemicals are leaching through soil directly from the sites of application (Troiano et al., 1992). On the other hand, in vulnerable sections with hardpan soils, we are recommending complete incorporation of residues into the soil by mechanical incorporation or supplemental irrigation because residues are moved offsite by runoff water which is then collected in nearby drainage wells (Braun and Hawkins, 1991; Troiano and Garretson, 1998).

Table 3. Comparison of the total use of norflurazon with simazine in sections identified as vulnerable to groundwater contamination for the second intensive well sampling in Fresno County, CA.

| Year | Norflurazon | Simazine |
|------|----------------|----------|
| | ----- kg ----- | |
| 1991 | 12 660 | 91 564 |
| 1992 | 16 517 | 93 721 |
| 1993 | 21 092 | 93 070 |
| 1994 | 17 948 | 93 517 |

Table 4. Estimated half-life and Koc values for pre-emergence herbicides that have been detected in California's groundwater and contact herbicides that has not yet been found to move into groundwater due to normal agricultural use.

| Active Ingredient | Type of Application | Estimated Value for ^H | |
|-------------------|---------------------|----------------------------------|--------------------------|
| | | Half-life | Koc |
| | | -- days -- | -- L Kg ⁻¹ -- |
| Atrazine | Pre-emergent | 60 | 100 |
| Bromacil | Pre-emergent | 60 | 32 |
| Diuron | Pre-emergent | 90 | 480 |
| Norflurazon | Pre-emergent | 90 | 600 |
| Prometon | Pre-emergent | 500 | 150 |
| Simazine | Pre-emergent | 60 | 130 |
| | | | |
| Glyphosate | Contact | 47 | 24 000 |
| Oxyflurfen | Contact | 35 | 100 000 |

^H Data from Wauchope and Hornsby, 1992.

CONCLUSIONS

The complex nature of pesticide movement to groundwater has led us to develop a statistical, empirical approach to assess spatial vulnerability to ground water contamination. The approach is designed to be dynamic and flexible, allowing for addition of geographic data that could produce further refinement in the definition of vulnerable areas. The detection of norflurazon in well water in this retrospective study indicates that:

1. The layering of a soil index that was produced from a multi-variate statistical investigation and depth to groundwater data was successful in delineating geographic areas of greater vulnerability to pesticide movement into groundwater. Implementation of the CALVUL modeling approach should result in more efficient use of monetary and personnel resources;
2. The presence of multiple residues for pre-emergence herbicides in well samples indicated a common pathway for movement into groundwater. Although all other current strategies are based on a pesticide-by-pesticide approach, a more effective preventative strategy will be to identify pathways specific to particular geographic features and site conditions, and then mitigate off-site movement of residues through the development of management practices based on those conditions.

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