PESTICIDE OCCURRENCE IN GROUNDWATER IN TULARE COUNTY, CALIFORNIA

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Abstract. Geographic Information Systems (GIS) and statistical methods were used to identify the major factors affecting pesticide leaching in groundwater from agricultural fields in Tulare County, California. Residues of bromacil, diuron, and simazine increased in groundwater during the 1980s. Bromacil, diuron, and simazine contamination were positively correlated to crop diversity and water demand. Diuron and simazine were positively correlated to groundwater depth and negatively correlated to soil water-holding capacity. DBCP concentration in groundwater was related to the crop coverage. The Goss model was used to examine soil-pesticide interactions and a Pesticide Contamination Index (PCI) was developed. Areas having high leaching potentials were mainly associated with citrus and orchards and coarse-textured sandy soils along the Sierra Nevada foothills, while areas having low leaching potentials were associated with field crops and clay soils of the southwest region. The PCI was largest for DBCP during the 1980s, suggesting that it was the most significant contaminant before 1977 when it was widely used; however, wells were not tested for this pesticide during that period. Twelve years after DBCP was banned, it was still the most significant health risk contaminant. Spatial maps showing the distribution of leaching potentials and soil interactions for these pesticides can provide useful information to regulatory and planning agencies for land use planning and pesticide management.

Key words: groundwater, pesticide contamination, Goss model, leaching potential, Pesticide Contamination Index, GIS.

1. Introduction

Agriculture uses 68% of the total pesticide produced in the United States (Cheng and Koskinen, 1986), and at least 46 different agricultural pesticides have been found in groundwater samples in 26 states (Williams et al., 1988). Thus, the leaching of pesticides from agricultural applications into groundwater is a major environmental concern. Groundwater contamination is critical in California, a state with major economic investment in intensively managed agricultural production and a semiarid climate with dependence on irrigated water. Residues of more than 50 pesticides were found in the groundwater of 23 California counties between 1970 and 1982 (Cohen, 1986). Forty-nine percent of the wells sampled in Tulare County (Troiano and Segawa, 1987) contained low levels of one or more of the following herbicides: simazine, diuron, atrazine and bromacil. As a result, 117 out of 263 Pesticide Management Zones (PMZs) in California are located in Tulare County

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Table I

Selected chemical properties and Health Advisory Levels (Data were compiled from the reports of the California EPA in 1991, US EPA in 1987, California Department of Food and Agriculture in 1990, and California Department of Health Services in 1990; Gustafson, 1989; and Jury et al., 1987)

	Bromacil	DBCP	Diuron	Simazine
Common name	Hyvar	–	Karmex	Princep
Chemical type	Herbicide	Nematicide	Herbicide	Herbicide
Application method	soil	soil	soil	soil
Water solubility (ppm)	929	1000	36	6
K_{oc} (adsorption coeff. cm^3/g)	17	40	499	340
Soil half-life (day)				
(aerobic soil metabolism HF)	346	225	372	110
Hydrolysis half-life (day)	30	7050	1285	28
HAL (Health Advisory Level, ppb)	90	0.02	10	1
Detected level (ppb)	0.09–6.7	0.002–8000	0.032–2.8	0.03–3.4

Major application use: (California Department of Pesticide Regulation) Bromacil, mostly citrus and rights-of-way. Diuron, mostly alfalfa, pasture, citrus, cotton, grape, olive and walnuts. Simazine, mostly citrus, almonds, avocado, grape and others. DBCP, mostly citrus, stone fruits and vineyards.

due to the accumulation of pesticides in groundwater (California Environmental Protection Agency, 1992).

Bromacil, diuron, and simazine, photosynthetic inhibitors that block photosystem II, have been used for many years for weed control. All are regularly used on citrus and non-agricultural land for both monocot and dicot weed control. Diuron and simazine are also used on fruit trees, vineyards, alfalfa and cotton. While all of these herbicides are effective on dicots and monocots, simazine is more commonly used to control monocot weeds. The use of these three herbicides was not regulated by state agencies until 1990 because of their relatively short aqueous half-lives. In contrast, Dibromochloropropane (DBCP), widely used in California until 1977 as a soil fumigant for nematode control, was banned in California after discovery of sterility among male workers manufacturing DBCP (Douglis, 1993). Furthermore, studies have shown that DBCP remains in the top soil layer for six to seven years after a single application (Cohen, 1986). Its hydrolysis half-life is about 20 years, although it is more rapidly degraded in aerobic soils (Table I).

The above pesticides are all widely used, are applied directly to the soil, and are water soluble, although solubility varies over three orders of magnitude (Table I). Patterns of contamination and transport among these pesticides illustrate the complexity of predicting their on-site behavior and the difficulty in developing site-specific management. These four pesticides have different solubilities, adsorption coefficient, persistence in the soil, and health risks. Chemical retention and effectiveness are affected by the properties of the pesticide, characteristics of the soil, climatic conditions at the site of application, and farm management practices.

Although the climate cannot be controlled, the other factors can be managed or altered to some extent in order to minimize potential pesticide contamination.

Previous studies have shown that pesticide contamination of groundwater occurs when normal or heavy applications of pesticides are coupled with poor management practices (Domagalski and Dubrovsky, 1992; Pickett et al., 1992). Proper water management is essential to minimize contamination, but may be difficult to achieve, especially in areas having shallow water tables or episodic high rainfall events. Such conditions are common in Tulare County. In recent years, many statistical and simulation models have been developed to describe and to predict pesticide leaching processes and transport into groundwater (Rao et al., 1985; Jury et al., 1987; Leonard and Knisel, 1988 and 1989; Goss, 1992; Shivkumar and Biksham, 1995). Most of the indices and statistical models were developed based on the soil characteristics and/or chemical properties of the pesticide (Gustafson, 1989).

The major factors contributing to pesticide leaching interact in a complex way within the agricultural landscape. Although much work has been done in assessing pesticide contamination in groundwater, the controlling factors and their interactions in relation to agriculture have not been sufficiently documented at a regional scale. Because of the potential for long distance transport to deep groundwater and the need to understand regional use and distribution patterns, new approaches and methods are needed for assessing pesticide contamination at a regional scale. Geographic Information Systems (GIS) are computer-assisted mapping and map analysis programs (Burrough, 1986) that have been widely used in geography and landscape ecology studies. Early GIS work mainly pertained to spatial mapping, while more recent GIS studies have integrated mapping and modeling (Wilson et al., 1992). A GIS-driven pesticide leaching model, such as the one developed for this study, provides a means to evaluate complex spatial and temporal patterns in pesticide use and transport.

This paper focuses on: (1) identifying the factors that cause pesticide leaching into groundwater, (2) understanding the relationship between the chemicals in groundwater as they are affected cropping systems and soil characteristics, and (3) mapping the potential contamination sites for given cultural practices and soil properties.

2. Materials and Methods

2.1. Study area

The agricultural region in the western third of Tulare County (35–36° N, 118–119° W) in the Central Valley of California was chosen as a case study because of its high agricultural productivity and the severity of its pesticide groundwater contamination problem. More than 40 commodities were produced in the 384460 ha of irrigated land in the county (Tulare County, 1990). A crop production map from

Figure 1. Major crops grown in Tulare County, California and their distributions in 1985.

1985 is shown in Figure 1 to illustrate the distributions of the major crops on which the herbicides of interest were used. The terrain is largely flat valley bottom land, although the location of citrus on the eastern side of the county marks the transition into the lower foothills of the Sierra Nevada range to the east. The lands along the eastern boundary of the agricultural region are managed as rangeland. Due to the comparatively uniform valley bottom topography of the agricultural lands in the county and the resolution of the available data, townships were used as the base mapping unit and well site and other point data were aggregated to townships for statistical analysis. Townships are a common administrative unit in the western United States, forming a square grid of 9.8 km^2 numbered from a north-south base line and an east–west meridian. Each township is further divided into 36 subgrid sections. In addition, most public and private agencies that collect and maintain agricultural databases use the township as their study unit because of its consistency in size.

2.2. Data sources

Monitored groundwater elevation (ground surface-to-water depth) data from 1219 wells in Tulare County were obtained from the U.S. Bureau of Reclamation for both spring and fall seasons between 1970 and 1990. These wells were within unconfined aquifers and have UTM (Universal Transverse Mercator) coordinates that permitted mapping their locations within the GIS database. Land use maps for 1985, with minimum mapping units of 0.81 ha were obtained from the San Joaquin District, California Department of Water Resources. Soil maps (1 : 63360) that were routinely used by farmers in the County were obtained from the University of California Cooperative Extension, Tulare County. U.S. Department of Interior Soil Conservation Service maps of comparable resolution were unavailable. Data on pesticide applications and pesticide residues in wells mapped with the township, range and section coordinates (1/36 township $\simeq$ 0.27 km^2, minimum mapping unit) were obtained from the California Department of Pesticide Regulation. Not all wells were monitored for pesticide residues, hence the pesticide residue data were not as well resolved as the well density. The number of wells sampled increased after 1985 and the frequency of sampling depended on detection of residues. Close to 1000 wells were monitored for pesticides and these were unevenly distributed in 42 townships with as many as 149 wells monitored and as few as one well monitored in a township. These data were averaged to obtain mean township values.

2.3. Materials and methods

Four pesticides (bromacil, diuron, simazine and DBCP) were selected for study because residues of these pesticides have been frequently detected in groundwater in Tulare County. Bromacil, diuron and simazine herbicides are used for weed control, and they can be persistent in soils for a few years after application. DBCP, a

Table II
The classes of the pesticide application rate (kg/ha)

Classes		Diuron and bromacil	Simazine
No application	1	< 0	< 0
Low	2	0 – 1.2	0 – 1.0
Medium	3	1.2 – 2.0	1.0 – 2.0
High	4	> 2.0	> 2.0

Table III
Combining soil and pesticide leaching loss potential (modified from Goss, 1992)

Soil leaching potential	Combined leaching potential for pesticide			
	Large	Medium	Small	Extra small
Very low	2	2	1	1
Low	3	2	2	1
Intermediate	4	3	2	1
High	4	4	3	2

nematicide, was widely used as a soil fumigant in orchards and vineyards beginning in the mid 1950s until it was banned in 1977. Nonetheless, bromacil and diuron have the longest half-lives in aerobic soil while DBCP has seven times the persistence of diuron in wet soils and persists in wet soils more than two orders of magnitude longer than bromacil and simazine. All of these pesticides are water soluble but have varied adsorption coefficients (Table I). Because the rate of pesticide application also varied spatially and temporally, the application rate of the selected pesticides used in the GIS analysis was based on a three-year average (in kg/ha using data for 1986, 1987 and 1988) for each pesticide (Table II) except for DBCP which had already been banned by this period although large amounts of DBCP (over 0.1 kg/ha) had been applied in a north–south swath across ranges 24, 25 and 26 on the eastern side of the cultivated townships.

Soil leaching potential and soil–pesticide interaction (Table III) were determined using the Goss model (1992), consisting of (1) soil ratings for potential pesticide leaching and potential surface loss, and (2) pesticide rankings for potential leaching. The soil leaching potential is based on the soil type, depth, and moisture. The leaching potential for soil–pesticide interactions uses the soil leaching potential and modifies it by the specific properties of the pesticide that determine its solubility and adsorption coefficients. Because the leaching process included the pesticide source, pesticide properties, and leachable media, the potential pesticide leaching sites in the county were identified in the GIS from map overlays of these factors. For example, the overall pesticide leaching potential in townships was determined from a derived map that combined overlay maps of pesticide applications, soil–pesticide

Table IV
Combined matrix of the classifications of soil–pesticide leaching potential and the classes of pesticide applications rates

Applications rate	Soil–pesticide leaching classes			
	Very low	Low	Medium	High
Very low	1	2	3	4
Low	2	4	6	8
Medium	3	6	9	12
High	4	8	12	16

interactions, and a soil map. The matrix in Table IV shows the possible classes of pesticide leaching potentials, calculated from the product of the classification of soil–pesticide interactions and the pesticide application rate. The definition of class boundaries is arbitrarily set and the product of the classification was used only for scaling the interactions. Therefore, in this case, values of 1 to 3 were classified as a low leaching potential, values of 4 to 6 as medium, values of 8 to 12 as high, and a value of 16 was a very high leaching potential. An examination of these classes shows a reasonable relative ranking in leaching potential for these pesticides and soils as based on the results of Goss (1992).

A Pesticide Contamination Index (PCI) was developed to compare the magnitude and degree of contamination among pesticides throughout the county. The PCI was defined as the weighted average residue concentrations (ppb) divided by the Health Advisory Level (HAL, ppb), i.e.,

$$\text{PCI} = \Sigma\{(N_i/N)^* PC_i\}/\text{HAL} \quad i = 1, ..., N$$

where N_i is the number of contaminated wells sampled in a township and N is the total number of wells sampled for pesticide residues in the county, and PC_i (ppb) is the average concentration of the pesticide residues measured in a township. HAL stands for Health Advisory Level and is an index published by the U.S. Environmental Protection Agency's Office of Drinking Water and Office of Water Regulations and Standards (1987). HAL values are a risk assessment guideline that includes a margin of safety to protect human health. Any pesticide residue value above the HAL is considered as unsafe for human consumption. Therefore, HAL is widely used by regulatory agencies for advisory purposes. PCI can be used to evaluate the toxicity of each pesticide in order to prioritize remediation processes when more than one chemical is detected.

Land use maps and soil type maps were digitized in ARC/INFO GIS (ESRI, 1990). All other data were stored in the GIS database. The ARC/INFO was used for data storage, spatial analysis, and illustrations, and SAS (SAS Inc., Cary, NC) was used for statistical analysis. Indices describing crops and soils are described more completely in Zhang (1993) and included crop diversity, crop water demand, and soil water-holding capacity. Crop diversity refers to the relative number of crops in a township, i.e.

$$R = S/S_{\text{max}}$$

where S is the number of the crops grown in a township and S_{max} is the maximum number of commodities in the county. Crop water demand represents the amount of water required for evapotranspiration for all crops grown in a township. The value was estimated according to the following formula:

$$TWD = \Sigma[(CWD_i/CWD_{\text{max}})^* I_i]$$

where TWD is the total crop water demand in a township, CWD_i is the annual water of ith crop in a township; and CWD_{max} is the maximum water demand of a crop in the county. I_i equals 1 of ith crop is present in a township and I_i equals 0 if ith crop is absent in a township. Soil water-holding capacity was estimated from soil texture for each soil type and then given a weighted average for each township. For example,

$$SAW\text{T(cm)} = ((\Sigma SAW^* SA)/\Sigma SA)^* 2.54$$

where SAW $((M_{\text{eq}}\text{-}W_p)^*A_s{}^*D_s)/100$, A_s=2.65*(1-S/100) and S=27+0.7M_{eq} (Roe, 1950). $SAWT$ and SAW represent the soil water holding capacity (cm) in a township and in a soil type, respectively; SA is the area of each soil type, M_{eq} is the moisture equivalent at a soil depth, where W_p is the wilting coefficient (M_{eq}/1.84), A_s is the apparent specific gravity; D_s is the thickness of soil horizon, and S is the soil pore space.

Correlation analysis was used to examine the spatial relationship between pesticide leaching, crop patterns and soil types.

3. Results

3.1. Pesticide application and its leaching potential

The applications of simazine and diuron in Tulare County increased up to 1986 and then decreased (Figure 2). Bromacil had a slight but steady increase in application during the 1980s. Because of specific crop-weed-herbicide applications, bromacil (Figure 3(a)) was used in the townships of the northwest, southeast, and in the agricultural lands along the eastern foothills of Tulare County. High and moderate application rates, as shown in Table II, were used in townships of the northwest and southeast, particularly in vineyards, citrus, and orchards. Diuron (Figure 3(b)) was widely used at moderate rates of application throughout the county except in a few townships. High and moderate application rates of simazine (Figure 3(c)) were used in townships along the foothills and in the northwest townships, while there was almost no application in the southwest townships.

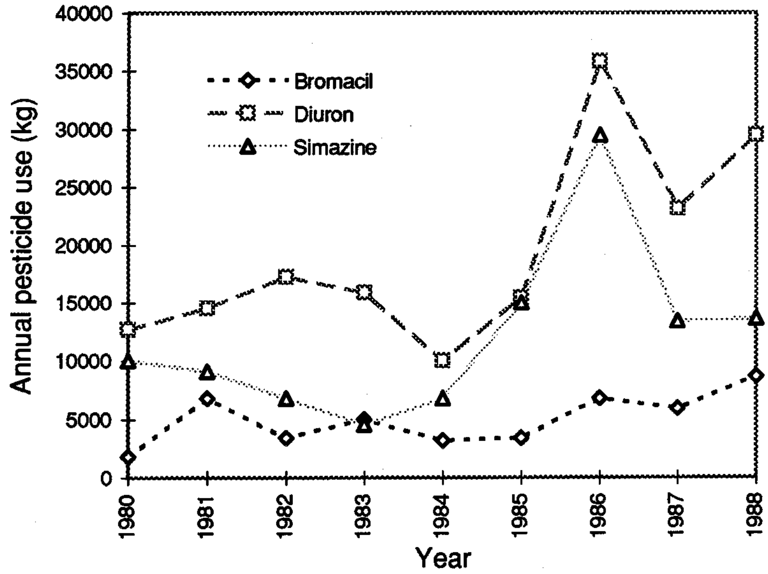

Figure 2. Estimated annual pesticide use (kg) in Tulare County, California for the years 1980–1988 for bromacil, diuron, and simazine.

The Goss model used attributes from the soil database including soil texture, depth, and soil water-holding capacity. Spatial variation in soil moisture capacity is shown in Figure 4(a). Generally, soils having highest leaching potentials have lowest water-holding capacities. Results of the Goss model showed that bromacil, diuron, DBCP and simazine all have high leaching potentials (Table III), primarily because they are water-soluble compounds. The soil types having medium to highest leaching potentials (Figure 4(b)) as estimated from the Goss model, were found in the townships of the extreme northwest and from the center of the county toward the foothills of the southeast. Very low soil leaching potentials were found only for the soils in the townships of the extreme southwest, in the center, and along the northern edge of the county. Because of soil variability, potential pesticide leaching patterns are complex. The most immediate observation is that many areas having medium and high potential for leaching are not the townships having the highest pesticide application rates, as shown in Figures 3(a)–(c). Because all the pesticides in the study were classified into the highest potential leaching class, similar spatial patterns were found between soil water-holding capacity, soil leaching potential maps and the soil–pesticide interaction maps (Figure 4(c)) except that there were no areas with with very low leaching potentials. Nonetheless, one could not directly infer locations of high potential soil–pesticide interaction directly from soil properties.

Considering the average bromacil application rates and the potential for soil–pesticide interactions, the area most susceptible to high and moderate bromacil

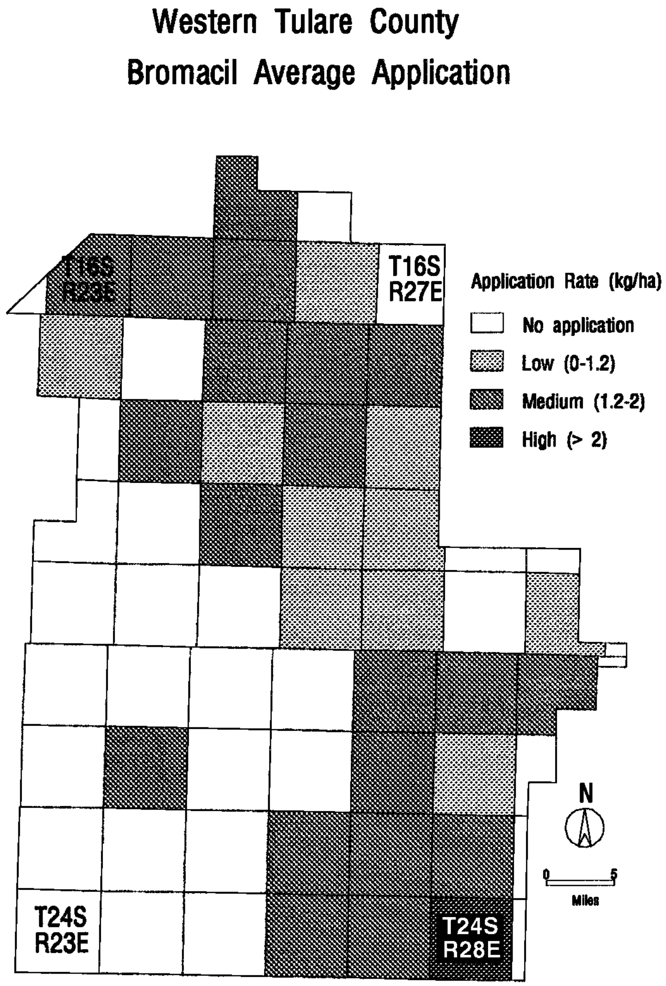

Figure 3(a)–(c). (a) The spatial pattern of average bromacil application rates (kg/ha) for townships in Tulare County. Offset observed in the figure between T20 and T21 is a map plane adjustment in the township survey data. (b) The spatial pattern of average diuron application rates (kg/ha) for townships in Tulare County. (c) The spatial pattern of average simazine application rates (kg/ha) for townships in Tulare County.

leaching potentials (Figure 5(a)) were found along the foothills and the townships of the northwest and were mainly associated with citrus and orchard crops. Clearly it would be possible to develop a monitoring and mitigation plan at the sub-township level if pesticide information at the resolution of the soil data were gathered at a larger number of wells. Almost all agricultural land in the county was classified as having moderate and/or high leaching potentials for diuron (Figure 5(b)), except for two townships at the southwest and northeast corners. For simazine, only four townships were classified as having the highest leaching potentials (Figure 5(c)).

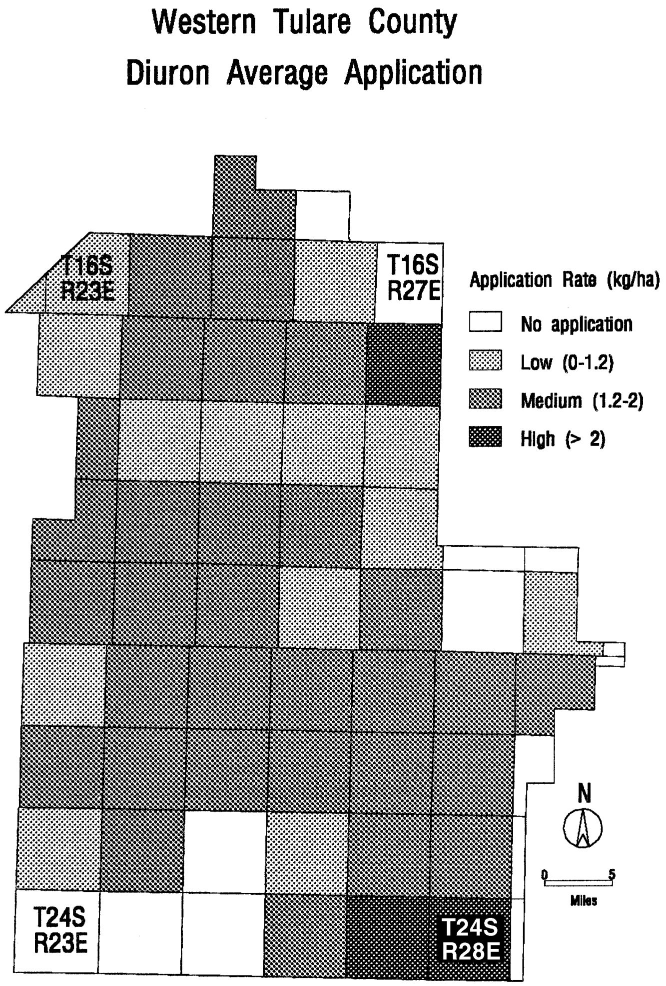

Figure 3b.

For both bromacil and simazine, the areas having high leaching potentials generally are citrus or orchards, while areas of lower leaching potentials were those planted with cotton and alfalfa crops (Figure 1). By comparing the differences in leaching potential among these pesticides it is clear that their spatial distributions in the soil are distinct despite similarities in their herbicide targets, crop types, and solubilities. The complexity of these spatial patterns are not apparent in the application maps shown in Figures 3(a)–(c)), despite general similarities.

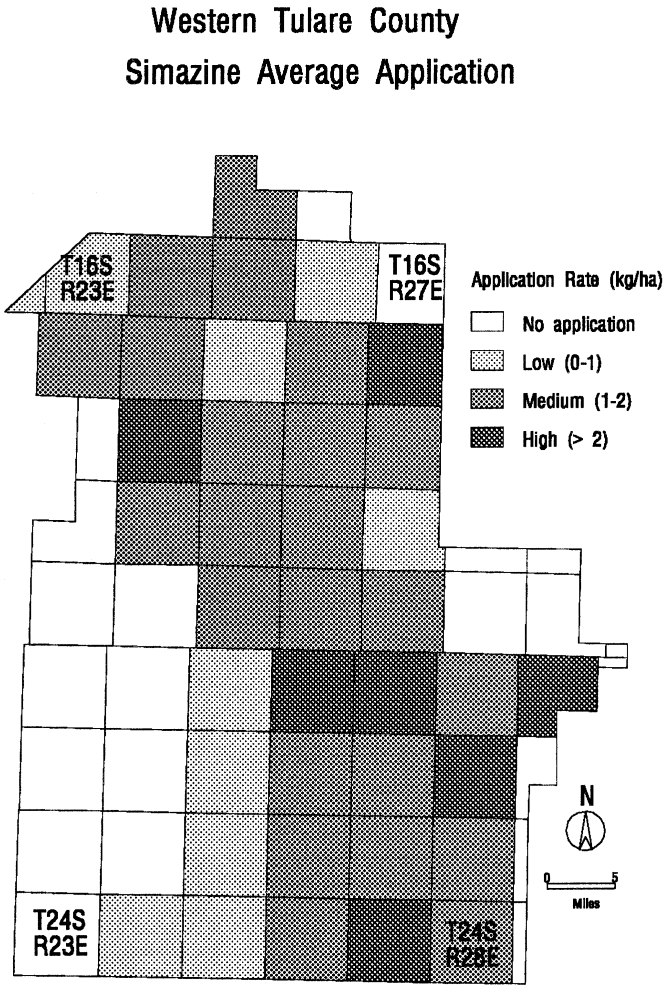

Figure 3c.

3.2. Pesticide contamination in groundwater and its relation to other factors

The well monitoring results showed that DBCP was first detected in 1979, simazine in 1982, and diuron and bromacil in 1986 (California Environmental Protection Agency, 1992). Following their initial detection, each of the pesticides has been continuously detected in county wells, and the number of wells reporting contamination has increased over time. Since 1986 residue concentrations in groundwater, as aggregated by township, have increased for bromacil, diuron, and simazine (Figure 6). Residues of DBCP in groundwater dramatically decreased in 1980 and have fluctuated in concentration around the values between 0.2 and 0.7 ppb since then.

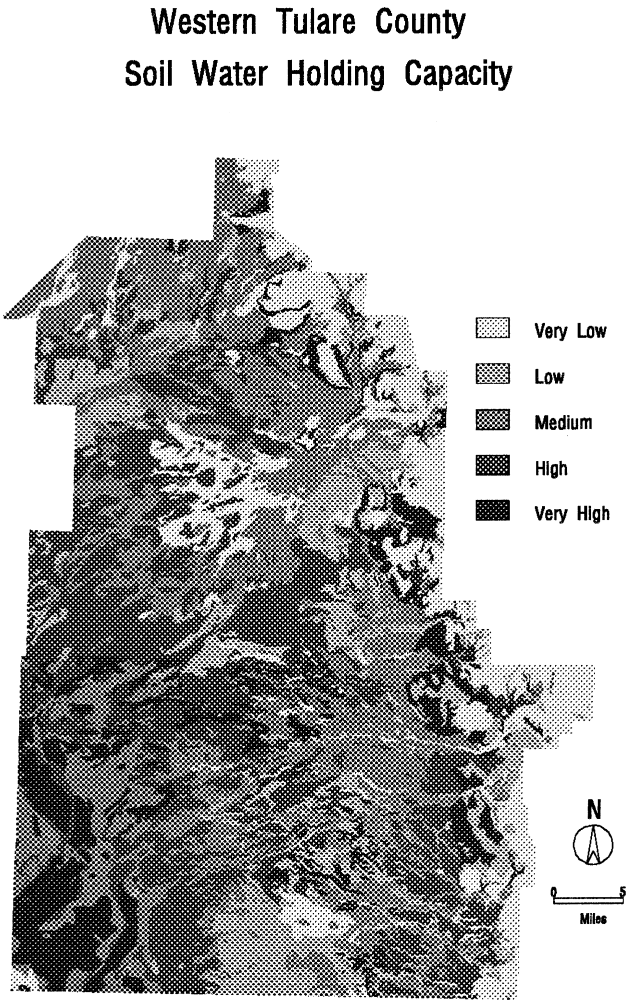

Figure 4(a)–(c). (a) Soil water-holding capacity as determined from the soil attribute database for western Tulare County. (b) The spatial distribution of soil leaching potential for four herbicides based on the Goss model. (c) Leaching potential for soil-pesticide interactions in Tulare County, California.

To evaluate the magnitude of contamination, a pesticide contamination index was constructed which was positively related to the average concentration of pesticide residues in groundwater (p<0.01), except that there was no significant relationship for simazine.

Because the monitoring program of the California Department of Pesticide Regulation was not fully established until 1985, and diuron and bromacil were not detected until 1986, the average pesticide residues in groundwater were calculated for two time intervals: before 1985 and after 1985 (Table V). Before 1985, the monitoring data showed that 88% of the wells contained detectable levels of DBCP

Western Tulare County
Pesticide Leaching Potential in Soils

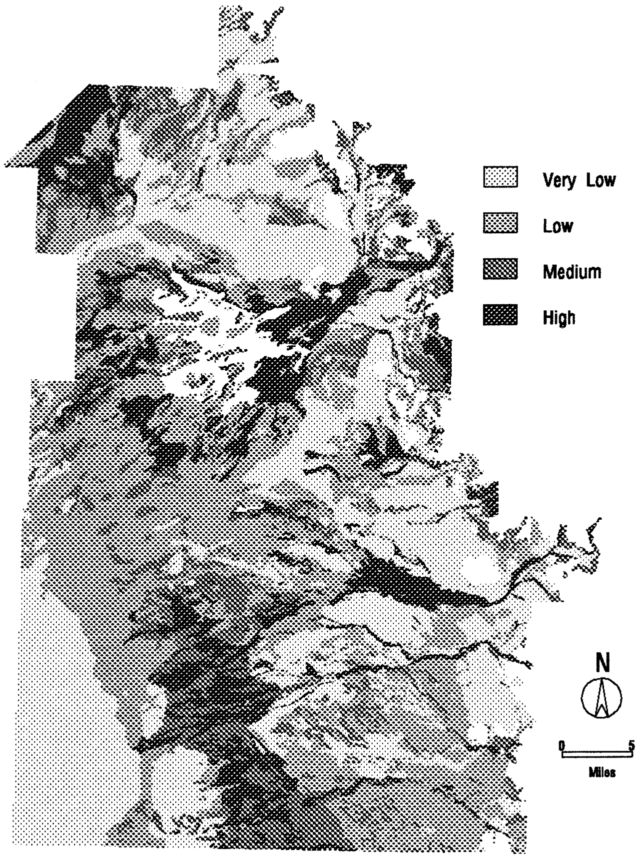

Figure 4b.

residues. The average DBCP concentration was 0.727 ppb with a standard deviation of 1.323 from 432 wells sampled. This concentration was more than 36 times the HAL advisory index for DBCP. Simazine was only detected in 6% of the wells, and the average concentration was 2.75 ppb with a standard deviation of 1.06 from 34 wells, a contamination about three times the HAL advisory level. On comparing the PCI values shown in Table V, we see that DBCP had the largest PCI value (55.10), followed by simazine (2.75). Because PCI incorporated the average concentration of the chemical and its health advisory level from U.S. E.P.A. standards, the value of the PCI should represent the composite contamination level. Therefore, one concludes that DBCP was the most significant contaminant when

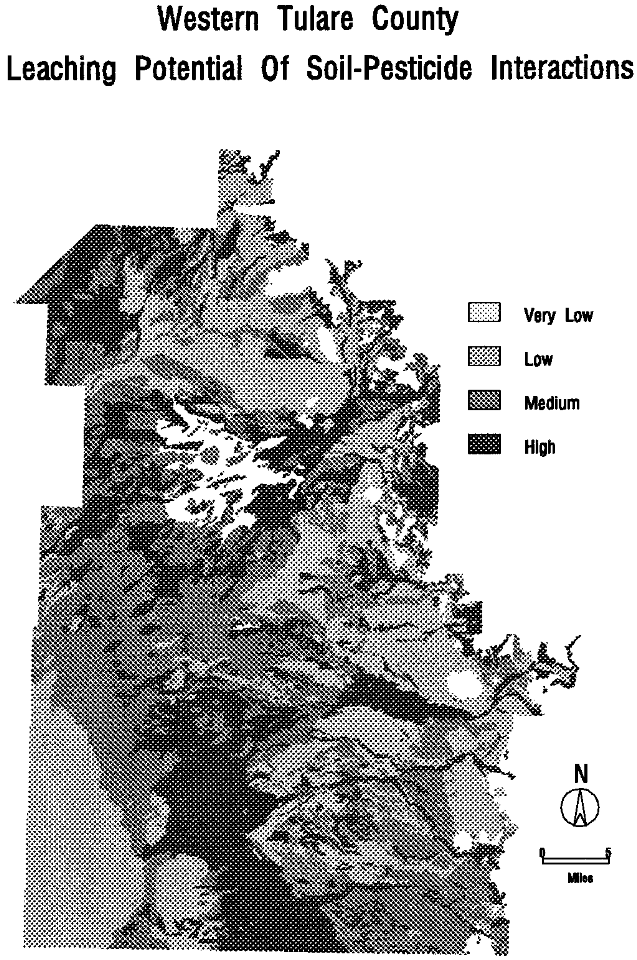

Figure 4c.

compared to the other pesticides. After 1985, the average concentration for DBCP residues in groundwater decreased to 0.626 ppb with a standard deviation of 0.569. Eleven years after the pesticide was first detected in Tulare County, the residues remained 30 times the HAL advisory level. The PCI had decreased to 23.75 by this time. The residues of bromacil and diuron appeared in groundwater with average concentrations of 0.337 and 0.282 ppb, respectively, much lower than the HAL advisory levels (Tables I, V). Therefore, on comparing the PCI values, we conclude that DBCP was still the most significant contaminant in groundwater (23.75); followed by simazine (0.20), diuron (0.0333) and bromacil (0.0033). Simazine residues were detected with a high frequency (84%) throughout the county, while bromacil was detected least often (58%) among the sampled wells.

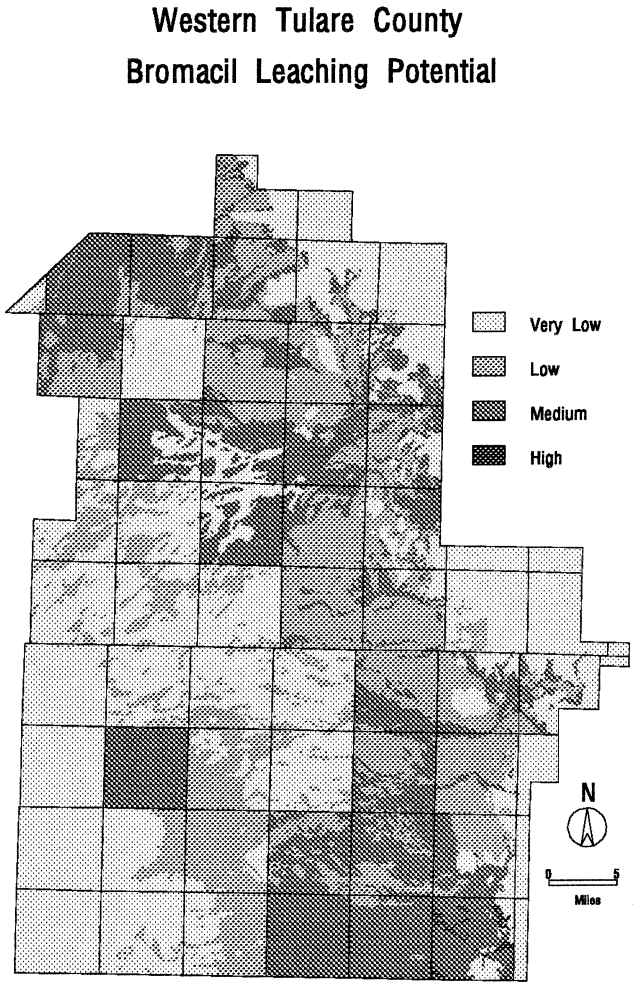

Figure 5(a)–(c). (a) Bromacil leaching potential in Tulare agricultural land. (b) Diuron leaching potential in Tulare agricultural land. (c) Simazine leaching potential in Tulare agricultural land.

The average pesticide residues after 1985 were used for illustrating the spatial contamination patterns and correlation analysis because of the availability of representative data. Bromacil contamination (Figure 7(a)) was found in the townships of T17S to T20S and ranges of R26E and R27E, and the township of T16S, R24E. A diuron contamination (Figure 7(b)) band was mainly associated with citrus production areas in the county. The spatial patterns of simazine (Figure 7(c)) in groundwater were similar to that of diuron. DBCP residues (Figure 7(d)) were detected from the north to south, and in the central portions of the county, where this compound was associated with tree fruit and grape production.

Groundwater contamination was statistically related to the characteristics of

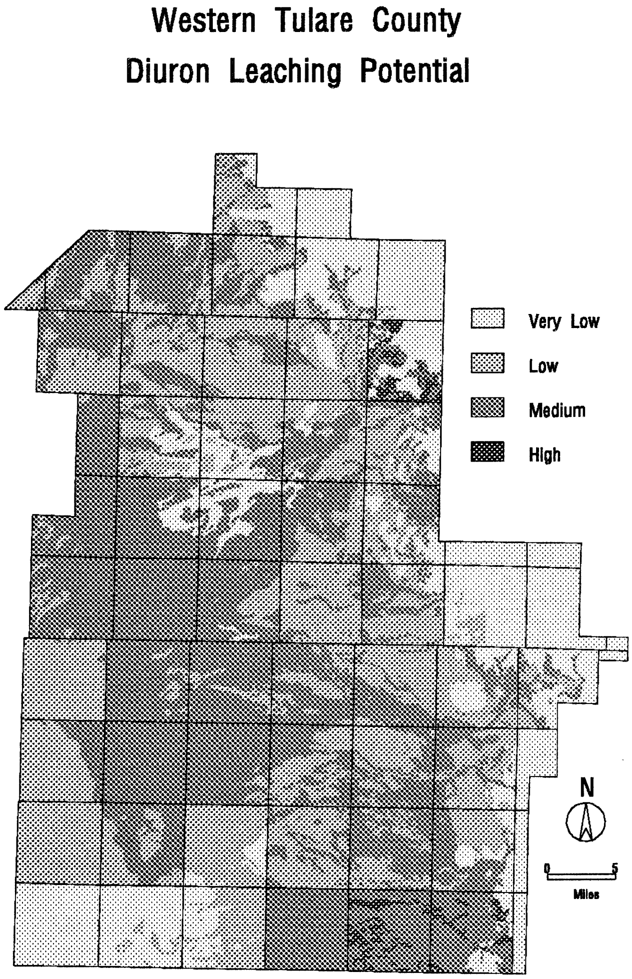

Figure 5(b).

the cropping system and soil types (Table VI). The distribution of major crops in Tulare County in 1985 is shown in Figure 1. Although the annual crops may change from year to year, fruit and vine crops represent a long-term commitment, and the distribution of these crops remains stable for a number of years. Thus, the map provides a realistic representation of agriculture in the county during the measurement period. Bromacil concentrations in groundwater (*PC, ppb* were significantly related to the relative number of crops in a township (*R*). Correlation analysis shows that as crop diversity increases in a township, higher bromacil concentrations are found in groundwater (Table VI). The number of wells sampled (*N*) for bromacil was strongly related to the relative number of crops and the crop water demand (*TWD*). DBCP concentration in groundwater and PCI were

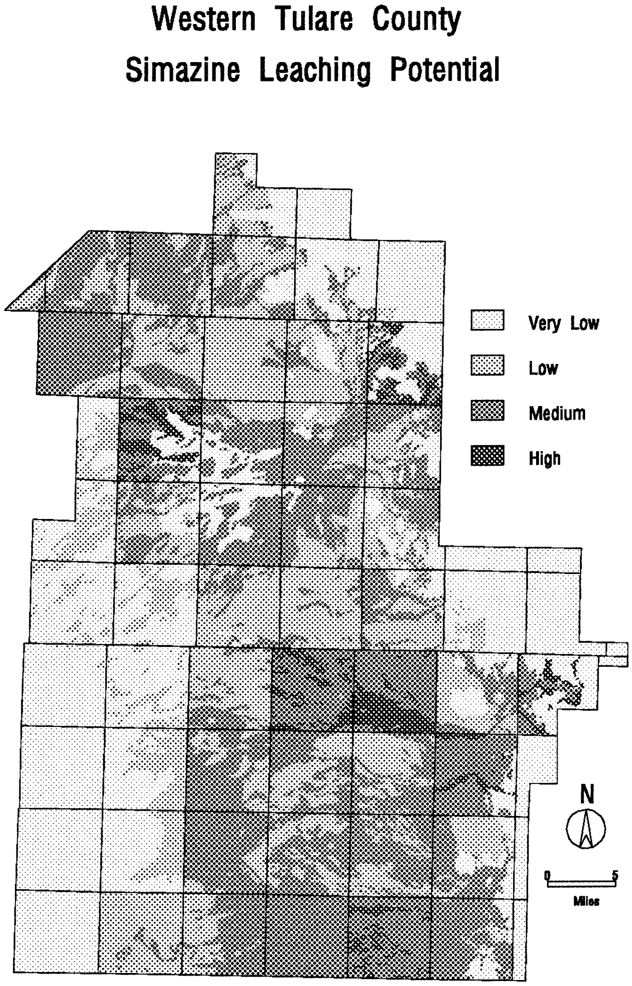

Figure 5(c).

significantly related to the average area of crops grown in the county (*MHA*). The number of wells sampled was not correlated with any crop or soil indices.

Diuron concentration in groundwater, the number of wells sampled, and PCI were positively correlated to the relative number of crops, crop water demand, and groundwater elevations at the end of the summer growing season. The PCI was negatively correlated to soil water holding capacity (SAWT) and average crop area in the county. The number of wells sampled for simazine and simazine PCI were positively correlated to the relative number of crops, crop water demand and groundwater elevation, and negatively related to soil water holding capacity. Average simazine concentration in groundwater did not correlate to the crop diversity, crop area, or to the soil indices.

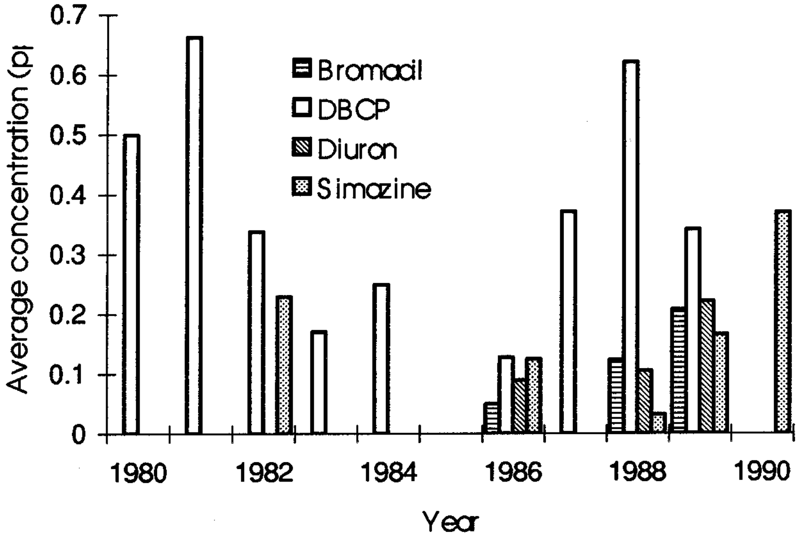

Figure 6. Pesticide residue concentrations in groundwater during the 1980s.

Table V

Number of wells sampled, number of positive wells, percentage of positive wells, average pesticide concentration (ppb), pesticide contamination index (PCI), and number of positive townships before and after 1985

Herbicide	Number of wells	Number of positive wells	Number of wells in Township	Detection (%) positive	Average (SD) concentration	PCI
Before 1985						
DBCP	432	381	20	88	0.7269(1.323)	55.10
Bromacil	9	0		0	0	0
Diuron	11	0		0	0	0
Simazine	34	2	2	6	2.75 (1.06)	2.75
After 1985						
DBCP	200	136	14	68	0.6257(0.569)	23.75
Bromacil	504	291	9	58	0.3368(0.168)	0.0033
Diuron	667	513	13	77	0.2823(0.201)	0.0333
Simazine	649	544	14	84	0.2029(0.160)	0.2000

4. Discussion

Bromacil, diuron and simazine have been used for many years in Tulare County for controlling both monocot and dicot weeds in citrus, orchards, vineyards, alfalfa and cotton crops. DBCP was widely used as a soil fumigant for nematode control but was banned in 1977 in California because it caused sterility in males who manu-

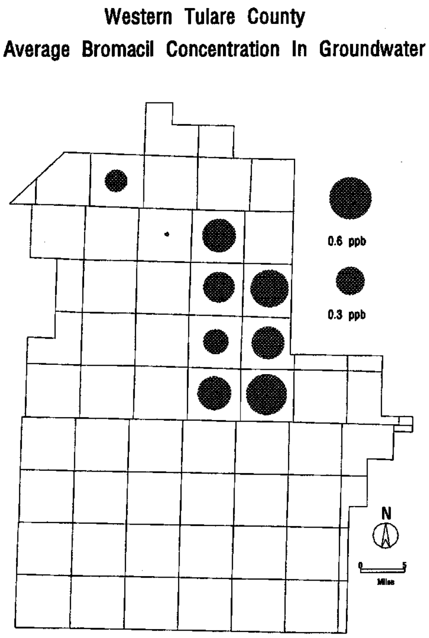

Figure 7(a)–(d). (a) Average bromacil residue concentrations detected in groundwater. (b) Average diuron residue concentrations detected in groundwater. (c) Average simazine residue concentrations detected in groundwater. (d) Average DBCP residue concentrations detected in groundwater.

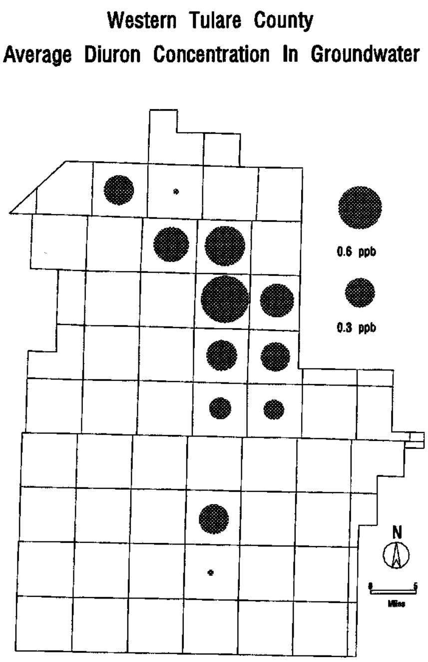

Figure 7b.

Western Tulare County
Average Simazine Concentration In Groundwater

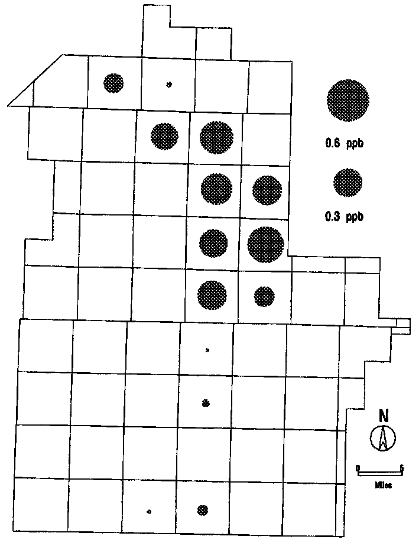

Figure 7c.

Western Tulare County
Average DBCP Concentration In Groundwater

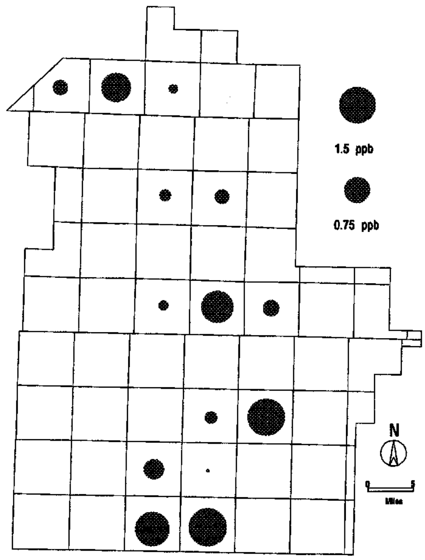

Figure 7d.

Table VI

Correlation coefficients among numbers of wells sampled after 1986, pesticide residue concentration in groundwater, county average of sums of the residue concentration and crops and soil characteristics

Pesticides	Crop and soil indices				
	R	TWD	SAWT	GWESM	MHA
Bromacil					
N	0.5454[a]	0.5348[a]	–0.2139	0.2249	–0.0059
PC	0.3916[a]	0.2782	–0.0574	0.0532	–0.0846
PCI	0.3835[a]	0.2684	–0.0561	0.0491	–0.0846
DBCP					
N	0.3646	0.3558	–0.3327	0.0210	0.4319
PC	0.4810	0.4470	–0.4650	0.0475	0.5848[b]
PCI	0.4161	0.3971	–0.3717	0.0653	0.6900[b]
Diuron					
N	0.5913[a]	0.6089[a]	–0.3600[a]	0.4069[a]	–0.3198[a]
PC	0.3648[a]	0.4318[a]	–0.3024[b]	0.4608[a]	–0.3563[a]
PCI	0.4366[a]	0.4832[a]	–0.3347[a]	0.4015[a]	–0.3198[a]
Simazine					
N	0.4269[a]	0.4464[a]	–0.2401[b]	0.2453[b]	–0.1794
PC	0.1769	0.2224	–0.1741	0.1625	–0.1437
PCI	0.3209[b]	0.3682[b]	–0.3000[b]	0.3134[b]	–0.1804

Notes:
N, The number of wells sampled after 1985. PC, Pesticide residue concentration in groundwater (ppb). PCI, Pesticide Contamination Index (ppb). R, Relative number of crops present in a township. TWD, Total crop water demand in a township. SAWT, Soil water holding capacity in a township. GWESW, Average groundwater elevation in spring in a township. MHA, Mean crop area in a township.
[a], [b] Represents the significance levels at 0.01 and 0.05, respectively.

factured this compound (Bouwer, 1990; Douglis, 1993). It was banned throughout the United States in 1979 because of potential carcinogenic risks and male infertility. Despite the fact that pesticide residues have been continuously detected in groundwater over a number of years and contamination issues have been raised by regulatory agencies, the application of pesticides has not decreased over time. These findings imply that farmers perceive agricultural production and economic benefit to be dependent on pesticide application to control weeds and other pests. To protect their economic investment farmers may not recognize other choices except those using current chemical technologies. However, farmers are aware of the environmental consequences of indiscriminate application of pesticides and would turn to other control mechanisms that are effective. For example, adapting biological controls such as crop and weed competition strategies and prey–predator relationships might be helpful in some cases.

Domagalski and Dubrovsky (1992) and Pickett et al. (1992) have pointed out that pesticide contamination of groundwater mostly occurs from normal or large applications when coupled with poor management practices. This suggests that significant reductions in contamination and pesticide residue transport could be obtained by altering farm management practices, especially pesticide application and water management.

The first factor to be considered is the soil potential for pesticide transport. Tulare County has diverse soil types including 30% having clay and clay loams and 28% having sandy loam or other sandy soils and generally low organic matter contents (U. California Cooperative Extension). Soil texture obviously affects pesticide movement, and soil permeability and erodibility affects loss by leaching and erosion. Soils with a high proportion of organic matter and clay absorb soluble pesticides better than soil that does not contain much organic matter (Bollag et al., 1992; Shaw et al., 1992). Fine textured soils with high organic matter contents will bind pesticides and limit off-site transport (Senesi, 1992). The pesticides in this study are highly soluble, and are likely to be leached or transported with eroded sediments. However, the specific soil–pesticide interactions and the chemical properties of the selected pesticides caused patterns of soil-pesticide leaching potentials to conform to the distribution of soil types (Figure 4(a),(b)).

Pesticide applications in low leaching potential soils have the least capacity for contributing to contaminant transport. For example, bromacil and simazine had low leaching potentials on the west side of Tulare county where heavy clay soils prevail. In contrast, application of highly soluble pesticides to coarse-textured soils are significantly more likely to result in leaching. The townships along the eastern foothills and the northwest corner of Tulare County that have high to moderate leaching potentials for bromacil, diuron, and simazine also have sandy soils (Figures 3(a)–(c)). This sensitivity to the soil medium provides a basis for a mitigation strategy if lower value crops or those that demand less investment in pesticides can be planted on sandy soils. The reduced crop economic benefit may be partially offset by lower management costs and lower risk of financial responsibility for off-site contamination.

Although we have discussed the source and media for potential pesticide leaching, farm water management and environmental factors such as rainfall and temperature influence both the speed of leaching and processes related to the rates of pesticide degradation. Water management is more important than temperaure in central California because of the Mediterranean climate and the low topographic relief. Tulare County has hot, dry summers and cool, wet winters, therefore summer irrigation practices are critical in mitigating transport. The correlation analysis indicated that diuron contamination decreased as the average pesticide application and average crop acreage increased. In reality, a large amount of the measured pesticide may have come from previous applications because of persistence in the soil, and may represent a contamination problem that existed decades before the sampling. Diuron has been regularly used in the county since the 1960s, and residues from previous applications may still persist. Therefore, it is necessary to carefully interpret correlations between applications and contamination.

Troiano and Segawa (1987) found that the type of irrigation system used was strongly related to the pesticide residue and the movement through the soil profile. Drip systems are considered best at minimizing pesticide residues in groundwater, while furrow and border irrigation are the worst systems. Pickett et al. (1992) have shown that frost protection from winter sprinkler irrigation in citrus is positively correlated with pesticide residues in groundwater. Therefore, winter farm practices can also contribute to mitigation strategies, by limiting pesticide leaching during frost protection activities when high groundwater table conditions exist. This suggests that leaching from citrus in the sandy northwest soils may be highly sensitive to winter irrigation practices. For this reason, the California Citrus Association has recommended adopting drip and sprinkler irrigation systems instead of surface irrigation methods.

Our results showed that soil contamination and transport is a combined function of many factors. Contamination usually occurred where high source loads were present (i.e. high rates or amounts of pesticide applications) and where efficient pathways were available (i.e. sandy soils with high water availability). Therefore, high concentrations of bromacil residue in groundwater were predicted at sites with crops having high water demand. Bromacil is highly soluble (929 ppm solubility in water) and has a low adsorption coefficient (17 cm^3/g K_{oc}). Hence, the residue concentrations of bromacil were not related to soil water-holding capacity. It is not clear from this work whether a high percentage of clay in soils will affect bromacil leaching potentials because its short hydrolysis half-life (30 days), should lead to rapid degradation. However, it should be noted that the health advisory level for bromacil is higher (90 ppb) than for the other pesticides, so its fate is of less concern.

DBCP also has a small adsorption coefficient (40 cm^3/g K_{oc}), and residues in groundwater are not affected by soil water-holding capacity. Residues were not related to crop type, crop diversity, or crop water demand because of its persistence and widespread usage as a soil fumigant. DBCP residue concentrations and PCI value corresponded to the average area of active cultivation and increased with the percent of crop area.

Diuron has the largest soil adsorption coefficient (499 cm^3/g K_{oc}) among these pesticides and is persistent in soils (Table I). In clay soils, diuron is largely adsorped after each application, minimizing leaching potential. Because diuron is commonly used for weed control, residues in groundwater have been frequently detected since 1986 when it was found for the first time in groundwater. Its widespread use may explain why diuron PC, N, and PCI were all significantly correlated to crop diversity, crop water demand, and to the height of the groundwater table.

Simazine, like diuron, has a high adsorption coefficient (340 cm^3/g K_{oc}), but has a low hydrolysis half-life (28 days). However, simazine has low water solubility (6 ppm) relative to the other pesticides (Table I). It is likely that simazine is adsorbed to soils after application. Increasing percentages of clay in the soil and higher water-holding capacity lowers the leaching potential for simazine.

More crops and greater demand for evapotranspiration requires more irrigation, so it is clear that irrigation is a major factor in determining pesticide leaching into groundwater. The question is how to apply irrigation properly such that the leaching potential can be minimized while agricultural production is optimized. The identified leaching potential maps for bromacil, diuron and simazine should provide information needed by farmers to apply these pesticides selectively.

5. Conclusions

Large pesticide applications, permeable soils and water management are primary factors affecting the quantity and patterns of pesticide leaching into groundwater. Pesticide properties, pesticide application rates, and soil types permitted us to identify and map sites of potential contamination for four pesticides in Tulare County. These sites were associated with high or moderate leaching of pesticides based on estimates of specific soil–pesticide interactions combined with moderate to high rates of pesticide applications. Increased pesticide residue concentrations of diuron and simazine in groundwater were found to be significantly related to the depth of the groundwater table (which in Tulare County is generally shallow), crop diversity and crop water demand, and soil water–holding capacity.

The frequency of well sampling for each pesticide was related to the concentrations of each pesticide residue measured in the wells. Sites sampled most frequently were found to have high herbicide residues. Thus, well information alone, because of sampling bias, is insufficient to evaluate leaching and contamination patterns on a regional basis. Furthermore, application rates and quantity of the selected chemicals varied spatially and temporally and required a GIS approach to evaluate county-wide patterns. The frequency of pesticide application was found to be linearly related to the economic value of crops. Application patterns did not coincide with well site information.

The modeled GIS estimates of pesticide concentration in groundwater and the identified areas of potential leaching provide a direct view of the degree of dispersion and spatial patterns of pesticide groundwater contamination in Tulare County. This type of information enhances public awareness of the potential for soil contamination and is of direct benefit to farmers, researchers, public officials for environmental planning, health and safety efforts, and mitigation activities. These maps also provide an improved understanding of the nature of the spatial interrelationships between pesticide contamination, cropping systems, soil characteristics and groundwater depth. These results can be used by regulatory agencies and health services to improve the efficiency of pesticide use and to suggest guidelines for management alternatives in sustainable agriculture.

Based on this research, we recommed that pesticide application procedures be revised to consider the potential for contamination and off-site transport. GIS appears to be a feasible method to track the spatial and temporal patterns of the many variables involved, to monitor and evaluate current conditions, and to model future trends. Furthermore, environmental protection, sustainable agriculture and timely guidance to farmers can be optimized through well designed monitoring programs that sample the potential pollutants regularly enough to permit accurate inferences from spatial statistical analysis.

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