WASHINGTON STATE
DEPARTMENT OF
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Washington State Pesticide Monitoring Program

Pesticide Residues in the Kittitas Valley Surficial Aquifer

Pesticides in Ground Water Report No. 10

April 1997

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by
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Olympia, Washington 98504-7710

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Abstract

Twenty-seven wells were sampled near Ellensburg, Washington for pesticides and nitrate+nitrite as N. Water temperature, pH, and specific conductance were also measured in the field. Wells were located in the surficial aquifer that underlies the Kittitas Valley. This water-table aquifer is shallow, with a depth to water ranging from as little as two feet to about 20 feet.

Seven pesticides were detected in the initial samples: **atrazine, simazine, prometon, bromacil, bentazon, diphenylamine, and 2,4-D**. The presence of **bentazon and 2,4-D** was not confirmed by the verification sampling. Pesticides were detected in nine of the 27 study wells, with more than one pesticide found in four wells. A breakdown product of atrazine, **atrazine desethyl**, was found in the six wells where atrazine was detected. Pesticides were not found in the deepest wells, but were restricted to depths less than about 50 feet. Concentrations of all pesticides were below the Maximum Contaminant Level or Lifetime Health Advisory Level set by the EPA for public drinking water.

Nitrate was detected in all nine wells with detected pesticides. In one well, the nitrate+nitrite as N concentration in the initial sample (11.9 mg/L in May) exceeded the 10.0 mg/L drinking water standard for nitrate. However, a verification sample collected in December had a concentration of 3.2 mg/L.

Acknowledgments

We thank the following people for their assistance with this project:

- Owners of the wells for allowing us to sample and for providing background information on their wells.
- Dick Carter, hydrogeologist with Ecology's Environmental Investigations and Laboratory Services (EILS) program, who selected the study wells, spoke with the farmers, and generally did all the "leg work." Dick also assisted with preliminary sampling.
- Norm Olson, Bob Carrell, and Dickey Huntamer at Manchester Laboratory for analyses of the pesticides.
- Stuart Magoon at the Manchester Laboratory for quality assurance review of the data.
- Robert Garrigues and Larry Goldstein of the EILS program for peer review.
- Kim Sherwood and Holly Cushman of the Water Quality Program, Ecology Central Regional Office, for peer review.
- David Nash of the Washington State Department of Health for reviewing all results for health implications and for writing health "consults" that were mailed to well owners explaining these implications.
- Joan LeTourneau for formatting and proofing this report.

Introduction

Twenty seven wells were sampled near Ellensburg, Washington for pesticides and nitrate+nitrite as nitrogen. Ellensburg, home of Central Washington State University and the major population center in Kittitas County, started as an agricultural and logging community in the late 1800s. In 1867, the first settlers in the Kittitas Valley found good range lands for grazing herds of cattle, and early agriculture was centered on raising livestock. One of the sampled wells was dug in 1878 on the Olmstead homestead, now an Historic Site and State Park. As farms were established along the stream bottoms, fields of hay and grain were irrigated by turning the water from the creeks into small ditches. As farming intensified, range cattle were replaced by sheep, which summered in the mountain forests and wintered in the valley. Presently, the area is irrigated by an extensive system of canals and ditches. The Highline Canal diverts water from the Yakima River at Easton and has provided irrigation to the east side of the valley since 1932. Other canals, principally the South Branch Canal, Taneum Ditch, and the West Side Canal, serve the west side of the valley.

The area studied encompasses the lands surrounding Ellensburg, roughly bordered by the town of Thorp to the north, the Yakima River canyon to the south, the town of Kittitas to the east, and the edge of the valley to the west (Figure 1). Study wells tap the Kittitas Valley Surficial Aquifer, although only a small portion of the aquifer was sampled. The Yakima River cuts through the study area, with about one-third of the wells to the west and the remainder east of the river.

The climate of the Kittitas Valley is continental (USDA, 1945). Winter snow is common, but the cold of winter is usually broken by mild west winds, often melting the snow in midwinter. Hot spells during the summer are of short duration, and the heat is seldom oppressive. The average temperature is about 28 degrees F. during the winter and 66 degrees F. in summer. Annual precipitation is 8.9 inches at Ellensburg (Miller, 1997). A large part of the precipitation comes as snow in winter and as low intensity rain in late fall and early spring. Because of light summer rainfall, farmers must irrigate to insure that crops will grow actively. Irrigation is primarily from water diverted from the Yakima River or its tributaries.

Agriculture in the area is best known for its timothy hay, most of which is exported to Japan. A local trucker estimated that several dozen semi-truck loads of compressed hay leave Ellensburg daily, year around, for the port of Seattle. Other crops include sweet and silage corn, wheat, oats, peas (seed), snap beans, potatoes, alfalfa and grass hay, and pasture. Although agriculture remains the major activity in the valley, residential and industrial development is replacing farming around the outskirts of Ellensburg and along the I-90 corridor.

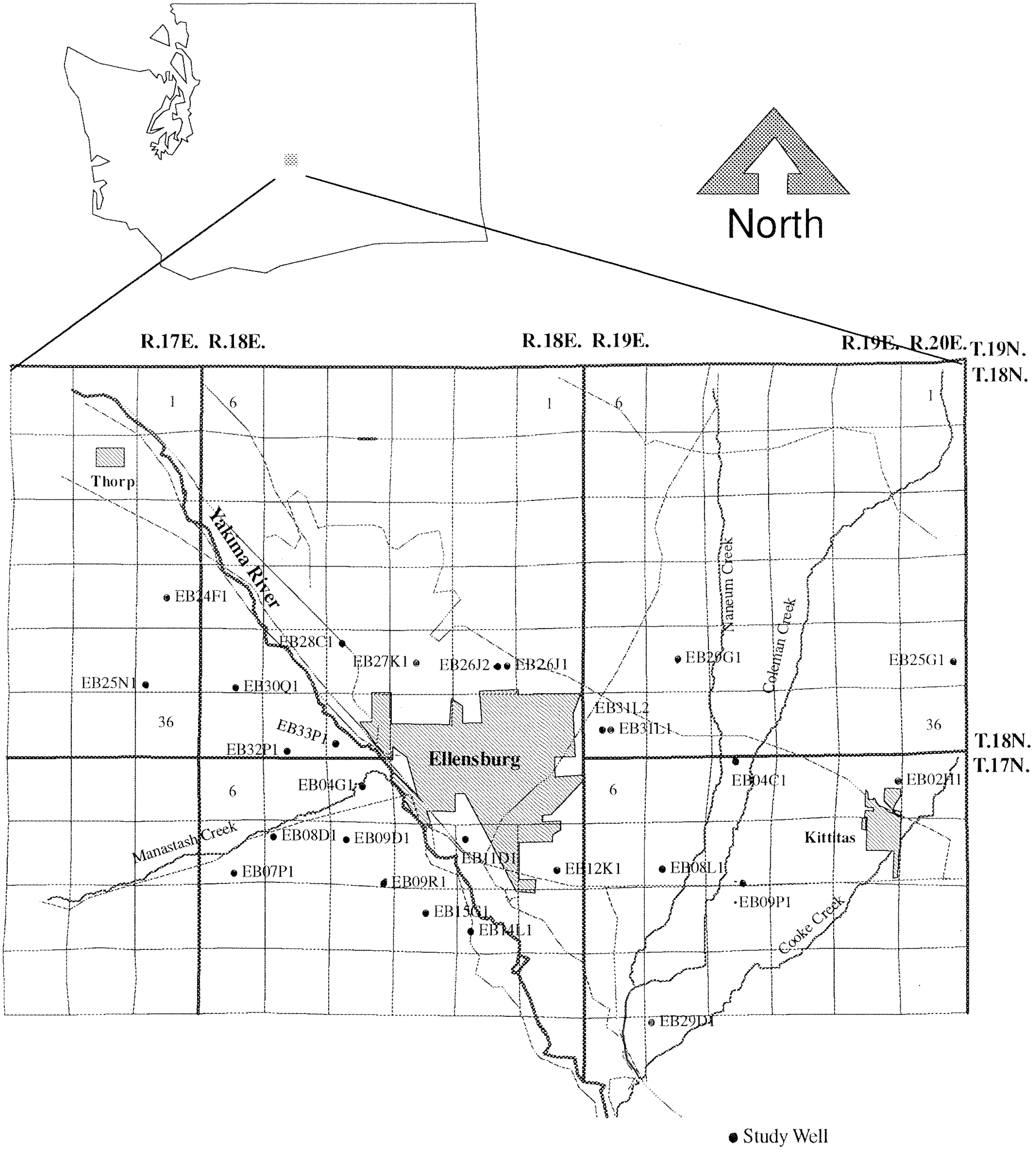

Figure 1. Location of the Kittitas Valley study area.

Background

Agricultural chemicals, specifically pesticides, are used throughout Washington. Although pesticides are used extensively on farmlands, they are also applied in urban and forest environments. Population growth and increasing urbanization are placing increasing demands on ground-water resources, and maintaining good water quality for a variety of beneficial uses is important. However, the effects of pesticide use on the state's ground-water quality is not well known.

Purpose

Sampling of the Kittitas Valley Surficial Aquifer is part of the Washington State Pesticide Monitoring Program which monitors pesticides in shallow ground water statewide. The focus is to provide data on the concentrations of pesticides in ground water where agriculture is interspersed with residential and industrial development.

Kittitas Valley Surficial Aquifer

The Kittitas Valley Surficial Aquifer, as the name implies, underlies the Kittitas Valley. The aquifer is dissected by the Yakima River, with which it is hydraulically connected, and feeds the river and its local tributaries. The Yakima River effectively separates the aquifer on one side of the river from the other; underflow is probably nil. The extent of the valley roughly defines the aquifer boundaries.

Hydrogeology

The Kittitas Valley is a downfolded mountain basin lying in the east-central part of Kittitas County. It is roughly oval in shape, about 25 miles long from northwest to southeast, and 14 miles wide. The Kittitas Valley is separated from the valley of the upper Yakima River by a high plateau between Green Canyon and Swauk Creek, Lookout Mountain, and Cle Elum Ridge. The valley is confined to the southeast by the Saddle Mountains, with the drainage via the Yakima Canyon.

The water table is shallow, generally within 20 feet of the land surface. The aquifer is hydraulically connected with the Yakima River, its tributaries, and the network of unlined ditches and canals that web the surface (Figure 2). Along with recharge from precipitation, the aquifer receives water from the infiltration of excess irrigation water. It is likely that the water table is higher now than it was before irrigation, but the 15 ft. deep (3 ft. to water) Olmstead well (dug in 1878) indicates that the water table was shallow even before irrigation.

Soils

The soils of the Kittitas Valley have a wide range in color, texture, topography, and profile character, but all have the characteristics common to soils formed under an arid or semiarid climate. When settlers arrived, the surface soil layers were relatively unleached; that is, they had not been impoverished of soluble mineral plant nutrients by downward movement of moisture through the soil. Since the advent of irrigation, some leaching has probably occurred. However, soils are inherently fertile and productive under irrigation. The lighter colored members are low in organic matter and nitrogen, but even the shallow and gravelly soils produce profitable crops where properly tilled, irrigated, and fertilized. (USDA, 1945).

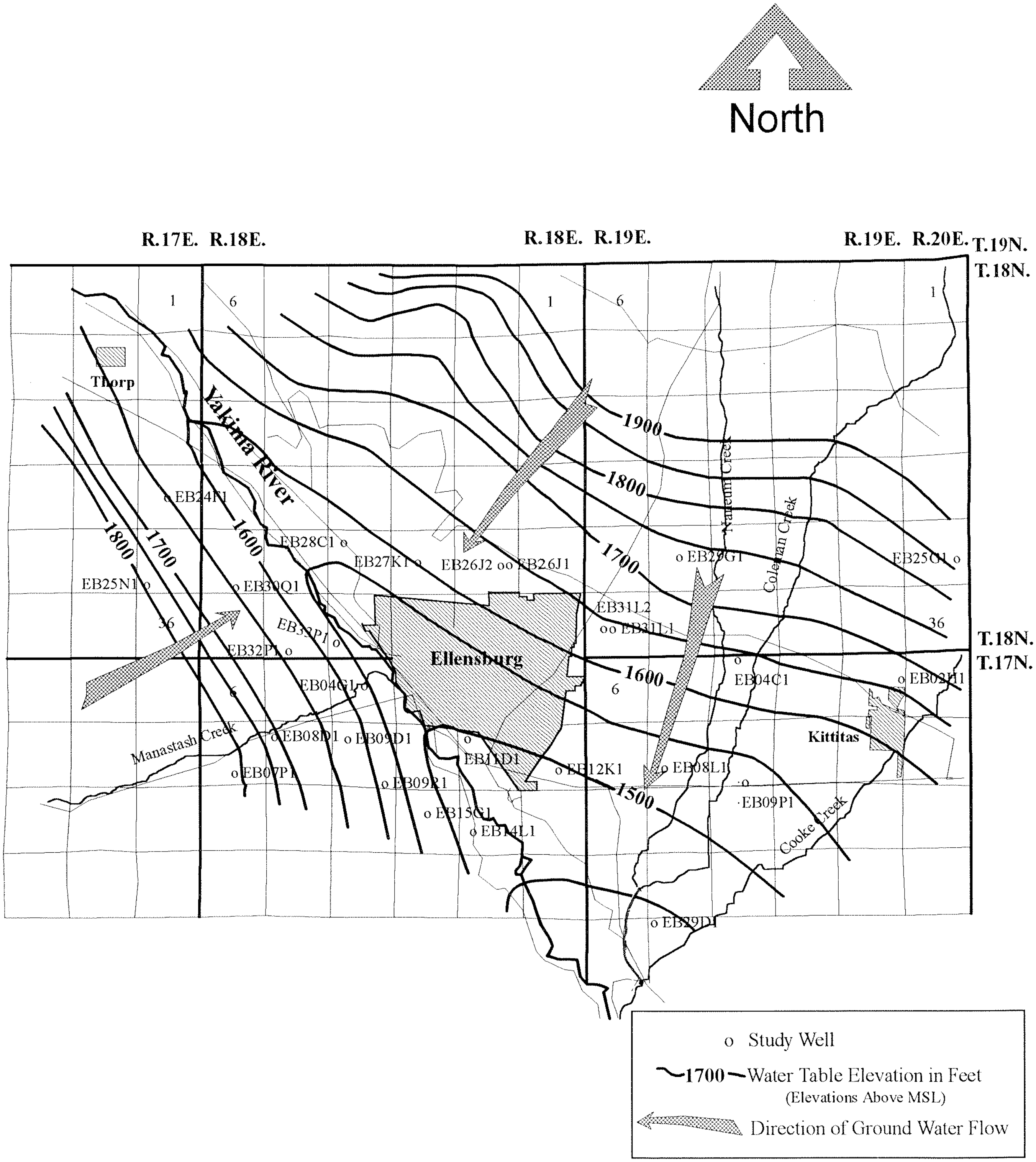

Figure 2. Water Table Contour Map.

Major soils include the Naches and Nanum soil series associations (USDA, 1945). Texture of the Naches soils are variable, and most are well drained. The lighter textured member is typically underlain by readily permeable gravel and finer materials. Some of the lower lying areas are subject to a high water table during wet periods in spring and early summer. Heavier soils, occurring in the low lying areas, may require artificial drainage for maximum utilization. The Nanum soils are also generally well drained. The most common Nanum soil in the study area is a clay loam that extends down to an underlying coarse gravel at one-half to five feet.

Methods

Appropriate wells were selected for sampling after researching the well-log files located at the Ecology Central Region Office in Yakima. Well logs were selected for further evaluation based on shallow depth, high water table, and location within the aquifer. Although well logs were useful for the selection of most wells, a few wells were selected following suggestions of local residents.

Criteria used in the well selection included:

- Water pumped only from the Kittitas Valley Surficial Aquifer
- Location of the well away from aquifer boundaries and from wells already selected
- A shallow well
- Ease of collecting a representative water sample
- The owner's permission to sample

Wells

Twenty-seven wells were selected for sampling the Kittitas Valley Surficial Aquifer, with uses including domestic (22), irrigation (4), and stockwatering (1). Wells are located within a 7 mile radius of Ellensburg (Figure 1). Wells range from 12 to 100 feet deep with a median depth of 65 feet. Screens, when present, usually allow water to enter the well over the deepest four to five feet. The depth to water ranges from 3 to 25 feet, and one well is a flowing artesian (capped). The type of well, surface elevation, total depth, and depth to water for the individual wells are presented in Appendix A. Two of the shallow wells are paired with nearby deeper wells (same owner and only a few feet apart). This allows a simple comparison between the water quality at two depths. The pairs are EB26J1 and 2, and EB31L1 and 2. The number two wells are shallow driven wells, originally used for domestic water, but since replaced by deeper drilled wells. The shallow wells are now used for supplemental irrigation only.

Sampling Schedule

The initial sampling occurred in May 1996. With one exception, wells in which pesticides were detected were resampled in December 1996 to confirm the initial results. Well EB31L2 was "winterized" and not accessible for verification sampling.

Sampling Procedures

Before sampling, all wells were purged until the temperature, pH, and specific conductance had stabilized and at least three casing volumes of water had been removed. An Orion model 250A meter was used to measure pH and temperature, and a Beckman type RB-5 meter was used to measure specific conductance. When the well had an installed pump, it was purged and sampled from an existing faucet located as close to the well as possible and upstream of any pressure tanks, where feasible. Well EB09P1 was sampled with a portable 4-inch submersible pump. The 5000 gallons of water in this hand dug well were not completely purged. Instead, it was pumped for one hour (approximately 1100 gallons) before sampling. Samples were collected in pre-cleaned, organic-free glass bottles and stored on ice until delivery to the lab. Carbamate samples were preserved with a monochloroacetic acid buffer. Field blanks were not collected. Since pesticides were not detected in the majority of samples, these were substituted for the field blanks.

Analytes Tested

Ground water was analyzed for 130 pesticides and pesticide-breakdown products (Appendix B) and for nitrate+nitrite as nitrogen. Many of the pesticides were chosen from the U.S. Environmental Protection Agency (EPA) list of leachable pesticides which have properties conducive to migration through soil to ground water (Cohen, 1985). Additional pesticides were added when available from the same analyses for little additional cost.

Nitrate was tested to investigate any link between elevated nitrate concentrations and pesticide detections.

Samples were analyzed by the Ecology/EPA Manchester Laboratory.

Quality Assurance

The quality of the results is good. The qualitative and quantitative accuracy, validity, and usefulness of data were independently reviewed by Stuart Magoon of the Ecology/EPA Manchester Environmental Laboratory and are summarized in Appendix C.

Results

Pesticides

In the initial sampling, pesticides were detected in nine of the 27 study wells, with more than one pesticide found in four of the nine wells. Pesticides detected were **atrazine, simazine, prometon, bromacil, bentazon, diphenylamine, and 2,4-D**. A breakdown product of atrazine, **atrazine desethyl**, was found in the six wells where atrazine was detected. The concentrations of detected pesticides are presented in Table 1, including results of both initial and verification sampling.

Table 1. Concentrations of pesticides and related breakdown products detected in the Kittitas Valley Surficial Aquifer (µg/L).

Site ID	Atrazine	Atrazine desethyl	Simazine	Prometon	Bromacil	Bentazon	Diphenylamine	2,4-D
EB04G1	0.005J/0.005NJ	0.007J/0.006NJ						
EB07P1				0.006J/U			0.19J/0.091J	
EB09D1	0.009J/0.003NJ VD/0.004NJ	0.005J/U VD/0.002NJ						
EB09P1	0.022J/0.022J	0.029J/0.031J	0.007J/0.004NJ		0.12J/U	0.17/U		
EB11D1				0.013J/0.006NJ				
EB15G1	0.07/0.034J	0.1J/0.059J	0.014J/0.007NJ					0.07/U
EB26J2	0.043J/0.024J	0.039J/0.026J	0.012J/0.003NJ				U/0.033J	
EB29G1	0.011J/0.012J	0.023J/0.017J						
EB31L2					0.037J/ns			

/ = initial sample followed by verification sample
VD/ = verification blind duplicate
ns = not sampled for verification
U = not detected
J = analyte detected but value is an estimate
NJ = evidence the analyte is present, the value is an estimate

Six of the seven pesticides detected are herbicides. Atrazine, simazine, and prometon are triazine herbicides, based on a symmetrical triazine structure with differences depending upon the attached radicals. Prometon is non-selective and used for total vegetation and brush control in noncrop areas. Atrazine and simazine are selective and used to control weeds on crop and pasture lands. Bromacil is also a herbicide used for general weed and brush control in non-crop areas. It is particularly useful against perennial grasses. Bentazon is a selective herbicide used after the weed emerges. It readily controls broadleaf weeds and may be applied by air. 2,4-D is a selective phenoxy herbicide used mostly after weeds have emerged. It is used on apples, corn, hay, wheat, and pasture.

The only non-herbicide was Diphenylamine (DPA). DPA is a fungicide and plant growth regulator commonly used postharvest to treat apple or pear scald. Additional pesticide information may be found in Thomson (1986).

Atrazine was detected in six wells during the initial sampling at concentrations between 0.005 and 0.07 micro-grams per liter (ug/L). Only the highest concentration, found at well EB15G1, was quantifiable; the other five were reported as estimates (J qualifier). Atrazine was again detected in the six verification samples. Concentrations ranged from 0.003 to 0.034 ug/L. Verification results were all estimates (J). **Atrazine desethyl** was also detected in these six wells at concentrations between 0.005 and 0.1 ug/L; and detected in all but one of the verification samples. All atrazine desethyl concentrations were reported as estimates.

Simazine was detected in three wells during the initial sampling and again in the verification samples from these wells. Initial concentrations ranged from 0.007 to 0.014 ug/L. Verification concentrations ranged from 0.003 to 0.007 ug/L. All initial and verification values were reported as estimates (J).

Prometon was detected in two wells, EB07P1 and EB11D1, during initial sampling at concentrations of 0.006 and 0.013 ug/L, respectively. The concentrations were low enough, however, that only estimated values were reported. Prometon was again detected in the verification sample from EB11D1 (0.006 ug/L) but was not detected in well EB07P1.

Bromacil was detected in two wells, EB09P1 and EB31L2, at concentrations of 0.12 and 0.037 ug/L, respectively. Concentrations were low enough in the initial samples that only estimated values were reported. Bromacil was not detected in the verification sample from EB09P1. Well EB31L2 was not resampled for verification

Bentazon was detected in well EB09P1 at a concentration of 0.17 ug/L. It may have been present in the verification sample, but the level was so low it could not be confirmed and was reported by the laboratory as "not detected."

Diphenylamine was detected in well EB07P1 during the initial sampling at a concentration of 0.19 ug/L. It was also detected in the verification sample from this well at a concentration of 0.091 ug/L. Both values were estimates. This pesticide was also detected in the verification sample from well EB26J2 (0.033 ug/L), although it was not detected in the initial sample.

2,4-D was detected in well EB15G1 at an estimated concentration of 0.07 ug/L. It was not detected in the verification sample.

Nitrate + Nitrite as N

Nitrate+nitrite as N was detected in 26 of the 27 wells sampled. Initial concentrations ranged from 0.04 to 11.9 mg/L (Table 2). The quantification limit was 0.01 mg/L. The median nitrate+nitrite as N concentration was 0.71 mg/L. The maximum concentration occurred in well EB15G1, 11.9 mg/L (initial) and 3.2 mg/L (verification). This well had an initial concentration greater than the Maximum Contaminant Level (MCL) (10.0 mg/L) for public drinking water, but the concentration in the sample collected for verification was below this limit.

Table 2. Nitrate + nitrite as nitrogen (mg/L), temperature (°C), pH, and specific conductance (µmhos/cm) of ground water.

Site ID	Nitrate	Temperature	pH	Conductance
EB02H1	0.71	11.6	6.7	340
EB04C1	U	7.7	6.6	130
EB04G1	2.03	12.3/10.4	7.0/6.6	280/250
EB07P1	0.34	8.8/10.4	6.7/6.5	125/105
EB08D1	0.27	11.5	7.4	180
EB08L1	0.33	11.3	7.2	350
EB09D1	1.09	11.1/10.6	6.4/6.7	150/160
EB09P1	5.15	7.6/8.3	7.2/6.7	550/485
EB09R1	0.53	12.1	7.2	170
EB11D1	1.01	11.0/10.8	6.9/6.9	200/200
EB12K1	0.73	12.1	7.2	240
EB14L1	0.25	12.0	7.6	180
EB15G1	11.9/3.2	11.0/10.8	7.1/6.7	420/330
EB24F1	1.52/1.53a	12.4	7.4	280
EB25G1	0.56	10.6	7.2	300
EB25N1	0.78	11.1	6.7	90
EB26J1	1.19	12.0	7.3	200
EB26J2	0.30	9.6/10.0	6.9/6.6	200/185
EB27K1	0.51	11.8	7.0	270
EB28C1	1.39	11.5	7.8	260
EB29D1	0.46	16.0	7.7	220
EB29G1	0.04	10.0/9.6	6.8/6.6	290/300
EB30Q1	1.39	12.6	6.9	240
EB31L1	0.59	12.0	7.2	220
EB31L2	0.08	10.2	6.9	285
EB32P1	5.02	12.3	7.2	650
EB33P1	3.26	11.8	6.7	250

U = not detected above the detection limit of 0.01 mg/L
/ = initial followed by verification sample (initial/verification)
a = field duplicate samples

Nitrate was detected in all nine wells with detected pesticides. The median nitrate+nitrite as N concentration in the nine wells was 1.01 mg/L (mean = 2.44) as compared to the median concentration for wells without pesticides of 0.72 mg/L (mean = 1.15). Pesticides were found in three of the five wells with highest nitrate concentrations. However, pesticides were also found in the two wells with the lowest detected nitrate concentrations

(EB29G1 and EB31L2). Although pesticides are more likely to be found in agricultural areas with elevated nitrate concentrations, the validity of using a single nitrate concentration to select an individual well for pesticide sampling is questionable.

Field Measurements

The water temperature, pH, and specific conductance of study wells are presented in Table 2. Values showed little seasonal variation between the initial sampling in May 1996 and the verification sampling in December 1996. The temperature of ground water averaged 11.3° C during the initial sampling and was cooler by about 1.1° C during the verification sampling. The initial pH ranged from 6.4 to 7.8. The average was 7.1, somewhat higher than the 6.7 pH found during verification sampling. The specific conductance, a rough measure of total dissolved solids, ranged from 125 to 650 umhos/cm. Average specific conductance was about 262 umhos/cm during the initial sampling, with little change noted during verification. The maximum allowed drinking water conductance is 700 umhos/cm and levels up to 500 umhos/cm are common in ground water.

Influence of Well Depth

The average depth of study wells was 60 feet with an average depth to water of about 13 feet (Appendix A). Pesticides were not detected in the nine deepest wells, ranging from 72 to 100 feet, even though the water levels in these wells averaged about 12 feet. The average depth of wells in which pesticides were detected was 40 feet; the deepest was 70 feet. The depths to water for wells with pesticides did not noticeably differ from those of wells without pesticides. Thus all wells were equally susceptible to pesticide contamination from the surface. However, it appears that the pesticides have not penetrated the aquifer to the depth of the deepest wells. Pesticides were detected in both shallow wells of the two sets of paired wells, but in neither of the deeper wells. The shallow wells (EB26J2 and EB31L2) were <20 and 15 feet deep, and the corresponding deeper wells (EB26J1 and EB31L1) were 72 and 55 feet deep. This study found no pesticides at depths greater than about 70 feet, and it appears that pesticides are presently restricted to about the top 50 feet of the aquifer.

A similar, although weak, relationship was found between well depth and nitrate concentration. The average nitrate+nitrite as N concentration in the nine deepest wells (72 to 100 feet deep) was 0.71 mg/L. In the nine shallowest wells (12 to 59 feet), the average concentration was 0.96 mg/L. However, the highest average nitrate concentration was for eight wells with depths between 60 and 70 feet. Six of the ten highest concentrations were found at these depths, with an average of 3.2 mg/L. The single well with no detectable nitrate was 65 feet deep. The depth to water for wells with nitrate concentrations greater than one mg/L ranged from 3 to 20 feet. The range for wells with concentrations less than one mg/L was similar.

Health Concerns

EPA has set Maximum Contaminant Levels (MCLs) or Lifetime Health Advisory Levels (LHALs) in drinking water for all of the detected pesticides. Consumption of water with pesticide concentrations above these levels increases the risk of adverse health effects. None of the pesticide concentrations exceeded these levels of concern.

- The MCL for atrazine in drinking water is 3.0 ug/L. Atrazine was detected at concentration between 0.003 and 0.043 ug/L. EPA has not established any standards for atrazine desethyl.
- The MCL for simazine has been set at 4.0 ug/L. Detected concentrations were less than 0.014 ug/L.
- EPA has set the LHAL for prometon at 100 ug/L. The two detections in this study were less than 0.013 ug/L.
- The LHAL for bromacil is 90 ug/L. Bromacil was detected at concentrations between 0.037 and 0.12 ug/L.
- The LHAL for bentazon is 20 ug/L. The one detection in this study was 0.17 ug/L.
- The LHAL for diphenylamine is 200 ug/L. The concentrations found in this study were less than 0.19 ug/L.
- EPA has set the MCL for 2,4-D at 70 ug/L. The one detection in this study was 0.07 ug/L, about 1/1000 of this value.

The MCL for public drinking-water systems for nitrate as N is 10.0 mg/L. The nitrate+nitrite as N concentration exceeded 10 mg/L in one well, and 5.0 mg/L (1/2 the MCL) in an additional two wells. Concentrations greater than one mg/L often indicate the influence of man, and concentrations greater than 5 mg/L are “high” for ground water and almost always indicate contamination.

Conclusions

- Pesticides were detected in one-third of the 27 wells sampled in the Kittitas Valley Surficial Aquifer.

- Seven pesticides were detected in ground water: **atrazine, simazine, prometon, bromacil, bentazon, diphenylamine, and 2,4-D**. A breakdown product of atrazine, **atrazine desethyl**, was also found in six wells where atrazine was detected. Two pesticides, **bentazon and 2,4-D**, were not detected during verification sampling.

- None of these pesticides was detected above concentrations established by EPA for health protection.

- No impairment of water use is indicated based on concentrations of pesticides.

- Pesticides were not detected in the nine deepest wells, ranging from 72 to 100 feet. Pesticide detections were limited to well depths less than about 70 feet.

- In one of the 27 study wells, the nitrate+nitrite as N concentration exceeded the 10.0 mg/L drinking water standard. Three wells had concentrations greater than 5 mg/L and 11 wells had concentrations greater than one mg/L. Contamination by nitrate from above the water table is the most likely cause of ground water nitrate concentrations greater than 2 or 3 mg/L. Additional study is necessary to identify the source of the nitrate or the source of both the oxygen and nitrogen necessary to sustain nitrate concentrations above 3 mg/L.

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Appendices

Appendix A. Kittitas Valley Surficial Aquifer study wells.

Site ID	Water Use	Ground Elevation (ft)	Well Depth (ft)	Depth to Water (ft)
EB02H1	Domestic	1690	64	18
EB04C1	Stockwater	1640	65	10
EB04G1	Domestic	1580	60	13
EB07P1	Domestic	1835	43	UN
EB08D1	Domestic	1735	35	15
EB08L1	Domestic	1535	80	15
EB09D1	Domestic	1640	60	UN
EB09P1	Irrigation	1540	15	3
EB09R1	Domestic	1595	100	15
EB11D1	Domestic	1495	63	12
EB12K1	Domestic	1490	80	9
EB14L1`	Domestic	1470	75	20
EB15G1	Domestic	1540	70	18
EB24F1	Domestic	1660	80	4
EB25G1	Domestic	1870	77	8
EB25N1	Domestic	1830	80	25
EB26J1	Domestic	1660	72	14
EB26J2	Irrigation	1660	<20	<20
EB27K1	Domestic	1600	58	A
EB28C1	Domestic	1570	59	3
EB29D1	Domestic	1440	80	2
EB29G1	Irrigation	1750	12	<12
EB30Q1	Domestic	1640	65	UN
EB31L1	Domestic	1640	55	20
EB31L2	Irrigation	1640	15	<15
EB32P1	Domestic	1660	70	18
EB33P1	Domestic	1590	70	20

UN = Unknown

A = Artesian, flows when not capped.

Appendix B. Target pesticides.

Pesticide	Method	Quantification Limit (µg/L)
1,2-Dibromo-3-Chloropropane (DBCP)	EPA 504	0.02
1,2-Dibromoethane (EDB)	EPA 504	0.02
1,2-Dichloropropane	EPA 846	1.0
1-Naphthol	EPA 531.1	1.0
2,3,4,5-Tetrachlorophenol	EPA 615	0.02
2,3,4,6-Tetrachlorophenol	EPA615	0.02
2,4,5-T	EPA 615	0.01
2,4,5-TB	EPA 615	0.01
2,4,5-TP (Silvex)	EPA 615	0.01
2,4,5-Trichlorophenol	EPA 615	0.02
2,4,6-Trichlorophenol	EPA 615	0.02
2,4-D	EPA 615	0.03
2,4-DB	EPA 615	0.06
3,5-Dichlorobenzoic Acid	EPA 615	0.03
3-Hydroxycarbofuran	EPA 531.1	0.50
4-Nitrophenol	EPA 615	0.07
Abate (Temephos)	EPA 1618	0.75
Acifluorfen (Blazer)	EPA 615	0.03
Alachlor	EPA 1618-N	0.20
Aldicarb	EPA 531.1	1.0
Aldicarb Sulfone	EPA 531.1	1.0
Aldicarb Sulfoxide	EPA 531.1	2.0
Ametryn	EPA 1618-N	0.08
Atraton	EPA 1618-N	0.25
Atrazine	EPA 1618-N	0.08
Azinphos Ethyl	EPA 1618	0.13
Azinphos Methyl (Guthion)	EPA 1618	0.15
Baygon (Propoxur)	EPA 531.1	1.0
Benefin	EPA 1618-N	0.13
Bentazon	EPA 615	0.11
Bolstar (Sulprofos)	EPA 1618	0.06
Bromacil	EPA 1618-N	0.50
Bromoxynil	EPA 615	0.01
Butachlor	EPA 1618-N	0.29
Butifos (DEF)	EPA 1618	0.12
Butylate	EPA 1618-N	0.13
Carbaryl	EPA 531.1	2.0
Carbofuran	EPA 531.1	2.0
Carbophenothion	EPA 1618	0.08
Carboxin	EPA 1618-N	0.92
Chlorothalonil (Daconil)	EPA 1618-N	0.20
Chlorpropham	EPA 1618-N	0.42
Chlorpyrifos	EPA 1618	0.06
Cis-1,3-Dichloropropene	EPA 846	1.0
Coumaphos	EPA 1618	0.10
Cyanazine	EPA 1618	0.10
Cycloate	EPA 1618-N	0.13
Dacthal (DCPA)	EPA 615	0.01
Demeton-O	EPA 1618	0.05
Demeton-S	EPA 1618	0.06
Di-allate (Avadex)	EPA 1618	0.30
Diazinon	EPA 1618	0.07

Appendix B. Continued.

Pesticide	Method	Quantification Limit (µg/L)
Dicamba	EPA 615	0.01
Dichlobenil	EPA 1618-N	0.10
Dichlorprop	EPA 615	0.03
Dichlorvos (DDVP)	EPA 1618	0.07
Diclofop Methyl	EPA 615	0.06
Dimethoate	EPA 1618	0.06
Dinoseb	EPA 615	0.06
Dioxathion	EPA 1618	0.13
Diphenamid	EPA 1618-N	0.25
Diphenylamine (DPA)	EPA 1618	0.20
Disulfoton (Di-Syston)	EPA 1618	0.05
Diuron	EPA 1618	0.10
EPN	EPA 1618	0.08
Eptam	EPA 1618-N	0.13
Ethalfluralin (Sonalan)	EPA 1618-N	0.13
Ethion	EPA 1618	0.06
Ethoprop	EPA 1618	0.07
Fenamiphos	EPA 1618	0.12
Fenarimol	EPA 1618-N	0.25
Fenitrothion	EPA 1618	0.06
Fensulfothion	EPA 1618	0.08
Fenthion	EPA 1618	0.06
Fenvalerate	EPA 1618	0.31
Fluridone	EPA 1618-N	0.67
Fonofos	EPA 1618	0.05
Hexazinone	EPA 1618-N	0.13
Imidan	EPA 1618	0.09
Ioxynil	EPA 615	0.01
MCPA	EPA 615	1.7
MCPP	EPA 615	1.7
MGK264	EPA 1618-N	0.59
Malathion	EPA 1618	0.07
Metalaxyl	EPA1618	0.50
Methiocarb	EPA 531.1	1.0
Methomyl	EPA 531.1	1.0
Methyl Chlorpyrifos	EPA 1618	0.06
Methyl Paraoxon	EPA 1618	0.15
Methyl Parathion	EPA 1618	0.06
Metolachlor	EPA 1618-N	0.25
Metribuzin	EPA 1618-N	0.08
Mevinphos	EPA 1618	0.08
Molinate	EPA 1618-N	0.22
Napropamide	EPA 1618-N	0.25
Norflurazon	EPA 1618-N	0.13
Oxamyl (Vydate)	EPA 531.1	2.0
Oxyfluorfen	EPA 1618-N	0.22
Parathion	EPA 1618	0.07
Pebulate	EPA 1618-N	0.20
Pendimethalin	EPA 1618-N	0.13
Pentachlorophenol	EPA 615	0.004
Permethrin	EPA 1618	0.16
Phenothrin	EPA1618	0.16

Appendix B. Continued.

Pesticide	Method	Quantification Limit (µg/L)
Phorate	EPA 1618	0.06
Phosphamidan	EPA 1618	0.20
Picloram	EPA 615	0.02
Profluralin	EPA 1618	0.20
Prometon (Pramitol 5p)	EPA 1618-N	0.08
Prometryn	EPA 1618-N	0.08
Pronamide (Kerb)	EPA 1618-N	0.25
Propachlor (Ramrod)	EPA 1618-N	0.17
Propargite	EPA 1618	0.16
Propazine	EPA 1618-N	0.08
Propetamphos	EPA 1618	0.17
Resmethrin	EPA 1618	0.16
Ronnel	EPA 1618	0.06
Simazine	EPA 1618-N	0.08
Sulfotepp	EPA 1618	0.05
Tebuthiuron	EPA 1618-N	0.08
Terbacil	EPA 1618-N	0.42
Terbutryn (Igran)	EPA 1618-N	0.08
Tetrachlorvinphos (Gardona)	EPA 1618	0.17
Trans-1,3-Dichloropropene	EPA 846	1.0
Treflan (Trifluralin)	EPA 1618-N	0.13
Triadimefon	EPA 1618-N	0.22
Triallate	EPA 1618-N	0.22
Tributylphosphorotrithioite(Folex),(Merphos)	EPA 1618	0.13
Trichlopyr (Garlon)	EPA 615	0.03
Vernolate	EPA 1618-N	0.13
Xylene, Total	EPA 846	1.0

Appendix C. Quality Assurance Review

Analyses were conducted at the Ecology/EPA Manchester Laboratory. The qualitative and quantitative accuracy, validity, and usefulness of data were reviewed by Stuart Magoon of Manchester Laboratory and are summarized here. Laboratory quality control (QC) followed standard Manchester guidelines and included laboratory blanks, surrogate spikes, and pesticide matrix spikes. The relative percent difference (RPD) was used to estimate analytical precision. The RPD is the ratio of the difference and the mean of duplicate (or replicate) samples expressed as a percentage.

In addition to laboratory QC samples, a single duplicate sample was collected for field quality assurance (QA) during the verification sampling. The sample was collected from a well that had detected pesticides in the initial sampling. A duplicate sample consisted of an identical sample submitted to the laboratory with different sample identification (a blind duplicate from site EB09D1). Because of the preponderance of below quantitation limit results, duplicate and replicate samples are usually not useful in determining precision of pesticide analyses. However, atrazine was detected in these duplicates. On the other hand, atrazine desethyl was detected in one but not the other. There was evidence of the presence of atrazine in both duplicate samples at estimated concentrations of 0.004 and 0.003 micrograms/L (qualified as NJ).

In general, the quality of the results is good. Specific comments on each laboratory method follow:

Chlorinated herbicides by (draft) EPA Method 8085: All samples were extracted and analyzed within the recommended 7-day holding time. No target compounds were detected in the laboratory blanks. Surrogate spike recoveries for 2,4,6-tribromophenol ranged from 53% to 106% for the initial samples, and 97% to 148% for the verification samples. No recovery limits have been established for this method.

A matrix spike and a matrix spike duplicate were collected during the initial sampling. No matrix spike was collected during verification. Most of the 25 compounds in the matrix spikes had recoveries between 37% and 99%, except 4-nitrophenol at 25% and 28%, dinoseb at 32% and 26%, and picloram at 14% and 21% recovery. The nitrophenol recoveries are typical for that analyte, and dinoseb and picloram were qualified 'UJ' (not detected above an estimated limit) throughout due to the poor precision these analytes have historically shown. No matrix spike recovery limits have been established for this method. No special problems were encountered with these analyses and the data are acceptable as qualified.

Volatile organics by EPA SW 846 Method 8260: All samples were analyzed within the recommended 14-day holding time. No pesticides were detected in the laboratory blanks with the exception of a low concentration of xylene in one. However, low levels of the common laboratory solvents acetone and methylene chloride were found as well as traces of toluene and benzene. Surrogate recoveries for 1,2-Dichloroethane-D4, D8-Toluene, D4-1,2-Dichlorobenzene, p-Bromofluorobenzene, and Fluorobenzene were within acceptable limits except for one surrogate that was slightly below acceptance criteria (p-Bromofluorobenzene). However, no target pesticides associated with this surrogate were detected so it was not necessary to qualify the data. Recoveries ranged from 78% to 117% for the initial samples. Matrix spikes were within acceptable limits for both percent recovery and RPD. No analytical problems were encountered in the analysis. The data are acceptable for use as qualified.

Ethylene dibromide(EDB) and dibromochloropropane (DBCP) by EPA Method 504: All samples were extracted and analyzed within the recommended holding times. No target compounds were detected in the laboratory blanks. Surrogate recoveries for methylated Dalapon ranged from 83% to 153%. No recovery limits have been established for this method. Matrix spike recoveries for EDB ranged from 88% to 92%. DBCP recoveries ranged from 80% to 93%. The RPD ranged from 4.4% to 15%. No special problems were encountered in the analysis. The data are acceptable for use as qualified.

Nitrogen containing pesticides by (draft) EPA Method 8085: All samples were extracted within 7 days and extracts were analyzed within the recommended holding time. No target analytes were detected in laboratory blanks. Dimethylnitrobenzene was used as the surrogate compound. No specific nitrogen containing pesticide surrogates were available for this analysis. Surrogate recoveries ranged from 64% to 94% for the initial samples, , and 64% to 87% for the verification samples. No surrogate recovery limits have been established for this method. Matrix spike recoveries for the 20 nitrogen containing compounds spiked in the initial samples, ranged from 74% to 123%. No matrix spikes were analyzed for the verification samples. No recommended recovery limits or RPD have been established for this method. No special problems were encountered in the analysis. The diphenylamine reported in one sample compared acceptably with a reference standard. Although reported as an estimate (J), it is possible that the compound is actually diphenylnitrosoamine or diphenylacetonitrile, a preemergence herbicide. These three compounds are indistinguishable by this method.

Organo-phosphorous pesticides by (draft) EPA Method 8085: All samples were extracted within 7 days and extracts were analyzed within the recommended holding time. No target analytes were detected in the laboratory blanks. Surrogate recovery for triphenyl phosphate (TPP) ranged from 77% to 116%. No recommended recovery limits have been established for this method. Matrix spike recoveries for 13 organo-phosphorous pesticide compounds ranged from 55% to 114%. No recommended recovery limits have been established for this method. No special problems were encountered in the analysis. The data are acceptable as qualified

Pyrethrin pesticides by modified EPA 1618 Method: All samples were extracted within 7 days and analyzed within the recommended holding time. No target analytes were detected in the laboratory blanks. No specific surrogates were available for this method and pyrethroid pesticides were not spiked during these analyses. No special problems were encountered in the analysis and the data are acceptable as qualified.

Sulfur pesticides by (draft) EPA Method 8085: All samples were extracted within 7 days and extracts were analyzed within the recommended holding time. The single target analyte, Propargite, was not detected in the laboratory blanks. The recovery of spiked Propargite was 83% and 85%. No special problems were encountered in the analysis and the data are acceptable as qualified.

Carbamate pesticides by EPA Method 531.1: Samples were preserved in the field at the time of collection. Samples from week 19 were analyzed within the recommended 28-day holding time. However, samples from week 20 and 21 were analyzed more than 28 days after collection. No carbamates were detected in any of the samples, but samples from week 20 and 21 were qualified with "UJ" for "not detected at the estimated concentration" No target compounds were detected in the laboratory blanks. No surrogate compound is specified for EPA Method 531.1. Since the method calls for direct injection of the sample, recovery is 100%. The compound 4-bromo-3,5-dimethylphenyl N-methylcarbamate (BDMC) is added as a surrogate when samples are extracted and concentrated before analysis but is used as an internal standard in Method 531.1. Consequently no surrogate recovery data are available from this analysis. Matrix spike recoveries for the 11 carbamate pesticides spiked ranged from 35% to 88%. No recovery limits have been established for this method although they typically range between 40% and 100%. One recovery of 1-Napthol was below 40%. This compound has demonstrated aberrations in past projects. Therefore, all quantitation limits for 1-Napthol have been raised to the same concentration as the matrix spikes, 2.5 ug/L. The data are acceptable for use as qualified.

Nitrate+nitrite as nitrogen by EPA Method 353.2: All samples were analyzed within recognized holding times. The procedural blanks showed no significant levels of nitrate-nitrite. Concentrations of blind field duplicates were within 2% and lab duplicates were within 1%. Recovery of a single spiked sample was 104%.