Shallow Ground-Water Quality Beneath Row Crops and Orchards in the Columbia Basin Irrigation Project Area, Washington

By Joseph L. Jones and Lonna M. Roberts

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<URL:http://wwwrvares.er.usgs.gov/nawqa/nawqa_home.html>

FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.

- Describe how water quality is changing over time.

- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of more than 50 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within these study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
acre	4,047	square meter
acre-foot (acre-ft)	1,233	cubic meter
pound	0.4536	kilogram
degree Fahrenheit (°F)	°C = 5/9 x (°F-32)	degree Celsius

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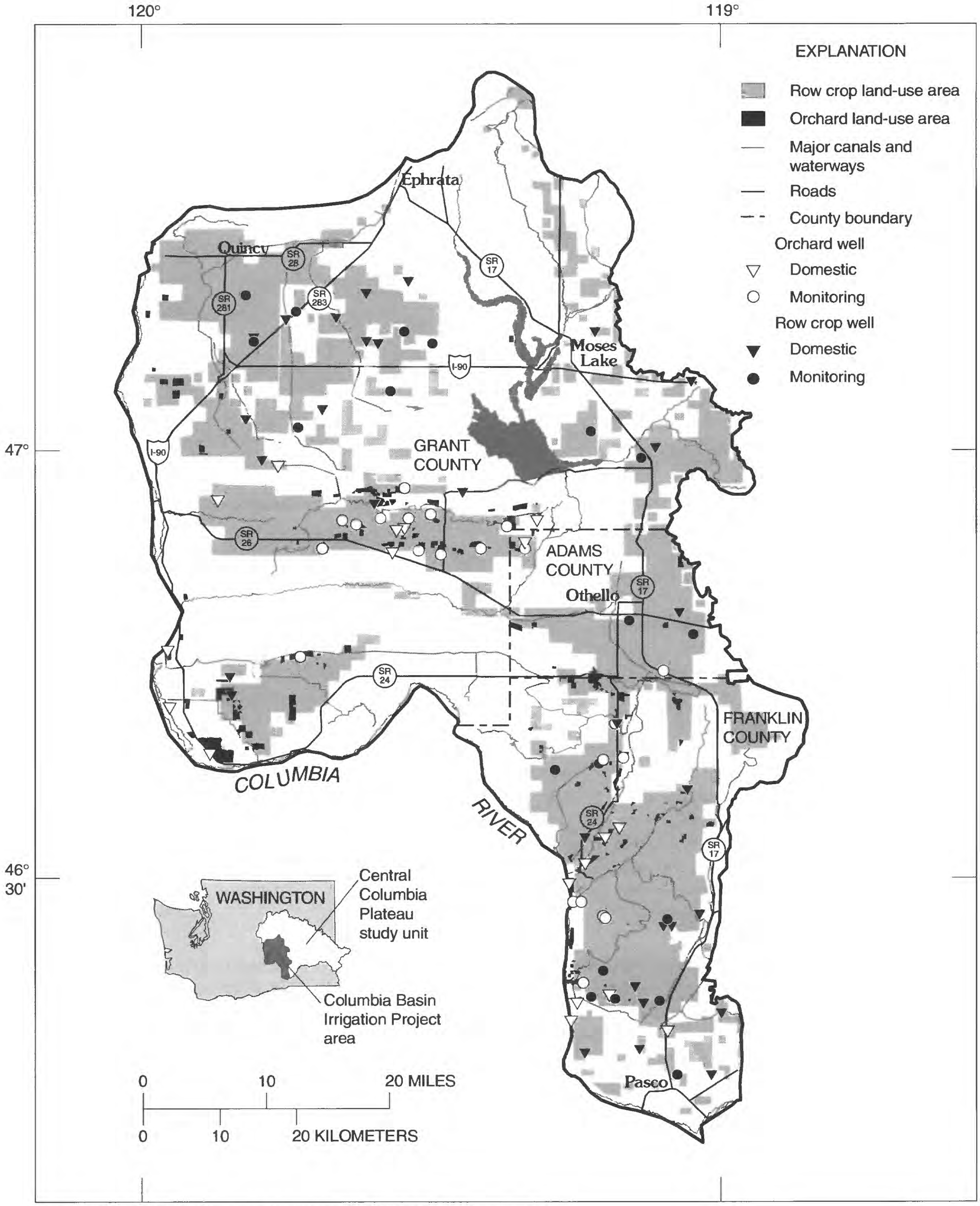
ABSTRACT

The impacts of two agricultural land uses—(1) row crop rotations, including potatoes and (2) orchards—on shallow ground-water quality were investigated as part of the National Water-Quality Assessment (NAWQA) Program. Eighty-nine wells were sampled from June 1993 through July 1995. The investigations were conducted in accordance with NAWQA protocols to allow comparisons among different areas of the United States and focused on the occurrence of nitrate and pesticides in shallow ground water. One hundred forty-five pesticides, pesticide degradates, and volatile organic compounds were targeted for analysis. The locations of shallow monitoring wells (average depth 43 feet) and existing shallow domestic wells (average depth 140 feet) were randomly selected. Well construction and sampling were carried out according to procedures that minimized the chances of contamination from the equipment used.

Over 30 percent of the domestic wells sampled had nitrate concentrations that exceeded the maximum contaminant level (MCL) established by the U.S. Environmental Protection Agency (USEPA), with a greater percentage of exceedances in row crop areas than in orchards. Three of 22 detected pesticide compounds with established USEPA human-health criteria—dieldrin, EDB (ethylene dibromide), and 1,2-dichloropropane—also were found at concentrations exceeding their criteria, although only EDB exceeded its criterion in domestic wells. Pesticide detections were related to pesticide use: pesticides used at higher average rates within a given land-use setting were generally detected at higher rates in wells in that setting. Otherwise, differences in the impacts of the two land uses on water quality were small when variations in well type (monitoring versus domestic) were not accounted for; pesticide detection rates were approximately 70 percent for both land-use settings, and the average numbers of pesticides detected per well were similar (approximately two pesticides detected per well in each setting), although a greater variety of pesticides was detected in row crop wells. In the domestic wells, the median desethylatrazine-to-atrazine concentration ratio (DAR), an indicator of ground-water residence time, was significantly higher in the orchards than in row crop areas. The comparison of DAR values suggests that atrazine (and perhaps other herbicides used on row crops) detected in shallow ground water beneath orchards may have either come from row crop areas upgradient or from row crops that preceded orchards on the same land.

INTRODUCTION

This report describes an investigation of the effects of two types of land-use activities on the quality of shallow ground water in the Columbia Basin Irrigation Project area (CBIP, fig. 1), which is composed of parts of Grant, Franklin, and Adams Counties in eastern Washington. These land-use studies are one component of the ground-water quality assessments conducted by the Central Columbia Plateau study unit of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program. The other major components of the NAWQA ground-water investigations are study-unit surveys, which are large-scale assessments of ground-water quality throughout entire basins, and flow-path studies, which are small-scale investigations that examine



Base from U.S. Geological Survey digital data, 1:100,000, UTM zone 11 projection

Figure 1. Location of the Columbia Basin Irrigation Project (CBIP) area and locations of domestic wells and newly installed monitoring wells sampled in the irrigated row crop and orchard land-use areas.

the evolution of ground-water quality along individual flow paths in the subsurface. Consistent procedures for study-area delineation, well-site selection, well construction, sample collection and chemical analyses used by all of the NAWQA study units across the United States, will allow the results of these ground-water investigations to be compared and synthesized on regional and national scales (Gilliom and others, 1995).

The land-use studies are designed to investigate relations between land use and shallow ground-water quality within specific, consistently defined land-use settings. In the CBIP, land use is predominantly agricultural, and these studies examined the potential impacts of the widespread application of agricultural chemicals on shallow ground-water quality in agricultural settings. As such, the studies were conducted in areas where agricultural chemicals were applied to crops, rather than locations where these chemicals may have been spilled. Adherence to nationally classified land-use categories allows national-scale comparisons to be made; the focus on shallow ground water provides the earliest indication of contamination or other water-quality changes and minimizes the influence of factors other than land use on water quality prior to sampling.

Purpose and Scope

This report describes and compares shallow ground-water quality beneath two land-use settings and presents possible explanations for the observed differences. Nitrate concentrations and pesticide detection rates are discussed in relation to agricultural chemical use and other controlling factors, and the relation of the data to human health criteria is briefly discussed. Potentially important factors influencing ground-water quality that are not discussed in this report are soil and aquifer characteristics (such as the occurrence of confining layers).

Land Use in the Study Area

Row crop rotations including potatoes (hereafter referred to as row crops) and orchards were selected for investigation. Row crops were selected because of their large acreage within the CBIP, their economic significance in the State (particularly potatoes), the large amounts of soil fumigants (primarily nematocides) applied to potatoes, and the widespread use of herbicides on row crops. Orchards were selected because of their rapid expansion within the CBIP, their economic significance to the State, and the fact that the highest rate of insecticide use in the CBIP is on orchards.

DESCRIPTION OF THE STUDY AREA

Geohydrology

The study area is underlain by massive basalt flows which are warped into a broad structural basin. Subbasins formed locally by steep folding and faulting of the basalts subsequently accumulated deposits of clay, silt, sand, and gravel from glaciofluvial action during the Pleistocene Epoch (Walters and Grolier, 1960; Drost and Whiteman, 1986). These unconsolidated deposits compose the aquifers sampled for these studies.

Agriculture and Agricultural Chemical Use

Over 5 thousand miles of canals distribute 3 million acre-feet of water imported from Franklin D. Roosevelt Lake throughout the CBIP annually. In the north, ground water augments this water supply. The introduction of such large amounts of water has led to a dramatic increase in the amount of recharge to the underlying aquifers. As a result, the water table in the CBIP has risen hundreds of feet in many areas (Drost and others, 1993). High aquifer recharge rates are commonly associated with an enhanced susceptibility to ground-water contamination (Mueller and others, 1995; Barbash and Resek, 1996).

A wide variety of crops is irrigated on over half a million acres of land in the CBIP. Table 1 presents acreage and pesticide use data for selected crops grown in the CBIP. Agricultural chemicals, primarily fertilizers, soil fumigants, and herbicides, as well as insecticides and fungicides, are used throughout the CBIP. Most of these chemicals are applied at rates of a few pounds per acre annually (table 2), but nitrogen fertilizers are applied at annual rates of hundreds of pounds per acre to potatoes, wheat, and corn, and the fumigant 1-3-dichloropropene (contained in Telone II, for example) is applied at comparable rates to potatoes. This widespread and intensive agricultural chemical use, combined with high recharge rates, presents a significant potential for ground-water contamination by these compounds throughout the CBIP.

Table 1.--*Row crop and orchard acreages and associated agricultural chemical use in the Columbia Basin Irrigation Project*
[--, not ranked or not known; <, less than]

Crop	Acreage[1]	Cash value rank in Washington State[2]	Total pesticide use[3] (tons of active ingredient per year)
		Row Crops	
Hay[4]	149,100	7	50
Wheat	94,500	4	40
Potatoes	59,900	5	4,693
Corn	55,600	18	34
Dry beans	33,900	27	36
Sweet corn	17,600	17	25
Pasture	13,900	--	<1
Asparagus	12,900	16	39
Pea seed	11,200	39	1
Mint	10,600	19	54
Alfalfa seed	9,100	32	2
Barley	6,200	25	2
Onions	3,900	14	12
Radish seed	3,900	--	10
Bean seeds	3,700	--	5
Green peas	3,300	23	2
Grass seed	3,300	29	<1
Grapes	2,900	15	8
Carrots	2,800	26	161
Carrot seed	2,500	--	6
Oats	700	--	<1
Onion seed	500	--	1
Sod	200	--	<1
Cucumber	100	--	<1
Squash	100	--	<1
Other crops	11,400	--	--
		Orchards	
Apples	27,433	1	631
Cherries	2,030	11	31
Peaches	876	34	16
Pears	638	9	18
Plums	136	--	3

[1] Calculated from irrigation block data (average of data from 1987 to 1991) and surrounding crop acreages from Van Metre and Seevers (1991) for the row crops and from Anderson and Gianessi (1995) for the orchards.

[2] From Washington Agricultural Statistics Service (1995).

[3] From Anderson and Gianessi (1995) for the orchards, and calculated from irrigation block crop data (U.S. Bureau of Reclamation, written commun., 1986), and Anderson and Gianessi (1995) for the row crops.

[4] Sum of alfalfa hay and other hay.

Table 2.--*Average application rates, acres treated, and total use for nitrogen fertilizer and selected agricultural pesticides ordered by total use under each land-use setting*
[Y, yes; N, no; --, not analyzed for]

Compound	Detected	Average application rate[1] (pounds of active ingredient per treated acre per year)	Acres treated	Total use (pounds of active ingredient per treated acre per year)
		Row crops		
Nitrogen fertilizer	Y	133.5	502,300	67,035,700
1,3-Dichloropropene	N	209.0	21,500	4,494,100
Metam sodium	--	147.1	23,900	3,516,100
Sulfuric acid	--	250.1	4,200	1,050,500
Chloropicrin	--	47.0	7,200	338,600
EPTC	Y	3.2	49,700	156,700
Methamidophos	--	1.7	43,600	74,600
Propargite	N	1.5	48,500	72,000
Disulfoton	N	2.1	34,800	71,400
Sulfur	--	5.1	14,000	71,000
Phorate	N	2.9	22,700	65,200
Mancozeb	--	1.9	33,600	62,500
Ethoprop	N	3.8	11,800	44,600
Metribuzin	Y	0.5	91,800	42,600
Chlorothalonil	N	1.8	23,300	42,300
Chlorpyrifos	N	1.2	29,500	34,200
Maleic hydrazide	--	1.9	17,700	33,800
2,4-D	Y	0.6	59,600	33,300
Alachlor	Y	2.3	13,400	31,400
Maneb	--	2.4	11,400	26,800
Iprodione	--	1.0	24,600	25,800
Diuron	Y	1.3	19,400	24,800
DCPA	N	9.5	2,600	24,600
Metolachlor	Y	1.7	12,800	21,400
Pendimethalin	N	0.9	23,100	21,200
Fonofos	N	1.8	11,900	21,100
Atrazine	Y	1.0	17,900	17,600
Bentazon	Y	1.6	11,100	17,500
Linuron	Y	1.0	10,900	11,000
2,4-DB	Y	0.5	15,100	7,600
Simazine	Y	1.8	2,300	4,200
Ethalfluralin	Y	0.8	4,600	3,800
		Orchards		
Nitrogen fertilizer	Y	68.6	30,977	2,124,441
Oil	--	37.5	26,500	993,800
Sulfur	--	15.9	3,700	59,000
Azinphos methyl	Y	2.0	23,700	47,000
Chlorpyrifos	N	2.3	18,500	42,100

Table 2.--*Average application rates, acres treated, and total use for nitrogen fertilizer and selected agricultural pesticides ordered by total use under each land-use setting--Continued*

Compound	Detected	Average application rate[1] (pounds of active ingredient per treated acre per year)	Acres treated	Total use (pounds of active ingredient per treated acre per year)
		Orchards--continued		
Ziram	--	4.5	6,900	31,200
Mancozeb	--	4.7	5,800	27,200
Carbaryl	N	1.5	17,600	25,600
Endosulfan	N	1.9	10,000	19,400
Methyl parathion	Y	2.2	7,800	17,100
Malathion	N	1.6	9,800	15,600
Phosmet	--	5.6	2,600	14,500
Methoxychlor	--	1.4	8,500	12,000
Glyphosate	--	0.9	10,400	9,800
Simazine	Y	0.9	6,500	6,000
2,4-D	N	0.9	6,100	5,300
Captan	--	2.9	1,800	5,200
Copper	--	3.4	1,400	4,800
Streptomycin	--	1.0	4,700	4,600
Propargite	N	2.4	1,900	4,600
Paraquat	--	0.6	6,500	4,100
Myclobutanil	--	0.2	18,700	3,900
Metiram	--	7.6	500	3,800
Dodine	--	2.2	1,700	3,700
Oxyfluorfen	--	1.1	3,300	3,500
Ethephon	--	0.8	3,800	3,000
Diuron	Y	0.6	2,800	1,700

[1] Actual application rate will vary by crop type. Data for orchards from Anderson and Gianessi (1995). Data for row crops is calculated from Franklin County Conservation District data on crop acreages (Hattrup, written commun., 1991), Van Metre and Seevers (1991) crop acreages and Anderson and Gianessi's (1995) pesticide use data.

SAMPLING DESIGN AND METHODS

Site Selection and Well Types

Sampling locations were selected at random (Scott, 1990) within row crop and orchard areas delineated using updated 1972 land-use maps (U.S. Geological Survey, 1986). These GIRAS (geographic information retrieval and analysis system) maps were updated by digitizing a map of irrigation blocks and center-pivot irrigation systems for the row crop areas (Phoenix Maps, 1990, approximately 1:93,000 scale, from mid-1980's aerial photography) and USGS 1:24,000 scale topographic maps (updated with mid-1980's aerial photography) for the orchard land-use areas. Row crops are areally much more extensive than orchards, and many orchards are small and often surrounded by row crops. The digitized updates of row crop and orchard locations within the CBIP were merged with GIRAS data using a computerized geographic information system (GIS); the GIS was then used for the random site selection. Precise well locations (fig. 1) were determined in the field.

Two types of wells were sampled. Shallow domestic wells were used because they could be sampled easily and because they provide water consumed by many residents in the basin. Shallow monitoring wells were installed specifically for these studies at locations and depths that would provide the earliest indication of potential water-quality concerns and would minimize the potential for physical, biological, and chemical processes in the saturated zone to affect the water sampled. Domestic wells listed in the USGS National Water Information System data base were selected as candidates for sampling if a well log was also available in USGS files and if the well was among the shallowest near the desired sampling location. Further screening of candidate domestic wells took place in the field; a well was selected if (1) it was within 100 feet of the target land use, (2) the sampling point was located upstream from any treatment systems, pressure reservoirs, or potential sources of contamination (such as PVC plumbing), and (3) a submersible pump was installed. Monitoring wells were installed within 50 feet of the target land use (typically much closer) and constructed according to NAWQA protocols (Lapham and others, 1995). These wells were constructed with threaded 2-inch PVC pipe, screened near the water table, and sealed with bentonite annular seals and cement surface seals. The monitoring wells were significantly more shallow than shallow domestic wells (p = 0.001, Wilcoxon rank-sum test); the average depth of monitoring wells was 43 feet and of domestic wells was 140 feet (fig. 2).

Initially, a limited number of monitoring wells were installed and samples collected from both domestic and monitoring wells to determine whether data from the two types of wells were comparable. After initial results indicated that data from the two types of wells would yield information about variations in pesticide occurrence with

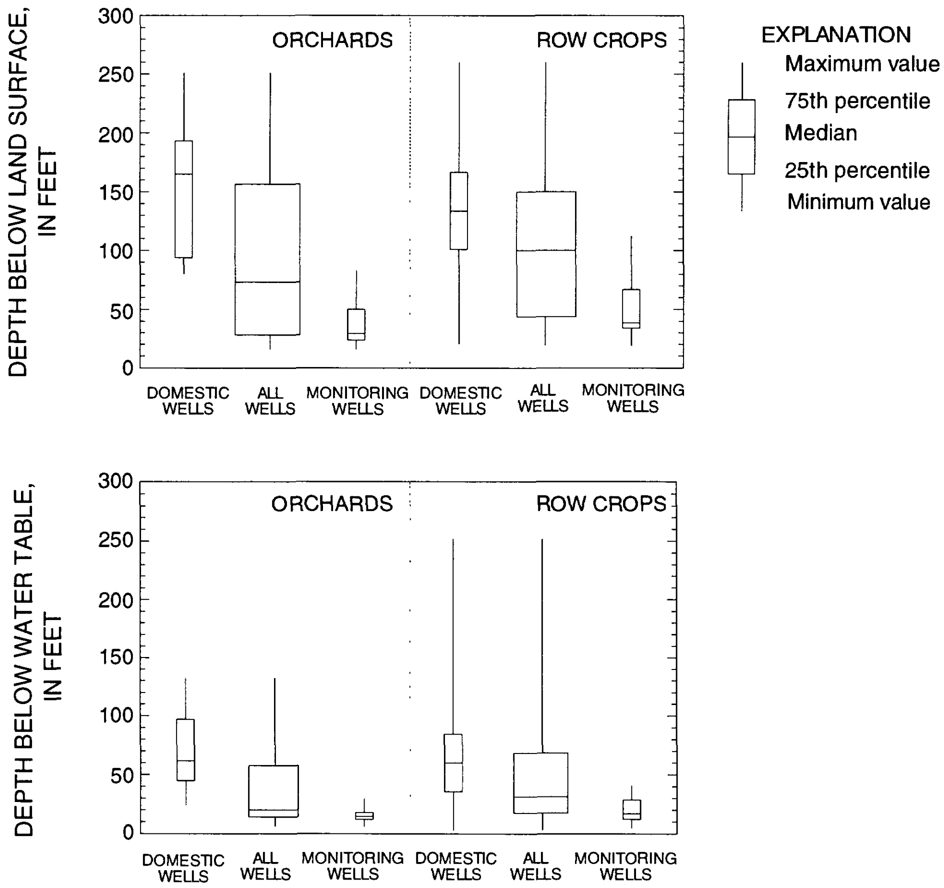


Figure 2. Depths of sampled wells below land surface and below water table for row crop and orchard land-use studies.

depth, additional monitoring wells were installed and a sufficient number of both types of wells were sampled in each of the two land-use settings to allow statistical comparisons between them (table 3). Wells were located (or drilled) and sampled during the irrigation seasons of 1993-95; sampling was carried out from June 1993 through July 1995.

Table 3.--*Numbers of wells sampled, by land-use setting and by well type*

Well type	Number of wells Row crops	 Orchards
Domestic	30	18
Monitoring	19	22

Sample Collection Method

Samples were collected using established NAWQA protocols (Koterba and others, 1995), which require the use of non-contaminating sampling equipment, well purging, and quality-assurance sampling. Wetted surfaces of sampling lines and plumbing fixtures were made of polytetraflouroethylene (Teflon) or stainless steel, including the submersible pump and lines used to sample monitoring wells. Prior to sampling, each well was purged of at least three times the wetted well volume and until general water-quality parameters (specific conductance, pH, and dissolved oxygen concentration) were stable to ensure samples were representative of the surrounding ground water. In addition to the actual samples (referred to herein as "environmental samples"), three different types of quality-assurance samples made up 32 percent of all samples taken (table 4):

> BLANKS—Contaminant-free water ("blank water") is submitted to the USGS National Water Quality Laboratory (NWQL) and analyzed to ensure that environmental samples have not been contaminated. Three types of blanks are prepared and analyzed: "trip blanks" prepared and sealed by the NWQL are shipped to the field and returned unopened for analysis to ensure that shipping, handling, and storage do not result in contamination; "source blanks" prepared by transferring blank water to sample containers to ensure that neither is a source of contamination; and "field blanks" prepared concurrently with environmental samples to ensure that field and lab procedures do not result in contamination or carry-over between sites.
>
> SPIKES—Known amounts of selected target analytes are added to an environmental sample to measure analyte recoveries and to determine whether other chemical species in the sample interfere with analyte detections.
>
> REPLICATES—Duplicate environmental samples from a site are submitted to the laboratory to determine whether the analytical results are reproducible.

More complete descriptions of these types of quality-assurance samples are in Koterba and others (1995).

Table 4.--*Numbers of environmental and quality-assurance samples taken from wells in each land-use setting*

Type of sample	Number (percent of group) of samples Row crop wells	 Orchard wells	 Total
Environmental	50 (62)	41 (77)	91 (68)
Field blanks	7 (9)	5 (9)	12 (9)
Trip blanks	3 (4)	1 (2)	4 (3)
Source blanks	0 (0)	1 (2)	1 (1)
Spikes	12 (15)	4 (8)	16 (12)
Lab spikes	5 (6)	1 (2)	6 (5)
Replicates	4 (5)	0 (0)	4 (3)
Total	81 (100)	53 (100)	134 (100)

Chemical Analyses

Ground-water samples were analyzed for nitrate and 145 pesticide compounds (pesticides and their transformation products, or "degradates") and volatile organic compounds, or VOCs (table 5). Concentrations of pesticide compounds were determined by the USGS National Water Quality Laboratory (NWQL) using two analytical methods developed for the NAWQA program (Zaugg and others, 1995; Werner and others, 1996). Both methods use solid-phase extraction (SPE) cartridges to adsorb the target analytes; pesticides and pesticide degradates are analyzed by high-performance liquid chromatography (HPLC) in one method and by capillary-column gas chromatography/mass spectrometry (GC/MS) with selected-ion monitoring in the other. These methods together target 85 pesticide compounds including 76 pesticides and 9 pesticide degradates. The VOC method (purge and trap capillary GC/MS) analyzes for 60 compounds (Rose and Schroeder, 1994) including nematocides, adjuvants, pesticide impurities (for example, the trichloropropanes—common impurities in fumigants containing 1,3-dichloropropene or 1,2-dichloropropane), and compounds that were once used to fumigate stored grain, such as the trichloroethanes. (In this report "VOCs" denotes all of the non-fumigant volatile organic compounds listed in table 5). A more sensitive method (gas chromatography, microextraction; minimum reporting limit 0.04 microgram/liter; Fishman, 1993) was used for analysis of the fumigant EDB (ethylene dibromide) because of its high toxicity and documented occurrence in ground water in the CBIP (Larson and Erickson, 1993). DBCP (1,2-dibromo-3-chloropropane) was also analyzed and reported at the lower reporting limit with this method.

In addition to the compounds discussed above, other VOCs targeted in the VOC method were included in this report because they may be adjuvants in agricultural chemical mixtures or may be included in materials used in agricultural areas for purposes other than pest control (for example, volatile compounds in fuels used for smudge pots and farm machinery). However, few of these non-agricultural VOCs were detected during this study. The VOC method also provided for reporting of compounds that are not included in table 5 but which were present at concentrations large enough to identify and quantify. As a result, two additional compounds are included in this report (see table 8, fig. 6): carbon disulfide, a grain fumigant (Howard, 1990), and 1,2,2-trichloropropane, an impurity in early soil fumigants (Szeto and others, 1994).

Statistical Methods

Statistical differences between groups of measurements (for example, concentrations of an analyte in each of the land-use settings) were determined using a nonparametric rank sum test for independent groups (the Wilcoxon rank sum test, sometimes called the Mann-Whitney test). Significance, or the lack of it, is based on the statistical probability (p) that the observed differences could be a result of chance alone; in this report the threshold of significance (α) is arbitrarily set at a 5 percent probability of chance accounting for the observed differences ($\alpha = 0.05$). In addition to reporting statistical significance, the p-value (probability that chance explains the differences) is generally included in the text parenthetically; for example, "($p = 0.01$)" means that the Wilcoxon rank sum test indicates that there is a 1 percent probability that chance alone explains the observed differences. (Therefore "$p = 0.04$" passes the test for significance, while "$p = 0.16$" does not.) With respect to comparisons of desethylatrazine-to-atrazine ratio (DAR) values between groups of wells, samples with detections of desethylatrazine but not atrazine (where the ratio is infinity) were represented by an arbitrary large value (99,999) in the calculations.

SUMMARY OF WATER-QUALITY DATA

Quality-Assurance Results

Quality-assurance and environmental samples were inspected for signs of contamination. As a result, several detections were eliminated from the data set. All detections of one pesticide (chlorpyrifos, an insecticide used on orchards) and four VOCs—1,2,4-trimethylbenzene, methyl chloride (chloromethane), methylene chloride (dichloromethane), and chloroform (trichloromethane)—are not reported because these compounds were also detected in blanks. The chlorpyrifos detections are assumed to have arisen from sample contamination because all four detections, including one in a blank, were in samples collected during a 3-day period when this pesticide was being applied (by fogging) to nearby orchards. For 1,2,4-trimethylbenzene, all three detections occurred over a 2-day sampling period, and all the samples were from monitoring wells where a gasoline generator was used to power the portable submersible pump. Although no blanks were obtained over this period, it was nevertheless assumed that the gasoline was the source of this

Table 5.--*Target analytes, method detection limits, and drinking water standards*

[µg/L, micrograms per liter; N, nutrient; H, herbicide; I, insecticide; D, pesticide degradate; U, fungicide; A, adjuvant; Z, no agricultural use known; F, fumigant; B, probable impurity in fumigants containing 1, 2-dichloropropane or 1,3-dichloropropene; α, alpha; γ, gamma; --, no drinking water standard or guideline established; drinking water standards are U.S. Environmental Protection Agency primary drinking water standards from Nowell and Resek (1994), unless otherwise noted; MCL, Maximum Contaminant Level; HA, Health Advisory]

Common name	Alternate or trade name(s)	Use class	Chemical Abstracts Service registry number	Method detection limit (µg/L)	Drinking water standard (MCL or HA[2]) (µg/L)
Nitrate	none	N		50 (as N)	10,000 (as N)
Gas Chromatography/Mass Spectrometry (GC/MS) analytical method					
Alachlor	Lasso	H	15972-60-8	0.002	2
Atrazine	AAtrex	H	1912-24-9	0.001	3
Azinphos-methyl[1]	Guthion	I	86-50-0	0.001	--
Benfluralin	Balan, Benefin	H	1861-40-1	0.002	--
Butylate	Sutan +, Genate Plus	H	2008-41-5	0.002	700
Carbaryl[1,3]	Sevin, Savit	I	63-25-2	0.003	700
Carbofuran[1,3]	Furandan	I	1563-66-2	0.003	40
Chlorpyrifos	Genpest, Lorsban	I	2921-88-2	0.004	20
Cyanazine	Bladex	H	21725-46-2	0.004	1
DCPA	Dacthal	H	1861-32-1	0.002	4,000
p,p'- DDE	none	D	72-55-9	0.006	--
Desethylatrazine[1]	none	D	6190-65-4	0.002	--
Diazinon	several	I	333-41-5	0.002	0.6
Dieldrin	Panoram D-31	I	60-57-1	0.001	--
2,6-Diethylaniline	none	D	579-66-8	0.003	--
Dimethoate[1,4]	Cygon	I	60-51-5	0.004	--
Disulfoton	Di-Syston	I	298-04-4	0.017	0.3
EPTC	Eptam, Eradicane	H	759-94-4	0.002	--
Ethalfluralin	Sonalan, Curbit EC	H	55283-68-6	0.004	--
Ethoprop	Mocap	I	13194-48-4	0.003	--
Fonofos	Dyfonate	I	944-22-9	0.003	10
α-HCH	none	D	319-84-6	0.002	--
γ-HCH	Lindane	I	58-89-9	0.004	0.2
Linuron[3]	Lorox, Linex	H	330-55-2	0.002	--
Malathion	several	I	121-75-5	0.005	200
Methyl parathion	Penncap-M	I	298-00-0	0.006	2
Metolachlor	Dual, Pennant	H	51218-45-2	0.002	100
Metribuzin	Lexone, Sencor	H	21087-64-9	0.004	200
Molinate	Ordram	H	2212-67-1	0.004	--
Napropamide	Devrinol	H	15299-99-7	0.003	--
Parathion	several	I	56-38-2	0.004	--
Pebulate	Tillam	H	1114-71-2	0.004	--
Pendimethalin	Prowl, Stomp	H	40487-42-1	0.004	--
cis-Permethrin	Ambush, Pounce	I	57608-04-5	0.005	--
Phorate	Thimet, Rampart	I	298-02-2	0.002	--
Prometon	Pramitol	H	1610-18-0	0.018	100

Table 5.--*Target analytes, method detection limits, and drinking water standards--Continued*

Common name	Alternate or trade name(s)	Use class	Chemical Abstracts Service registry number	Method detection limit (µg/L)	Drinking water standard (MCL or HA[2]) (µg/L)
Gas Chromatography/Mass Spectrometry (GC/MS) analytical method--Continued					
Pronamide	Kerb	H	23950-58-5	0.003	50
Propanil	Stampede	H	709-98-8	0.004	--
Propachlor	Ramrod	H	1918-16-7	0.007	90
Propargite	Comite, Omite	I	2312-35-8	0.013	--
Simazine	Aquazine, Princep	H	122-34-9	0.005	4
Tebuthiuron	Spike	H	34014-18-1	0.01	500
Terbacil[1]	Sinbar	H	5902-51-2	0.007	90
Terbufos	Counter	I	13071-79-9	0.013	0.9
Thiobencarb	Bolero	H	28249-77-6	0.002	--
Triallate	Far-Go	H	2303-17-5	0.001	--
Trifluralin	Treflan, Trilin	H	1582-09-8	0.002	5
High-Performance Liquid Chromatography (HPLC) analytical method					
Acifluorfen	Blazer	H	50594-66-6	0.035	--
Aldicarb[6]	Temik	I	116-06-3	0.016	3
Aldicarb sulfone[6]	Standak	D	1646-88-4	0.016	2
Aldicarb sulfoxide	none	D	1646-87-3	0.021	4
Bentazon	Basagran	H	25057-89-0	0.014	20
Bromacil	Hyvar, Urox B	H	314-40-9	0.035	90
Bromoxynil	Buctril, Brominal	H	1689-84-5	0.035	--
Carbaryl[3,6]	Sevin, Savit	I	63-25-2	0.008	700
Carbofuran[3,6]	Furadan	I	1563-66-2	0.028	40
Chloramben	Amiben, Vegiben	H	133-90-4	0.011	100
Chlorothalonil[5]	Bravo	U	1897-45-6	0.035	--
Clopyralid	Stinger, Lontrel	H	1702-17-6	0.05	--
2,4-D	several	H	94-75-7	0.035	70
Dacthal,mono-acid	none	D	887-54-7	0.017	--
2,4-DB	Dublex	I	94-82-6	0.035	--
Dicamba	Banvel	H	1918-00-9	0.035	200
Dichlobenil[5]	Barrier, Casoron	H	1194-65-6	0.02	--
Dichlorprop	2,4-DP, Seritox 50	H	120-36-5	0.032	--
Dinoseb	DNBP, Dinitro	H	88-85-7	0.035	7
Diuron	Karmex, Direx	H	330-54-1	0.02	10
DNOC[5]	Trifocide, Elgetol 30	I, U, H	534-52-1	0.035	--
Esfenvalerate[5]	Asana XL	I	66230-04-4	0.019	--
Fenuron	Beet-Kleen	H	101-42-8	0.013	--
Fluometuron	Flo-Met, Cotoran	H	2164-17-2	0.035	90
3-Hydroxycarbofuran	none	D	1563-38-8	0.014	--
Linuron[3]	Lorox, Linex	H	330-55-2	0.018	--
MCPA	Metaxon, Kilsem	H	94-74-6	0.05	10
MCPB	Can-Trol, Thistrol	H	94-81-5	0.035	--
Methiocarb[6]	Grandslam, Mesurol	I	2032-65-7	0.026	--
Methomyl	Lannate, Nudrin	I	16752-77-5	0.017	200

Table 5.--*Target analytes, method detection limits, and drinking water standards--Continued*

Common name	Alternate or trade name(s)	Use class	Chemical Abstracts Service registry number	Method detection limit (µg/L)	Drinking water standard (MCL or HA^2) (µg/L)
High-Performance Liquid Chromatography analytical method--Continued					
1-Naphthol^{5,6}	none	D	90-15-3	0.007	--
Neburon	Neburex, Noruben	H	555-37-3	0.015	--
Norflurazon	Evital, Solicam	H	27314-13-2	0.024	--
Oryzalin	Surflan	H	19044-88-3	0.019	--
Oxamyl^6	Vydate	I	23135-22-0	0.018	200
Picloram^6	Tordon	H	1918-02-1	0.05	500
Propham	Chem-Hoe, IPC	H	122-42-9	0.035	100
Propoxur	Baygon	I	114-26-1	0.035	--
2,4,5-T	several	H	93-76-5	0.035	70
2,4-5-TP^6	Silvex	H	93-72-1	0.021	50
Triclopyr^6	Garlon, Grazon	H	55335-06-3	0.05	--
Purge and trap capillary gas chromatography/mass spectrometry analytical method					
Benzene	none	A	71-43-2	0.2	5
Bromobenzene	none	Z	108-86-1	0.2	--
Bromochloromethane	none	Z	74-97-5	0.2	--
Bromodichloromethane	none	Z	75-27-4	0.2	100
Bromomethane	none	F,A	74-83-9	0.2	--
n-Butylbenzene	none	Z	104-51-8	0.2	--
sec-Butylbenzene	none	Z	135-98-8	0.2	--
tert-Butylbenzene	none	Z	98-06-6	0.2	--
1-Chloro-2-methylbenzene	2-Chlorotoluene	A	95-49-8	0.2	--
1-Chloro-4-methylbenzene	4-Chlorotoluene	Z	106-43-4	0.2	--
Chlorobenzene	none	A	108-90-7	0.2	100
Chloroethane	none	A	75-00-3	0.2	--
Chloroethene	Vinyl chloride	Z	75-01-4	0.2	2
Chloromethane	none	F,A	74-87-3	0.2	--
1,2-Dibromo-3-Chloropropane	DBCP	F	96-12-8	0.03	0.2
Dibromochloromethane	none	Z	124-48-1	0.2	100
1,2-Dibromoethane	EDB	F	106-93-4	0.04	0.05
Dibromomethane	none	Z	74-95-3	0.2	--
1,2-Dichlorobenzene	*o*-Dichlorobenzene	F,H,I,A	95-50-1	0.2	600
1,3-Dichlorobenzene	*m*-Dichlorobenzene	Z	541-73-1	0.2	600
1,4-Dichlorobenzene	*p*-Dichlorobenzene	F,U,I,A,	106-46-7	0.2	75
Dichlorodifluoromethane	none	Z	75-71-8	0.2	--
1,1-Dichloroethane	none	Z	75-34-3	0.2	--
1,2-Dichloroethane	none	F,A	107-06-2	0.2	5
1,1-Dichloroethene	none	Z	75-35-4	0.2	7
cis-1,2-Dichloroethene	none	F	156-59-4	0.2	70
trans-1,2-Dichloroethene	none	F	156-60-5	0.2	100
Dichloromethane	Methylene chloride	F,A	75-09-2	0.2	5
1,2-Dichloropropane	none	F	78-87-5	0.2	5
1,3-Dichloropropane	none	B	142-28-9	0.2	--

Table 5.--*Target analytes, method detection limits, and drinking water standards--Continued*

Common name	Alternate, or trade name(s)	Use class	Chemical Abstracts Service registry number	Method detection limit (µg/L)	Drinking water standard (MCL or HA[2]) (µg/L)
Purge and trap capillary gas chromatography/mass spectrometry analytical method--Continued					
2,2-Dichloropropane	none	B	590-20-7	0.2	--
1,1-Dichloropropene	none	B	563-58-6	0.2	--
cis-1,3-Dichloropropene	none	F	10061-01-5	0.2	--
trans-1,3-Dichloropropene	none	F	10061-02-6	0.2	--
Dimethylbenzene	Xylene	A	1330-20-7	0.2	10,000
Ethylbenzene	none	A	100-41-4	0.2	700
Hexachlorobutadiene	none	Z	87-68-3	0.2	--
1-Methyl-4-Methylethylbenzene	*p*-Isopropyltoluene	Z	99-87-6	0.2	--
Methylbenzene	Toluene	A	108-88-3	0.2	1,000
1-Methylethylbenzene	Isopropylbenzene, Cumene	Z	98-82-8	0.2	--
Methyl-tert-butylether	MTBE	Z	1634-04-4	0.2	--
Napththalene	none	I,F	91-20-3	0.2	--
n-Propylbenzene	none	Z	103-65-1	0.2	--
Styrene	Ethenylbenzene	Z	100-42-5	0.2	100
1,1,1,2-Tetrachloroethane	none	Z	630-20-6	0.2	--
1,1,2,2-Tetrachloroethane	none	Z	79-34-5	0.2	--
Tetrachloroethene	none	F,A	127-18-4	0.2	5
Tetrachloromethane	Carbon tetrachloride	F,A	56-23-5	0.2	5
Tribromomethane	Bromoform	F	75-25-2	0.2	100
1,2,3-Trichlorobenzene	none	Z	87-61-6	0.2	--
1,2,4-Trichlorobenzene	none	Z	102-82-1	0.2	70
1,1,1-Trichloroethane	none	F,A	71-55-6	0.2	200
1,1,2-Trichloroethane	none	A	79-00-5	0.2	5
Trichloroethene	none	F,A	79-01-6	0.2	5
Trichlorofluoromethane	none	Z	75-69-4	0.2	--
Trichloromethane	Chloroform	F,A	67-66-3	0.2	100
1,2,3-Trichloropropane	none	B	96-18-4	0.2	--
Trichlorotrifluoroethane	none	Z	76-13-1	0.2	--
1,2,4-Trimethylbenzene	Pseudocumene	Z	95-63-6	0.2	--
1,3,5-Trimethylbenzene	none	Z	108-67-8	0.2	--

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[1] Concentrations for these pesticides could only be estimated because of analytical difficulties (Zaugg and others, 1995).

[2] U.S. Environmental Protection Agency lifetime health advisory for a 70-kilogram adult, from Nowell and Resek (1994).

[3] Analyzed by both gas chromatography/mass spectrometry and high-performance liquid chromatography methods.

[4] Pesticide demonstrated small and variable recovery and was thus deleted from the analyte list in November 1994.

[5] The concentration values for these analytes could only be estimated because of poor overall recovery and precision (NAWQA/NWQL Quality Assurance Committee for the Schedule 2050/2051 Pesticide Analysis Method, written commun., 1995).

[6] Pesticide is heat- and light-sensitive and therefore susceptible to degradation. This may result in poor overall recovery and precision (NAWQA/NWQL Quality Assurance Committee for the Schedule 2050/2051 Pesticide Analysis Method, written commun., 1995).

detection because this compound is a component of gasoline (Kraemer and Stetzenbach, 1990). Contamination by the chlorinated methanes (chloromethane, dichloromethane, and chloroform) was believed to have resulted from the concentrated hydrochloric acid added as a preservative to the VOC samples (J.S. Zogorski, written commun., 1995). All other unreported detections are described in table 6.

Reported concentrations of analytes in spikes were compared with predicted concentrations to estimate recoveries. These values were compared with recoveries determined at the NWQL (Pritt and Raese, 1992) to infer whether chemical constituents in the environmental samples interfered with the analyses. Results from these comparisons indicate that recoveries in environmental samples were within acceptable ranges. Although no modifications were made to the data set on the basis of these comparisons, some qualifications need to be made on the basis of the laboratory recoveries themselves. Several target analytes of the HPLC method (table 5)—carbaryl, chlorothalonil, dichlobenil, DNOC, esfenvalerate, and 1-naphthol—had poor overall recoveries and precision (Werner and others, 1996); six other compounds—aldicarb, aldicarb sulfone, carbofuran, MCPB, methiocarb, and oxamyl—were potentially subject to similar analytical difficulties during the time period when samples were collected (NAWQA/NWQL Quality Assurance Committee for the Schedule 2050/2051 Pesticide Analysis Method, written commun., 1995). Although confidence in a detection of one of these compounds would be high had any been detected (none was), the likelihood of a false negative (failure to detect a compound that is actually present at detectable levels) is higher for these compounds than others, especially for aldicarb and aldicarb sulfone, which have been used as fumigants on row crops and have been detected in ground water elsewhere in the U.S. (for example, Jones, 1986). Six target analytes of the GC/MS method—azinphos-methyl, carbaryl, carbofuran, desethylatrazine, dimethoate, and terbacil—were also subject to variable performance and low recoveries and precision (Zaugg and others, 1995), but these problems were not as severe as those for the HPLC compounds.

Replicate samples were reviewed for large variations in reported concentrations. No modification of the data set resulted from this review. Concentrations reported are from the environmental samples. Most wells were resampled for nitrate; the concentration for the sample taken concurrently with the pesticide samples is reported. Two wells were resampled for pesticides—ON07 and PN37—and data from the first samples are used in analyses (table 7). The two samples from PN37, the first taken in the summer of 1993 and the second in the fall of 1994, contained similar suites of pesticides, indicating both that detections are reasonably consistent and that seasonal effects are minimal. The two samples from ON07 also demonstrated consistent results for the VOC compounds, 1,2,3-trichloropropane and 1,2-dichloropropane; however, the triazine compounds—atrazine, desethylatrazine, and simazine—and diuron were detected in only the first sample and at low concentrations. Because the concentrations of simazine, desethylatrazine, and diuron were only slightly above their method detection limits (table 5), it is reasonable to assume that these compounds were not detected in the second sample because concentrations were below those limits. This assumption does not appear reasonable for the detection of atrazine, however. A detection of chlorpyrifos in the first ON07 sample was deleted on the basis of quality-assurance samples (table 6), but the data did not suggest that the atrazine detection was the result of contamination or carry-over.

Nitrate

The median nitrate concentration for all samples was 6.4 mg/L (milligrams per liter as nitrogen). Samples from 31 percent of wells exceeded the 10 mg/L maximum contaminant level (MCL) established by the USEPA for drinking water (exceeded in 33 percent of the domestic wells overall, 37 percent in row crop areas and 28 percent in orchard areas). Nitrogen fertilizers are applied to row crops at a higher annual rate (more than 130 pounds per acre) than to orchards (less than 70 pounds per acre), and the median nitrate concentration in row crop wells (6.7 mg/L as N, fig. 3) was higher than that in orchard wells (6.0 mg/L), but this difference is not statistically significant ($p = 0.16$).

The highest nitrate concentration was 59 mg/L (viewed as an outlier, because the second highest concentration was 20 mg/L), and the lowest was less than the detection limit of 0.05 mg/L. This wide range of nitrate concentrations (fig. 4) is consistent with other data reported for the CBIP. Drost and others (1993) report median nitrate concentrations of 22.5 mg/L (as nitrogen) beneath row crops, 9.6 mg/L in agricultural drains (shallow ground water), and less than 1 mg/L in canal water (the source of most of the ground water in the area). Jones and Wagner (1995) report that shallow wells have the highest median and the broadest range of nitrate concentrations of all wells sampled on the Central Columbia Plateau.

Table 6.--*Analytical results from environmental samples and quality assurance samples, supporting deletion of data for selected compounds, in the order in which the samples were obtained*

[Well types: P, row crop land use; O, orchard land use; E, domestic well; N, monitoring well; µg/L, micrograms per liter; --, not applicable]

Type of sample	Date	Type of well	Compound	Concentration (µg/L)	Comments
Environmental	7/8/93	PE07	No detections	--	
Spike	7/8/93	PE07	*p,p'*-DDE	0.086	Other spike compounds not shown.
Spike replicate	7/8/93	PE07	*p,p'*-DDE	0.093	
Blank	7/8/93	PE07	*p,p'*-DDE	0.002	Carry-over from spikes.
Environmental	7/8/93	PE25	Atrazine	0.970	Next environmental sample after blank, no contamination.
			Desethylatrazine	0.050	
			Ethalfluralin	0.090	
Environmental	3/28/94	ON16	No detections	--	
Blank	3/29/94	ON08	1,1-Dichloroethene	0.3	This was the only detection of this compound. No likely source of contamination was identified.
			MTBE	0.3	This was the only detection of this compound. MTBE is a volatile "oxygenate" added to some gasolines.
			Chlorpyrifos	0.013	All chlorpyrifos detections, including one in a blank, occurred in a three-day period. Therefore, they are thought to be contamination from nearby applications taking place during this time period.
Environmental	3/30/94	ON08	Chlorpyrifos	0.010	Data deleted.
			Atrazine	0.039	Data retained.
			Simazine	0.012	Data retained.
Environmental	3/30/94	ON07	Chlorpyrifos	0.100	Data deleted.
Environmental	3/31/94	ON10	Chlorpyrifos	0.020	Data deleted.
Environmental	5/11/94	PE02	Atrazine	0.040	
			Desethylatrazine	0.010	

Table 6.--*Analytical results from environmental samples and quality assurance samples, supporting deletion of data for selected compounds, in the order in which the samples were obtained--Continued*

Type of sample	Date	Type of well	Compound	Concentration (µg/L)	Comments
Blank	5/11/94	PE02	Ethylbenzene	0.2	The detection of BTEX (benzene, toluene, ethylbenzene and xylene) compounds together suggests contamination from gasoline; these compounds are constituents of gasoline.
			Xylene	0.3	
			Toluene	2.0	
			Styrene	1.6	
			Chloroethane	3.8	Data retained.
Environmental	5/11/94	PE2A	Atrazine	0.030	Next environmental sample after PE02 blank, no contamination.
			Metribuzin	0.010	
Environmental	10/4/94	PN84	Atrazine	0.007	
			Desethylatrazine	0.007	
			Diuron	2.000	
			Bromacil	1.800	
Blank	10/5/94	PN84	Diuron	0.020	Possible carry-over from previous day's sample.
			Bromacil	0.010	Possible carry-over from previous day's sample.
Environmental	10/5/94	PN93	Atrazine	0.070	Next environmental sample after PN84 blank, no contamination.
			Desethylatrazine	0.100	
Environmental	10/25/94	ON12	1,2,4-Trimethylbenzene	0.5	All detections occurred at monitoring wells in a two-day period, and are presumed to have been derived from a gasoline generator used to power the submersible pump; data deleted.
Environmental	10/25/94	ON02	1,2,4-Trimethylbenzene	0.2	Data deleted (see comments for site ON12).
			DCPA	0.001	Data retained.
			Desethylatrazine	0.003	Data retained.
Environmental	10/26/94	ON99	1,2,4-Trimethylbenzene	0.3	These BTEX compounds are believed to represent contamination from the gasoline generator used to power the submersible pump; data deleted.
			Toluene	0.20	
			Xylene	0.20	
Environmental	10/26/94	OE05	no detections	--	Next sample after ON99; no contamination.

Table 7.--*Compounds detected at sites with two environmental samples*

[µg/L, micrograms per liter; see table 6 for explanation of well naming convention]

Well ON07

Compound in first sample (3/30/94)	Concentration (µg/L)	Compound in second sample (10/6/94)	Concentration (µg/L)
1,2,3-Trichloropropane	0.8	1,2,3-Trichloropropane	1.1
1,2-Dichloropropane	7.3	1,2-Dichloropropane	7.5
Atrazine	0.039		
Simazine	0.012		
Desethylatrazine	0.004		
Diuron	0.02		

Well PN37

Compound in first sample (6/15/93)	Concentration (µg/L)	Compound in second sample (10/6/94)	Concentration (µg/L)
1,3-Dichloropropane	0.5	1,3-Dichloropropane	0.4
1,2-Dichloropropane	0.5	1,2-Dichloropropane	0.3
Alachlor	0.008	Alachlor	0.004
Atrazine	0.018	Atrazine	0.019
EPTC	0.012	EPTC	0.006
Desethylatrazine	0.006	Desethylatrazine	0.008
EDB	0.04		
		1,2,3-trichloropropane	0.6
		Metribuzin	0.013

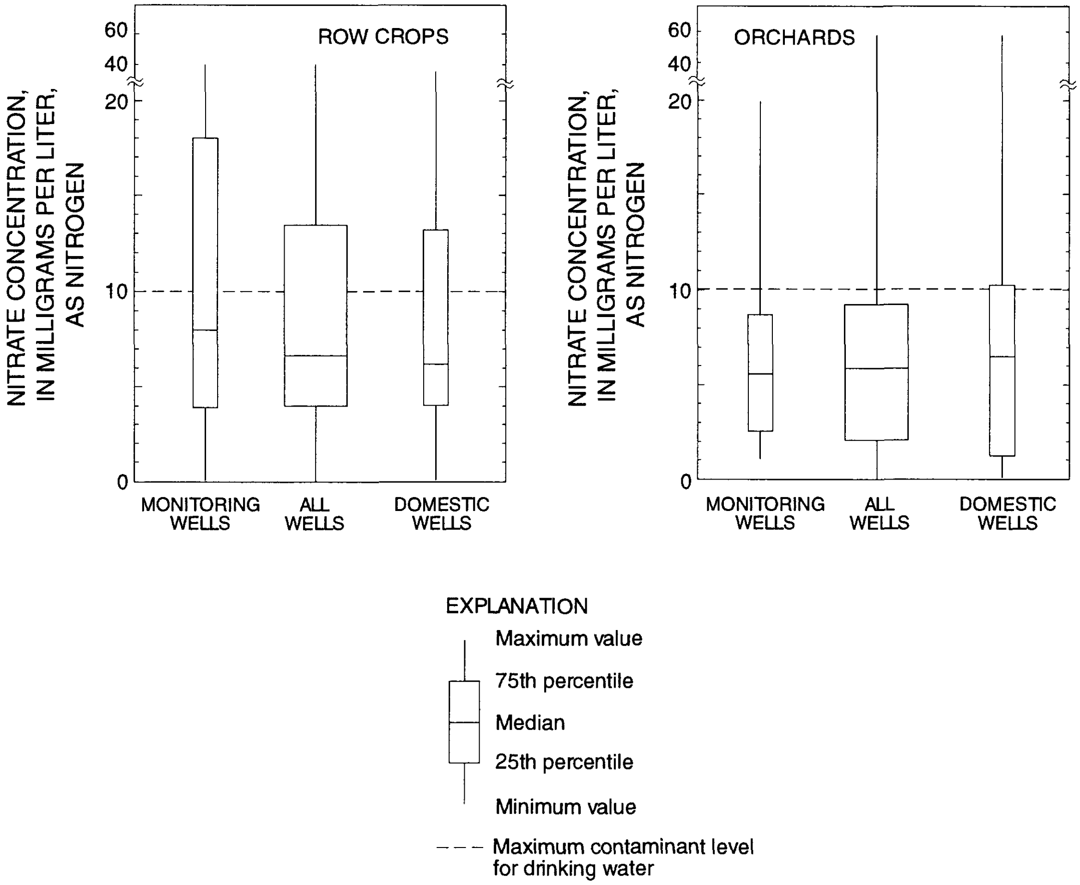

Figure 3. Nitrate concentrations in sampled wells.

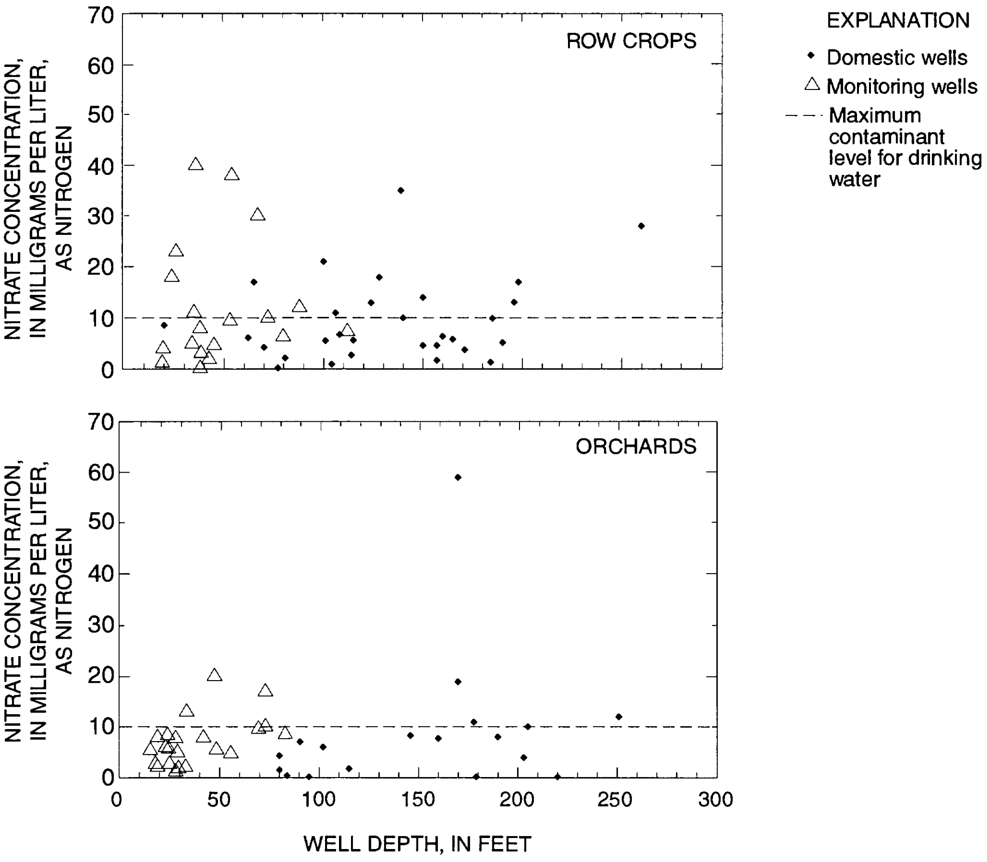

Figure 4. Nitrate concentrations in relation to depth of sampled wells.

The primary source of nitrate in ground water in this area appears to be nitrogen fertilizer applied to agricultural lands. Both Drost and others (1993) and Ebbert and others (1995) investigated potential sources of nitrate other than direct applications; they concluded that flushing of natural nitrate salts by irrigation water could temporarily cause high nitrate concentrations in ground water, but that this mechanism would not be an ongoing source of nitrate. Other sources of nitrate include livestock, manures, septic systems, non-agricultural use of nitrogen fertilizers, and atmospheric deposition, but these are deemed to be less significant sources than fertilizers in the CBIP (Greene and others, 1994).

Pesticides and Volatile Organic Compounds

A total of 34 pesticide compounds or VOCs was detected (table 8). Although most of the detected compounds were herbicides (19, including 2 herbicide degradates), compounds from all classes that were targeted for analysis were detected: insecticides (5 compounds, including 1 insecticide degradate), fumigants (3 compounds), and VOCs (7 compounds). Of the 22 compounds for which human health criteria have been established, 3 were detected at concentrations above their criteria. Both detections of the banned insecticide dieldrin exceeded the health criterion of 0.002 µg/L (the risk-specific dose, or the concentration estimated to cause a one-in-a-million increase in the chance of developing cancer); however, these detections were in shallow monitoring wells. The discontinued fumigant EDB exceeded its MCL in samples from two domestic wells; 1,2-dichloropropane, another discontinued fumigant, exceeded its MCL in one monitoring well sample. These compounds were historically applied at high rates to potatoes; use of EDB for this purpose is well documented, and 1,2-dichloropropane was an ingredient in 1,3-dichloropropene-based fumigants, which are still used in the study area (1,3-dichloropropene, however, was not detected although it is applied at a high rate (table 2).

A greater variety of compounds was detected in row crop wells than in orchard wells (table 8, fig. 5), though the percentage of wells in each group with detections of any pesticide compound and the average number of compounds detected per well were approximately the same. A total of 25 compounds was detected in row crop wells, with detections of at least one pesticide compound in 69 percent of the sampled wells. A total of 20 compounds was detected in orchard wells, with detections of at least one pesticide compound in 68 percent of the sampled wells. An average of two pesticide compounds was detected in the wells sampled in both settings.

Detected compounds were generally found more frequently in the land-use setting where they were used at higher rates (fig. 6). Two out of four of the detected compounds used at higher rates on orchards (azinphos-methyl and methyl parathion, table 9) were detected only in orchard wells; another (simazine) was detected more frequently in orchard wells than row crop wells. Although average rates of diuron application based on total areas for each land use were only slightly higher for orchards, it was also detected more frequently in orchard wells; this may be explained by the fact that almost 10 percent of orchard acres were treated with diuron compared to less than 5 percent of row crop acres.

Among the 12 detected parent compounds applied at higher rates to row crops, 10 were found more frequently in row crop wells; 9 of these compounds, including degradates, were detected only in row crop wells. Discontinued fumigants (1,2-dichloropropane, EDB, and bromoform) that were used in large quantities on row crops prior to the late 1970's were also detected either exclusively or more frequently in row crop wells. For unknown reasons, two herbicides currently in use at higher rates on row crops (DCPA and pendimethalin) were detected only in the orchard areas. Desethylatrazine might have been expected to be detected at locations similar to those for its parent compound atrazine, but it was detected more frequently in orchard wells (see "Desethylatrazine-to-Atrazine Ratio" below for a possible explanation).

The most frequently detected compounds are not those that are applied at the highest rates in either land-use setting (fig. 6); in fact, many compounds that were not detected at all are applied at higher rates than compounds that were detected. Chemical or biological degradation, and sorption to minerals or organic matter, are processes that could be responsible for these observations.

Comparisons of Ground-Water Quality from Monitoring and Domestic Wells

Because the monitoring wells were significantly shallower than the domestic wells ($p = 0.001$), the water-quality data were divided into four groups (domestic wells and shallow monitoring wells in each of the two land-use settings) to determine if differences in water

Table 8.--*Frequencies with which pesticide compounds were detected in row crop and orchard areas*

[µg/L, micrograms per liter; --, not established or not applicable; MDL, method detection limit; MRL, minimum reporting level]

			Row crops				Orchards			
Compound	Detection threshold MDL or MRL[1] (µg/L)	Human health criterion[2] (µg/L)	Percentage of wells with detections	Median concen-tration of detections (µg/L)	Maximum concen-tration (µg/L)	Percentage of wells exceeding health criterion	Percentage of wells with detections	Median concen-tration of detections (µg/L)	Maximum concen-tration (µg/L)	Percentage of wells exceeding health criterion
				Herbicide compounds						
Atrazine	0.001	3	45	0.017	0.97	0	40	0.008	0.52	0
Desethylatrazine	0.002	--	35	0.007	0.12	--	52	0.006	0.039	--
Metribuzin	0.004	200	10	0.013	0.028	0	2	--	0.007	0
Metolachlor	0.002	100	10	0.003	0.009	0	0	--	--	0
Simazine	0.005	4	10	0.009	0.011	0	28	0.004	0.04	0
Alachlor	0.002	2	6	0.005	0.006	0	0	--	--	0
EPTC	0.002	--	6	0.006	0.006	--	0	--	--	--
2,4-D	0.035	70	4	0.275	0.54	0	0	--	--	0
2,6-Diethylaniline	0.003	--	4	0.0045	0.008	--	0	--	--	--
Diuron	0.02	10	2	--	2.0	0	5	0.02	0.02	0
Bromacil	0.035	90	2	--	1.8	0	2	--	0.02	0
Ethalfluralin	0.004	--	2	--	0.09	--	0	--	--	--
2,4-DB	0.035	--	2	--	0.06	--	0	--	--	--
Bentazon	0.014	20	2	--	0.07	0	0	--	--	0
Prometon	0.018	100	2	--	0.005	0	2	--	0.002	0
Linuron	0.002	--	2	--	0.001	--	0	--	--	--
DCPA	0.002	4,000	0	--	--	0	15	0.002	0.011	0
Pendimethalin	0.004	--	0	--	--	--	2	--	0.012	--
Butylate	0.002	350	0	--	--	0	2	--	0.002	0
				Insecticide compounds						
Dieldrin	0.001	0.002	4	0.01	0.013	4	0	--	--	0
p,p'-DDE	0.006	0.01	2	--	0.001	0	0	--	--	0
Azinphos-methyl	0.001	87.5	0	--	--	--	10	0.039	0.18	0
Methyl parathion	0.006	2	0	--	--	--	5	0.042	0.062	0
Dinoseb	0.035	7	0	--	--	--	2	--	0.7	0

Table 8.--*Frequencies with which pesticide compounds were detected in row crop and orchard areas--Continued*

			Row crops				Orchards			
Compound	Detection threshold MDL or MRL[1] (µg/L)	Human health criterion[2] (µg/L)	Percentage of wells with detections	Median concen-tration of detections (µg/L)	Maximum concen-tration (µg/L)	Percentage of wells exceeding health criterion	Percentage of wells with detections	Median concen-tration of detections (µg/L)	Maximum concen-tration (µg/L)	Percentage of wells exceeding health criterion
				Fumigants						
1,2-Dichloropropane	0.2	5	12	0.25	0.5	0	10	0.45	7.3	2
EDB	0.04	0.05	7	0.3	1.1	5	0	--	--	0
Tribromomethane	0.2	--	2	--	0.12	--	0	--	--	--
				Volatile organic compounds						
1,2,2-Trichloropropane	0.2	--	8	0.26	0.55	--	5	0.26	0.42	--
1,2,3-Trichloropropane	0.2	--	6	0.5	1.0	--	2	--	0.8	--
1,3-Dichloropropane	0.2	--	2	--	0.4	--	5	0.16	0.2	--
1,1,1-Trichloroethane	0.2	200	0	--	--	0	2	--	0.2	0
1,2-Dichloroethane	0.2	5	0	--	--	0	2	--	0.3	0
Tetrachloroethylene	0.2	5	0	--	--	0	5	0.26	0.4	0
Carbon disulfide	0.2	--	2	--	0.15	--	0	--	--	--

[1] The MDL is reported for the herbicide and insecticide compounds; the MRL is reported for the fumigants and volatile organic compounds.

[2] Human health criteria are either the maximum contaminant level (MCL), set by the U.S. Environmental Protection Agency to be the maximum concentration allowed in drinking water, the lifetime health advisory level (HA), which is the maximum concentration in drinking water that would not cause adverse human health effects, excluding cancer (based on a 150-pound adult consuming about 2 quarts of water per day for 70 years) or the risk-specific dose (RSD), which is the concentration that corresponds to an increase of a one-in-a-million chance of developing cancer (Nowell and Resek, 1994).

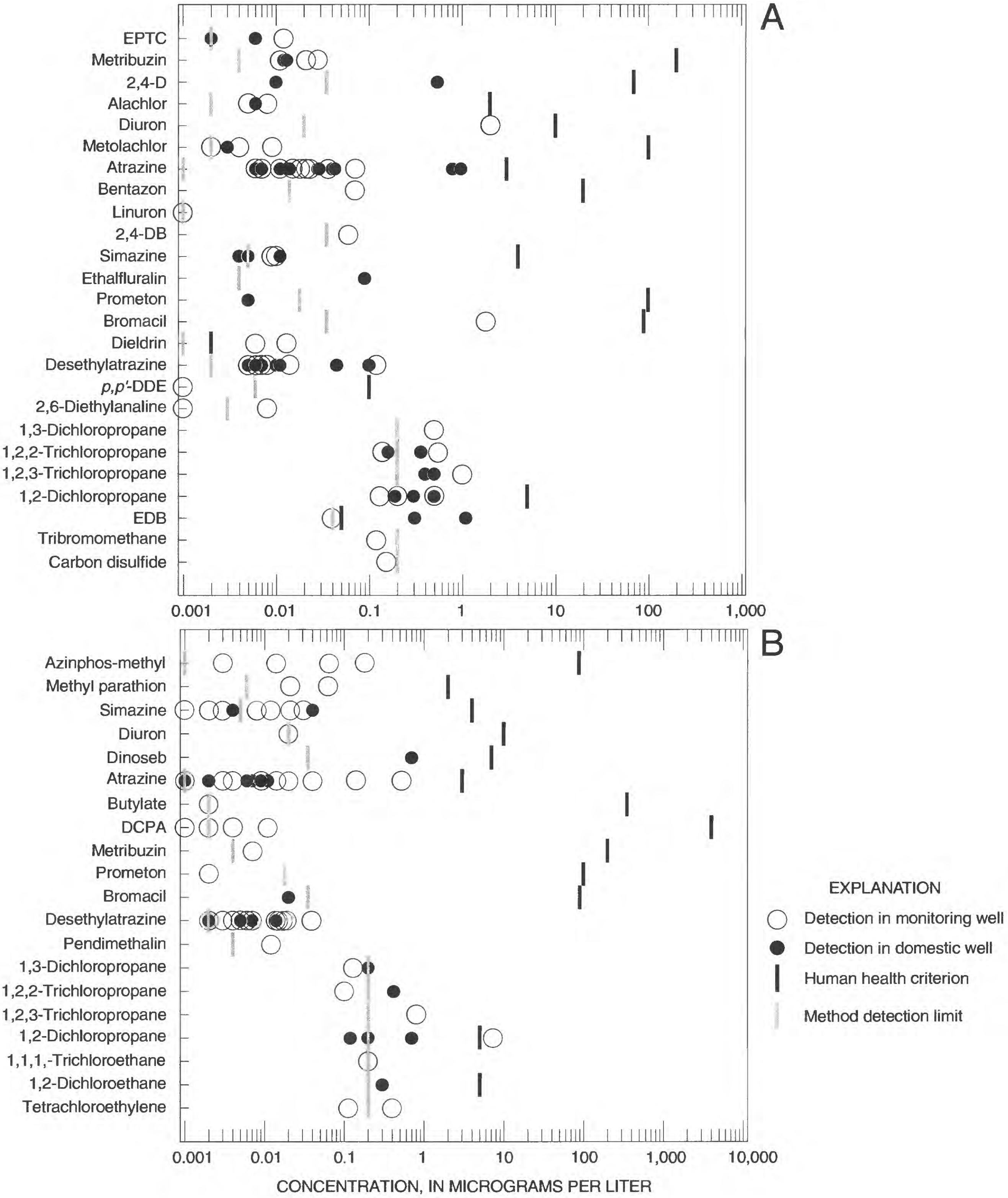

Figure 5. Concentrations of pesticides and volatile organic compounds in (A) row crop and (B) orchard wells.

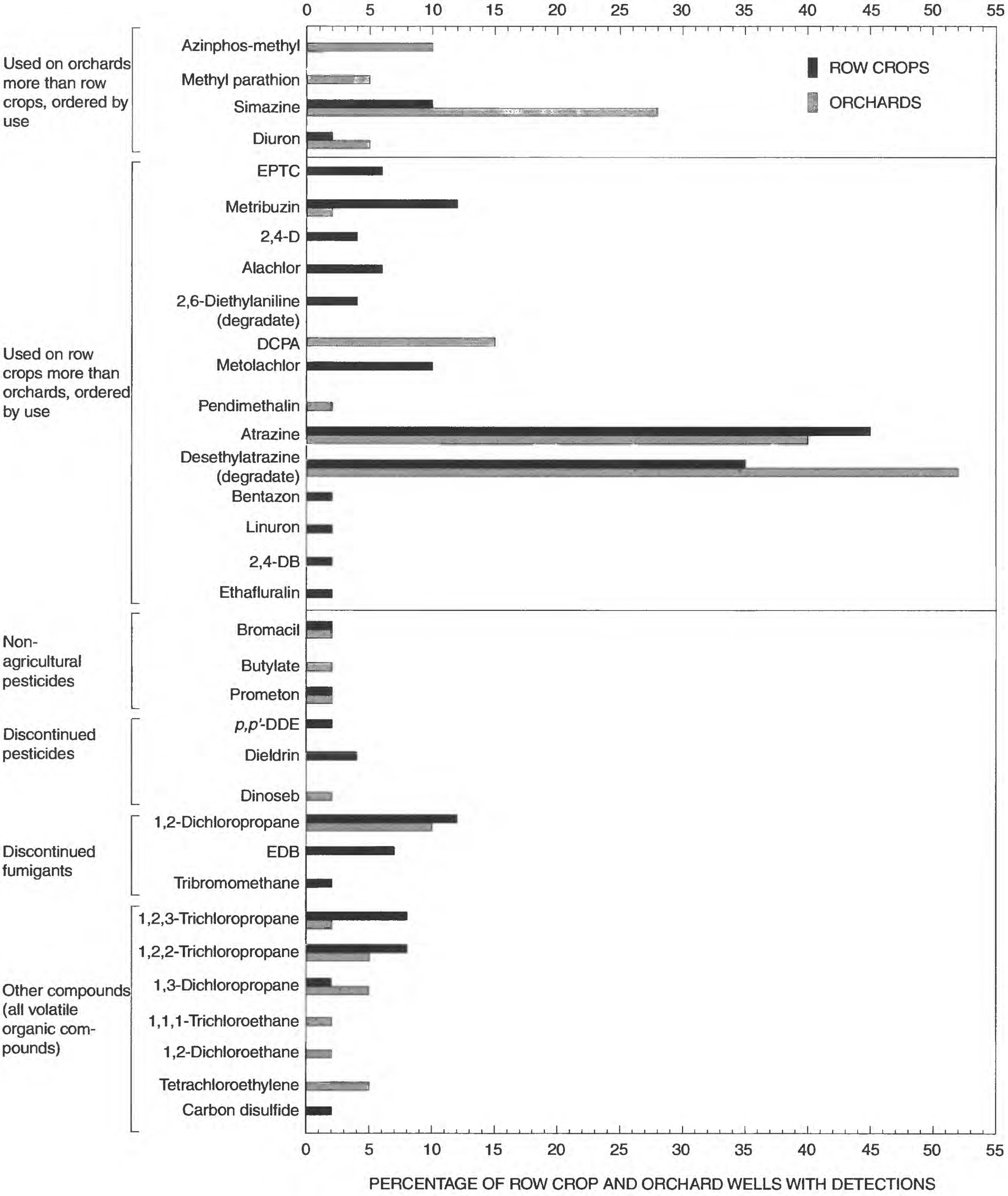

Figure 6. Detection rates of pesticides and other compounds in row crop and orchard areas. Degradates are listed directly below their parent compounds.

Table 9.--*Average application rates of detected agricultural chemicals*

Compound	Average application rate over entire land-use area (pounds of active ingredient per acre per year)	
	Orchard	Row crops
1,3-Dichloropropene	0	8.9
EPTC	0	0.31
Metribuzin	0	0.08
2,4-D	0	0.07
Alachlor	0	0.060
Diuron	0.05	0.050
DCPA	0	0.050
Metolachlor	0	0.04
Pendimethalin	0	0.04
Atrazine	0	0.04
Bentazon	0	0.03
Linuron	0	0.02
2,4-DB	0	0.02
Simazine	0.2	0.008
Ethalfluralin	0	0.008
Azinphos-methyl	1.5	0.007
Methyl parathion	0.6	0.008

quality with depth were similar for the two land uses. Differences in the well types other than depth also had potential to affect the quality of water samples: monitoring wells were pumped only to develop the well and to take samples, whereas domestic wells are pumped regularly and may have affected ground-water flow paths locally; monitoring wells were placed as close to the target land use as feasible and consequently are generally closer than the domestic wells to the targeted land use; monitoring wells were constructed of non-contaminating materials, whereas detailed knowledge of the materials used to construct domestic wells is lacking; the type and condition of the surface seals in domestic wells are generally unknown; and some domestic well houses in the area are used for pesticide storage (although these wells were excluded from the study, historical conditions are unknown).

Nitrate

The median nitrate concentration in monitoring wells was higher for row crops than for orchards (8 mg/L and 5.6 mg/L, respectively, fig. 3) though the difference was not statistically significant ($p = 0.28$). The median nitrate concentrations for the domestic wells near row crops and orchards were nearly the same: 6.2 mg/L and 6.5 mg/L, respectively ($p = 0.32$). Within the row crop areas, nitrate concentrations are higher for the monitoring wells than the (relatively) deeper domestic wells; within the orchard areas nitrate concentrations are lower in the monitoring wells. These differences, however, are not statistically significant.

Desethylatrazine-to-Atrazine Ratio

Because atrazine undergoes de-alkylation to desethylatrazine over a time scale from weeks to months in water, the desethylatrazine-to-atrazine ratio, or DAR, has been used as a surrogate for atrazine residence time in ground water (Adams and Thurman, 1991; Thurman and others, 1992). Sufficient detections of both compounds occurred in both land-use areas to allow the computation of DAR values. Comparison of these values for the four groups of wells is possible despite the fact that desethylatrazine had low analytical recoveries, because all wells were subject to the same recoveries. However, because of these low recoveries, comparisons based on DAR values should be reinforced by other water-quality information.

DAR values for the shallow ground water beneath the orchards (median 1.67) were found to be significantly higher ($p = 0.002$) than those from the row crop areas (median 0.26). Considering only the domestic wells, DAR values for the orchard areas (median 1.27) were also significantly higher ($p = 0.011$) than those from the row crop areas (median 0.18); however, the differences were not statistically significant for the monitoring wells despite a larger difference between the medians—1.71 for orchards, 0.40 for row crops; $p = 0.124$. No statistically significant differences in the DAR were detected between the monitoring and domestic wells in either land-use area ($p = 0.820$ in orchards, $p = 0.0616$ in row crops). The comparison of DAR values suggests a longer residence time for the atrazine detected in the shallow ground water beneath the orchards than for the atrazine detected beneath row crops. Given that atrazine is routinely applied to corn, sorghum, and other row crops, as well as to rights-of-way, but rarely applied to orchards, it is not surprising that atrazine residence time appears to be shorter beneath row crops. The atrazine detected in shallow ground water beneath the orchards thus appears to have been either (a) transported from application areas upgradient from the orchards (row crops or rights-of-way) or (b) present as a result of applications to the orchard areas before the orchards were established.

Pesticides

The relations between agricultural chemical use and pesticide detections observed for the two land-use areas (see "Pesticides and Volatile Organic Compounds") are more evident in the monitoring wells than in the domestic wells, presumably because the monitoring wells are shallower (fig. 2). All of the detections of currently used orchard insecticides in orchard wells were from monitoring wells (fig. 5b) (dinoseb was banned in 1988 and was detected in a domestic well). Simazine, which is used on row crops, but at lower rates than in orchards, was detected primarily in orchard wells (fig. 6), and 78 percent of those detections were in monitoring wells. In contrast, of the four detections of the discontinued row crop fumigant 1,2-dichloropropane in the orchard land-use area, three were in domestic wells. As was also inferred for atrazine (on the basis of comparing DAR values), the more frequent detection of 1,2-dichloropropane in the deeper wells suggests that it was present beneath the orchards as a result of historical use, either on surrounding row crops or before the orchards were planted.

SUMMARY

The effects of agricultural chemical use on shallow ground-water quality in two agricultural land-use settings were investigated and compared in the Columbia Basin Irrigation Project (CBIP) using data from 89 existing shallow domestic wells and newly installed monitoring wells during 1993-95, as part of the National Water-Quality Assessment (NAWQA) Program. Areas characterized by row crop rotations (including potatoes) and orchards were selected for study on the basis of large (or in the case of orchards, rapidly increasing) acreages, heavy use of pesticides (fumigants on row crops, and insecticides on orchards), and the economic significance of the crops in Washington State.

Analyses for 145 pesticide compounds (pesticides and pesticide degradates), and volatile organic compounds (VOCs, including several agricultural fumigants) were carried out. Sampling locations were selected at random and wells were selected (in the case of domestic wells) or constructed (in the case of monitoring wells) to (a) obtain the shallowest samples possible, in order to ensure the sample reflects the target land use and (b) avoid potential contamination from construction materials or treatment systems. Shallow domestic wells averaged 140 feet deep and were located within 100 feet from the targeted land use, whereas the monitoring wells averaged 43 feet deep and were less than 50 feet from the targeted land use. Samples were obtained from both types of wells in both land-use settings to facilitate statistical comparisons among each of the four subsets of well type and land-use setting.

Sampling methods followed nationally consistent procedures and included thorough well purging, using non-contaminating sampling equipment, and quality-assurance sampling. Quality-assurance samples made up 32 percent of all samples and included blanks, spikes, and replicates. Examination of the results from these samples led to the deletion of some of the data because of demonstrated or suspected contamination or carry-over between successive samples.

The maximum contaminant level (MCL) for nitrate (10 mg/L nitrate as N) was exceeded in 31 percent of the domestic wells (37 percent of domestic row crop wells and 28 percent of domestic orchard wells). Of the 22 detected compounds with USEPA-established MCLs (or other applicable human-health criteria), 3 were found to exceed their respective criteria: dieldrin (in 2 monitoring wells), ethylene dibromide (EDB, in 2 domestic wells), and 1,2-dichloropropane (in 1 monitoring well).

When the differences in well type (monitoring versus domestic) were not accounted for, no significant difference in overall agricultural chemical occurrence was observed between wells in the orchard and the row crop setting ($p > 0.05$). The median nitrate concentration for row crop wells was 6.7 mg/L and in orchard wells was 6.0 mg/L, despite the pronounced differences in annual nitrogen application rates (more than 130 pounds per acre on row crops compared to less than 70 in orchards). Similarly, overall rates of pesticide detection were not significantly different between the two land uses, although compounds were generally detected at the higher rates in the land-use setting where they were applied more extensively. The overall pesticide detection rates for row crops and orchards were 69 and 68 percent, respectively, with an average of approximately two pesticides detected per well in each setting. Furthermore, a larger number of different compounds were found in row crop wells.

Relations between pesticide detection rates and use were more evident in both land-use settings when specific compounds were examined. Three out of the five detected compounds that were used at higher rates on orchards were detected only in orchards, and the remaining two were detected at highest rates in orchards. Similarly, 9 of 12 (parent) compounds applied at higher rates to row crops were detected only in row crop wells, and 2 of the remaining 3 were found more frequently in row crop wells.

When the influence of well types was examined, the monitoring wells were found to provide a clearer picture of the differing effects of pesticide use on shallow groundwater quality in the two land-use settings than did the domestic wells, presumably because the latter are significantly deeper ($p = 0.001$).

The median nitrate concentrations in monitoring wells in the two land uses (fig. 3) are not significantly different (8.0 mg/L for row crop monitoring wells, and 6.5 mg/L for orchards), nor are there significant differences between the monitoring wells and the domestic wells in either setting ($p > 0.05$). Desethylatrazine-to-atrazine ratios (DAR), which increase with residence time, suggest a greater residence time for the atrazine detected beneath orchards relative to that detected beneath row crops. The median DAR value for orchard wells, 1.67, is significantly higher than the median value of 0.26 measured in the wells in the row crops ($p = 0.002$). There is a statistically significant difference in median DAR values considering only domestic wells (1.27 for orchards versus 0.18 for row crops, $p = 0.011$) however, considering only monitoring wells, the difference in median DAR values is numerically larger but not statistically significant (1.71 for orchards versus 0.40 for row crops, $p = 0.124$). The significant differences between median DAR values suggest that the atrazine detected beneath orchards may have come from row crops located upgradient from orchards or was applied prior to the establishment of the orchards.

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