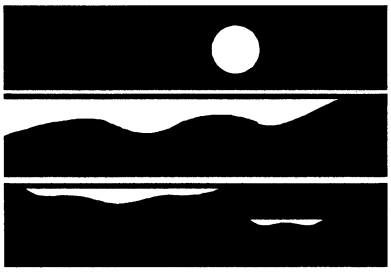

Pesticide Residues in the Walla Walla Surficial Aquifer

Pesticides in Ground Water Report No. 7

September 1995

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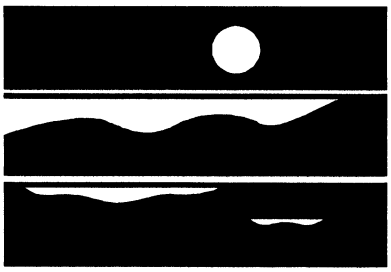

Pesticide Residues in the Walla Walla Surficial Aquifer

Pesticides in Ground Water Report No. 7

by
Arthur G. Larson

Toxics Investigations Section
Environmental Investigations and Laboratory Services Program
Olympia, Washington 98504-7710

September 1995

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Abstract

From December 1993 to February 1994, 27 wells were sampled near Walla Walla, Washington for pesticides and nitrate+nitrite as N. Field measurements of water temperature, pH, and specific conductance were also made. Wells were located in the Walla Walla Surficial Aquifer underlying the Walla Walla River valley.

Eight pesticides were detected in the initial samples: **dacthal (DCPAs), atrazine, simazine, prometon, picloram, oxamyl,** and **methiocarb**. However, only atrazine, simazine, and prometon were confirmed by the verification sampling. An additional pesticide, **aldicarb**, was detected in one well during the verification sampling. Pesticides were detected in 14 of the 27 study wells, with more than one pesticide found in seven wells.

Concentrations of all pesticides were below the Maximum Contaminant Level (MCL) or Lifetime Health Advisory Level set by the EPA for public drinking water. In seven wells, the nitrate+nitrite as N concentration exceeded the 10.0 mg/L drinking water standard for nitrate. Four wells also had specific conductance values greater than or equal to the 700 µmhos/cm MCL for drinking water. Two of these four wells were also included in the seven wells with high nitrates.

Summary

The Washington State Pesticide Monitoring Program was initiated in 1991 by the Department of Ecology to characterize pesticide residues geographically and over time in ground water and surface water throughout Washington. Ground water of the Walla Walla Surficial Aquifer was selected for study during 1994, and samples were collected from 27 wells during December 1993, and January and February 1994. Agriculture is the major land use in the valley.

Ground water was tested for 124 pesticides and pesticide-breakdown products and for nitrate+nitrite as nitrogen. Wells in which pesticides were detected were resampled in November 1994.

In the initial sampling, pesticides were detected in 14 of the 27 study wells, with more than one pesticide found in seven of the 14 wells. Pesticides detected were **dacthal (DCPA), atrazine, simazine, prometon, picloram, oxamyl,** and **methiocarb**. During the verification sampling, one additional pesticide, **aldicarb**, was detected in one well.

The herbicide **dacthal** was detected in 11 wells with concentrations ranging from 0.12 to 9.9 µg/L. All eleven wells were resampled for verification, but dacthal was not detected in these samples. The EPA has set a Lifetime Health Advisory Level (LHAL) for dacthal (DCPA's) in drinking water at 4,000 µg/L. The maximum concentration detected in this study was only 0.25% of this value.

Atrazine, another herbicide, was detected in both the initial and verification samples from three wells. Estimated concentrations ranged from 0.015 to 0.078 µg/L. Atrazine was also detected in the verification sample from one well in which it was not detected during the initial sampling. The Maximum Contaminant Level (MCL) for atrazine in drinking water is 3.0 µg/L; the detected concentrations were 100 times lower.

The herbicide **simazine** was detected in both the initial and verification samples from three wells. Like atrazine, concentrations were low enough that only an estimate of the concentration was possible. Estimated concentrations ranged from 0.011 to 0.080 µg/L. Concentrations were 50 times lower than simazine's 4.0 µg/L MCL.

Prometon, another herbicide, was detected in one well at an estimated concentration of 0.015 µg/L and in the verification sample from this well at an estimated concentration of 0.059 µg/L. EPA has established an MCL of 500 µg/L for picloram, 8,000 times greater than concentrations found in this study.

The herbicide **picloram** was detected in two wells at concentrations of 0.073 and 0.031 µg/L. Picloram was also detected in the verification samples from both wells, but at lower concentrations that could not be confirmed. The LHAL for prometon is 100 µg/L, 1,500 times greater than these concentrations.

The carbamate insecticides **oxamyl** and **methiocarb** were detected in one well each at concentrations of 3.8 µg/L and 1.05 µg/L, respectively. The concentration of oxamyl was only 2% of the 200 µg/L MCL; the EPA has not established an MCL or LHAL for methiocarb.

Aldicarb, a carbamate insecticide, was not detected in any well during the initial sampling; however, it was detected in the sample collected for verification of methiocarb. The carbamate analysis detected an aldicarb concentration of 2.75 µg/L with a quantification limit of about 1.0 µg/L. The LHAL for aldicarb is 10 µg/L; the single detection was about 30 percent of this value.

Nitrate+nitrite as N was detected in all 27 wells sampled. Initial concentrations ranged from 0.10 to 23.0 mg/L. The average concentration of nitrate in all wells was 6.4 mg/L. In seven of the 27 study wells, the nitrate+nitrite as N concentration exceeded the 10.0 mg/L drinking water standard for nitrate. Eleven wells had concentrations greater than 5 mg/L.

No impairment of water use is indicated based on concentrations of detected pesticides. All pesticide concentrations were below currently recognized contaminant levels. Concentrations of nitrate, however, were high enough to be of concern.

Acknowledgements

I thank the owners of the wells for allowing me to sample and for providing background information on their wells.

Thanks to Norm Olson, Bob Carrell, and Dickey Huntamer at Manchester Laboratory for their analyses of the pesticides. Without their work there would be nothing to report. I also thank Stuart Magoon at the laboratory for his quality assurance review of the data.

Peer review was provided by Denis Erickson, Larry Goldstein, and Will Kendra of the Environmental Investigations and Laboratory Services Program and by Carl Neuchterlein of the Water Quality Program, Eastern Regional Office.

David Nash of the Washington State Department of Health reviewed all results for health implications and wrote health consults that were mailed to well owners explaining these implications.

Finally, thanks to Joan LeTourneau for formatting and proofing this report.

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Introduction

From December 1993 to February 1994, 27 wells were sampled near Walla Walla, Washington for pesticides and nitrate+nitrite as nitrogen. Wells were located in the Walla Walla Surficial Aquifer underlying the Walla Walla River valley. Most of the population of Walla Walla County lives in this valley or tributary valleys. The study area, between Walla Walla and Touchet, is situated just north of the Oregon-Washington border (Figure 1). The aquifer underlies one of the oldest agricultural areas in Washington. The Whitman Mission, located in the center of the study area, had about 30 acres under cultivation by 1847 (SCS, 1964). In addition to the locally famous Walla Walla sweet onions, crops include wheat, canola, sugar beets, sweet and silage corn; a large variety of vegetables including peas, lettuce, asparagus, rhubarb, and squash; and fruits including grapes. Pasture for cattle, both beef and dairy, is also common. Farming is still the major activity in the valley, although several new housing developments were noted on farmland south of Walla Walla.

Background

Agricultural chemicals, specifically pesticides, are used throughout Washington. Although pesticides are used extensively on farmlands, they are also applied in the urban and forest environment. Population growth and increasing urbanization are placing increasing demands on the ground-water resource. At the same time, the effect of pesticide use on the state's ground-water quality is largely unknown.

Purpose

Sampling of the Walla Walla Surficial Aquifer is part of ongoing efforts to monitor pesticides in ground water, statewide. It provides data on the concentrations of pesticides in ground water where agriculture is interspersed with residential and industrial development.

Walla Walla Aquifer

The Walla Walla Surficial Aquifer is the uppermost aquifer in the valley of the Walla Walla River. It is unconfined, with a shallow water table, and is hydraulically connected to local surface water. The aquifer, as much as 700 feet thick in the western part of the basin, averages about 200 feet in thickness and discharges to tributaries of the Walla Walla River

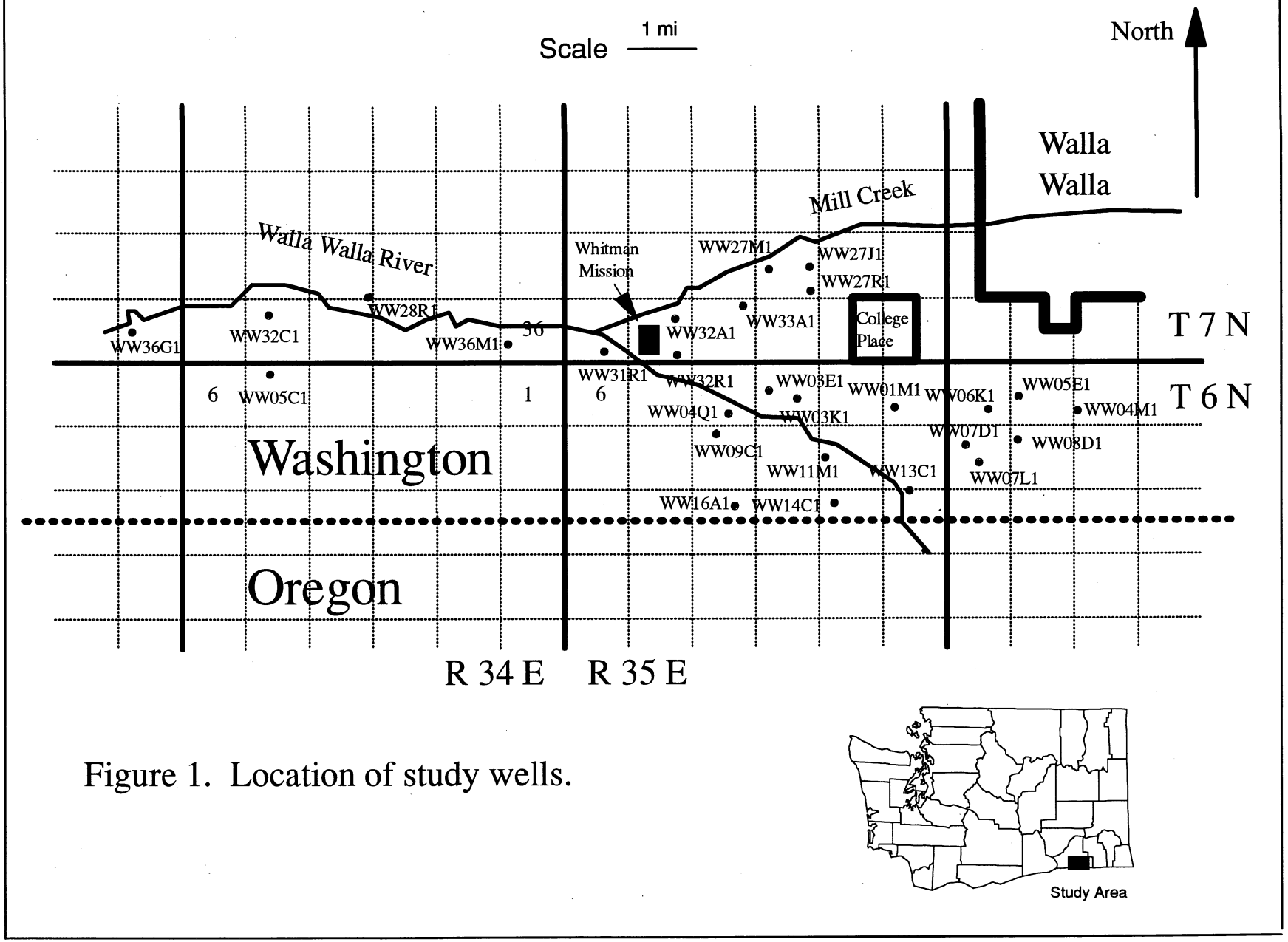

Figure 1. Location of study wells.

(MacNish et. al., 1973). It is underlain continuously by Columbia River basalts and associated confined aquifers. Regional ground water flow, like surface water flow, is toward the Columbia River.

The climate is predominantly dry, with mild winters and hot summers. Winter snow accumulations in the valley are three to eight inches, with annual precipitation of 14 to 18 inches (SCS, 1964). Most of the valley bottoms are irrigated while the uplands are dryland farmed.

Hydrogeology

The water table is shallow, generally within 20 feet of the land surface. It is shallowest near the river and deepest near the valley edges. Ground water flow follows topography toward the Walla Walla River or down valley to the west toward the Columbia River. Exchange of water also occurs between the Walla Walla aquifer and the underlying basalt aquifer. In the past, flow was upward in some areas with the basalt aquifer contributing water to the Walla Walla aquifer. However, excessive pumping has reduced the hydraulic head of the basalt aquifer, increasing the vertical leakage of the Walla Walla aquifer to the basalt (MacNish et.al., 1973). The aquifer within the main valley is primarily river deposits. The eastern portion of the study area, underlying the cities of Walla Walla and College Place, is composed of silts and gravels of the Mill Creek fan. This fan, located at the mouth of Mill Creek Canyon, is about two miles wide and five miles long.

The Walla Walla aquifer is hydraulically connected with the network of streams, canals and ditches that web its surface. Along with recharge from precipitation, the aquifer receives water from stream and canal leakage and infiltration of excess irrigation water. Only a very small acreage is drained via ditches or pipe. In turn, water from the aquifer discharges to springs and streams at lower elevations and contributes water by downward leakage to the basalt aquifers. In addition to these natural discharges, water is drawn from the aquifer by many irrigation and domestic wells.

Soils

Major soils on the Mill Creek fan are the Yakima-Hermiston-Ahtanum association. These soils, formed on alluvial fans, stream bottoms, and small outwash plains, are moderately to excessively drained. Yakima soils are shallow, medium textured and overlie gravel or cobbles of basalt. The Hermiston soils are deep and medium textured and have a weakly calcareous upper subsoil. Ahtanum soils are medium textured, saline, and moderately to strongly alkaline (SCS, 1964). Soils of the lower valley are the Umapin-Stanfield association, saline or alkaline soils. These soils are moderately well drained and medium in texture, often with a hardpan at 1.5 to 4 feet. Crops require irrigation, both to provide supplemental moisture and to leach away excess salts.

Methods

To select appropriate wells for sampling, I searched the well log files located at Ecology's Eastern Region Office in Spokane. I selected well logs based on shallow depth, high water table, and location within the aquifer. Although well logs were useful for the selection of a few wells, most wells were located and selected after a door-to-door survey in areas of interest.

Criteria used in the well selection included:

- Water pumped only from the Walla Walla 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

I selected 27 wells for sampling the Walla Walla Surficial Aquifer: 26 domestic and one irrigation. Wells were located in a 75 square-mile area along the Walla Walla River between the towns of Walla Walla and Touchet (Figure 1).

Many of the study wells were shallow, driven wells (sand points). Wells ranged from 15 to 100 feet deep and averaged 48 feet. Screens, when present, usually allowed water to enter the well over the deepest four to five feet. The type of well, surface elevation, total depth, and depth to water for the individual wells are presented in Appendix A.

Sampling Schedule

Initial sampling occurred in late December 1993 and January and February 1994. Wells in which pesticides were detected were resampled in November 1994 (verification sampling), to confirm the initial analyses.

Sampling Procedures

Before sampling, I purged all wells until the temperature, pH, and specific conductance had stabilized and at least three casing volumes of water had been removed. I used an Orion model 250A meter for pH and temperature measurements, and a Beckman type RB-5 meter to measure specific conductance. I purged and sampled the wells from

existing faucets located as close to the well as possible and upstream of any pressure tanks, where feasible. 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. No field blanks were collected.

Analytes Tested

Ground water was analyzed for 124 pesticides and pesticide-breakdown products (Appendix B) and for nitrate+nitrite as nitrogen. Most of the pesticides were chosen from the Environmental Protection Agency's (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 concentrations and pesticide detections.

Samples were analyzed by the Ecology/EPA Manchester Laboratory.

Quality Assurance

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

Results

Pesticides

In the initial sampling, pesticides were detected in 14 of the 27 study wells, with more than one pesticide found in seven of the 14 wells. Pesticides detected were **dacthal (DCPA), atrazine, simazine, prometon, picloram, oxamyl,** and **methiocarb**. During the verification sampling, one additional pesticide, **aldicarb**, was detected in one well. The concentrations of detected pesticides are presented in Table 1, including results of both initial and verification sampling.

Of the eight pesticides detected, five (dacthal, atrazine, simazine, prometon, and picloram) are herbicides, and three (oxamyl, methiocarb, and aldicarb) are carbamate insecticides (Thomson, 1986). Dacthal, atrazine, and simazine are herbicides used to control perennial

and annual weeds such as crabgrass, foxtail, horsetail, and chickweed. Prometon is a nonselective triazine herbicide used for total vegetation control and brush control in noncrop areas. Picloram is an herbicide often used to control weeds on pasture and range lands. Oxamyl, methiocarb, and aldicarb are insecticides that kill by contact and/or stomach-poison action.

Davis and Johnson (1994) detected the herbicides dacthal (DCPA), atrazine, and simazine in the Walla Walla River during 1993. They also detected several other pesticides that were not found in this study's ground water samples.

Table 1. Concentrations of pesticides detected (µg/L).

Site ID	Dacthal* (DCPA's)	Atrazine	Simazine	Prometon (Pramitol 5p)	Picloram	Oxamyl	Methiocarb	Aldicarb
WW03E1	6.8/U					3.8/U		
WW03K1	0.29/U							
WW05C1	3.2/U		0.011J/0.027J					
WW05E1		0.032J/0.067						
WW09C1	7.5/U	0.015J/0.061J	0.026J/0.057J					
WW27J1	0.037/U				0.031/0.019NJ			
WW27M1	0.14/U							
WW27R1	9.9/U				0.073/0.014NJ			
WW27R1 (dup)					NS/0.015NJ			
WW28R1		0.032J/0.078	0.018J/0.080					
WW28R1 (dup)		0.025J/NS	0.013J/NS					
WW31R1							1.05/U	U/2.75
WW32A1	0.12/U							
WW32R1	0.091/U							
WW33A1	0.17/U	U/0.052J		0.015J/0.059J				
WW36G1	0.13/U							

* Dacthal - Both the initial and verification sampling quantification limits were 0.03 ug/L.

(dup) = duplicate sample

"/" =initial sample followed / by verification sample.

U = not detected.

J = positively identified, but an estimated value.

NJ = there is evidence the analyte is present, the value is an estimate.

NS = no sample was collected.

Dacthal was detected in 11 wells during the initial sampling. Concentrations ranged from 0.12 to 9.9 µg/L. Nine of the detections were located near the center of the study area, between College Place and the Whitman Mission (see Figure 1). The remaining two detections were near the western limit of the study. Laboratory quality assurance during the initial analyses was good. Initial samples were collected and analyzed in three groups (10 samples) spaced several weeks apart. Quantification limits were similar for each set, and although dacthal was not detected in samples from the first set, it was detected in both the remaining sets. The first set consisted of sites in the southeast portion of the study area, between Walla Walla and the Washington/Oregon border. A duplicate and triplicate sample was collected from well WW09C1, and dacthal was detected at concentrations of 7.5, 7.2, and 7.8 µg/L in these samples.

All 11 wells were resampled for verification, but dacthal was not detected in these samples. All verification samples were collected and analyzed as one group. The quantification limit (0.03-0.04 µg/L) was similar to the initial analyses and no significant problems were encountered in the analyses, yet no dacthal was detected in any sample. The reason for this anomaly is unknown, but may be due to the 10 to 11 months lag between the initial and verification sampling. Changes in ground-water quality occurred during this period as shown by differences in temperature and specific conductance between initial and verification sampling (see Table 2)..

Atrazine was detected in both the initial and verification samples from three wells (WW05E1, WW09C1, WW28R1). Although positively identified in the samples, concentrations were low enough that only an estimate of the concentration was possible in most cases. Estimated concentrations in the initial samples ranged from 0.015 to 0.032 µg/L. Duplicate samples were collected from well WW28R1; estimated concentrations were 0.025 and 0.032 µg/L. Atrazine in the verification samples ranged from 0.061 to 0.078 µg/L. Atrazine was also detected in the verification sample from well WW33A1 (0.052 µg/L) although it was not detected in the initial sample from this well. There is no apparent relationship between the locations of the wells in which atrazine was detected; two are near the center of the study area, and one each to the east and west, all several miles apart.

Simazine was detected in both the initial and verification samples from three wells (WW05C1, WW09C1, WW28R1). Like atrazine, concentrations were low enough that only an estimate of the concentration was possible. Estimated concentrations ranged from 0.011 to 0.026 µg/L in the initial samples and 0.027 to 0.080 µg/L in the verification samples. Two of the wells were the same wells in which atrazine was detected, and like atrazine, there is no apparent relationship between well locations. Duplicate samples were collected from well WW28R1; estimated concentrations were 0.013 and 0.018 µg/L.

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
WW01M1	1.78	13	7.1	300
WW03E1	3.11	12.2	7	330
WW03K1	0.10	10.5/13.7	6.8/6.9	250/340
WW04M1	11.20	12.2	7.1	320
WW04Q1	1.68	11.7	7.3	160
WW05C1	2.02	13.8/13.8	7.5/7.6	500/540
WW05E1	19.1/19.3	12.1/12.4	7.1/6.9	410/500
WW06K1	8.11	11.9	7.8	500
WW07D1	8.87	13.3	7.6	700
WW07L1	10.40	12.2	7.4	535
WW08D1	1.62	9.4	7.5	110
WW09C1	5.47	10.5	6.8	250
WW11M1	2.80	12.5	7.4	335
WW13C1	5.21	12.5	7.5	450
WW14C1	0.80	12.5	7.8	280
WW16A1	2.06	12.9	7	150
WW27J1	10.6/8.46	13.8/14.4	6.9/6.9	460/510
WW27M1	3.86	12.9/13.6	7.2/6.9	390/370
WW27R1	13.0/12.2	13.4/13.5	6.9/6.9	370/500
WW28R1	4.95	11.7/14.1	6.7/7.3	1000+/750
WW31R1	0.78	12.5/13.0	6.6/7.6	170/160
WW32A1	4.86	12.5/13.0	7.1/7.0	575/660
WW32C1	0.68	12.1	7.4	610
WW32R1	23.0/28.6	11.5/15.1	7.2/7.1	500/960
WW33A1	21.9/27.5	13.8/12.9	7.3/7.1	490/1000+
WW36G1	3.81	12.2/12.4	7.5/7.3	500/480
WW36M1	0.44	13	7.2	290

/ = Initial sample / followed by verification sample.
Initial samples = December 1993, January, February 1994.
Verification samples = November 1994.
1000+ = greater than 1000

Prometon was detected in one well (WW33A1) at an estimated concentration of 0.015 µg/L. It was also detected in the verification sample from this well at an estimated concentration of 0.059 µg/L.

Picloram was detected in two wells (WW27R1 and WW27J1) at concentrations of 0.073 and 0.031 µg/L. Picloram was also detected in the verification samples from both wells, but at lower concentrations that could not be confirmed. There was evidence that picloram was present, but the reported values are estimates. Duplicate verification samples collected from WW27R1 had estimated concentrations of 0.014 and 0.015 µg/L.

The sample from WW27J1 had an estimated concentration of 0.019 µg/L. Both wells are located within one-fourth mile of each other near Blalock Lake. Dacthal was also detected in these wells.

Oxamyl was detected in one well (WW03E1) at a concentration of 3.8 µg/L. The quantification limit for the analysis was about 0.5 µg/L. However, oxamyl was not detected in the verification sample (quantification limit = 1.0 µg/L).

Methiocarb was detected in one well (WW31R1) at a concentration of 1.05 µg/L. The quantification limit for this analysis was about 0.5 µg/L. However, methiocarb was not detected in the verification sample. The quantification limit of 1.0 µg/L for this suite of analyses was very near the initial sample concentration.

Aldicarb was not detected in any well during the initial sampling. However, it was detected in the sample collected from well WW31R1 for verification of methiocarb. The carbamate analysis detected an aldicarb concentration of 2.75 µg/L with a quantification limit of about 1.0 µg/L.

Nitrate + Nitrite as N

Nitrate+nitrite as N was detected in all 27 wells sampled. Initial concentrations ranged from 0.10 to 23.0 mg/L (Table 2). The maximum concentration of nitrate+nitrite as N occurred in well WW32R1, 23.0 mg/L (initial) and 28.6 mg/L (verification). The average concentration of nitrate in all wells was 6.4 mg/L, probably reflecting the effects of agriculture. The locations of the higher concentrations were scattered throughout the study area.

The average nitrate+nitrite as N concentration for wells with pesticides was 8.3 mg/L. This was about double the 4.3 mg/L average for wells without pesticides. However, nitrate concentrations were not useful in predicting in which well I would detect pesticides. The wells with a detected pesticide included the wells with both the greatest and least nitrate concentration. Also, no pesticide was detected in four wells with nitrate+nitrite as N concentrations greater than 8 mg/L.

Influence of Well Depth

Pesticides were detected throughout the range of well depths with the exception of the two deepest wells (both 100 feet deep) in which no pesticides were detected.

Well depth did not have a consistent influence on nitrate concentrations. The two deepest wells, both 100 feet, had concentrations of 8.9 and 10.4 mg/L. The highest nitrate

concentration was from a well with a reported depth of 80 feet. In turn, the lowest nitrate concentration (0.10 mg/L) was found in a 15-foot-deep well.

Field Measurements

The water temperature, pH, and specific conductance of study wells are shown in Table 2. Values showed some seasonal variation. The average temperature of the ground water was 12.3° C during the initial sampling in December, January and February and a slightly warmer 13.5° C during the verification sampling in November. The average initial pH was 7.2, similar to the average pH of 7.1 during verification sampling. The average specific conductance was about 400 µmhos/cm during the initial sampling, rising to 560 µmhos/cm during verification.

Samples from four wells equaled or exceeded the MCL (700 µmhos/cm) for specific conductance of public drinking water. Also, the average specific conductance was slightly greater, at 442 µmhos/cm, for wells with pesticide detections than for wells without pesticides (364 µmhos/cm). Wells with nitrate + nitrite as N concentrations greater than the MCL also had a slightly greater average specific conductance (440 µmhos/cm) than wells with nitrate + nitrite as N less than the MCL (392 µmhos/cm).

Health Concerns

The Environmental Protection Agency (EPA) has set Maximum Contaminant Levels (MCLs) or Lifetime Health Advisory Levels (LHALs) -- concentrations considered protective of non-cancer health effects -- for all of the detected pesticides except methiocarb. None of the pesticide concentrations exceeded these levels of concern.

- EPA has set a LHAL for dacthal (DCPA's) at 4,000 µg/L. The maximum concentration detected in this study was only 0.25% of this value.

- The MCL for atrazine in drinking water is 3.0 µg/L and the MCL for simazine is 4.0 µg/L. Detected atrazine concentrations were 100 times lower than the MCL and simazine detections were 50 times lower than the MCL. EPA has established an MCL of 500 µg/L for picloram, 8,000 times greater than concentrations found in this study.

- The LHAL for prometon is 100 µg/L, 1,500 times greater than concentrations found in this study.

- Oxamyl was detected at 2% of the 200 µg/L MCL.

- The LHAL for aldicarb is 10 µg/L. The single detection was about 30% of this value.

- The EPA has not established an MCL or LHAL for methiocarb.

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 seven wells, and 5.0 mg/L (1/2 the MCL) in 11 wells.

Specific conductance in four wells equaled or exceeded the 700 µmhos/cm secondary drinking water standard. Two of these wells also exceeded the nitrate MCL

Conclusions

- Eight pesticides were detected in ground water from the Walla Walla Surficial Aquifer: **dacthal (DCPA), atrazine, simazine, prometon, picloram, oxamyl, methiocarb, and aldicarb**. However, the presence of only three of these pesticides was confirmed by the verification sampling.

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

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

- Nitrate concentrations averaged 6.4 mg/L. In seven of the 27 study wells, the nitrate+nitrite as N concentration exceeded the 10.0 mg/L drinking water standard. Eleven wells had concentrations greater than 5 mg/L.

- Four wells had specific conductance values greater than or equal to the 700 µmhos/cm MCL for public drinking water. Pesticides were detected in three of these wells.

- Pesticides were not detected in the two deepest wells (at 100 feet); however, nitrate + nitrite as N concentrations were high at 8.87 and 10.40 mg/L, as were the specific conductances of 700 and 535 µmhos/cm.

- Although dacthal was detected most often near the center of the study area, other pesticide detections were scattered. There is no evidence to suggest that any portion of the study area has a greater or lesser risk of pesticide contamination than another.

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Appendices

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Appendix A. Walla Walla Surficial Aquifer study wells.				
Site ID	Water Use	Ground Elevation (ft)	Well Depth (ft)	Depth to Water (ft)
WW01M1	Domestic	760	27	UN
WW03E1	Domestic	685	20	UN
WW03K1	Domestic	700	15	6
WW04M1	Domestic	938	80	UN
WW04Q1	Domestic	670	70	UN
WW05C1	Domestic	500	22	UN
WW05E1	Domestic	875	50	7.5
WW06K1	Irrigation	860	30	UN
WW07D1	Domestic	834	100	UN
WW07L1	Domestic	850	100	UN
WW08D1	Domestic	875	22	6
WW09C1	Domestic	675	UN	UN
WW11M1	Domestic	725	UN	UN
WW13C1	Domestic	769	40	UN
WW14C1	Domestic	753	40	UN
WW16A1	Domestic	730	20	UN
WW27J1	Domestic	748	UN	10
WW27M1	Domestic	708	UN	UN
WW27R1	Domestic	744	90	UN
WW28R1	Domestic	512	17	UN
WW31R1	Domestic	605	42	UN
WW32A1	Domestic	655	40	10.6
WW32C1	Domestic	480	UN	UN
WW32R1	Domestic	638	80	UN
WW33A1	Domestic	680	UN	24
WW36G1	Domestic	460	UN	<20
WW36M1	Domestic	565	UN	UN
UN = Unknown, but shallow (< 20 feet).				

Appendix B. Target pesticides, test methods, and quantitation limits (µg/L).

EPA method 1618.

Abate (Temephos)	0.75
Alachlor	0.19
Ametryn	0.085
Atraton (Atron, Atratone)	0.25
Atrazine	0.086
Avadex (Di-Allate)	0.32
Azinphos (Guthion)	0.16
Benefin	0.13
Bolstar (Sulprofos)	0.053
Bromacil	0.47
Butachlor	0.28
Butifos (Def)	0.11
Butylate	0.13
CIPC (Chlorpropham)	0.4
Carbophenothion	0.081
Carboxin	0.85
Chlorothalonil (Daconil)	0.19
Chlorpropham	0.4
Chlorpyriphos (Chlorpyrifos)	0.059
Coumaphos	0.098
Cycloate	0.13
Demeton-O	0.06
Demeton-S	0.058
Devrinol (Napropamide)	0.25
Di-allate(Avadex)	0.32
Diazinon	0.067
Dichlobenil	0.1
Dichlorvos (Ddvp)	0.068
Dimethoate	0.062
Dioxathion	0.14
Diphenamid	0.23
Disulfoton (Di-Syston)	0.051
Epn	0.087
Eptam (EPTC)	0.13
Ethalfluralin (Sonalan)	0.13
Ethion	0.057
Ethoprop	0.065
Ethyl Azinphos (Ethyl Guthion)	0.14
Fenamiphos	0.12
Fenarimol	0.25
Fenitrothion	0.059
Fensulfothion	0.085
Fenthion	0.058
Fenvalerate	0.34
Fluridone	1.4
Fonofos	0.047
Hexazinone	0.12

Imidan	0.09
Malathion	0.07
Merphos I	0.12
Metalaxyl	0.58
Methyl Chlorpyrifos	0.061
Methyl Paraoxon	0.14
Methyl Parathion	0.058
Metolachlor	0.25
Metribuzin	0.081
Mevinphos	0.085
Mgk 264	0.6
Molinate (Ordram)	0.22
Napropamide (Devrinol)	0.25
Norflurazon	0.12
Oxyfluorfen (Goal)	0.22
Parathion	0.062
Pebulate (S-Propyl butylethylthiocarbamate)	0.19
Pendimethalin (Prowl)	0.13
Permethrin (CIS and trans)	0.17
Phenothrin	0.17
Phorate	0.059
Phosphamidan	0.2
Profluralin	0.2
Prometon (Pramitol 5p)	0.084
Prometryn (Caparol, Gesagard, Primatol Q)	0.084
Pronamide (Kerb)	0.25
Propachlor (Ramrod)	0.17
Propargite	0.18
Propazine	0.085
Propetamphos	0.16
Resmethrin	0.17
Ronnel	0.054
Simazine	0.086
Sulfotepp (Tetraethyl Dithiopyrophosphate)	0.052
Tebuthiuron	0.087
Terbacil	0.42
Terbutryn (Igran)	0.084
Tetrachlorvinphos (Gardona, Striofos)	0.16
Treflan (Trifluraline)	0.12
Triadimefon	0.22
Triallate	0.22
Vernolate	0.12

Appendix B. Continued.

Chlorinated Herbicides by method EPA SW 8150.

2,3,4,5-Tetrachlorophenol	0.026
2,4,5-T	0.036
2,4,5-Tb	0.042
2,4,5-Tp (Silvex)	0.036
2,4,5-Trichlorophenol	0.027
2,4,6-Trichlorophenol	0.029
2,4-D	0.047
2,4-Db	0.061
3,5-Dichlorobenzoic	0.05
4-Nitrophenol	0.087
5-Hydroxydicamba	0.046
Acifluorfen (Blazer)	0.19
Bentazon	0.068
Bromoxynil	0.038
Chloramben	0.05
Dacthal (DCPA)	0.037
Dalapon (Dpa)	0.033
Dicamba	0.049
Dichloroprop	0.051
Diclofop-Methyl	0.07
Dinoseb	0.068
Ioxynil	0.04
Mcpa	0.094
Mcpp	0.094
Pentachlorophenol	0.023
Picloram	0.047
Triclopyr (Garlon)	0.039

Volatile Organics by method EPA SW 846

1,2-Dichloropropane	0.5
Cis-1,3-Dichloropropene	0.26
Total Xylenes	1
Trans-1,3-Dichloropropene	0.24

Urea pesticides by method NPS-4.

Cyanazine	0.12
Diuron	0.48

Ethylene Dibromide by method EPA 504

1,2-Dibromo-3-Chloropropane (Dbcp)	2.5
EDB (Ethylene Dibromide)	0.5

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. 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). A duplicate sample consisted of an identical sample submitted to the laboratory with different sample identification. 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 and simazine were detected in both the initial and duplicate samples at concentrations of 0.032/0.025 and 0.018/0.013 µg/L respectively, and nitrate-nitrite as N was detected at 4.91 and 4.98 mg/L. Although positively detected, atrazine and simazine concentrations were below the quantification limit and were reported as estimated values with the "J" qualifier.

A duplicate sample was also collected during the verification sampling. Because pesticides were detected in the initial sample from this well, the duplicate was expected to have a greater than detection limit concentration of pesticides. Picloram was detected in the duplicate samples at estimated concentrations of 0.014 and 0.015 ug/L.

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

Chlorinated herbicides by EPA Method 1658 and 515.1: All samples were extracted and analyzed within recommended holding times. No target compounds were detected in the laboratory blanks. Surrogate spike recoveries for 2,4,6-tribromophenol ranged from 42% to 116% for the initial samples and 57% to 113% for the verification samples. No recovery limits have been established for this method. Most of the compounds in the matrix spike had recoveries between 35% and 98%. Four compounds, Dalapon (DPA), Dinoseb, Acifluorfen (Blazer) and Chloramben, had recoveries of less than 20%, and the "J" qualifier was added to the analytical results for these compounds. The relative percent differences (RPD) ranged from 0% to 120%. No matrix spike recovery limits or RPD have been established for this method. No special problems were encountered with these analyses, and only one compound, Dacthal, was detected. Since Dacthal was not used in the matrix spikes but was detected in the source sample and in the matrix spike, a triplicate analysis for this sample was achieved. Results were 7.5, 7.2, and 7.8 µg/L with an RPD of 4%. The data are acceptable for use 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, although low levels of the common laboratory solvents acetone and methylene chloride were found. Surrogate recoveries for 1,2-Dichloroethane-D4, D8-Toluene, D4-1,2-Dichlorobenzene, p-Bromofluorobenzene, and Fluorobenzene were within acceptable limits, ranging from 87% to 109% for the initial samples. Matrix spikes were within acceptable limits for both percent recovery and RPD with the exception of dichlorodifluoromethane, acetone, and methylene chloride. The "J" qualifier was added to the results for these compounds in the matrix source sample. The dichlorodifuoromethane was not recovered and consequently the data were rejected "REJ". Both methylene chloride and acetone had high recoveries due to the high native concentrations which could not be corrected for. 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 71% to 117%. No recovery limits have been established for this method. Matrix spike recoveries for EDB were 92% and 95%. DBCP recoveries were 90% and 96%. The RPD was 3.2% and 6.6% respectively. No special problems were encountered in the analysis. The data are acceptable for use without additional qualifiers.

Nitrogen containing pesticides by EPA Method 1618: 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 48% to 94% for the initial samples and 80% to 93% for the verification samples. No surrogate recovery limits have been established for this method. Matrix spike recoveries for the 18 nitrogen containing compounds spiked, ranged from 27% to 133%, and the RPD from 3.6% to 40%. No recommended recovery limits or RPD have been established for this method. No special problems were encountered in the analysis.

Urea pesticides by modified EPA 1618 Method: All samples were extracted within 7 days and extracts were analyzed within the recommended holding time. No target analytes were detected in laboratory blanks. Surrogate recoveries for dimethylnitrobenzene ranged from 52% to 94%. No surrogate recovery limits have been established for this method.

Neither of the target compounds, diuron and cyanazine, was used in the matrix spikes. The spike recoveries were 27% to 133% with a RPD range of 3.6% to 40%. No recommended recovery limits or RPD have been established for this method. No special problems were encountered in the analysis. The data are acceptable for use as qualified.

Organo-phosphorous pesticides by EPA 1618 Method: 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 33% to 102%. No recommended recovery limits have been established for this method. Matrix spike recoveries for nine organo-phosphorous pesticide compounds ranged from 69% to 107%, and the RPD ranged from 0% to 29%. No recommended recovery limits or RPD have been established for this method. No special problems were encountered in the analysis. The data are acceptable for use 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. Matrix spike recoveries for the pyrethrin, fenvalerate (2 isomer), ranged from 66% to 81% and the RPD was 20%. No recommended recovery limits or RPD have been established for this method. No special problems were encountered in the analysis and the data are acceptable for use as qualified.

Sulfur pesticides by modified EPA 1618 Method: 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. No specific sulfur pesticide surrogate has been identified for this method, and no matrix spikes were analyzed with these samples. No special problems were encountered in the analysis and the data are acceptable for use as qualified.

Carbamate pesticides by EPA Method 531.1: Samples were preserved in the field at the time of collection and initial samples were analyzed within the recommended 28-day holding time. Verification samples were analyzed 2 days over the recommended holding time; however, experience indicates that samples are stable for at least 60 days and no qualifiers were added to the results. One compound, Baygon (Propoxur), was detected in the first laboratory blank. No target compounds were detected in the other blanks. The EPA five times rule was applied to all target compounds which were found in the blank. Compounds that were found in the sample and in the blank were considered real and not the result of contamination if the levels in the sample are greater than or equal to five times the amount of compounds in the associated method blank. An unidentified peak which interfered with aldicarb was seen in one laboratory blank during the verification analyses, but not in any samples. 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 56% to 118% and the RPD ranged from 6.7% to 11%. No recovery or RPD limits have been established for this method. 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. No laboratory blank was analyzed, but a field duplicate was within 2% of the original sample value.