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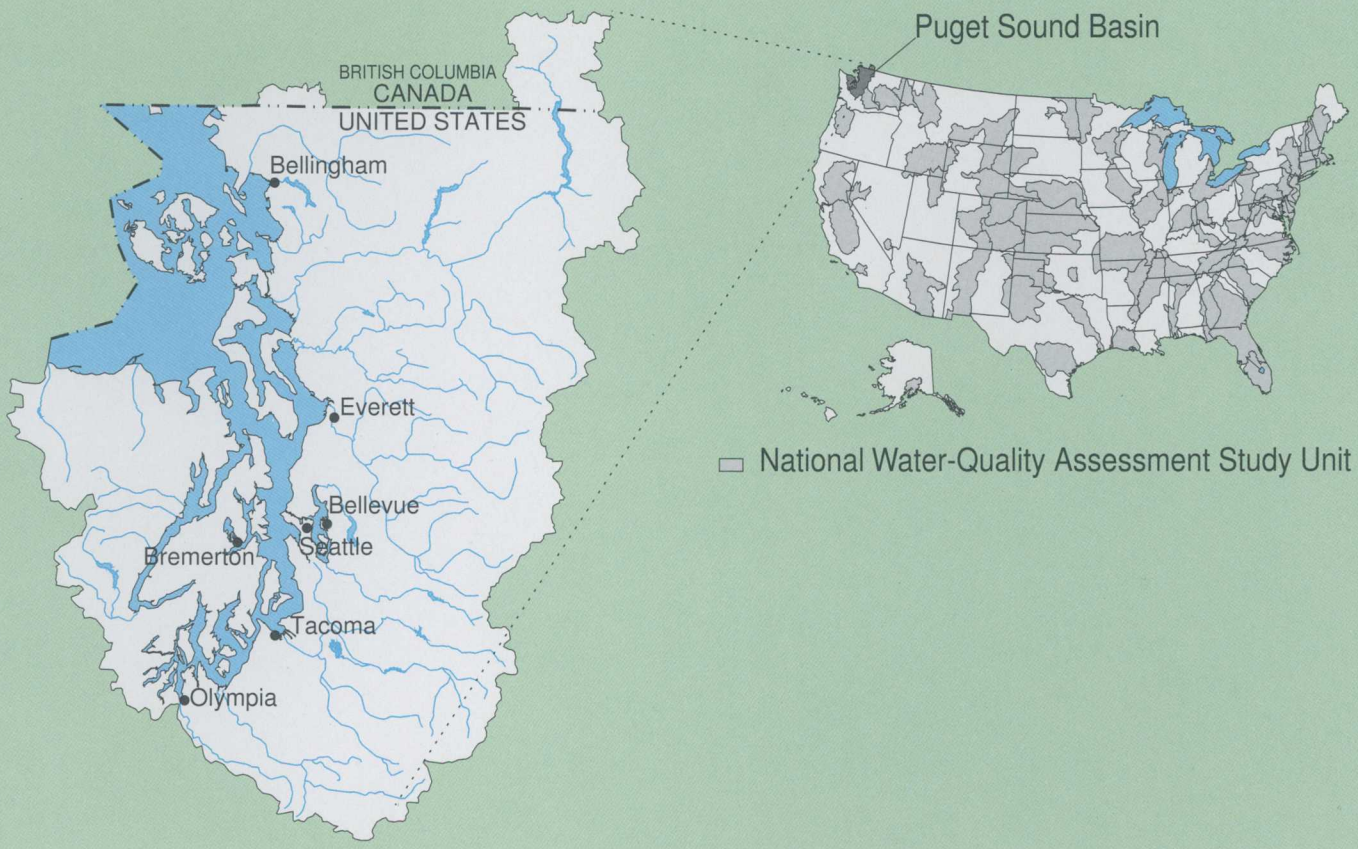
Ground-Water Quality in Regional, Agricultural, and Urban Settings in the Puget Sound Basin, Washington and British Columbia, 1996-1998

By Emily L. Inkpen, Anthony J. Tesoriero, James C. Ebbert, Steven R. Silva, and Mark W. Sandstrom



U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 00-4100

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2000

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
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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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ABBREVIATIONS

DBCP	1,2-dibromo-3-chloropropane
DO	dissolved oxygen
EDB	1,2-dibromoethane
GC/EC	gas chromatography/electron capture
GC/MS	gas chromatography/mass spectrometry
HA	health advisory for drinking water
HPLC/DAD	high-performance liquid chromatography/photodiode-array detection
ICP/MS	inductively coupled plasma/mass spectrometry
km	kilometer
L	liter
LRL	laboratory reporting level
LUS	Land-use study
MCL	maximum contaminant level for drinking water
MDL	method detection limit
mm	millimeter
MRL	minimum reporting level
N	nitrogen
NAWQA	National Water-Quality Assessment Program
NWQL	National Water Quality Laboratory
P	phosphorus
pCi/L	picocuries per liter
RSDHA	risk-specific-dose health advisory
SUS	Study-unit survey
µg	microgram
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound
1,2-DCP	1,2-dichloropropane
1,2,4-TMB	1,2,4-trimethylbenzene

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ABSTRACT

A regional study, a study focused on agricultural raspberry production, and a study focused on post-1970 urban residential areas were conducted from 1996-98 as part of the U.S. Geological Survey's National Water-Quality Assessment Program to characterize the quality of shallow ground water in the unconfined portions of the Fraser aquifer in the Puget Sound Basin, Washington and British Columbia. Relations between water quality, land use, and natural and anthropogenic factors were also investigated using results for primarily nutrients, volatile organic compounds, pesticides, and radon.

In the regional study, or study-unit survey, the quality of ground water was generally good; no samples had concentrations of pesticides or volatile organic compounds that exceeded any drinking-water guidelines or health advisories, and only one concentration of nitrate exceeded the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for drinking water of 10 milligrams per liter (mg/L). The median nitrate concentration was low at 1.0 mg/L. The presence of pesticides, detected in 20 percent of the samples, and volatile organic compounds (VOCs), detected above their laboratory reporting level in 40 percent of the samples, indicates that while concentrations of contaminants are low and do not pose an immediate health risk, contaminants used at the land surface were able to migrate to ground water. Radon was detected in all samples from the study-unit survey, ranging from 100 to 860 picocuries per liter (pCi/L).

In the study of agricultural raspberry production, or agricultural land-use study, concentrations of nitrate exceeded the USEPA MCL for drinking water in 64 percent of the samples, with a median value of 12.9 mg/L. These nitrate concentrations were significantly greater than the nitrate concentrations in samples from the study-unit survey. Sources of nitrate to ground water in the agricultural land-use study area were reported by earlier studies to be primarily animal manure and inorganic fertilizers.

Pesticide compounds were widely detected in the agricultural land-use study, being found in 77 percent of the samples. The most commonly detected compounds, oxamyl, atrazine, and simazine, were known or inferred to be used in Washington or in British Columbia on raspberries and corn, which are also grown in the agricultural land-use study area. All pesticide concentrations were well below any health advisories or drinking-water guidelines.

Volatile organic compounds were detected in 82 percent of the samples from wells near raspberry production in agricultural areas. Fumigant-related compounds, mainly 1,2-dichloropropane, comprised the majority of the VOC detections. Two concentrations of 1,2-dichloropropane and one concentration of 1,2-dibromo-3-chloropropane exceeded their respective USEPA MCLs. Four samples had concentrations of 1,2-dichloropropane that exceeded the health advisory level for 10^{-6} (1 in a million) cancer risk. Concentrations of 1,2-dichloropropane in fumigant formulation have decreased markedly over the past few decades. As a result, much of the 1,2-dichloropropane detected may be due to historical uses of fumigants and may not be derived from current practices.

In the urban residential study, or urban land-use study, nitrate concentrations in ground-water samples were significantly greater than those from the study-unit survey when comparing samples from wells of similar depths. Differences in chemistry between sewered and unsewered areas were analyzed to determine whether septic systems were a source of nitrate to ground water in the urban area. Although analysis of chloride concentrations and isotopic ratios of nitrate nitrogen from unsewered and sewered urban areas

indicated septic effluent was mixing with ground water, median nitrate concentrations in both areas were similar. These results likely reflect the fact that while septic systems are a source of nitrate where they are used, nitrate in the urban land-use study area is likely derived from multiple sources, which vary in intensity in the study area.

Pesticides were detected in 14 percent of the samples from the urban land-use study and were likely from nonresidential applications of pesticides. Volatile organic compounds were detected more often and in higher concentrations in the urban land-use study than in samples from the regional study. Forty-eight percent of the samples from the urban land-use study had detections of VOCs above laboratory reporting levels, consisting mostly of solvents and fuel-related compounds.

INTRODUCTION

In 1991 the U.S. Geological Survey (USGS) began the National Water-Quality Assessment Program (NAWQA) to describe the status and trends in the quality of the Nation's surface- and ground-water resources and to identify the major natural and human factors that affect the quality of these resources. The Puget Sound Basin study unit, which is one of more than 50 study areas selected to meet the objectives of the NAWQA program, encompasses the 13,700-square-mile area that drains to Puget Sound and its adjacent waters (fig. 1). From 1996 to 1998, the Puget Sound Basin NAWQA conducted ground-water investigations to characterize the quality of regional shallow ground water and to determine whether shallow ground water associated with urban or agricultural land use showed any degradation of water quality.

The quality of ground water of the Puget Sound Basin area is of concern because of its importance for municipal and domestic supplies of potable water. The major aquifers in the Puget Sound Basin are largely contained within unconsolidated glacial drift of the Puget Sound Lowlands, and are most vulnerable to contamination where they are shallow, coarse-grained, unconfined, and overlain by urban or agricultural land use (Tesoriero and Voss, 1997). For example, the chance of having elevated nitrate concentrations (greater than or equal to 3 milligrams per liter) in shallow ground water in the intensive agricultural areas in Whatcom County and in the urban areas in the vicinity of Everett, Seattle,Tacoma, and Olympia was equal to or greater than 50 percent (Tesoriero and Voss, 1997). Other contaminants, such as pesticides and volatile organic compounds, may also be more likely to migrate to ground water in vulnerable aquifers.

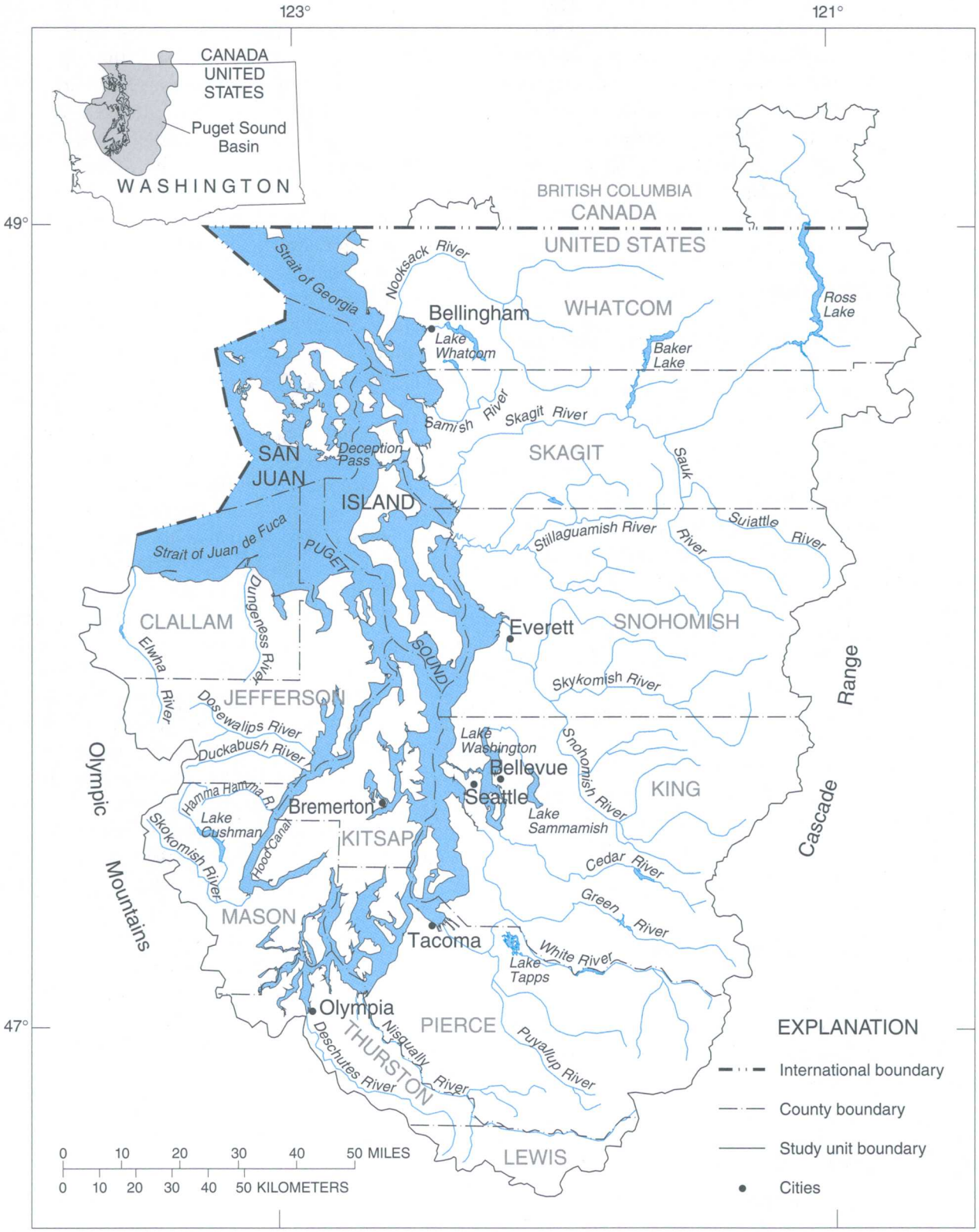
Studies conducted in some of the agricultural and urban areas in the Puget Sound Basin have indicated some water-quality degradation of ground water. Pesticides were detected at low levels in 4 percent of the samples in the Puget Sound Basin in a statewide survey of pesticides in public-supply wells (Ryker and Williamson, 1996). Some concentrations of nitrate and the fumigants 1,2-dibromoethane (EDB) and 1,2-dichloropropane (1,2-DCP) in ground water in the agricultural areas of Whatcom County and southern British Columbia were greater than the U.S Environmental Protection Agency's primary drinking-water standards for these compounds (Cox and Kahle, 1999; Liebscher and others, 1992). Pesticides, volatile organic compounds, and elevated concentrations of nitrate were also found in urban areas in the vicinity of Tacoma, Wash. (Jones and others, 1999).

By the year 2010, an additional 1.1 million people are expected to move to the Puget Sound region (Puget Sound Water Quality Authority, 1988), bringing increased development and demands for water of good quality. Understanding the current status of ground-water quality and how water quality is influenced by natural and anthropogenic factors will be useful for protecting ground-water resources for future use.

Purpose and Scope

This report characterizes the quality of shallow ground water in unconfined, coarse-grained glacial aquifers using results from (1) a regional assessment of these aquifers by sampling randomly selected wells; without regard to land use, termed a study-unit survey, (2) a study focusing on the effects of agricultural land use, particularly raspberry production, termed an agricultural land-use study (LUS), (3) a study focused on new (post-1970) urban residential areas in Pierce and Thurston Counties, termed an urban land-use study. Nutrients, pesticides, volatile organic compounds, and radon are the focus of this report.

This report discusses the sources of ground-water contamination and relations between ground-water quality and hydrogeologic and anthropogenic factors. It discusses the occurrence and distribution of nutrients, pesticides, and volatile organic compounds for each study, which are compared with natural and



Base from U.S. Geological Survey digital data, 1:2,000,000, 1972
Albers Equal-Area Conic Projection
Standard parallels 47° and 49°, central meridian 122°

Figure 1. Puget Sound Basin NAWQA study unit.

anthropogenic factors to identify possible sources. This report also discusses an additional study conducted in the agricultural LUS to define possible relations between applications of fumigants and detections of fumigant-related compounds in ground water. Isotopic ratios of nitrate nitrogen and concentrations of chloride in ground water in the urban LUS were used to help determine whether septic effluent was a source of nitrate to ground water.

Acknowledgments

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DESCRIPTION OF THE STUDY AREA

The hydrology, land use, and water use are described in the following sections. A more detailed description of the study area can be found in Staubitz and others (1997).

Hydrogeology

The Puget Sound Basin study unit encompasses the 13,700-square-mile area that drains to Puget Sound and its adjacent waters, including lands that drain to the Strait of Georgia south of the Canadian border and to the eastern part of the Strait of Juan de Fuca. Aquifers in the Puget Sound Basin, which are contained mostly within the Puget Sound Lowland and the upper reaches of the alluvial valleys, are composed primarily of unconsolidated sediments (Jones, 1999). The Puget Sound Lowland is a structural basin filled with alluvial, glacial, and interglacial unconsolidated sediments, which can be locally more than 3,000 feet thick. Coarse-grained glacial outwash and alluvial deposits form the major aquifers in the Puget Sound Basin. Fine-grained interglacial, lacustrine, and till deposits are layered in between the outwash and serve as confining and semiconfining units. Bedrock consisting of consolidated rocks of sandstone, limestone, and basalt defines the lateral and basal extent of the Puget Sound aquifer system (fig. 2) (Vaccaro and others, 1998).

Repeated glaciations resulted in variable deposits over the Puget Sound Basin. In order to more easily assess hydrologic properties across the study unit, Jones (1999) grouped local stratigraphic units into hydrogeologic units, which include the Fraser aquifer, a semiconfining unit, and alluvial aquifers.

The Fraser aquifer, locally known in Whatcom County as the Sumas aquifer, is the aquifer of interest in this report. It is composed primarily of coarse-grained outwash deposited during glacial advances and retreats, with some drift (Jones, 1999). Of particular interest are the areas where the Fraser aquifer is unconfined and thus most vulnerable, although it is semiconfined in some areas. The extent of the unconfined Fraser aquifer generally corresponds to the coarse-grained glacial deposits in figure 2. The Fraser aquifer is a source of water for many domestic and public-supply wells and has a median depth to water of 20 feet (Staubitz and others, 1997).

The fine-grained deposits generally consist of till, lacustrine, glaciomarine, and mudflow deposits and, where present, act as a semiconfining unit at the surface (fig. 2). Alluvial aquifers are composed primarily of alluvium deposited by rivers during interglacial and glacial periods (fig. 2).

Land Use and Cover

Forest, urban, and agricultural are the three principal land uses and covers in the Puget Sound Basin. It is estimated that forest covers 75 percent of the basin, urban land use covers 11 percent, and agricultural land use covers about 6 percent (Staubitz and others,

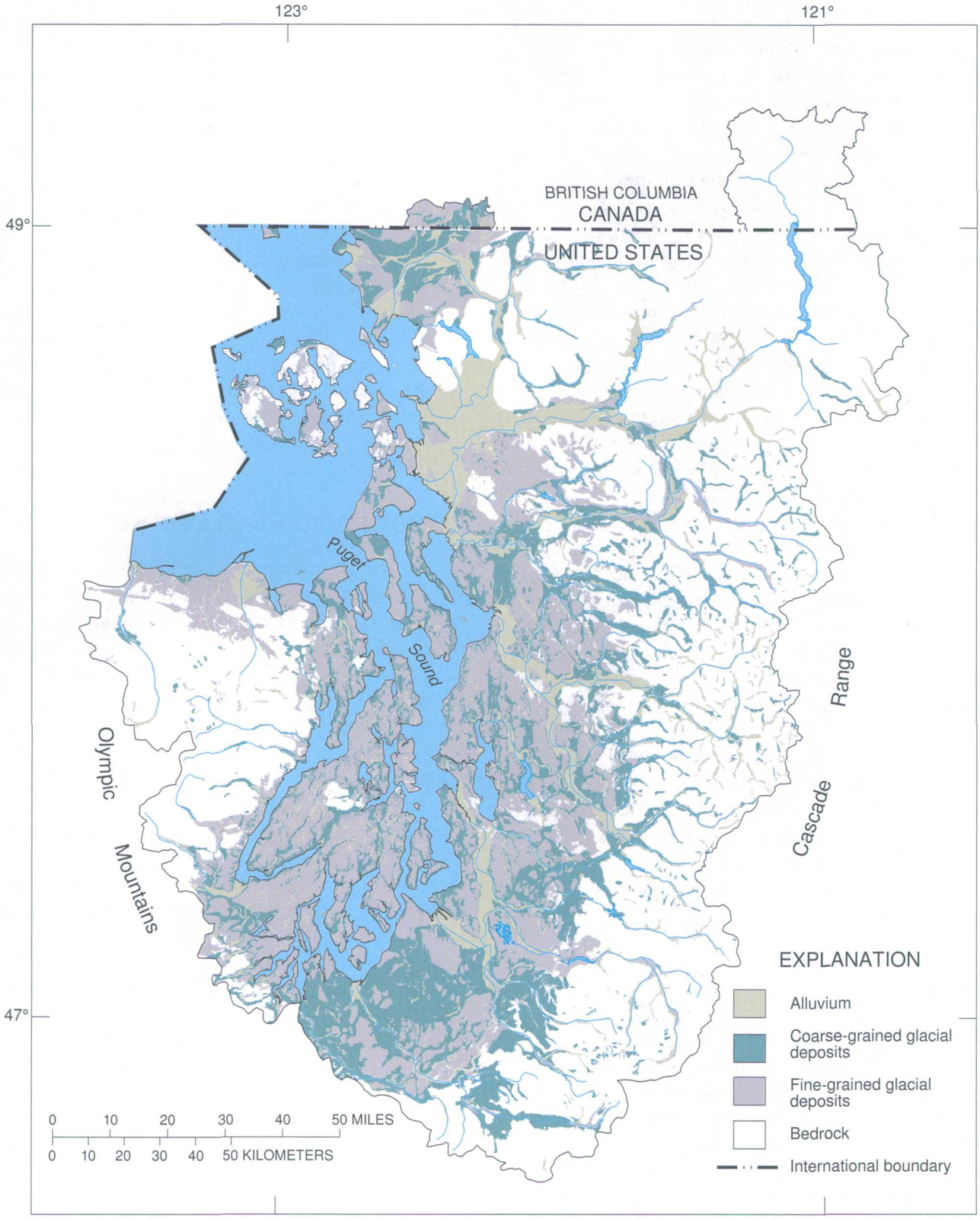

Figure 2. Generalized surficial geology of the Puget Sound Basin. (Modified from Vaccaro and others,1998.)

1997) (fig. 3a). The impacts of urban and agricultural land uses on ground-water quality are of particular interest because greater amounts of potential contaminants are used in these areas.

Agricultural land use is located primarily in the Puget Sound Lowlands mostly in the Whatcom, Skagit, Snohomish, King, and Clallam Counties (fig. 3a). About 60 percent of agricultural areas in Puget Sound Basin are used to grow hay, corn (silage), peas, potatoes, raspberries, wheat, barley, and oats. Another 37 percent of the agricultural area is used as pasture and supports many dairy and poultry farms throughout the U.S. and Canadian portions of the study unit (Staubitz and others, 1997). Possible sources of nitrate in agricultural areas include fertilizers and manure applied to crops, manure storage, domestic septic systems, and dairy and poultry farms (Cox and Kahle, 1999; Embrey and Inkpen, 1997; Erickson, 1998; Wassenaar, 1995). Pesticides and fumigants applied to crops are also possible sources of contaminants to ground water.

Urban land use, including residential, commercial and industrial uses, is mainly located near the shores of Puget Sound and is concentrated in the Cities of Seattle, Tacoma, Bellevue, Bremerton, Everett, Olympia, and Bellingham (figs. 3a-3c). Most of the new urban growth has occurred around the periphery of these areas. Possible sources of contaminants in ground water in urban areas include nitrate from septic systems, fertilizers applied to lawns, or exhaust from cars; pesticides applied to lawns, golf-courses, or other areas such as rights-of-way; VOCs from dry-cleaners, runoff from road surfaces, gas or chemical spills, or exhaust from vehicles. Chemicals used by homeowners or by industry are also possible contaminants to the ground water.

Water Use

Approximately 810 million gallons (Mgal) of water are withdrawn from surface or ground water each day in the Puget Sound Basin (Vaccaro and others, 1998). These estimates do not include hydropower use or water use in the Canadian portion of the study unit. Domestic use (411 Mgal/d) is the greatest water use, followed by industrial (174 Mgal/d), irrigation (145 Mgal/d) and commercial use (95 Mgal/d). Approximately 44 percent of the water comes from ground-water sources, with the remaining 56 percent being derived from surface water (Vaccaro and others, 1998). Ground water is an important source of water in rural areas where water is often self-supplied and in areas designated as having a sole source aquifer, like western Pierce County, where ground water provides more than 50 percent of the drinking water (Staubitz and others, 1997).

Total water use from 1965-1990 has been estimated as decreasing, possibly due to the reduction in the size and number of industries that use water, such as paper manufacturing. Despite the decrease in overall water use, however, water supplied from ground-water sources in 1990 was two to three times greater than in 1965 (Vaccaro and others, 1998). As surface-water resources are increasingly appropriated and growth continues in more rural areas, ground-water resources will likely be considered more often for water supply (Vaccaro and others, 1998).

STUDY DESIGN AND METHODS

The three components of the Puget Sound Basin NAWQA study were a study-unit survey (SUS), an agricultural land-use study (LUS), and an urban LUS. The SUS was conducted to characterize the regional quality of shallow ground water in the unconfined Fraser aquifer throughout the Puget Sound Basin. The agricultural LUS characterized the quality of shallow ground water in the unconfined portions of the Fraser aquifer that underlie agricultural areas, with an emphasis on raspberry production. The urban LUS characterized the quality of shallow ground water in the unconfined portions of the Fraser aquifer that are overlain by post-1970 urban residential land use. A subsection also assessed whether septic systems are a source of nitrate to ground water.

Selection and installation of wells for the SUS and urban and agricultural LUS followed NAWQA protocols (Koterba and others, 1995). Existing domestic wells and sites for well installation for each study were selected using a GIS-based, stratified random selection program (Scott, 1990) that targeted the unconfined Fraser aquifer. Additional criteria, as put forth by NAWQA (Lapham and others, 1995), included (1) not selecting or installing wells in areas with known or suspected point source contamination; (2) not selecting existing wells with plumbing that might alter water quality; and (3) selecting wells with submersible or water-lubricated pumps. Wells were drilled using either hollow-stem auger or air-rotary auger drill rigs,

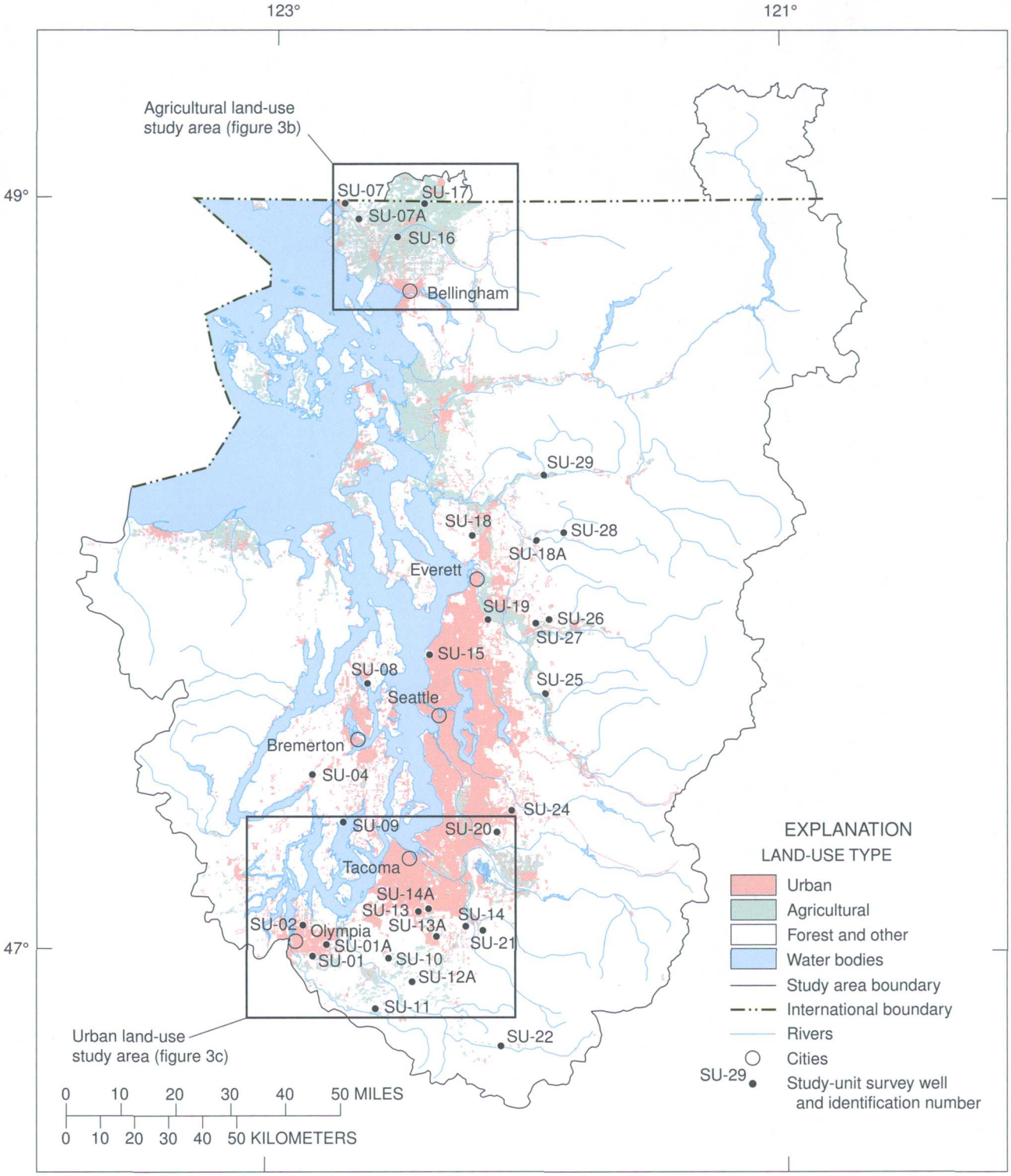

Figure 3a. Generalized land use in the Puget Sound Basin study unit with locations of study-unit survey wells and agricultural and urban land-use study areas. Enlargements of the land-use study areas are shown in figures 3b and 3c.

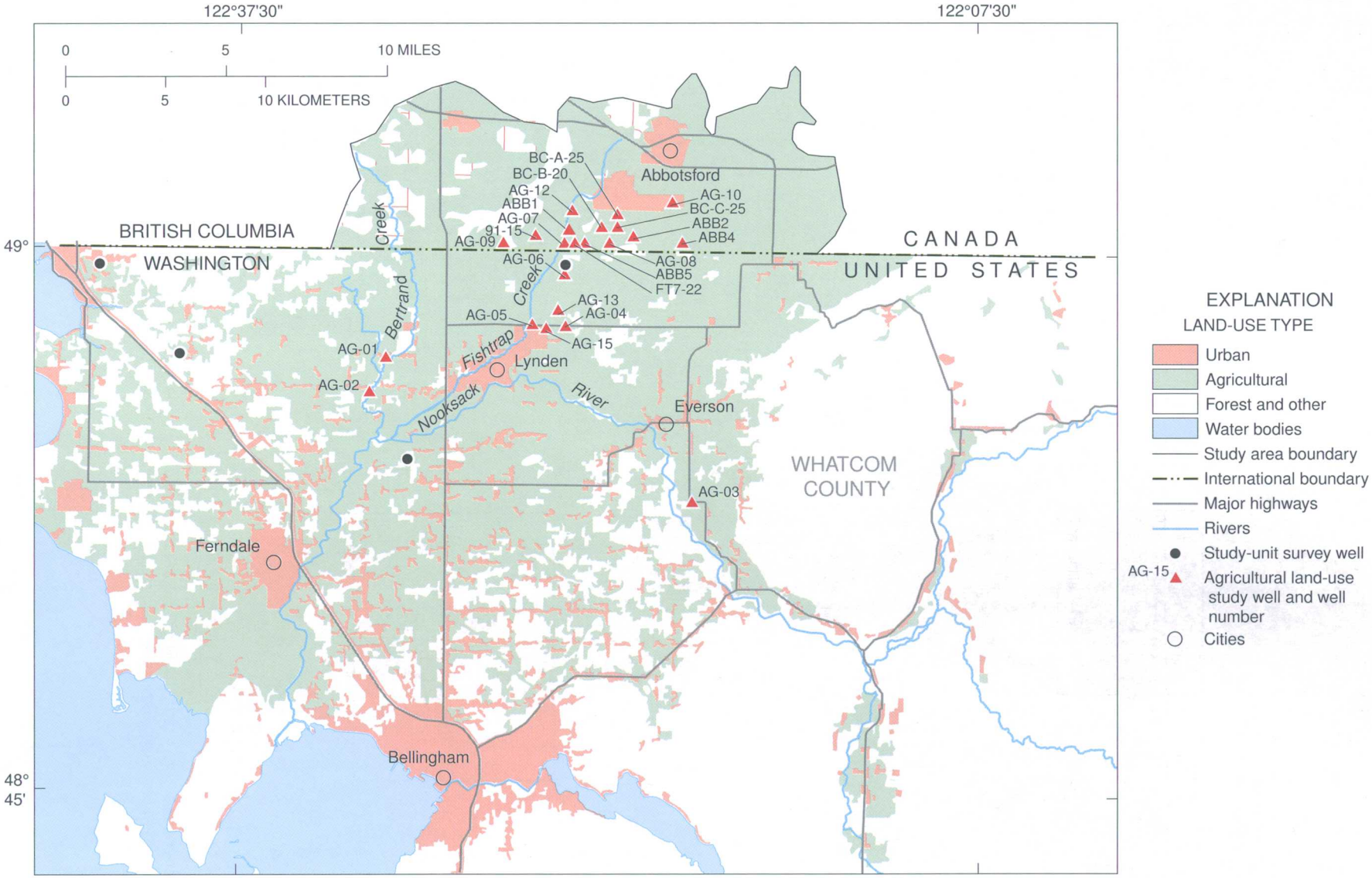

Figure 3b. Location of agricultural land-use study wells and nearby study-unit survey wells.

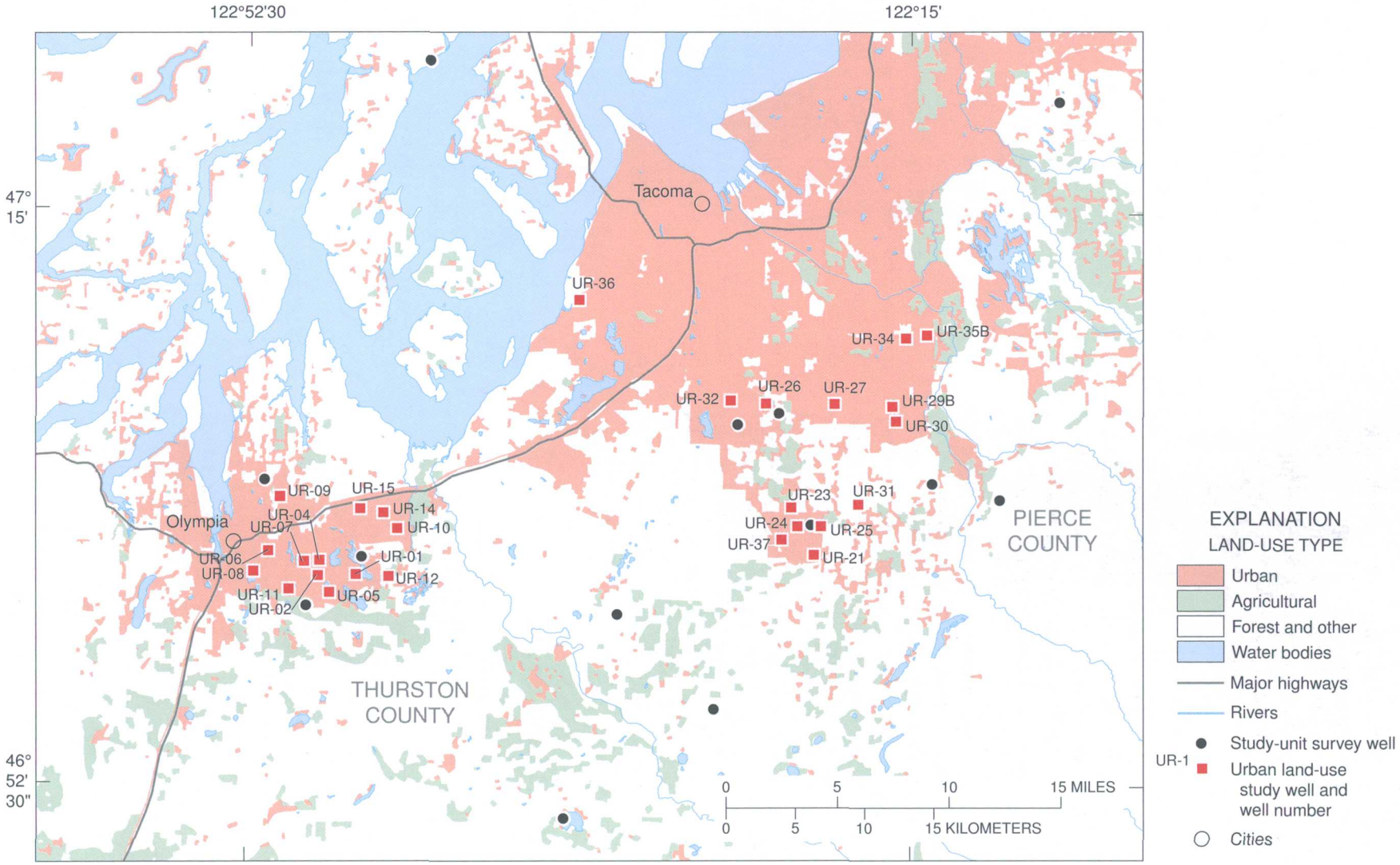

Figure 3c. Location of urban land-use study area wells and nearby study-unit survey wells.

constructed using threaded 2-inch polyvinyl chloride (PVC) pipe, and screened in the Fraser aquifer. Bentonite and cement were used to provide annular and surface seals, respectively. A more detailed description of each study's design and well selection follows.

Study-Unit Survey

The objective of the study-unit survey was to provide a broad assessment of the quality of shallow ground water in the unconfined Fraser aquifer--the most important aquifer in the study unit because of its wide use as a source of domestic and municipal water supplies.

Thirty existing domestic wells were selected for sampling by using a geographical-information-system-based random, equal-area algorithm (Scott, 1990; fig. 3a). Thirty cells of equal area were created based on coarse-grained surficial geology (representative of the lateral extent of the Fraser aquifer; fig. 2) in the Puget Sound Basin. Within each cell, primary and alternate wells were selected for sampling based on well construction, their completion in the unconfined Fraser aquifer, and other criteria described by Lapham and others (1995). If the primary well did not meet the criteria, then an alternate well was used. The depth of the study-unit survey wells ranged from 23 to 186 feet, with a median depth of 66 feet (see App. table 1).

Agricultural Land-Use Study

The agricultural land-use study was located in the Fishtrap and Bertrand Creek areas of northern Whatcom County and southern British Columbia (fig. 3b). The primary objective of this study was to assess the quality of shallow ground water in the unconfined Fraser aquifer that is overlain by raspberry fields, dairies, and areas where manure is applied to crops. The impact of raspberry production on water quality was selected for study because raspberries are one of the most important crops in Whatcom County, their production extensively uses fumigants, and more data are needed about the possible impact of their production on water quality.

A joint study in cooperation with Whatcom County was conducted to assess possible relations between fumigant applications and occurrence of fumigant-related compounds in the ground water. VOC data from the joint study, the agricultural LUS, and another NAWQA study located in the agricultural LUS area to investigate the transport of fumigant-related compounds along a ground-water flowpath (Tesoriero and others, 2000) were combined and compared to fumigant application data.

Well Selection

Sites for the agricultural land-use monitoring wells were selected in areas where raspberry fields were overlying the unconfined Fraser aquifer. Twenty-two wells were installed or selected in or downgradient from raspberry fields and were screened in this aquifer. Well depths ranged from 18 to 96 feet, with a median of 28 feet (see App. table 1).

Twenty domestic wells, ranging in depth from 19.7 to 57 feet, were sampled as part of a joint study with Whatcom County. These wells were not randomly selected, but were located close to raspberry fields and distributed throughout the area where the fumigant application data were available. The wells sampled as part of the flowpath study were also within the agricultural LUS area. Selection criteria for these wells were related to studying the flow of ground water, although they were often also situated near raspberry fields (Tesoriero and others, 2000).

Processing of the Fumigant Application Data

The Washington State Department of Agriculture obtained fumigant application data for the years 1991 through 1997 from registered pesticide applicators for the areas within the agricultural LUS area. The amount of active ingredient per application was calculated for each quarter section and summed to produce a map showing amounts of active ingredient applied over the 7-year period. Data were summarized for the applications of fumigants containing the active ingredients methyl bromide, 1,3-dichloropropene, and metham sodium. Data for applications of chloropicrin were not used because no corresponding analyses of ground-water samples were performed.

Urban Land-Use Study

The urban land-use study was conducted from November 1996 to July 1998 in southern Pierce and northern Thurston Counties (fig. 3c). The objective was to characterize the quality of shallow ground water in the unconfined Fraser aquifer underlying primarily

new (post-1970) residential areas with some commercial areas. Residential land use was selected because, while it comprises a large percentage of land use in urban areas, little is known about water quality associated with it (Squillace and Price, 1996).

New residential developments were selected for study because older areas might be affected by past practices, and thus the current land-use practices would not be easily associated with the quality of ground water. The residential areas of Pierce and Thurston Counties were selected because (1) they are the largest contiguous residential areas overlying the unconfined Fraser aquifer, (2) they lie over a vulnerable aquifer and are increasingly being developed, and (3) the aquifer in this area is a major source of drinking water.

In addition to determining general quality of shallow ground water overlain by residential areas, the urban LUS also assessed whether septic systems were a source of nitrate to ground water. Concentrations of chloride and stable-isotope ratios of nitrate nitrogen in ground water were compared between sewered and unsewered areas for this assessment. Septic systems are used in the unsewered areas.

Well Selection

Twenty-seven monitoring wells were installed by the Puget Sound NAWQA for the urban LUS. Sites for well installation were selected based on guidance and protocols described by Squillace and Price (1996), and Lapham and others (1995). Areas of potential sampling sites were defined by the intersection of the unconfined Fraser aquifer and post-1970 urban residential land use. The 27 primary and alternate sites selected within the target areas were at least 1 kilometer away from heavy industry, railways and freeways, and known sources of contaminants. The depths of the urban LUS wells ranged from 22 to 137 feet, with a median of 47 feet (see App. table 1).

Methods for Assessing Nitrate in Ground Water from Septic Systems in Urban Areas

The use of chloride as an indicator of septic system effluent is based on the assumption that chloride from sources other than septic systems in unsewered and sewered areas in the urban LUS area are about equivalent. If chloride concentrations in septic system effluent, which range from 45 to 55 mg/L (Robertson and others, 1991), are higher than background concentrations of chloride (represented by samples from the SUS), then higher concentrations of chloride in ground water in unsewered areas compared with sewered areas would indicate that septic system effluent is mixing with ground water.

The use of stable-isotope ratios of nitrate nitrogen to assess sources of nitrate in ground water is based on relating the isotopic composition of the nitrate nitrogen to the isotopic composition of different sources of nitrogen. Two naturally occurring stable isotopes of nitrogen are known: ^{14}N and ^{15}N. The ^{15}N atom, which is the heavier of the two isotopes, makes up only about 0.4 percent of the nitrogen in the earth's atmosphere. Although the isotopic composition of nitrogen in the earth's atmosphere is relatively constant, the isotopic composition of nitrogen in other compounds is variable.

Stable-isotope ratios of nitrogen are generally expressed in delta units (δ) given in per mil (0/00) or parts per thousand relative to atmospheric nitrogen (Gat, 1980) and are defined as

$$\delta^{15}N = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \times 1,000 \quad , \qquad (1)$$

where

R_{sample} = ratio of isotopic concentration ($^{15}N/^{14}N$) of the sample, and

$R_{standard}$ = ratio of isotopic concentration ($^{15}N/^{14}N$) of atmospheric nitrogen.

The most common ranges of $\delta^{15}N$ values of nitrate derived from various sources (Kendall, 1998) are

Source	$\delta^{15}N$ per mil
Sewage and animal wastes	10 to 20
Ammonia fertilizers	-4 to 4
Soils	2 to 5

Based on the ranges given, the $\delta^{15}N$ values of nitrate in ground water should be higher if some of the nitrate is derived from septic system effluent. Nitrogen

cycling, principally microbial denitrification, can complicate the use of nitrogen isotope ratios to infer sources of nitrate. Denitrifying bacteria, which occur in reducing environments, preferentially select $^{14}NO_3$ leaving the remaining nitrate pool isotopically enriched in $^{15}NO_3$. Therefore, denitrification must be considered particularly for samples with high $\delta^{15}N$ values. Denitrification is generally insignificant in well-oxygenated environments like the urban LUS area where the unsaturated zone is relatively permeable, the water table is near the land surface, and the ground water is generally oxygenated. One exception is well UR-01, which was not used in data analysis because the sample contained no oxygen, had a low nitrate concentration, and a high $\delta^{15}N$ value indicating possible denitrification.

Sample Collection

Wells for the SUS and the LUSs were sampled for field parameters, dissolved organic carbon (DOC), major ions, nutrients, pesticides, and volatile organic compounds (VOCs). In addition, nitrogen and oxygen isotope data were collected at selected urban LUS wells. Radon was collected at all SUS wells and selected urban LUS wells. Typically, all constituents, excluding isotopes, were collected on the same day. Quality control samples were also collected for DOC, nutrients, major ions, pesticides and VOCs and are explained in the Appendix.

Ground-water samples from the 20 wells in the cooperative study with Whatcom County and from the 15 wells in the flowpath study were analyzed for the 86 volatile organic compounds included in the analytical schedule used for the agricultural LUS. Only the samples from the joint study were analyzed for methyl isothiocyanate (MITC), a transformation product of the fumigant metham sodium (Boesten and others, 1991).

Samples were collected using established NAWQA protocols (Koterba and others, 1995), which require the use of sampling equipment and techniques that minimize the introduction of contamination. For domestic wells, sampling points were located before any water treatment, pressure tanks, or holding tanks. 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, a well was purged of at least three times the wetted well volume until general water-quality parameters (specific conductance, pH, dissolved oxygen (DO), and water temperature) were stable to ensure that samples were representative of the surrounding ground water.

Calibration procedures and measurements of temperature, DO, specific conductance, pH and alkalinity/bicarbonate followed the procedures outlined in Koterba and others (1995). Water temperature, DO, specific conductance, and pH were measured in the field using a flow-through chamber so that measurements were made prior to contact between sample water and the atmosphere. Alkalinity, bicarbonate and carbonate concentrations were determined using water filtered through a polypropylene encapsulated filter with a pore size of 0.45 µm (micrometer).

Nutrient and major ion samples were filtered through a polypropylene encapsulated filter with a pore size of 0.45 µm. The cation complement of the major ions was preserved with nitric acid. Pesticides were filtered through a 142-millimeter (mm) diameter, 0.7-µm pore size, baked, glass-fiber filter on an aluminum filter holder (Sandstrom and others, 1992). DOC samples were filtered under nitrogen pressure through a 47-mm diameter, 0.45-µm pore size, silver filter held in a stainless steel filtration unit. Volatile organic compounds (VOCs) were collected in baked amber vials and preserved with 1:1 hydrochloric acid. Nutrient, DOC, pesticide, and VOC samples were all stored at less than 4 degrees Celsius for shipment to the laboratory. Radon was collected using a glass syringe needle. More detailed descriptions of the collection procedures are described by Koterba and others, (1995). Isotopes of nitrate nitrogen and nitrate oxygen were collected by nitrate concentrated on an anion exchange resin in the field (Silva and others, 2000; Chang and others, 1999).

Analytical Methods

Analyses for pesticides, VOCs, nutrients, and major ions, dissolved organic carbon, and radon were performed at the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. (table 1). Nitrite concentrations were significantly smaller than nitrite plus nitrate concentrations; thus nitrite plus nitrate will be referred to as nitrate throughout this report. Major ions and nutrients and their respective method reporting limits are listed in table 2. Analyses for stable oxygen and nitrogen isotopes were performed by USGS in Menlo Park (table 1).

Table 1. Inorganic and organic analytes and schedules, analytical methods, and references

[O, oxygen; N, nitrogen; ICP/MS, inductively-coupled plasma/mass spectrometry; SPE, solid-phase extraction; HPLC/DAD, high-performance liquid chromatography, with photodiode-array detection; GC/MS, gas-chromatography with detection by mass spectrometry; UV, ultraviolet]

Analyte or schedule	Analytical method	Reference
	Inorganic Compounds	
Isotopes		
$^{18}O/^{16}O$ ratio from nitrate	Nitrate concentrated in the field on exchange resin and then analyzed by combustion with graphite and mass spectrometry	Silva and others, 2000
$^{15}N/^{14}N$ ratio from nitrate	Nitrate concentrated in the field on exchange resin and then analyzed by combustion with Cu, CuO, and CaO, and mass spectrometry	Silva and others, 2000 Chang and others, 1999
Major ions		
bromide	colorimetry, fluorescein	Fishman and Friedman, 1989
calcium	ICP/MS	Fishman, 1993
chloride	ion-chromatography	-- do --
magnesium	ICP/MS	-- do --
manganese	ICP/MS	-- do --
silica	ICP/MS	-- do --
sodium	ICP/MS	-- do --
sulfate	ion-chromatography	-- do --
Nutrients		
ammonia	colorimetry, salicylate-hypochlorite	Fishman, 1993
ammonia plus organic nitrogen	colorimetry, microkjeldahl digestion	Patton and Truitt, 1992
nitrite	colorimetry, diazotization	-- do --
nitrite plus nitrate	colorimetry, cadmium reduction	-- do --
orthophosphorus	colorimetry, phosphomolybdate	-- do --
phosphorus	colorimetry, microkjeldahl digestion	Patton and Truitt, 1992
Radon	Liquid scintillation	American Society for Testing and Materials, 1996
	Organic Compounds	
Dissolved organic carbon	UV-promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett, 1993
Pesticides		
Schedule 2010	SPE technology on a C-18 cartridge and GC/MS	Zaugg and others, 1995
Schedule 2051	SPE technology with a Carbopak-B cartridge and HPLC/DAD with UV detection	Werner and others, 1996
Volatile organic compounds	Purge and trap capillary-column GC/MS	Connor and others, 1998

Table 2. Minimum reporting limits and drinking-water standards for field parameters, nutrients, major ions, dissolved organic carbon, and radon

[MRL, minimum reporting limit; MCL, maximum contaminant level (U.S. Environmental Protection Agency, 1996a); mg/L, milligrams per liter; ≥, greater than or equal to; <, less than; µS/cm, microsiemens per centimeter; N, nitrogen; P, phosphorus; +, plus; pCi/L, picocuries per liter; na, not applicable; %, percent]

Parameter	Chemical Abstracts Service registry number	MRL (unless otherwise noted) (mg/L)	MCL (unless otherwise noted) (mg/L)
	Field Parameters		
Alkalinity	471-34-1	1	
Dissolved oxygen	na	[1]± 0.3 mg/L	
pH, units	na	[1]± 0.1 units of pH	[2]6.5-8.5
Specific conductance	na	[1]± 5% when sample is ≥ 100 µS/cm [1]± 3% when sample is < 100 µS/cm	
Temperature, degrees Celsius	na	[1]± 0.2 degrees Celsius	
	Nutrients		
Ammonia, as N	7664-41-7	0.02	
Ammonia + organic nitrogen, as N	17778-88-0	0.1	
Nitrite, as N	14797-65-0	0.01	1
Nitrite + nitrate, as N	na	0.05	10
Orthophosphorus, as P	14265-44-2	0.01	
Phosphorus, as P	7723-14-0	0.01	
	Major Ions		
Bromide	24959-67-9	0.010	
Calcium	7440-70-2	0.020	
Chloride	16887-00-6	0.100	[2]250
Fluoride	16984-48-8	0.100	4
Iron, µg/L	7439-89-6	10.0	[2]300
Magnesium	7439-95-4	0.004	
Manganese, µg/L	7439-96-5	3.0	[2]50
Potassium	7440-09-7	0.100	
Silica	7631-86-9	0.05	
Sulfate	14808-79-8	0.100	[2]250
Sodium	7440-23-5	0.06	
	Other		
Dissolved organic carbon	na	0.1	
Radon, pCi/L	14859-67-7	26	[3]300 or 4,000

[1] Precision of instruments.
[2] Secondary maximum contaminant level (U.S. Environmental Protection Agency, 1996b).
[3] U.S. Environmental Protection Agency, 1999.

Samples were analyzed for 83 pesticides and transformation products by gas chromatography/mass spectrometry (GC/MS) (Zaugg and others, 1995, and Lindley and others, 1996) and by high-performance liquid chromatography with photodiode-array detection (HPLC/DAD) (Werner and others, 1996; table 3). Of the 83 analytes, 44 were analyzed by GC/MS only, 36 by HPLC/DAD only, and 3 (carbaryl, carbofuran, and linuron) by both GC/MS and HPLC/DAD. Concentration values for both of the GC/MS and HPLC/DAD methods are reported to a method detection limit (MDL). The MDL is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero (Wershaw and others, 1987).

A suite of 86 VOCs including chlorofluorohydrocarbons, aromatic hydrocarbons, reformulated fuel components and halogenated hydrocarbons was analyzed using purge and trap capillary-column GC/MS (Connor and others, 1998; table 4). Between April 1996 and May 1997, a minimum reporting level (MRL) was used to censor data values (Childress and others, 1999). The MRL is defined by the NWQL as the smallest concentration of a substance that can be reliably measured using a given analytical method (Timme, 1995). For the VOC method, the MRL for each compound was usually set at 0.05 or 0.1 µg/L, but ranged up to 5 µg/L for some compounds. In May 1997, the NWQL began censoring data using a laboratory reporting level (LRL) (Childress and others, 1999). Although some of the LRL values are lower than the previous MRLs, compounds positively detected below the MRL were reported, so subsequent lower LRLs did not cause an increase in detection frequencies. The LRL is statistically based and is set so that the chance that a detected concentration is a false negative or false positive is less than or equal to 1 percent. The LRL is reassessed each year and may change for some compounds.

Sample analysis of methyl isothiocyanate (MITC) was conducted by solid-phase microextraction (SPME) (Gorecki and Pawliszyn, 1995; James and Stack, 1997; Santos and others, 1996; and Shirey, 1995), with GC/MS used to identify MITC and chloropropanes. Briefly, MITC and other compounds are adsorbed from water samples by immersion of the SPME fiber into 3.8-mL samples. MITC and other compounds adsorbed on the fiber are then thermally desorbed into the injection port of the GC/MS system. Identification and quantification of each compound is confirmed by analyzing reference material under the same conditions as the samples and comparing retention times and mass spectra and peak areas with reference standards. Initial method validation involved analysis of three blanks and seven reagent-water spiked samples to document method performance.

Estimation of method detection levels (MDLs) was conducted by analysis of a series of replicate standards at a concentration of 1.0 µg/L. Results indicate an estimate MDL of 0.40 µg/L for MITC. A laboratory reporting level (LRL) was set at twice the MDL or 0.8 µg/L (Childress and others, 1999).

Statistical Methods

Nonparametric statistics were used in this report because they are resistant to the effects of outliers, do not assume that data are normally distributed, and can handle censored values (i.e., unquantified data reported below a detection limit) (Helsel and Hirsch, 1992). A Wilcoxon rank-sum test was used to evaluate the differences in median values of (1) ratios of $\delta^{15}N$ and concentrations of nitrate and concentrations of chloride between unsewered and sewered areas of the urban LUS; and (2) concentrations of nitrate between each of the land-use studies and the study-unit survey (Helsel and Hirsch, 1992). A probability of less than or equal to 0.05 for the Wilcoxon test was considered to be significant. An exact test was applied to the $\delta^{15}N$ values, and a large sample approximation was applied to the chloride and nitrate data.

Land-Use and Land-Cover Data Collection

Ancillary land-use and land-cover data were collected for each well sampled for the Puget Sound Basin NAWQA according to Koterba (1998). Using aerial photos and field observations, a 500-meter buffer around each well was delineated by specific land uses and possible point sources of contamination. Table 5 summarizes the overall total land use within 500 meters of each well for the land-use studies. In agricultural areas, delineated land use and land cover could include specific crops, livestock farms, roads, and farm-related infrastructure, which included houses, small gardens, barns, silos, and dirt roads on the farm. Land-use and land-cover data were not collected for one well in the agricultural LUS because of limited access to the area.

Table 3. Pesticide analytes, method detection limits, drinking-water standards, and health advisories [µg/L, micrograms per liter; H, herbicide; I, insecticide; T, transformation product; F, fungicide; --, no criteria established; MCL, drinking-water maximum contaminant level (U.S. Environmental Protection Agency, 1996a); **HA-L**, health advisory, 70-kilogram adult, lifetime (U.S. Environmental Protection Agency, 1996a); *RSD*, risk-specific dose health advisory for drinking water associated with a 10^{-6} (1 in a million) cancer risk (U.S. Environmental Protection Agency, 1996a); U.S. Environmental Protection Agency lifetime-health advisory for a 70-kilogram adult, from Nowell and Resek (1994); U.S. Environmental Protection Agency risk-specific dose health advisory associated with a cancer risk of 10^{-6} (1 in a million), from Nowell and Resek (1994)]

Pesticide target analyte	Trade or common name(s)	Type of pesti-cide	Chemical Abstracts Service registry number	Method detection limit (µg/L)	MCL, **HA-L** or *RSD* (µg/L)
		Gas Chromatography/Mass Spectrometry analytical method			
Acetochlor	Acenit, Sacenid	H	34256-82-1	0.002	--
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	**350**
Carbaryl[1,2]	Sevin, Savit	I	63-25-2	0.003	**700**
Carbofuran[1,2]	Furadan	I	1563-66-2	0.003	40
Chlorpyrifos	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	T	72-55-9	0.006	*0.1*
Desethylatrazine[1]	none	T	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	*0.002*
2,6-Diethylanaline	none	T	579-66-8	0.003	--
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**
alpha-HCH	none	T	319-84-6	0.002	*0.006*
gamma-HCH	Lindane	I	58-89-9	0.004	0.2
Linuron[2]	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	**100**
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	--

Table 3. Pesticide analytes, method detection limits, drinking-water standards, and health advisories--Continued

Pesticide target analyte	Trade or common name(s)	Type of pesticide	Chemical Abstracts Service registry number	Method detection limit (µg/L)	MCL, **HA-L** or *RSD* (µg/L)
		Gas Chromatography/Mass Spectrometry analytical method--Continued			
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**
Pronamide	Kerb	H	23950-58-5	0.003	**50**
Propachlor	Ramrod	H	1918-16-7	0.007	**90**
Propanil	Stampede	H	709-98-8	0.004	--
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 analytical method			
2,4-D	several	H	94-75-7	0.15	70
2,4-DB	none	I	94-82-6	0.24	--
2,4,5-T	several	H	93-76-5	0.035	**70**
2,4,5-TP[3]	Silvex	H	93-72-1	0.021	50
3-Hydroxy-carbofuran[3]	none	T	1563-38-8	0.014	--
Acifluorfen	Blazer	H	50594-66-6	0.035	*1*
Aldicarb[3,1]	Temik	I	116-06-3	0.55	7
Aldicarb sulfone[3]	Standak	T	1646-88-4	0.1	7
Aldicarb sulfoxide	none	T	1646-87-3	0.021	7
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[2,3]	Sevin, Savit	I	63-25-2	0.008	**700**
Carbofuran[2,3]	Furadan	I	1563-66-2	0.12	40
Chloramben	Amiben, Vegiben	H	133-90-4	0.42	**100**
Chlorothalonil	Bravo	F	1897-45-6	0.48	*1.5*
Clopyralid	Stinger, Lontrel	H	1702-17-6	0.23	--
Dacthal, (mono-acid)	none	T	887-54-7	0.017	--
Dicamba	Banvel	H	1918-00-9	0.035	**200**
Dichlobenil	Barrier, Casoron	H	1194-65-6	1.2	--
Dichlorprop	2,4-DP, Seritox 50	H	120-36-5	0.032	--

Table 3. Pesticide analytes, method detection limits, drinking-water standards, and health advisories--Continued

Pesticide target analyte	Trade or common name(s)	Type of pesticide	Chemical Abstracts Service registry number	Method detection limit (µg/L)	MCL, **HA-L** or *RSD* (µg/L)
		High-Performance Liquid Chromatography analytical method--Continued			
Dinoseb	DNBP, Dinitro	H	88-85-7	0.035	7
Diuron	Karmex, Direx	H	330-54-1	0.02	**10**
DNOC	Trifocide, Elgetol 30	I,F,H	534-52-1	0.42	--
Fenuron	Beet-Kleen	H	101-42-8	0.013	--
Fluometuron	Flo-Met, Cotoran	H	2164-17-2	0.035	**90**
Linuron[2]	Lorox, Linex	H	330-55-2	0.018	--
MCPA	Metaxon, Kilsem	H	94-74-6	0.17	**10**
MCPB	Can-Trol, Thistrol	H	94-81-5	0.14	--
Methiocarb[3]	Grandslam, Mesurol	I	2032-65-7	0.026	--
Methomyl	Lannate, Nudrin	I	16752-77-5	0.017	**200**
Neburon	Neburex, Noruben	H	555-37-3	0.015	--
Norflurazon	Evital, Solicam	H	27314-13-2	0.024	--
Oryzalin	Surflan	H	19044-88-3	0.31	--
Oxamyl[3]	Vydate	I	23135-22-0	0.018	200
Picloram[3]	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	--
Triclopyr[3]	Garlon, Grazon	H	55335-06-3	0.25	--

[1] Concentrations for these pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction (Zaugg and others, 1995).

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

[3] Pesticide target analyte 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).

Table 4. Volatile organic compounds, laboratory reporting levels, drinking-water standards, and health advisories [µg/L, micrograms per liter; --, no criteria established; MCL, drinking-water maximum contaminant level (U.S. Environmental Protection Agency, 1996a); **HA-L**, health advisory, 70-kilogram adult, lifetime (U.S. Environmental Protection Agency, 1996a); *RSD*, risk-specific dose health advisory for drinking water associated with a 10^{-6} (1 in a million) cancer risk (U.S. Environmental Protection Agency, 1996a)]

Volatile organic compounds	Trade or common name(s)	Chemical Abstracts Service registry number	Laboratory reporting level[1] (µg/L)	MCL, **HA-L** or *RSD* (µg/L)
1,1-Dichloroethane	Ethylidine chloride	75-34-3	0.066	--
1,1-Dichloroethylene	Vinylidine chloride	75-35-4	0.044	7
1,1-Dichloropropene	--	563-58-6	0.026	--
1,1,1-Trichloroethane	1,1,1-TCA	71-55-6	0.032	200
1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA	630-20-6	0.044	70
1,1,2-Trichloroethane	Vinyl trichloride	79-00-5	0.064	5
1,1,2-Trichlorotrifluoroethane	Freon 113, CFC-113	76-13-1	0.032	--
1,1,2,2-Tetrachloroethane	1,1,2,2,-TeCA	79-34-5	0.13	--
1,2-Dibromo-3-chloropropane	DBCP	96-12-8	0.21	0.2
1,2-Dibromoethane	Ethylene dibromide, EDB	106-93-4	0.036	0.05
1,2-Dichlorobenzene	*o*-Dichlorobenzene	95-50-1	0.048	600
1,2-Dichloroethane	Ethylene dichloride	107-06-2	0.13	5
cis-1,2-Dichloroethylene	*cis*-Acetylene dichloride	156-59-2	0.038	70
trans-1,2-Dichloroethylene	*trans*-Acetylene dichloride	156-60-5	0.032	100
1,2-Dichloropropane	Propylene dichloride, 1,2-DCP	78-87-5	0.068	5
1,2,3-Trichlorobenzene	--	87-61-6	0.27	--
1,2,3-Trichloropropane	--	96-18-4	0.16	40
1,2,3-Trimethylbenzene	--	526-73-8	0.12	--
1,2,3,4-Tetramethylbenzene	Prer-nitine	488-23-3	0.23	--
1,2,3,5-Tetramethylbenzene	Isodurence	527-53-7	0.24	--
1,2,4-Trichlorobenzene	--	120-82-1	0.19	70
1,2,4-Trimethylbenzene	Pseudocumene, 1,2,4-TMB	95-63-6	0.056	--
1,3-Dichlorobenzene	*m*-Dichlorobenzene	541-73-1	0.054	600
1,3-Dichloropropane	--	142-28-9	0.12	--
cis-1,3-Dichloropropene	*cis*-1,3-Dichloropropylene	10061-01-5	0.092	2
trans-1,3-Dichloropropene	*trans*-1,3-Dichloropropylene	10061-02-6	0.13	2
1,3,5-Trimethylbenzene	Mesitylene	108-67-8	0.044	--
trans-1,4-Dichloro-2-butene	--	110-57-6	0.7	--
1,4-Dichlorobenzene	*p*-Dichlorobenzene	106-46-7	0.05	75
2-Butanone	Methyl-ethyl ketone	78-93-3	1.6	--
2-Chlorotoluene	--	95-49-8	0.042	--
2-Hexanone	--	591-78-6	0.7	--
2,2-Dichloropropane	--	594-20-7	0.078	--
3-Chloropropene	--	107-05-1	0.20	--
4-Chlorotoluene	--	106-43-4	0.056	--
4-Isopropyl-1-methylbenzene	--	99-87-6	0.11	--
4-Methyl-2-pentanone	Methyl isobutyl ketone	108-01-1	0.37	--
Acetone	--	67-64-1	5	--
Acrolein[2]	--	107-02-8	1.4	--
Acrylonitrile	--	107-13-1	1.2	*0.06*
Benzene	--	71-43-2	0.10	5
Bromobenzene	Phenyl bromide	108-86-1	0.036	--
Bromochloromethane	Methylene chlorobromide	74-97-5	0.044	**10**
Bromodichloromethane	Dichlorobromomethane	75-27-4	0.048	100

Table 4. Volatile organic compounds, laboratory reporting levels, drinking-water standards, and health advisories--Continued

Volatile organic compounds	Trade or common name(s)	Chemical Abstracts Service registry number	Laboratory reporting level[1] (µg/L)	MCL, **HA-L** or *RSD* (µg/L)
Bromoethene	Vinyl bromide	593-60-2	0.1	--
Bromoform	--	75-25-2	0.10	100
Bromomethane	Methyl bromide	74-83-9	0.15	**10**
Butylbenzene	--	104-51-8	0.19	--
sec-Butylbenzene	2-Phenylbutane	135-98-8	0.048	--
tert-Butylbenzene	2-Methyl-2-phenylpropane	98-06-6	0.096	--
Carbon disulfide	Carbon bisulfide	75-15-0	0.37	--
Chlorobenzene	Monochlorobenzene	108-90-7	0.028	100
Chloroethane	Ethyl chloride	75-00-3	0.12	--
Chloroethene	Vinyl chloride	75-01-4	0.12	2
Chloroform	trichloromethane	67-66-3	0.052	100
Chloromethane	Methyl chloride	74-87-3	0.25	**3**
Dibromochloromethane	Chlorodibromomethane	124-48-1	0.18	100
Dibromomethane	Methylene bromide	74-95-3	0.05	--
Dichlorodifluoromethane	Chlorofluorocarbon-12, CFC-12	75-71-8	0.14	**1,000**
Dichloromethane	Methylene chloride	75-09-2	0.38	5
Diethylether	--	60-29-7	0.17	--
Diisopropyl ether	--	108-20-3	0.098	--
Ethyl methacrylate	--	97-63-2	0.28	--
Ethyl *tert*-butyl ether	ETBE	637-92-3	0.054	--
o-Ethyl toluene	--	611-14-3	0.1	--
Ethylbenzene	--	100-41-4	0.03	700
Hexachlorobutadiene	HCBD	87-68-3	0.14	50
Hexachloroethane	--	67-72-1	0.36	1
Isopropylbenzene	Cumene	98-82-8	0.032	--
Methyl acrylate	--	96-33-3	1.4	--
Methyl acrylonitrile	--	126-98-7	0.57	--
Methyl iodide	--	74-88-4	0.21	--
Methyl methacrylate	--	80-62-6	0.35	--
Methyl *tert*-butyl ether	MTBE	1634-04-4	0.17	[3]**20-40**
Naphthalene	--	91-20-3	0.25	**20**
tert-Pentyl methyl ether	--	994-05-8	0.11	--
Propylbenzene	--	103-65-1	0.042	--
Styrene	Vinyl benzene	100-42-5	0.042	100
Tetrachloroethylene	Perchloroethylene, PCE	127-18-4	0.1	5
Tetrachloromethane	Carbon tetrachloride	56-23-5	0.088	5
Tetrahydrofuran	--	109-99-9	9	--
Toluene	Methylbenzene	108-88-3	0.05	1,000
Trichloroethylene	Trichloroethene, TCE	79-01-6	0.038	5
Trichlorofluoromethane	Chlorofluorocarbon-11, CFC-11	75-69-4	0.032	**2,000**
m- and *p*-Xylene	*meta*- and *para*-Xylene		0.064	--
o-Xylene	--	95-47-6	0.064	--

[1] Laboratory reporting levels are updated every year by the National Water Quality Laboratory. The laboratory reporting levels listed in this table are from 1999.
[2] Acrolein was deleted from the volatile organic compound schedule on April 1998 because of poor recovery of the compound.
[3] The health advisory for MTBE was released in a separate publication (U.S. Environmental Protection Agency, 1997).

Table 5. Summary of land use within 500 meters of wells in the urban and agricultural land-use studies

Land use	Percentage of area		
	Mean	Minimum	Maximum
Agricultural Land-Use Study (22 wells)			
Raspberries	58	30	93
Farm-related infrastructure	9	0	17
Silage	6	0	25
Undeveloped buffer zone	6	0	31
Other berries	3	0	14
Nonproductive cropland	3	0	37
Corn	3	0	24
Dairy pasture	2	0	15
Urban residential	2	0	29
Horse pasture	1	0	16
Miscellaneous cropland	1	0	12
Airport	1	0	17
Other	5		
Urban Land-Use Study (27 wells)			
Urban residential	63	37	92
Undeveloped, wooded	20	0	42
Barren	7	0	34
Water (lakes and ponds)	2	0	21
Parks	1	0	25
Construction	1	0	8
Other	6		

Land use recorded in the urban LUS included different types of residences, businesses, parks, roads, railways, and construction sites.

GROUND-WATER QUALITY IN REGIONAL, AGRICULTURAL, AND URBAN SETTINGS

Ground-water quality is described using results of nutrients, pesticides, VOCs, and radon analyses. In each section, results from the SUS are used to describe the background water-quality conditions of the Puget Sound Basin. Then the SUS results are compared to detections of nutrients, pesticides, VOCs, and radon in ground water from wells in the agricultural and urban LUS to determine what effects land use has on ground-water quality. Major ion and DOC data were collected for this study but are used to supplement analysis of other constituents and are not discussed in this report. A comprehensive summary of major ions in Puget Sound Basin ground water can be found in Turney (1984). Tables of data for field parameters, nutrients, DOC, major ions, pesticides, VOCs, and radon can be obtained from the Puget Sound NAWQA web site at URL http://wa.water.usgs.gov/ps.nawqa.html.

Results from the SUS showed that regional ground-water quality was generally good. Only one constituent, nitrate, exceeded any drinking-water standards, and only 1,2,4-trimethylbenzene and radon were prevalent (for the purposes of this report, *prevalent* refers to analytes detected in 30 percent or more of the samples) (table 6). Nitrate was at elevated concentrations (greater than 3.0 mg/L) in 17 percent of the SUS samples (table 6). In contrast, the agricultural LUS showed that ground water in Whatcom County had much higher concentrations of nitrate and was influenced by past and possibly present fumigant applications. Sixty-four percent (14 samples) of nitrate detections, 9 percent (2 samples) of the 1,2-dichloropropane detections, and 5 percent (1 sample) of 1,2-dibromo-3-chloropropane detections were above drinking-water standards. Nitrate and 1,2-DCP were

Table 6. Summary of ground-water quality in the study-unit survey and agricultural and urban land-use studies

Compound or group of compounds	Location of interest	Highlights of chemical conditions[1]	Sources and influences
Nitrate	Study-unit survey	**Cautionary concentration**--3 percent **Elevated concentration**--17 percent	
	Agricultural land-use study	**Cautionary concentration**--64 percent **Elevated concentration**--82 percent	Derived mostly from cow manure and fertilizers.
	Urban land-use study	**Cautionary concentration**--4 percent **Elevated concentration**--63 percent	Lawn and garden fertilizers, and septic systems.
Pesticides	Study-unit survey	**Cautionary concentration**--none **Prevalent detection**--none	
	Agricultural land-use study	**Cautionary concentration**--none **Prevalent detection**--atrazine (41 percent), desethylatrazine (45 percent), oxamyl (41 percent), simazine (36 percent)	Atrazine and simazine are registered in Washington for use on crops that are grown within the agricultural land-use study area; oxamyl is a recommended pesticide for raspberries in British Columbia, Canada.
	Urban land-use study	**Cautionary concentration**--none **Prevalent detection**--none	
Volatile organic compounds	Study-unit survey	**Cautionary concentration**--none **Prevalent detection**--1,2,4-trimethylbenzene (30 percent)	1,2,4-trimethylbenzene is a fuel-related compound.
	Agricultural land-use study	**Cautionary concentration**--1,2-dichloropropane (9 percent) 1,2-dibromo-3-chloropropane (5 percent) **Prevalent detection**--1,2-dichloropropane (73 percent), 1,2,4-trimethylbenzene (41 percent)	1,2-dichloropropane is derived from past, and possibly current, applications of fumigants to raspberries and other crops. 1,2-dibromo-3-chloropropane was used as a fumigant in the past. 1,2,4-trimethylbenzene is an inert ingredient in some pesticides applied to raspberries.
	Urban land-use study	**Cautionary concentration**--none **Prevalent detection**--none	
Radon	Study-unit survey	**Cautionary concentration**--47 percent **Prevalent detection**--100 percent	Radon is formed from the radioactive decay of uranium-238, which is present in geologic formations.
	Urban land-use study	**Cautionary concentration**--65 percent **Prevalent detection**--100 percent	

[1] Categories of chemical conditions: Cautionary concentration--based on a comparison of chemical concentrations with EPA Maximum Contaminant Levels (MCLs) or health advisories for drinking water. The cautionary concentration for radon is based on the EPA proposed MCL of 300 pCi/L; Prevalent detection--detection of a chemical in 30 percent or more of samples in the location of interest. Elevated concentration--the percentage of samples with concentrations of nitrate above 3.0 mg/L, a level suggested by Madison and Brunett (1985) that indicates anthropogenic sources of nitrate.

also prevalent in ground water, as were atrazine, desethylatrazine, oxamyl, simazine, and 1,2,4-trimethylbenzene (table 6). The urban LUS results indicated that ground water in Olympia and Tacoma overlain by urban, residential areas showed more anthropogenic influences than the ground water sampled for the SUS. Sixty-three percent (17 samples) of the nitrate detections were elevated (table 6), and a higher number of different compounds were detected in the urban LUS (8 VOCs, 6 pesticides) than in the SUS (4 VOCs, 5 pesticides). No VOCs or pesticide compounds were prevalent in the urban LUS.

Nutrients

Nitrate is a nutrient of primary interest in ground water. Nitrate concentrations above the USEPA MCL of 10 mg/L for drinking water have been associated with "blue-baby" syndrome (methemoglobinemia). This discussion of nutrients will focus on nitrate because concentrations of phosphorus, orthophosphorus, ammonia, ammonia plus organic nitrogen, and nitrite were quite low and were not significant in the interpretation of ground-water quality (table 7).

Table 7. Summary of detections and concentrations of nutrients and dissolved oxygen in ground-water samples from the study-unit survey and agricultural and urban land-use studies
[MRL, method reporting level; mg/L, milligrams per liter; n, number of samples; <, less than; N, nitrogen; P, phosphorus; bold numbers exceed maximum contaminant level (U.S. Environmental Protection Agency, 1996a; LRL, laboratory reporting level; nc, not computed]

Compound	MRL (mg/L)	Detection frequency, in percent	Minimum (mg/L)	Median (mg/L)	Maximum (mg/L)
		Study Unit Survey (n=30)			
Dissolved oxygen	0.01	nc	<0.01	5.6	9.9
Ammonia as N	0.015	70	<0.015	0.02	0.42
Ammonia and organic nitrogen as N	0.2	7	<0.2	<0.2	0.4
Nitrite as N	0.01	23	<0.01	<0.01	0.01
Nitrate as N (nitrite plus nitrate)	0.05	93	<0.05	0.98	**12**
Orthophosphorus as P	0.01	93	<0.01	0.03	0.32
Phosphorus as P	0.01	57	<0.01	0.015	0.26
		Agricultural Land-Use Study (n=22)			
Dissolved oxygen	0.01	nc	<0.01	7.4	9.6
Ammonia as N	0.015	29	<0.015	<0.02	0.20
Ammonia and organic nitrogen as N	0.1	19	<0.1	<0.2	0.23
Nitrite as N	0.01	38	<0.01	<0.01	0.042
Nitrate as N (nitrite plus nitrate)	0.05	95	<0.05	**12.9**	**36**
Orthophosphorus as P	0.01	52	<0.01	0.015	0.12
Phosphorus as P	0.01	14	<0.01	<0.01	0.037
		Urban Land-Use Study (n=27)			
Dissolved oxygen	0.01	nc	<0.01	7.2	9.4
Ammonia as N	0.015	41	<0.015	<0.015	0.22
Ammonia and organic nitrogen as N	0.1	7	<[1]0.1	<0.2	0.27
Nitrite as N	0.01	33	<0.01	<0.01	0.02
Nitrate as N (nitrite plus nitrate)	0.05	93	<0.05	4.2	**10**
Orthophosphorus as P	0.01	82	<0.01	0.02	0.21
Phosphorus as P	0.01	48	<0.01	<0.01	0.38

[1] On October 1, 1998, the MRL for ammonia of 0.02 mg/L was changed to an LRL of 0.1 mg/L. Only one sample was collected at the lower reporting level.

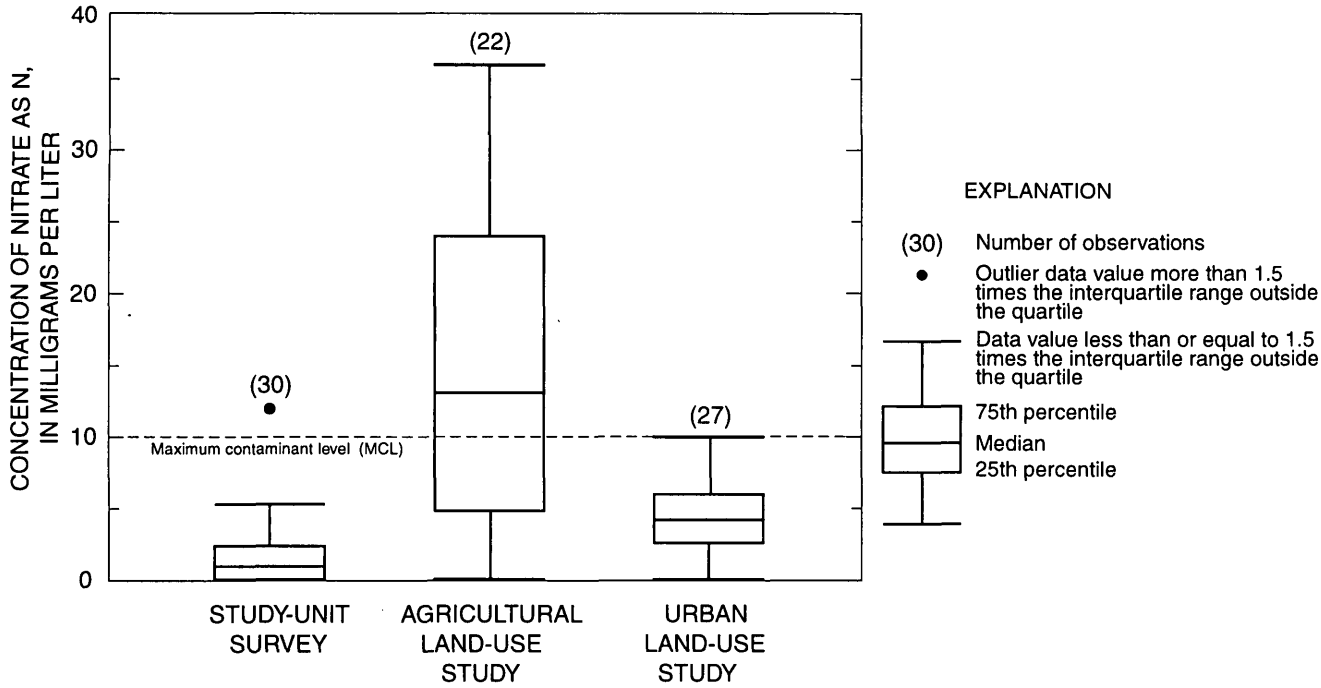

Figure 4. Concentrations of nitrate in ground-water samples from the study-unit survey and agricultural and urban land-use studies.

Comparison of Nitrate in Ground Water in Regional, Agricultural, and Urban Settings

Concentrations of nitrate in ground-water samples from the SUS were generally low, having a median concentration of about 1.0 mg/L (table 7). The nitrate concentration in one sample from the SUS was greater than the USEPA MCL for drinking water of 10.0 mg/L (table 7). This sample was taken in the agricultural LUS area.

In the agricultural LUS, concentrations of nitrate in 64 percent of the samples were greater than the USEPA MCL for drinking water (10 mg/L) (fig. 4). Nitrate concentrations in samples ranged from less than 0.05 mg/L to 36 mg/L, with a median value of 12.9 mg/L (table 7). Median concentrations of nitrate in samples from the agricultural LUS were significantly higher than background median concentrations of nitrate in samples from the SUS ($p<0.01$), indicating an anthropogenic influence on the aquifer in the agricultural LUS area.

High nitrate concentrations in Whatcom County have been well documented by other studies (Obbert, 1973; Cox and Kahle, 1999; Erickson, 1998; Liebscher and others, 1992). Possible sources of nitrate to ground water in the agricultural LUS area include inorganic fertilizer and manure application to crops, storage of barnyard manures, and residential septic systems (Cox and Kahle, 1999). In a study that encompassed the agricultural LUS area, including Everson, Abbotsford, and Lynden, Cox and Kahle (1999) estimated that 63 percent of the nitrogen reaching ground water was from applications of manure or manure storage, 21 percent was from inorganic fertilizers, and about 5 percent was from residential sources. However, the study was more broadly focused with respect to land use than the agricultural LUS. Of the land within a 500-meter radius of each well in the agricultural LUS, about 65 percent is field crops, whereas in the Cox and Kahle study (1999), only about 31 percent is used for crops. As such, fertilizers could be a more significant source of nitrogen for the agricultural LUS than estimated by Cox and Kahle (1999).

In the urban LUS, the concentration of nitrate in one sample was equal to the drinking-water standard of 10 mg/L (table 7). However, median concentrations of nitrate in samples from the urban LUS were significantly greater than those from the SUS from wells with similar depths (25-100 feet) ($p<0.001$), indicating a widespread anthropogenic influence on nitrate concentrations in the aquifer in the urban LUS area.

The prevalence of nitrate in this aquifer at elevated concentrations is likely a result of both natural and anthropogenic influences. Ground water in the urban LUS was well oxygenated (median DO, 7.2 mg/L), and had low levels of dissolved organic carbon (DOC) (median 0.4 mg/L; from data collected, but not tabled in this report), both of which may have minimized the chemical transformations of nitrate to other forms, providing a stable environment for nitrate introduced into the system (Hem, 1989).

Potential anthropogenic sources of nitrate to ground water in the urban LUS include effluent from septic systems, fertilizers applied to lawns and gardens, leakage from sewer lines, waste from pets, and atmospheric deposition, which includes exhaust from automobiles. Installing sewers in urban and suburban areas that rely on septic systems is often considered as a management option for lowering concentrations of nitrate and other constituents in ground water. Because of the expense of installing sewers, it is important to determine if the removal of septic systems will lower concentrations in ground water to target levels. The urban LUS was not designed specifically to assess the effects of septic systems, but because the monitoring wells were installed in both sewered and unsewered areas, the data from the study were used for this purpose.

Assessment of Septic Systems as Sources of Nitrate in Ground Water in the Urban Land-Use Study Area

Of 27 wells sampled for the urban LUS, 16 were located in predominantly unsewered areas (70 percent of residential areas within 500 meters of the well), 10 were located in predominantly sewered areas, and 1 was in a mixed sewered-unsewered area (fig. 5). Concentrations of nitrate in ground water from unsewered and sewered areas were not statistically different ($p = 0.98$) (fig. 6), which suggests that septic systems have little overall effect on nitrate concentrations in ground water in this area. However, concentrations of chloride and $\delta^{15}N$ values were significantly higher in ground water in unsewered areas (chloride, $p = 0.01$; $\delta^{15}N$, $p < 0.001$) (fig. 6), indicating that effluent from septic systems is mixing with ground water.

In unsewered areas, concentrations of nitrate and chloride generally increase with increasing $\delta^{15}N$ values in ground water (fig. 7), indicating that nitrate and chloride concentrations increase as the amount of septic system effluent mixing with ground water increases and that septic-derived nitrate is a significant source of nitrate in ground water in these areas. As expected, chloride concentrations and $\delta^{15}N$ values in ground water in unsewered areas are generally higher than in sewered areas, indicating septic system effluent was mixing with ground water. The wide range of nitrate concentrations in ground water in the sewered areas (table 8) indicates that sources of nonseptic-derived nitrate in ground water in this area are highly variable.

The relation between $\delta^{15}N$ values and concentrations of chloride in ground water in unsewered areas suggests that much of the chloride in excess of the background level of 4 mg/L, the mean concentration of chloride in the SUS samples, is due to mixing of septic system effluent with ground water. If it is assumed that all chloride in excess of 4 mg/L is derived from septic system effluent, then the fraction of effluent in ground water can be computed using a chloride mass-balance equation. This fraction can then be used to compute the concentration of nitrate in ground water derived solely from septic system effluent.

The relation between the concentration of chloride and the fraction of septic system effluent in ground water is given by the equation

$$Cl = (50 \text{ mg/L})\,(x) + (4 \text{ mg/L})\,(1-x), \qquad (2)$$

where Cl is the concentration of chloride in ground water, in mg/L, x is fraction of septic system effluent in ground water, 4 is the background concentration of 4 mg/L chloride in ground water, and 50 is the concentration of chloride in septic system effluent in mg/L based on the average given by Robertson and others (1991).

The concentration of nitrate in ground water derived solely from septic system effluent is then

$$NO_3 = x\,(37 \text{ mg/L as N}), \qquad (3)$$

where NO_3 is the concentration of nitrate nitrogen derived from septic system effluent, x is the fraction of septic system effluent in ground water, and 37 is the concentration of nitrate in nitrogen septic system effluent reaching the ground-water system.

The value of 37 mg/L nitrate nitrogen in septic system effluent reaching the ground-water system is based on work in Whatcom County by Cox and Kahle (1999). They estimated nitrogen loading to ground water in a setting with coarse-textured, well-aerated

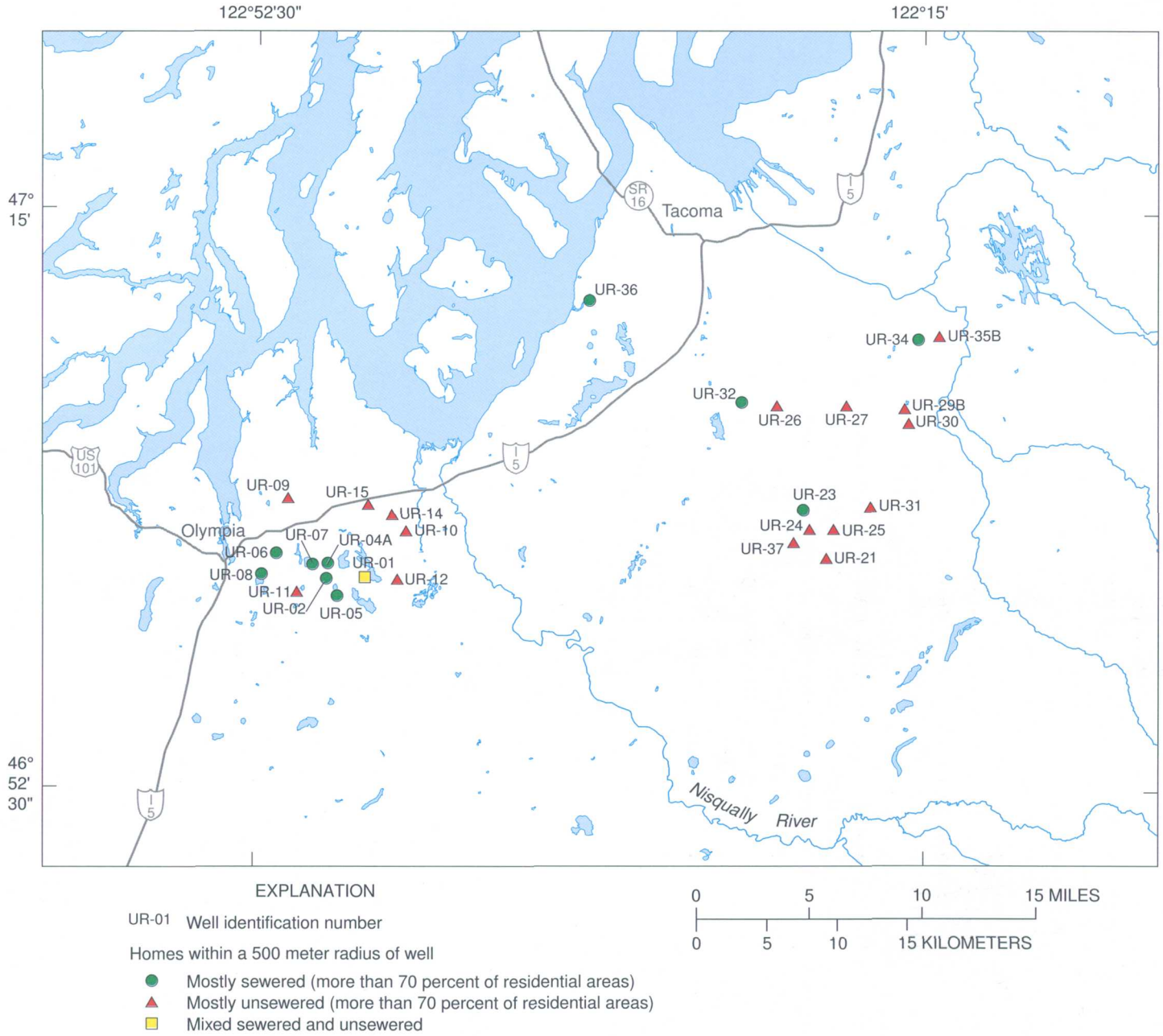

Figure 5. Locations of wells sampled for the urban land-use study.

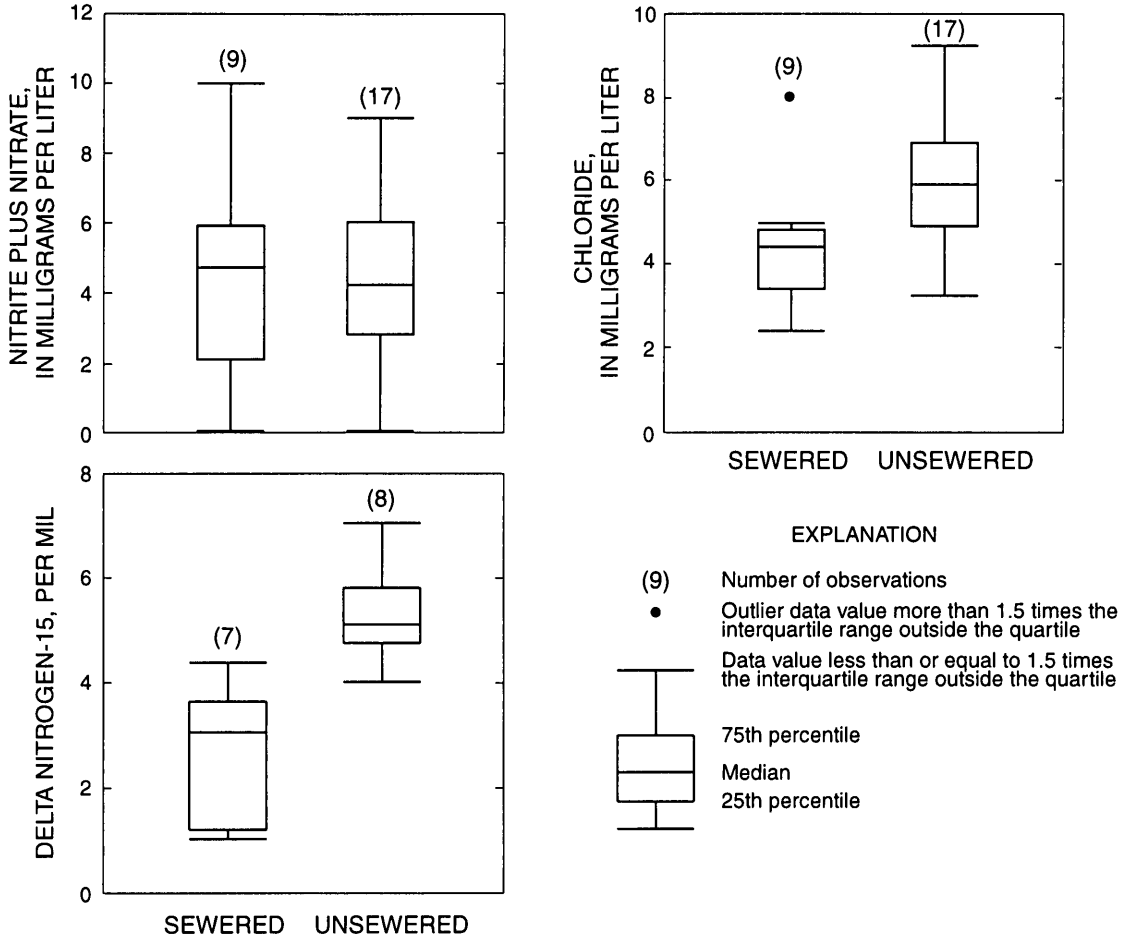

Figure 6. Concentrations of nitrate and chloride and the isotopic composition of nitrate nitrogen in ground water in sewered and unsewered areas.

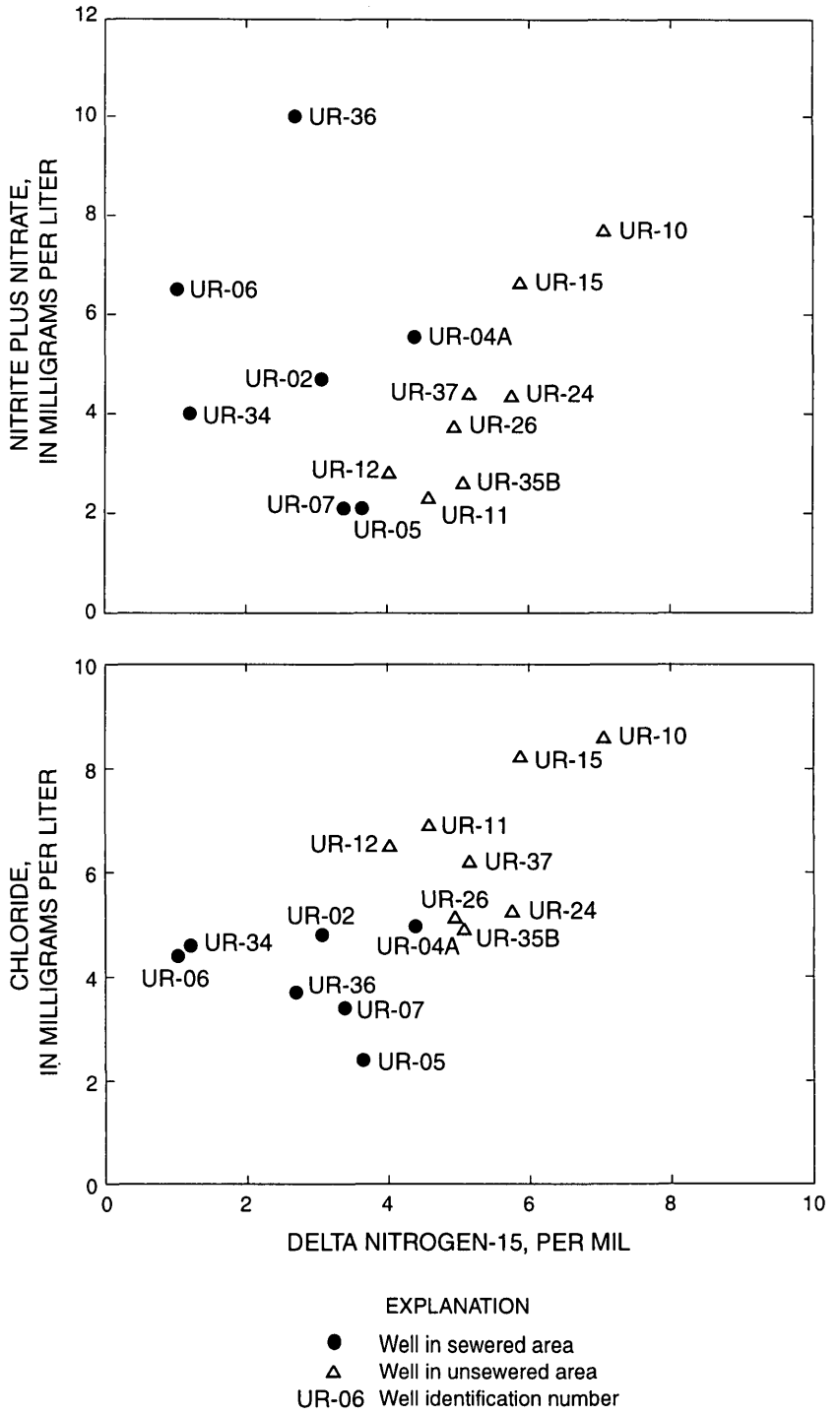

Figure 7. Concentrations of nitrate and chloride as a function of the isotopic composition of nitrate nitrogen in ground water in sewered and unsewered areas.

Table 8. Concentrations of dissolved oxygen, chloride, and nitrate, and the isotopic composition of nitrate nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) in water samples from urban land-use wells

[s, sewered area; u, unsewered area; m, mixed sewered and unsewered; mg/L, milligrams per liter; per mil, parts per thousand; <, less than; --, no data]

Well number	Sewerage setting	Well depth (in feet)	Date sampled	Dissolved oxygen (mg/L)	Chloride (mg/L)	Nitrate (mg/L as N)	$\delta^{15}N$ (per mil)	$\delta^{18}O$ (per mil)
UR-01	m	24	12-02-96	<0.1	7.7	2.8	10	9.24
UR-02	s	48	11-25-96	8.9	4.8	4.7	3.06	6.69
UR-04A	s	67	07-28-97	9.4	5.0	5.5	4.38	8.54
UR-05	s	48	11-22-96	8.8	2.4	2.1	3.64	--
UR-06	s	39	11-21-96	8.3	4.4	6.5	1.02	4.02
UR-07	s	29	11-26-96	8.4	3.4	2.1	3.38	6.1
UR-10	u	27	12-03-96	4.7	8.6	7.7	7.05	2.46
UR-11	u	57	11-22-96	3.1	6.9	2.3	4.58	--
UR-12	u	51	12-02-96	8.5	6.5	2.8	4.02	6.57
UR-15	u	46	05-02-97	8.6	8.2	6.6	5.87	2.55
UR-24	u	47	07-30-97	5.4	5.2	4.4	5.75	3.76
UR-26	u	37	08-12-97	7.3	5.1	3.7	4.94	1.97
UR-34	s	33	12-04-96	2.4	4.6	4.0	1.2	--
UR-35B	u	52	12-04-96	7.3	4.9	2.6	5.07	4.62
UR-36	s	97	11-18-96	8.3	3.7	10	2.69	1.81
UR-37	u	22	11-27-96	7.6	6.2	4.4	5.15	3.5

subsurface sediments similar to those in the urban LUS area. They assumed a concentration of 55 mg/L total nitrogen in septic system effluent based on a range of values reported in the literature. Ammonia generally makes up more than 75 percent of the total nitrogen in the effluent, with the remaining 25 percent mostly organic nitrogen. The organic nitrogen is largely retained in the septic drain field, while most of the ammonia fraction is converted to nitrate and percolates to ground water. They reduced the amount of nitrogen reaching the ground-water system by another 10 percent to account for denitrification of some of the nitrate in the percolate.

Using equations 2 and 3, fractions of the total nitrate in ground water added from septic system effluent range from 0.23 to 1.01 (23 to 101 percent), with concentrations of nitrate in ground water attributed to effluent ranging from 0.72 to 3.7 mg/L (table 9). These results are rough estimates and should be used as a starting point for future investigations. For example, the result for well UR-11 (table 9) showing that 101 percent of the nitrate is derived from septic system effluent is not feasible. More realistic are the results for wells UR-10 and UR-15 with the highest $\delta^{15}N$ values (table 9), which indicate that up to one-half of the nitrate in ground water in the unsewered areas can be derived from septic system effluent. The central problem of why there was no difference between nitrate concentrations in sewered and unsewered areas remains unresolved other than to acknowledge that sources of nitrate are highly variable in the urban LUS area.

Pesticides

Pesticides are used to kill unwanted plants or insects. They are applied to crops, pasture and fallow land in agricultural areas and are applied to lawns, gardens, rights-of-way, and along highway margins in urban areas. Pesticides can be harmful to humans if they are present in high concentrations in drinking water.

Samples from each study were analyzed for 83 pesticides and transformation products. At least one pesticide compound was detected in the 20 percent of the SUS samples, 77 percent of the agricultural LUS samples, and 14 percent of the urban LUS samples, for a total of 74 pesticide detections. Concentrations of all pesticides were low and none exceeded maximum contaminant levels or health advisories for drinking water (fig. 8).

Atrazine, desethylatrazine, simazine, and oxamyl were the most commonly detected compounds overall (fig. 9a). However, comparing detection frequencies between pesticides can be misleading because pesticides with lower reporting limits tend to have a higher frequency of detection (Kolpin and others, 1998). In order to compare detection frequencies

Table 9. Estimates of nitrate contributed to ground water from septic systems in unsewered parts of the urban land-use study area
[mg/L, milligrams per liter; NO_3-N, nitrate as nitrogen]

Well number	Chloride in ground water (mg/L)	NO_3-N in ground water (mg/L)	Percent of septic system effluent mixed with ground water	NO_3-N added from effluent (mg/L)	Percent of total NO_3-N added from effluent
UR-10	8.6	7.7	10	3.70	48
UR-15	8.2	6.6	9	3.40	52
UR-24	5.3	4.4	3	1.00	23
UR-37	6.2	4.4	5	1.77	40
UR-35B	4.9	2.6	2	0.72	28
UR-26	5.1	3.7	3	0.91	25
UR-11	6.9	2.3	6	2.33	101
UR-12	6.5	2.8	5	2.01	72
Average	6.5	4.3	5	1.98	46

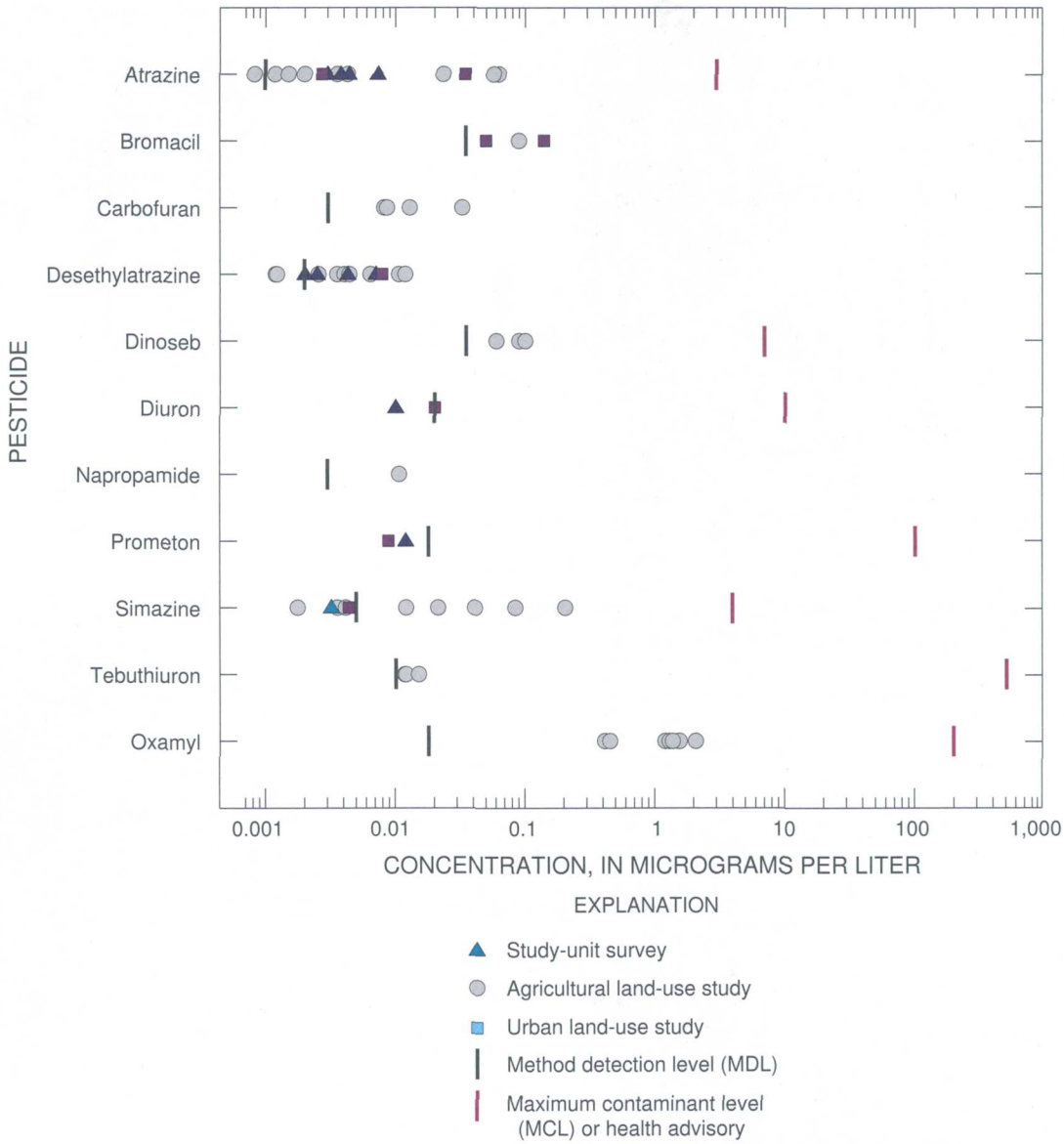

Figure 8. Concentrations of pesticides detected in ground-water samples from the study-unit survey and agricultural and urban land-use studies.

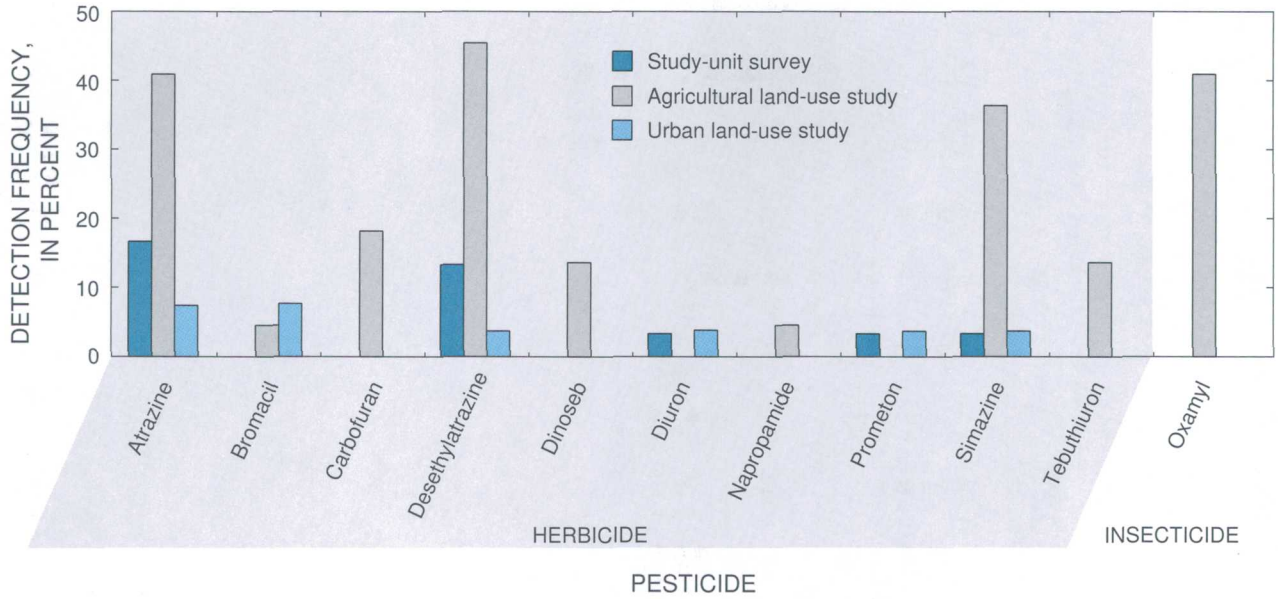

Figure 9a. Detection frequency of pesticides in ground-water samples from the study-unit survey and agricultural and urban land-use studies.

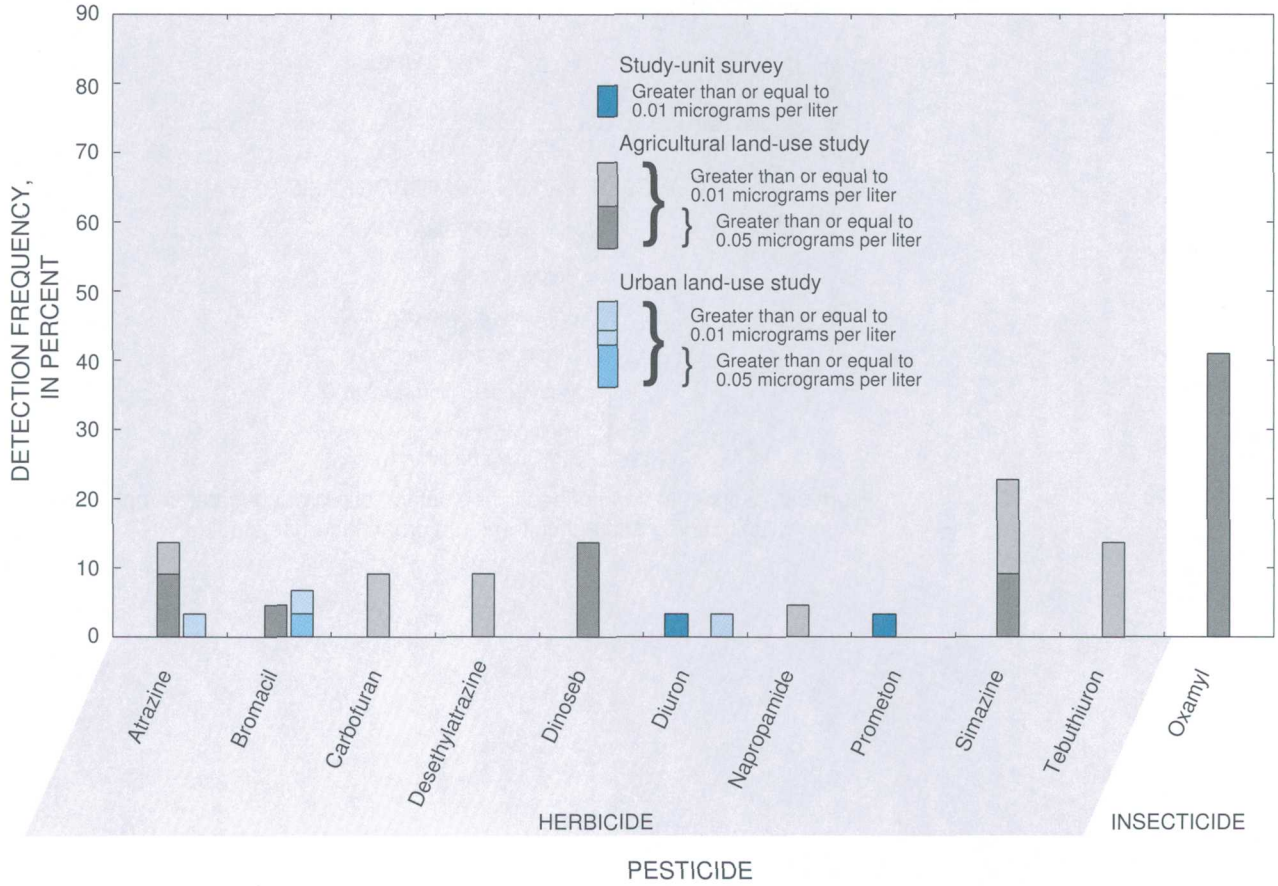

Figure 9b. Detection frequency of pesticides in ground water with concentrations greater than or equal to 0.01 micrograms per liter, or greater than or equal to 0.05 micrograms per liter in samples from the study-unit survey and agricultural and urban land-use studies.

between different pesticides, two common censoring limits were chosen: 0.01 µg/L and 0.05 µg/L (fig. 9b). The first censoring limit of 0.01 µg/L is equal or greater than almost all of the MDLs for pesticides analyzed by the GC/MS method, whereas 0.05 µg/L is greater or equal to nearly all pesticides analyzed by both the GC/MS and HPLC methods (table 3).

Pesticides were detected in only 20 percent of the SUS samples. Five different compounds were detected in the SUS, and the majority of the detections were atrazine and its transformation product desethylatrazine (fig. 9a). However, only prometon and diuron were detected above the common censoring limit of 0.01 µg/L (fig. 9b). Atrazine and desethylatrazine were detected in samples from urban, agricultural and undeveloped areas of the SUS. Atrazine is used on cropland in agricultural areas, on fallow land, and in industrial parks in urban areas (Barbash and Resek, 1996).

Pesticides were much more commonly detected in samples from the agricultural LUS than in samples from the SUS; at least one compound was detected in 77 percent of samples from the agricultural LUS. Greater usage of pesticides in the agricultural area and a shallower depth to the ground water are likely reasons why more pesticides were detected. Atrazine, desethylatrazine, simazine, and oxamyl were detected much more frequently in wells from the agricultural LUS than in wells from the SUS or urban LUS (fig. 9a). However, at concentrations above 0.01 µg/L, oxamyl was the most commonly detected pesticide, followed by simazine. Oxamyl was also the pesticide most commonly detected above 0.05 µg/L, followed by dinoseb (fig. 9b).

Pesticides commonly detected in the agricultural LUS (oxamyl, simazine, and atrazine) tended to be the ones used in Washington or in British Columbia for crops grown near sampled wells. Simazine and oxamyl were potentially used on raspberries in British Columbia, as they are among the pesticides recommended for raspberry production (Madeline Waring, British Columbia Ministry of Agriculture and Food, oral commun., October 1999) and are reported as being sold by vendors in Region 2 of Environment Canada, which includes the Canadian portion of the agricultural LUS area (Norecol Dames & Moore, 1997). All but one of the oxamyl detections were in Canada. Oxamyl is not registered for use on raspberries in Washington, but is registered for use on potatoes, which are grown in Whatcom County. Simazine was reported as having been applied to raspberries in Washington in 1995 and 1997 in a survey conducted by the Washington State Department of Agriculture (1998). In the same survey, atrazine was also reported by farmers as being applied to corn crops in Washington, also an important crop in the agricultural LUS area. Atrazine can also be used on fallow cropland and along road sides and rights-of-way.

Other pesticides detected in the agricultural LUS were possibly used on crops or elsewhere. Carbofuran was detected in 18 percent of the agricultural LUS samples and is potentially used on raspberries, although not enough data were available for statistics to be calculated (table 10). Tebuthiuron was detected in 14 percent of the samples and has uses on grazing land (Gianessi and Puffer, 1990). Dinoseb was also detected in 14 percent of the samples and is used primarily on corn and potatoes, two crops that are grown within the vicinity of the agricultural LUS area. Bromacil was detected once and is often used for brush control on noncropland areas (Farm Chemicals Handbook, 1994).

In the urban LUS, pesticides were detected in 14 percent of the samples and were generally the same compounds detected in samples from the SUS (fig. 9a). The detected pesticides, atrazine, bromacil, diuron, prometon, and simazine are all herbicides used to control weeds and unwanted grasses (Fuhrer and others, 1999; Tetra Tech, 1988; Barbash and Resek, 1996).

Detection of the same compounds at similar detection frequencies in the urban LUS and the SUS suggests that pesticides in ground water in the urban LUS area are not derived from residential pesticide use. Data from a recent study also suggest that most pesticides in the urban LUS area were not from residential applications. Voss and others (1999) reported residential use of pesticides based on pesticide sales data from 10 home and garden stores in King and Snohomish Counties. Although the data were not from Pierce and Thurston Counties where the urban LUS was conducted, the data represent pesticide use in urban residential areas similar to the land use in the urban LUS. Of the pesticides detected in the urban LUS, only prometon was sold at the retail outlets. Therefore, most detections were probably the result of nonresidential uses, such as applications along road rights-of-way, around buildings, and in parks and golf courses. For example, the Washington State Department of Transportation uses many different pesticides, including atrazine, bromacil, and diuron (Tom Clay, Washington State Department of Transportation, written commun.,

Table 10. Reported pesticide applications to raspberry crops in Washington State, 1995 and 1997[1]
[--, not available; Application data from Washington State Department of Agriculture, 1998; bold numbers indicate pesticides included in analysis of ground-water samples]

Agricultural chemical [2]	Percent of total bearing acres receiving application		Number of applications		Rate of pesticide application (pounds per acre): Rate per application		Rate of pesticide application (pounds per acre): Rate per crop year		Total pesticides applied (1,000 pounds)	
	1995	1997	1995	1997	1995	1997	1995	1997	1995	1997
					Herbicides					
Diuron	**4**	**31**	**1.0**	**1.0**	**1.54**	**0.97**	**1.54**	**0.97**	**0.4**	**2.5**
Norflurazon	**13**	**4**	**1.0**	**1.0**	**0.86**	**1.25**	**0.86**	**1.25**	**0.6**	**0.4**
Oryzalin	62	62	1.1	1.0	1.16	1.21	1.26	1.23	4.6	6.4
Oxyfluorfen	48	74	1.0	1.0	0.12	0.10	0.12	0.11	0.3	0.7
Paraquat	75	85	1.1	1.1	0.32	0.32	0.37	0.36	1.6	2.6
Sethoxydim	--	5	--	1.0	--	0.19	--	0.19	--	0.1
Simazine	**74**	**56**	**1.1**	**1.1**	**0.70**	**0.62**	**0.75**	**0.67**	**3.3**	**3.2**
					Insecticides					
Bifenthrin	67	81	1.0	1.0	0.10	0.10	0.10	0.10	0.4	0.7
Bt (Bacillus thur.) [3]	64	46	1.5	2.1	--	--	--	--	--	--
Diazinon	**60**	**77**	**1.0**	**1.4**	**1.26**	**1.14**	**1.28**	**1.58**	**4.5**	**10.3**
Esfenvalerate	**--**	**36**	**--**	**1.0**	**--**	**0.06**	**--**	**0.06**	**--**	**0.2**
Fenamiphos	13	--	1.0	--	2.77	--	2.77	--	2.2	--
Fenbutatin-oxide	45	--	1.1	--	0.95	--	1.06	--	2.8	--
Malathion	**54**	**44**	**1.0**	**1.0**	**1.12**	**1.07**	**1.14**	**1.09**	**3.7**	**4.1**
					Fungicides					
Benomyl	66	76	1.6	1.7	0.42	0.49	0.68	0.83	2.7	5.3
Calcium polysulfide	43	70	1.0	1.0	9.43	9.16	9.47	9.26	24.1	55.1
Captan	91	94	3.4	5.0	1.73	1.17	5.82	5.80	31.3	46.4
Ferbam	40	61	1.2	1.3	1.28	1.23	1.49	1.59	3.5	8.3
Iprodione	72	71	1.2	1.3	0.59	0.60	0.72	0.77	3.1	4.7
Metalaxyl	26	49	1.3	1.2	0.84	0.49	1.09	0.58	1.7	2.4
Vinclozolin	66	58	2.0	2.6	0.54	0.54	1.08	1.37	4.2	6.7

Note: Data may not multiply across due to rounding.

[1] Bearing acres in 1995 and 1997 for Washington State were 5,900 acres and 8,500 acres, respectively.

[2] Insufficient reports to publish data for the following agricultural chemicals: 1995 Herbicides: 2,4-D, Triclopyr. 1997 Herbicides: Dichlobenil, Fluazifop-P-butyl, Glyphosate, Napropamide, Pronamide. 1995 Insecticides: Azinphos-methyl, Carbaryl, Carbofuran, Esfenvalerate, Petroleum distillate. 1997 Insecticides: Azinphos-methyl, Carbofuran, Fenamiphos, Fenbutatin-oxide, Petroleum distillate. 1995 Fungicides: Copper hydroxide, Copper oxide, Copper sulfate, Ziram. 1997 Fungicides: Copper hydroxide, Copper sulfate, Mefenoxam, Sulfur. 1995 Other chemicals: Sulfcarbamide. 1997 Other chemicals: Metaldehyde, Monocarbamide dihyd.

[3] Rates and total applied are not available because amounts of active ingredient are not comparable between products.

July 1999) all of which were detected in the urban LUS, but were not reported as being sold in home and garden stores.

Although the pesticides concentrations were well below established drinking-water standards and health advisories, their presence indicates that they are indeed reaching the ground water in the Fraser aquifer. In particular, samples of ground water from the agricultural LUS show that more pesticides are present in ground water than in samples from the SUS, and at higher concentrations. While the results of pesticide detections and concentrations in samples from the urban LUS were not very different from those in the SUS, as the urban areas continue to increase in density and development, some of these patterns may change.

Volatile Organic Compounds

Volatile organic compounds (VOCs) are used in many products including fuels, solvents, paints, adhesives, deodorizers, and refrigerants, and are present in combustion exhaust and chlorinated drinking water. These chemicals have uses in both agricultural and urban land uses, and can reach the ground water by leaching from spills or leaks at the surface or underground, from atmospheric dispersion into ground water, and through recharge of ground water from rain, which could contain VOCs from the atmosphere.

At least one of 14 VOCs was detected at concentrations above its respective laboratory reporting level (LRL) in 40 percent of the SUS samples, 82 percent of the agricultural LUS samples, and in 48 percent of the urban LUS samples (see "Appendix: Quality Control: Volatile Organic Compounds" for an explanation of using only values above the LRL). The higher frequency of VOC detections in samples from the agricultural LUS compared with the other two studies is most likely the result of fumigant use in the agricultural LUS area. Fumigant-related compounds comprised 73 percent of all VOCs detected in samples from the agricultural LUS.

1,2-dichloropropane (1,2-DCP) and 1,2,4-trimethylbenzene were the most commonly detected compounds overall (fig. 10a). As with pesticides, analytical reporting levels for VOCs vary by compound, which affects detection frequencies. A common censoring level of 0.2 µg/L was selected for computing detection frequencies. This level is greater than or equal to nearly all of the VOC LRLs and is the same detection level for the VOC method used by NAWQA study units that began investigations in 1991. 1,2-dichloropropane (1,2-DCP) was the most commonly detected compound above 0.2 µg/L, followed by 1,2,3-trichloropropane and 1,2,4-trimethylbenzene (fig. 10b).

Concentrations of VOCs were generally low. Only two compounds, 1,2-DCP and 1,2-dibromo-3-chloropropane were detected at concentrations greater than their respective MCLs (fig. 11). However, even though most of the VOC detections were low, their presence in the Fraser aquifer shows that the quality of ground water was affected by surface activities, particularly in the agricultural LUS. As the Puget Sound region increases in population, it is likely that the urban LUS area will continue to develop, potentially introducing more VOCs into the environment. Monitoring the quality of ground water as land-use practices change may be beneficial in further understanding the impact of land use on the quality of ground water.

VOCs detected in the SUS, agricultural, and urban LUSs were grouped into four categories to assess possible sources of these compounds: (1) fumigant-related compounds, (2) solvents and fuel-related compounds, (3) trihalomethanes (THMs), and (4) refrigerants. Fumigant-related compounds were detected only in the agricultural LUS (fig. 10a) and comprised 73 percent of all detections; solvents and fuel-related compounds were most frequently detected VOCs in samples from the SUS (70 percent of all VOC detections) and urban LUS (67 percent of all VOC detections). Trihalomethanes and refrigerants were detected infrequently and did not seem to be related to a particular land use.

Fumigant-Related Compounds

Fumigants currently used in the agricultural LUS area contain the active ingredients 1,3-dichloropropene, methyl bromide, chloropicrin, and metham sodium (sodium N-methyldithiocarbamate) (Cindy Moore, Washington State Department of Agriculture, written commun., 1998). Of the four compounds, 1,3-dichloropropene (both *cis*- and *trans*- isomers) and methyl bromide were among the 83 VOCs analyzed. Historically, fumigants containing the active ingredients 1,2-DCP, and 1,2-dibromoethane (EDB) were used in this area (Erickson and Norton, 1990). Use of fumigants containing 1,2-dibromo-3-chloropropane (DBCP) as an active ingredient in this area is inferred by its presence in the ground water (Erickson and Norton, 1990). All three of these compounds were

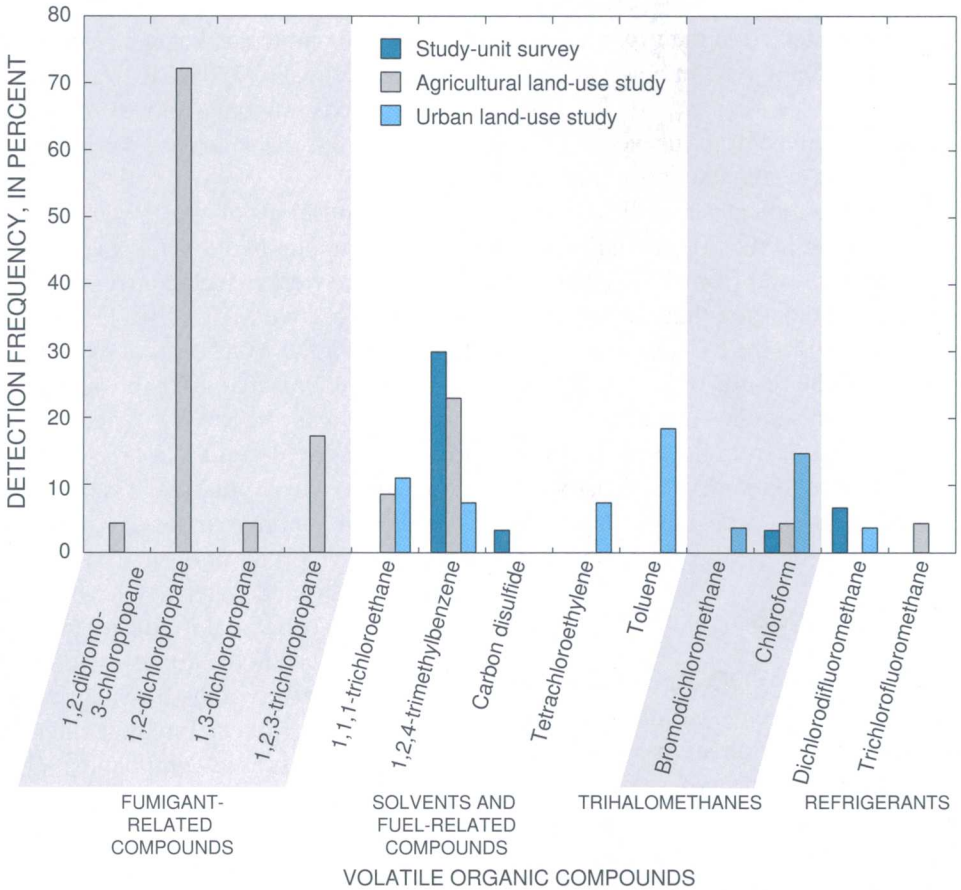

Figure 10a. Detection frequency of volatile organic compounds in ground water with concentrations above their laboratory reporting levels in samples from the study-unit survey and agricultural and urban land-use studies.

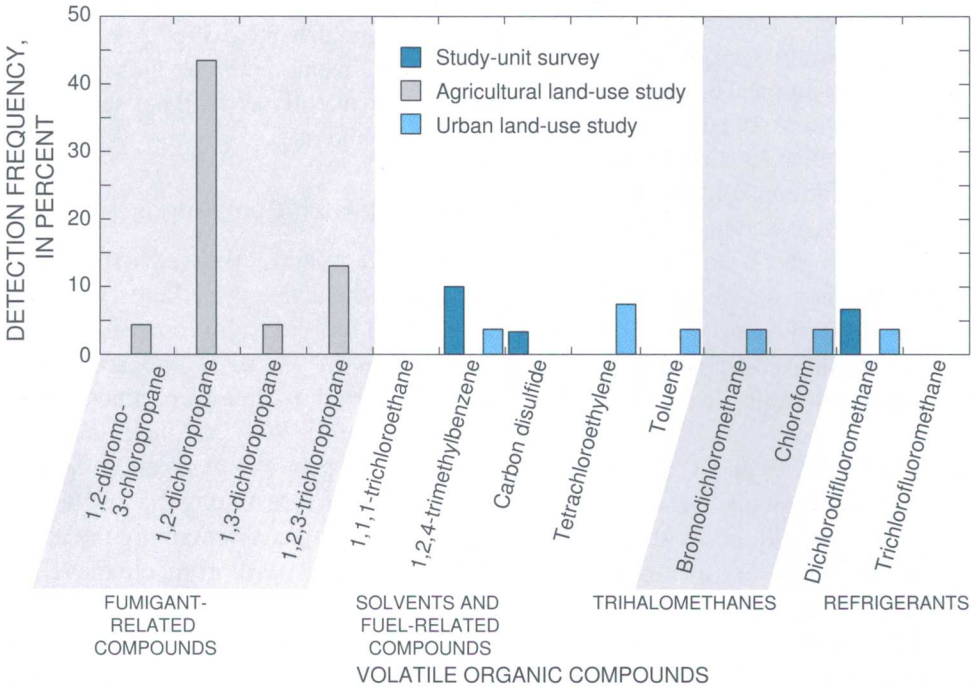

Figure 10b. Detection frequency of volatile organic compounds in ground water with concentrations greater than or equal to 0.2 micrograms per liter in samples from the study-unit survey and agricultural and urban land-use studies.

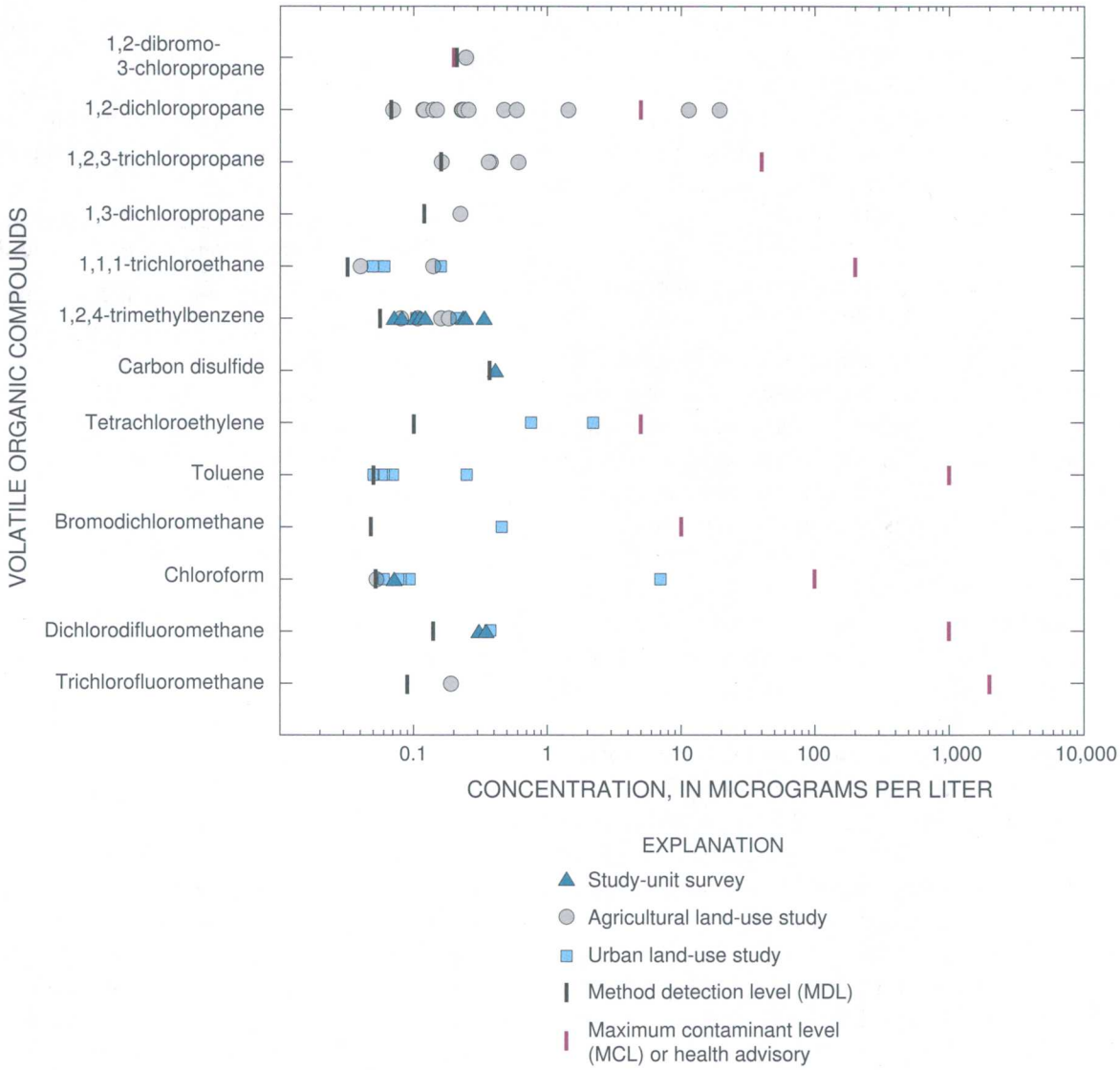

Figure 11. Concentrations of volatile organic compounds detected above their laboratory reporting levels in ground-water samples from the study-unit survey and agricultural and urban land-use studies.

among the 83 VOCs analyzed. Other fumigant-related compounds for which ground-water samples were analyzed include 1,2,3-trichloropropane and 1,3-dichloropropane, which were both present at low concentrations in formerly used fumigants containing 1,3-dichloropropene and 1,2-DCP as active ingredients (Zebarth and others, 1998).

Presence of Fumigant-Related Compounds in Ground Water

Methyl bromide and 1,3-dichloropropene, the two currently used active ingredients included in the analytical schedule, were not detected in any samples in the agricultural LUS. Of the historically used active ingredients, 1,2-DCP and DBCP were found, but EDB was not. 1,2-DCP was present in every sample where fumigant-related compounds were detected (fig. 10a) and was the most commonly detected compound both above its LRL and above 0.2 µg/L (fig. 10b). One or more fumigant-related compounds (1,2-DCP, DBCP, 1,3-dichloropropane, and 1,2,3-trichloropropane) were present in 73 percent of the samples.

Concentrations of fumigant-related compounds were low; 92 percent were less than 1 µg/L (fig. 11). However, concentrations of 1,2-DCP in two samples (9 percent) (19.4 µg/L and 11.4 µg/L) were greater than the MCL for drinking water of 5 µg/L, and four detections (18 percent) exceeded the 10^{-6} (one in a million) cancer risk health advisory of 0.6 µg/L for this compound. DBCP at a concentration of 0.245 µg/L in one sample violated the maximum contaminant level for drinking water of 0.2 µg/L (fig. 11).

Potential sources of 1,2-DCP include older fumigant formulations in which 1,2-DCP was an active ingredient and newer formulations in which 1,3-dichloropropene is the active ingredient and 1,2-DCP is an impurity. Concentrations of 1,2-DCP in fumigant formulations were once as high as 50 percent, although more typically about 15 percent (Cohen and others, 1983), but have decreased over the years to less than 0.1 percent (Zebarth and others, 1998). However, even at these low concentrations, 1,2-DCP concentrations in ground water in the part-per-billion level have been observed after application of fumigants (Knuteson and others, 1997). This suggests that the newer formulations also may be a source of 1,2-DCP in ground water. Grove and others (1998) also suggest that build-up of 1,2-DCP in the soil from historical applications of older formulations of fumigants containing 1,2-DCP is leaching to the ground water, providing an ongoing source of the fumigant. Newer fumigant formulations containing 1,3-dichloropropene as the active ingredient are still used in Washington State, but have not been sold in British Columbia since 1993 (Grove and others, 1998), although they are still registered for use.

Effects of Fumigant Applications on the Presence of Fumigant-Related Compounds in Ground Water

Because of the presence of 1,2-dichloropropane in many of the samples from the agricultural land-use study wells and the continued use of other fumigants over a vulnerable aquifer, the USGS conducted a study in cooperation with Whatcom County 1998 in the agricultural LUS area to determine the relation between the application of fumigants and the occurrence of fumigant-related compounds in ground water. Cumulative applications, from 1991 to 1997, of the active ingredients of fumigants applied within the study area were compared with detections of fumigant-related compounds in ground water.

Fumigant application data were obtained from the Washington State Department of Agriculture for the areas within boundaries shown in figures 12-14 (Cindy Moore, Washington State Department of Agriculture, written commun., 1998). Fumigants containing the active ingredients 1,3-dichloropropene, methyl bromide, chloropicrin, and metham sodium were applied in the area. Comparisons are made between (1) applications of metham sodium and detections of MITC (a transformation product of metham sodium); (2) applications of methyl bromide and detections of methyl bromide; (3) applications of fumigants containing the active ingredient 1,3-dichloropropene and detections of 1,3-dichloropropene and of 1,2-DCP (an impurity in this fumigant) (figs. 12-14). Data from the agricultural LUS wells, the 20 wells from the cooperative study, and the 15 wells sampled as part of a flow-path study (Tesoriero and others, 2000) were combined for a total of 57 wells to determine detections of fumigant-related compounds in ground water.

In the Washington portion of the study area, from 45 to 8,050 pounds of metham sodium as an active ingredient in fumigants were applied to quarter sections from 1991 to 1997 (fig. 12). Although metham sodium has been used regularly in the recent past and applications have been in the proximity of sample collection, there were no detections of MITC in the ground water. The lack of MITC detections in ground water could be caused, in part, by the rapid degradation of MITC in the soil. Reported half-lives of

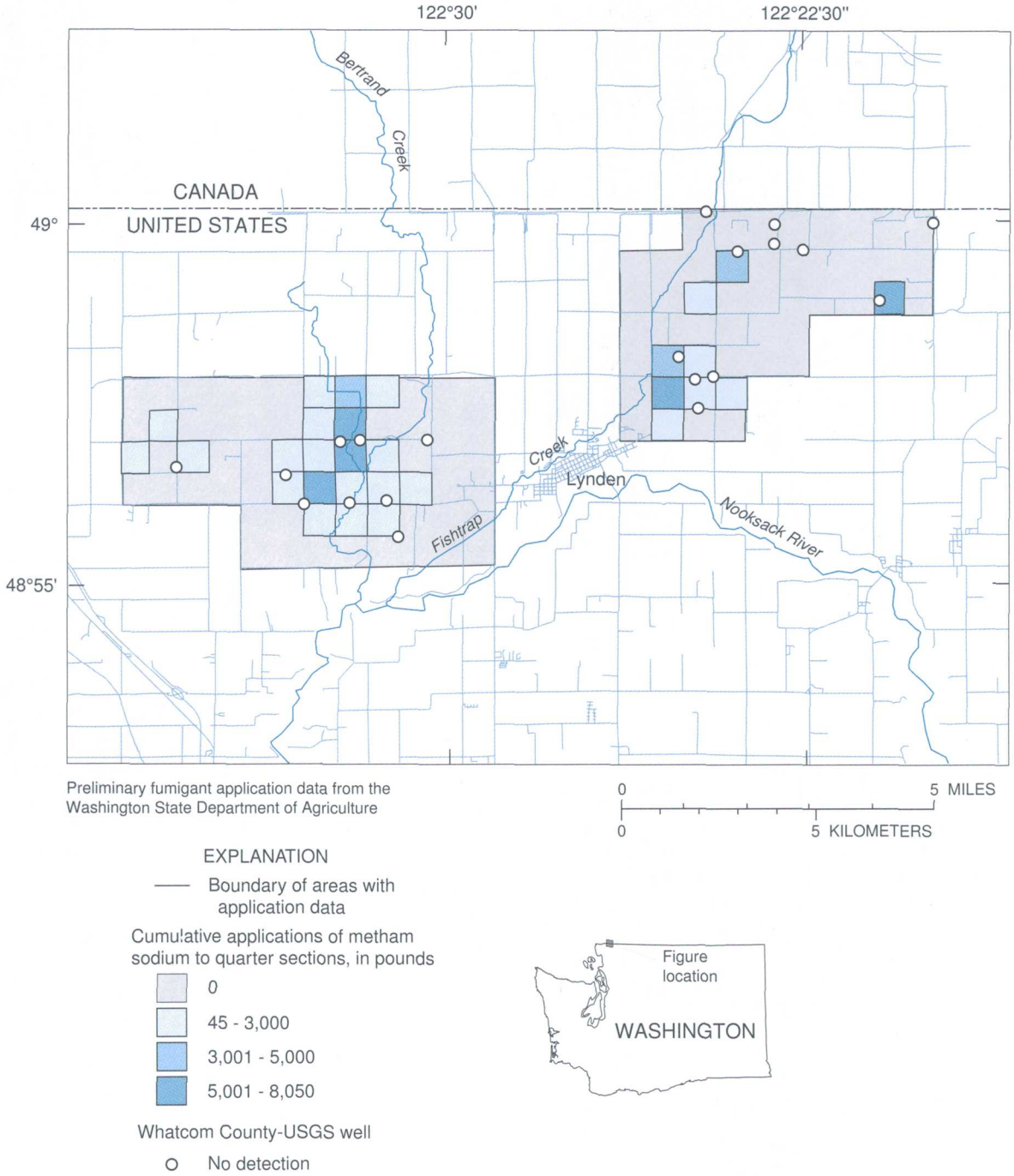

Figure 12. Well locations, cumulative applications of metham sodium as an active ingredient in fumigants from 1991 through 1997, and detections of methyl isothiocyanate (MITC) in ground water. MITC is a breakdown product of metham sodium.

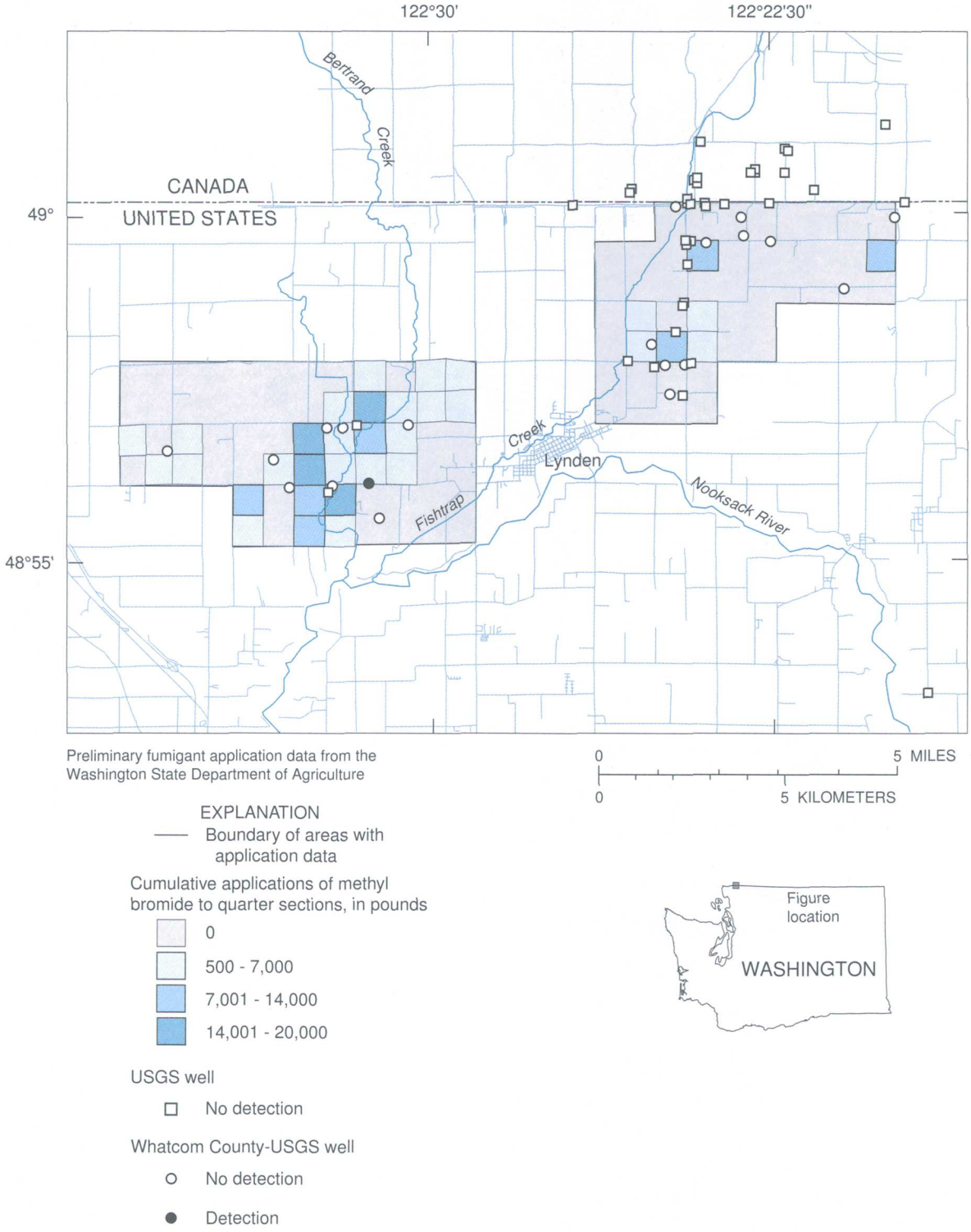

Figure 13. Well locations, cumulative applications of the fumigant methyl bromide from 1991 through 1997, and detections of methyl bromide in ground water

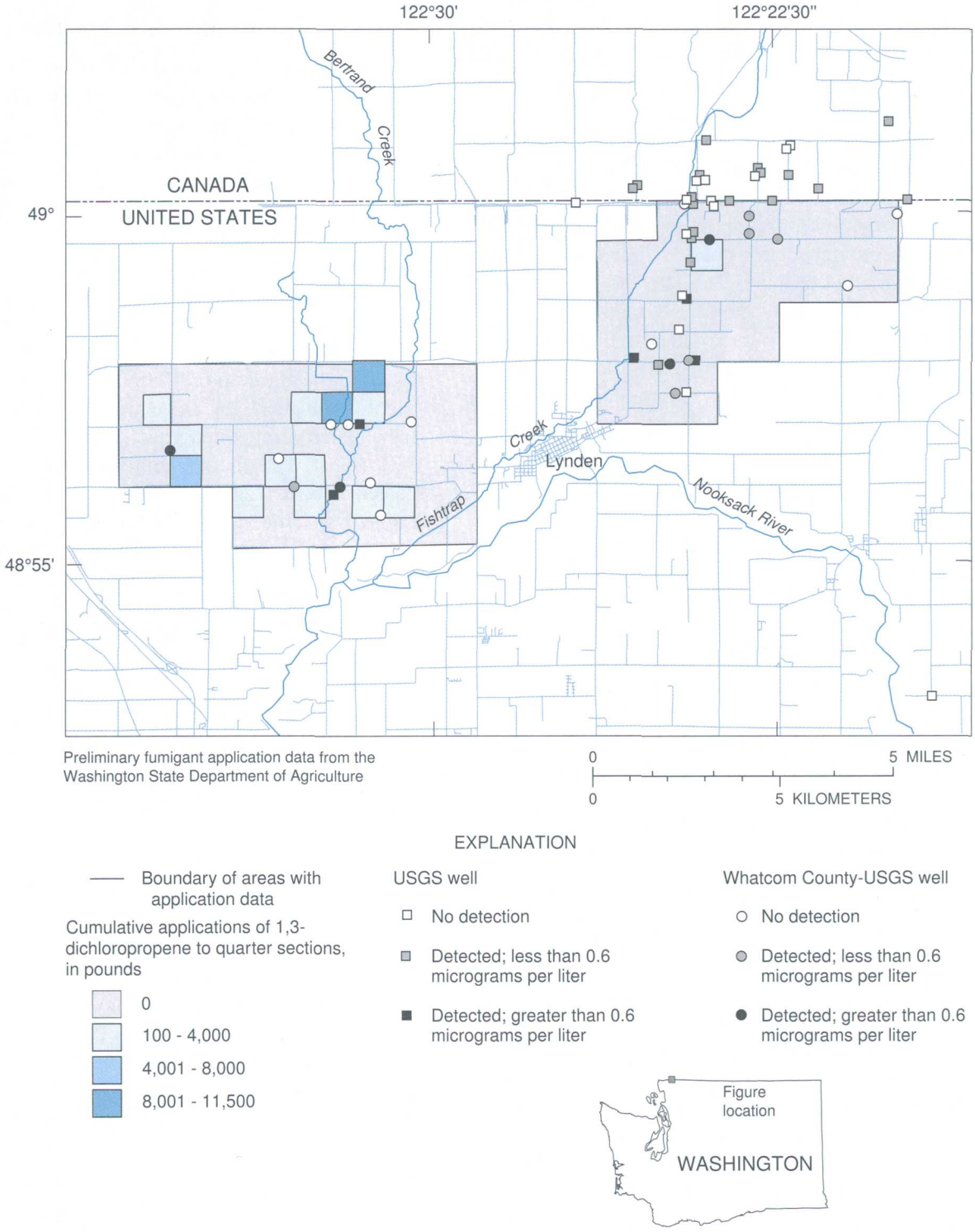

Figure 14. Well locations, cumulative applications of 1,3-dichloropropene as an active ingredient in fumigants from 1991-1997, and detections of 1,2-dichloropropane in ground water. 1,2-dichloropropane is a trace impurity in fumigant formulations containing 1,3-dichloropropene.

MITC are predominantly between 5 and 15 days, generally decreasing with increasing temperature and increasing clay and organic matter content in soil (Frick and others, 1998; Gan and others, 1999).

Methyl bromide was more heavily applied than metham sodium or 1,3-dichloropropene in this study area. From 1991 to 1997, approximately 500 to 20,000 pounds of methyl bromide (as active ingredient) were applied to quarter sections of the study area (fig. 13); however, methyl bromide was detected in only one ground-water sample. The lack of methyl bromide detections in ground water could be explained by rapid degradation and some volatilization after application (Wegman and others, 1981). Although it breaks down quickly and is not likely to be a long-term ground-water contaminant, use of methyl bromide is planned to be phased out completely by the year 2005 because it contributes significantly to the depletion of the stratospheric ozone layer (U.S. Environmental Protection Agency, 1996c).

Between 1991 and 1997, from 100 to 11,500 pounds of 1,3-dichloropropene as an active ingredient in fumigants were applied to quarter sections of the study area (fig. 14). Like MITC, 1,3-dichloropropene also was not detected in any ground-water samples and has been found to degrade quickly in the environment (for example, Zebarth and Szeto, 1999; Gan and others, 1999). The degradation of 1,3-dichloropropene was shown to increase with temperature and moisture content, both of which might be increased if tarping methods are used in the application of this fumigant (Gan and others, 1999).

As discussed previously, 1,2-dichloropropane is not currently applied as an active ingredient in a fumigant, although it is a trace contaminant in fumigants containing 1,3-dichloropropene. Unlike the other fumigants discussed in this section, however, 1,2-DCP was detected in 33 of 57 ground-water samples (58 percent) (fig. 14). Concentrations of 1,2-DCP ranged from 0.027 to 19.4 µg/L, with a median of 0.229 µg/L. The occurrence of 1,2-DCP does not seem to correlate with the areas of 1,3-dichloropropene application (fig. 14). The lack of relation between application and occurrence in ground water and the persistence of 1,2-DCP in soils (Zebarth and Szeto, 1999) suggest that the presence of 1,2-DCP is not related to current applications of fumigants and may be the result of applications prior to 1991.

Solvents and Fuel-Related Compounds

Only two solvent and fuel-related compounds were detected above the LRL in samples from the SUS (fig. 10a). 1,2,4-trimethylbenzene (1,2,4-TMB) and carbon disulfide were detected in 30 percent (9 detections) and three percent (1 detection) of the samples from the SUS, respectively. 1,2,4-TMB is commonly found in gasoline, but did not occur together with other gasoline-related compounds such as toluene or benzene. Carbon disulfide, which was detected in the SUS in a well located in the agricultural LUS area, is used as a solvent.

In the agricultural LUS, 1,2,4-TMB and 1,1,1-trichloroethane (1,1,1-TCA) were the only solvent and fuel-related compounds detected above their respective LRL (fig. 10a), although neither compound was detected above 0.2 µg/L (fig. 10b). In addition to being found in gasoline, 1,2,4-TMB is also an inert ingredient in some pesticides, such as bifenthrin, that are used on raspberries throughout Washington (Information Ventures, 1995) (Table 10). Other uses of 1,1,1-TCA include degreasing of metal parts in repair shops and in electronic manufacturing (Pankow and Cherry, 1996).

Use of methyl *tert*-butyl ether (MTBE), an oxygenate added to gasoline to reduce emissions from vehicles, has been discontinued in some states because it has contaminated ground-water resources (Squillace and others, 1996). MTBE is highly soluble in water and can be easily transported to ground water from road-surface runoff or from precipitation in areas where MTBE is present in the air (Squillace and others, 1996). MTBE was detected in four samples from the agricultural LUS, although all were below the LRL of 0.17 µg/L. Concentrations of MTBE in the agricultural LUS study area ranged from 0.05 to 0.12 µg/L. Three samples with MTBE detections were from British Columbia near the U.S.-Canadian border, with one detection in Washington. While MTBE has never been used in Washington as part of a program to reduce CO_2 emissions from cars, it has been used to increase octane in gasoline (Washington State Department of Ecology, 2000). Another possible source of MTBE is British Columbia, where MTBE is used in gasoline (Duncan Ferguson, BC Environment, oral commun., June 1999).

The urban LUS had the most solvents and fuel-related compounds detected (four) of the SUS and two LUSs, which is not surprising as many of the activities associated with these compounds tend to be urban related (fig. 10a). Tetrachloroethylene was the most commonly detected above 0.2 µg/L, followed by toluene and 1,2,4-TMB (fig. 10b). Sources of tetrachloroethylene include dry cleaning. 1,2,4-TMB and toluene are both possibly fuel-related, but other sources for toluene include paint strippers, lacquers, adhesives, and antifreeze (Pankow and Cherry, 1996).

Trihalomethanes

Chloroform was detected in all three studies, although at very low concentrations (fig. 10a); only one sample from the urban LUS showed detections above 0.2 µg/L. Bromodichloromethane was detected in only one sample from the urban LUS above the LRL.

Chloroform is used as a solvent in industry and is also formed during the chlorination of drinking water supplies (Minear and Amy, 1995). Potential sources of chloroform to ground water include releases from industry, leaking water-supply lines or septic tanks that contain chlorinated water, and lawn sprinklers. Bromodichloromethane is also formed during the chlorination of drinking water when bromine is naturally available (Rathbun, 1996). It is unusual for bromodichloromethane to be formed naturally, so its presence in one sample above the LRL and in two samples below the LRL suggests that at least some portion of the chloroform found in ground-water samples could be from recharge of chlorinated water.

Refrigerants

Refrigerants are used in cooling systems in the home, in automobiles, and in industry. Two detections of dichlorodifluoromethane occurred in the SUS and one in the urban LUS. Trichlorofluoromethane was detected in one agricultural LUS sample. Refrigeration units used to preserve raspberries were a suggested source of trichlorofluoromethane in another study conducted in the vicinity of the agricultural LUS (British Columbia Ministry of Health and Ministry Responsible for Seniors, 1995).

Radon

Radon is a gas produced by the decay of the parent radioactive element Uranium-238 (Hem, 1989), and it occurs naturally in rocks, ground water, and air. Radon in ground water is a concern because breathing radon in indoor air can cause lung cancer. The primary source of radon in indoor air is soil underneath a home, although water can also be a source. The median concentration of radon in 30 SUS wells was 290 picocuries per liter (pCi/L), with values ranging from 100-860 pCi/L. These radon values are similar to those in other ground-water studies in other parts of the country (Wanty and Nordstrom, 1993). Forty-seven percent of the radon values were greater than the proposed MCL for radon in drinking water of 300 pCi/L, a standard proposed for water systems supplying areas that have not adopted a program to reduce the amount of radon entering houses through the soil (U.S. Environmental Protection Agency, 1999). No radon values were greater than the alternative maximum contaminant level (AMCL) of 4,000 pCi/L, a standard proposed for water systems supplying areas with programs to prevent radon from entering houses through the soil (U.S. Environmental Protection Agency, 1999).

Radon concentrations in ground water from 17 urban LUS wells ranged from 160 to 630 pCi/L, with a median concentration of 385 pCi/L. Sixty-five percent (11 samples) of the samples from the urban LUS had radon concentrations that exceeded the proposed MCL of 300 pCi/L; no samples had concentrations of radon that exceeded the AMCL of 4,000 pCi/L.

SUMMARY AND CONCLUSIONS

Three ground-water studies, a study-unit survey, an agricultural land-use study, and an urban land-use study, were conducted in the Puget Sound Basin, Washington and British Columbia from 1996 to 1998 as part of the NAWQA program. The purpose of these studies was to characterize the current quality of ground water in shallow, unconfined glacial aquifers (referred to collectively as the Fraser aquifer) and to determine any

relations between water quality, land use, and natural and anthropogenic factors. The SUS was a regional assessment of water quality in the Puget Sound and was conducted in 1996. Thirty domestic wells were randomly selected throughout the Puget Sound Basin based on surficial geology, well construction, and site suitability. The agricultural LUS was conducted in the years 1997 and early 1998. Twenty-two wells were installed or selected by Puget Sound NAWQA downgradient from raspberry fields overlying a shallow, unconfined aquifer in Whatcom County. The urban LUS was conducted from 1996 to 1998. Twenty-seven wells were installed by the Puget Sound NAWQA in generally post-1970, urban residential areas of Pierce and Thurston Counties.

An additional study was conducted in cooperation with Whatcom County in the agricultural LUS using 20 domestic wells near raspberry fields. Data from these wells, the agricultural LUS wells, and wells used for a flowpath study were used to assess possible relations between applications of fumigants and the occurrence of fumigant-related compounds in ground water.

Ground-water samples for the SUS and two LUS were analyzed for nutrients, pesticides, volatile organic compounds, dissolved organic carbon, and major ions; however, dissolved organic carbon and major ion data are not summarized in this report but are used to supplement the analysis of other constituents. All study-unit survey wells were also sampled for radon, and some urban land-use study wells were sampled for radon and oxygen and nitrogen isotopes. Ground-water samples for the joint study with Whatcom County were sampled for VOCs and MITC, a degradation product of the fumigant metham sodium. The flowpath study wells were analyzed for VOCs.

Results from the SUS showed that regional quality of the Fraser aquifer was generally good, although somewhat affected by land-use activities as indicated by the presence of pesticides and VOCs. Nitrate concentrations were generally low, with a median concentration of 1.0 mg/L. One concentration of nitrate (12.0 mg/L) was above the USEPA MCL of 10 mg/L for drinking water. Pesticides were detected in 20 percent of the samples from the SUS at very low concentrations; only prometon and diuron were found at a concentration above 0.01 microgram per liter (µg/L). Volatile organic compounds were detected in 40 percent of the samples from the SUS. 1,2,4-trimethylbenzene was the most commonly detected compound above 0.2 µg/L. No VOCs or pesticides were detected above drinking-water standards or guidelines in samples from the SUS. Radon, which is naturally occurring, was detected in all study-unit survey samples, ranging from 100 to 860 piCi/L. Forty-seven percent of the detections exceeded the proposed MCL for drinking water of 300 pCi/L, but no detections of radon exceeded the alternative MCL of 4,000 pCi/L.

Elevated nitrate concentrations and prevalent detections of pesticides and VOCs in the agricultural LUS indicate a more intense anthropogenic impact on the quality of ground water than is shown in the SUS. Nitrate concentrations exceeded the USEPA MCL for drinking water in 64 percent of the agricultural land-use samples (median of 12.9 mg/L; maximum of 36 mg/L). Sources of nitrate in the agricultural land-use study area have been identified by previous studies and are mainly animal manure and inorganic fertilizers applied to crops in an area of highly permeable soils and a shallow water table. Concentrations of nitrite, ammonia, ammonia plus organic nitrogen, phosphorus, and orthophosphorus were generally low and were not related to either natural or anthropogenic factors.

At least one pesticide compound was detected in 77 percent of the agricultural LUS wells. The high frequency of pesticide detections in the agricultural LUS compared with the other studies is likely the result of different usage practices, higher application rates than in urban areas, and the shallow depth to ground water in the agricultural land-use study area. The most commonly detected pesticides above the laboratory reporting limit were oxamyl, atrazine, and simazine. No pesticide concentrations exceeded any drinking-water standards or guidelines.

Based on pesticide use surveys in 1995 and 1997 for Washington State and on recommendations for pesticide use in British Columbia, the most commonly detected pesticides in samples from the agricultural LUS were known to be used in Washington or were likely used in British Columbia on crops, mainly raspberries and corn, that are also grown in the agricultural LUS area.

At least one VOC compound was detected above the laboratory reporting limit in 82 percent of the agricultural LUS samples. The high frequency of VOC detections in the agricultural LUS was likely because of the applications of fumigants in the study area. Fumigant-related compounds comprised 73 percent of all VOC detections in samples from the agricultural

LUS. 1,2-dichloropropane was the most commonly detected VOC, present in 73 percent of the samples. Two concentrations of 1,2-dichloropropane and one concentration of 1,2-dibromo-3-chloropropane were greater than the USEPA MCLs for these compounds (5 µg/L, and 0.2 µg/L, respectively). Solvents and fuel-related compounds were the second most commonly detected group of VOCs in the agricultural LUS, consisting mostly of 1,2,4-trimethylbenzene, which is also found in some pesticides likely used in the vicinity of the agricultural LUS.

Relations between fumigant applications and the presence of fumigants in ground water in the agricultural land-use study area were investigated by combining data from the agricultural land-use study, a fumigant study conducted in cooperation with Whatcom County, and a flowpath study. Cumulative applications of metham sodium, methyl bromide, and 1,3-dichloropropene during the period 1991 to 1997 were compared to detections of methyl isothiocyanate (MITC), methyl bromide, and 1,3-dichloropropene and 1,2-DCP, respectively.

No relation between fumigant applications and detections of fumigant-related compounds was observed. MITC and 1,3-dichloropropene were not detected in any samples, and methyl bromide was detected only once, all possibly due to the rapid degradation or volatilization of the fumigant or parent compound in the environment. 1,2-DCP, used as a fumigant in the past and found in trace amounts in fumigants containing 1,3-dichloropropene, was detected in 58 percent of the samples, although most of the detections were not near known recent applications of 1,3-dichloropropene. This may indicate that most of the detections of 1,2-DCP are from fumigant applications prior to 1991.

In the urban land-use study, nitrate concentrations in ground-water samples were significantly higher than background nitrate concentrations from SUS samples, indicating effects of nitrate sources on ground-water quality in urban areas. Ground-water chemistry was compared between sewered and unsewered areas to determine if septic systems were a source of nitrate. Nitrate concentrations in sewered and unsewered areas were not statistically different, indicating septic systems do not have a significant effect on nitrate in ground water overall. However, chloride concentrations and isotopic ratios of nitrate nitrogen were significantly different between sewered and unsewered areas, indicating that septic system effluent is indeed mixing with ground water. When chloride concentrations were used to compute percentages of septic system effluent mixing with ground water, an average of 46 percent of nitrate in ground water in unsewered areas was estimated to be from septic systems. The central problem of why there is no difference between nitrate concentrations in sewered and unsewered areas remains unresolved other than to acknowledge that sources of nitrate are highly variable in the urban LUS area. Concentrations of nitrite, ammonia, ammonia plus organic nitrogen, phosphorus, and orthophosphorus in samples from the urban LUS were generally low.

Pesticides were detected in 14 percent of the samples from the urban LUS and were generally the same compounds detected in samples from the SUS. The similarity in detected compounds and overall detection frequency between samples from the SUS and urban LUS could indicate that pesticides detected in samples from the urban LUS are from more general pesticide use, and not necessarily related to residential uses. Most pesticides detected in the urban LUS were not sold in retail outlets indicating that homeowners were probably not using pesticides detected in the urban LUS, but rather commercial applicators or government agencies for maintaining roadsides, highways, and rights-of-way. No pesticide concentrations exceeded any drinking-water standards or guidelines.

Volatile organic compounds were detected in 48 percent of the samples from the urban LUS. Solvents and fuel-related compounds (i.e. toluene, tetrachloroethane, and 1,1,1-trichloroethane), comprised 62 percent of all VOC detections in samples from the urban LUS. These compounds are more likely to be found in urban areas as they are usually related to sources more often found in urban areas, such as dry cleaning, degreasers in auto repair shops, and fuel. No VOCs were detected in the urban LUS at concentrations above any drinking-water standards or guidelines.

Radon concentrations in ground water from 17 urban LUS wells ranged from 160 to 630 pCi/L, with a median concentration of 385 pCi/L. Sixty-five percent (11 samples) of the samples from the urban LUS had radon concentrations that exceeded the proposed MCL of 300 pCi/L; none exceeded the alternative MCL of 4,000 pCi/L.

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APPENDIX

QUALITY CONTROL DATA

Quality control data collected to evaluate the quality of the chemical data collected for the study-unit survey and LUS, followed the design described by Koterba and others (1995). Blank samples were used to measure possible contamination or bias; replicate samples were used to measure variability; surrogates were added to each pesticide or VOC environmental sample to facilitate evaluation of method performance; and field-matrix-spike samples were used to measure bias of the recovery of VOC and pesticide analytes.

Four different types of blanks were collected for the SUS and two LUSs. Equipment blanks were collected for the urban and agricultural LUSs to determine whether cleaning procedures were adequate to eliminate contamination. The equipment blanks were collected at the District Field Services Unit before and sometimes after a sampling trip by running blank water (water free of the analyte of interest) through the sampling equipment in the same manner as an environmental sample. Field blanks were collected for each study to determine if sample collection procedures introduced any contamination to the sample. Using blank water and standard sample collection protocols, field blanks were collected on-site after the environmental sample had been collected and all sampling equipment was cleaned. Trip blanks, sealed sampling bottles containing analyte-free water, were taken to a sample site and then sent to the NWQL for analysis. Trip blanks measure whether contamination occurs during the transport of the samples. Source solution blanks, blank water poured directly into a sample bottle, test the water used for blanks.

Replicate samples were collected at the same time as the environmental samples and were used to measure variability. Field-matrix spikes are environmental samples to which are added known concentrations of VOCs and pesticides that are included in the analyte schedules for the environmental samples. Analytical results are compared with the expected concentrations to determine percent recoveries and whether the recoveries are biased.

Surrogate samples are environmental samples to which known concentrations of pesticides or VOCs are added. The surrogate compounds are compounds that would not be expected in the environment, but that have chemical behavior similar to analytes included in regular pesticide and VOC schedules.

Nutrients

Seven blanks and four replicate pairs were analyzed for ammonia, ammonia plus organic nitrogen, nitrite, nitrite plus nitrate, orthophosphorus, and phosphorus (App. table 2). Blank samples included one equipment blank and six field blanks.

Phosphorus and nitrite were each detected once in separate field blanks (App. table 2). Both phosphorus and nitrite were present in the blanks at concentrations similar to those of the environmental samples. However, contamination was not systematic, and the concentrations in question did not affect interpretation, so the data were not modified.

Three detections of nitrate in two field blanks and one equipment blank (0.05-0.06 mg/L) were much lower than the associated environmental samples (3.7-4.85 mg/L); thus the environmental values for nitrate were considered to be uncontaminated.

Ammonia was detected in three field blanks, all at 0.02 mg/L (App. table 2). Two of the associated environmental samples were of equal concentration, and one environmental sample did not have detectable concentrations of ammonia. Ammonia concentrations in samples from the SUS may have some low-level contamination as many of the environmental samples had concentrations similar to detected blank concentrations taken during the same time period (table 7, App. table 2). This amount of contamination did not affect interpretations made in this report. As such, the data were not modified.

Orthophosphorus was detected in three field blanks with concentrations ranging from 0.01-0.033 mg/L (App. table 2). These concentrations were similar to concentrations in the associated environmental samples from the SUS and agricultural LUS, which ranged from 0.02-0.116 mg/L. Low-level contamination (<0.03 mg/L) of some environmental samples from the SUS and agricultural LUS may have occurred. This amount of contamination did not affect interpretations made in this report. As such, the data were not modified.

All of the nitrogen species of nutrients showed a 5 percent or less difference between environmental and replicate samples (App. table 3). One orthophosphorus replicate and three phosphorus replicates had relatively large relative percent differences, although these differences were near the reporting level where greater analytical variability is expected and may account for some of the difference. Environmental

detections near the method reporting level for phosphorus may show some variability of 0.01-0.02 mg/L, but these differences did not affect interpretation of the data. No changes were made to the data based on these results.

Dissolved Organic Carbon

A total of 4 replicate samples and 15 blanks, (7 field blanks, 1 equipment blank, and 7 source-solution blanks) were collected for dissolved organic carbon (DOC) (App. table 2). Over half of the field blanks had detections of DOC, ranging from 0.1-0.4 mg/L (App. table 2). Many of these detections, however, could be attributed to contamination in the source solution. Four of the seven source-solution blanks had detections ranging from 0.1-0.2 mg/L. Based on the prevalence of DOC in source-solution blanks at a level similar to that in the field and equipment blanks, the DOC environmental detections were considered to be uncontaminated. Relative percent differences of replicate samples for DOC were 0 and 22 percent (App. table 3).

Pesticides

Seven field blanks and six field-matrix spikes were collected for pesticides among the three studies. No pesticides were detected in any blanks, indicating that samples were not contaminated during sample collection and analysis. Six field-matrix-spike replicates were collected for pesticides to assess the bias of analytical recovery of these compounds (App. table 4).

Mean recoveries of pesticides ranged from 36 to 164 percent. In general, mean recoveries for the HPLC/DAD method (80 percent) were lower than mean recoveries for the GC/MS method (102 percent). Rose and Schroeder (1995) suggested a mean recovery of 60 percent for volatile organic compounds as an acceptable lower limit. Applying this standard to pesticides, five compounds, aldicarb, chloramben, clopyralid, chlorothalonil and *cis*-permethrin, had mean recoveries that were lower than 60 percent, ranging from 36 to 56 percent (App. table 4). Analyses of these compounds may show more false negatives than true concentrations show. No changes were made to the data based on these recoveries as none of these analytes was detected in the environmental samples.

Percent recoveries for carbaryl (164 percent) and carbofuran (151 percent) using the GC/MS method were much higher than for the HPLC/DAD method (carbaryl, 89 percent; carbofuran 95 percent) and also showed considerable variability (App. table 4). Carbaryl and carbofuran are reported with an "estimated" code for the GC/MS method (table 3) because of their variable performance related to GC injection port breakdown for these compounds (Zaugg and others, 1995). Carbofuran was detected in environmental samples using the GC/MS method, and concentrations may be overestimated. Carbaryl was not detected in environmental samples.

Surrogate compounds for the GC/MS method were diazinon-d_{10}, alpha-HCH-d_6, and terbuthylazine. BDMC was the only surrogate compound for the HPLC/DAD method. Surrogate recoveries for *alpha*-HCH-d_6 and diazinon-d_{10} seemed reasonable; both had medians near 100 percent, and only one sample for each analyte showed poor recovery (46 and 49 percent, respectively) (App. table 5). Percent recoveries for terbuthylazine were high; percent recoveries ranged from 51 to 163, with a median of 111. Percent recoveries for BDMC were also within reason, ranging from 76 to 113 with a median of 96.

Volatile Organic Compounds

Seventeen blanks and six field-spike replicates were collected for volatile organic compounds for the SUS and two LUSs. Blanks included one trip blank, three equipment blanks, four source-solution blanks, and nine field blanks.

Detections of VOCs in the source-solution blanks were compared with VOC detections in equipment and field blanks and environmental samples to determine whether contamination was a result of the blank water or of the sample-collection procedures. In August, 1997, the NWQL began purging the blank water with nitrogen gas (N_2) to remove as many VOCs from the water as possible. Of the four source-solution blanks, the two source-solution blanks that used non-N_2 purged water had a total of nine VOC detections, whereas the source-solution blanks that used N_2-purged water had only two detections. The more frequent detections of VOCs in the nonpurged blank water suggest that detections in equipment and field blanks could be due to the blank water and may not be the result of contamination.

Only one compound, acetone, was detected in the trip blank, indicating that the transport of samples generally did not introduce contaminants. The equipment blanks had several VOC detections at low levels; however, many of the same compounds were also detected in the associated source-solution blank at concentrations similar to those in the equipment blank. All of the field blanks had at least one VOC detection; 23 different VOCs were detected altogether (Apps. tables 6, 7). However, only eight of these compounds (1,2,4-trimethylbenzene, chloroform, Freon 113, *m,p*-xylene, methyl chloride, *o*-xylene, tetrachloroethylene, and toluene) were detected in both the field blank and associated environmental sample, possibly indicating contamination of the environmental sample. As such, these results were examined further to determine whether or not the environmental sample might have been contaminated and if the environmental value should be removed from the data set.

Several criteria were used for determining whether or not an environmental detection was contaminated: (1) there is direct evidence of contamination, (2) the field blank concentration was significant compared to the environmental sample concentration (10 percent or more), and (3) the contamination was understood well enough to interpret the environmental data, which usually includes showing that the contamination was systematic and that the source and magnitude of contamination can be identified (U.S. Geological Survey, 1997).

Using these guidelines, some detections of the following compounds were considered to be the result of contamination (the number of contaminated samples removed from the data set are shown in parentheses): 1,2,4-trimethylbenzene (5), Freon 113 (34; all detections), ethylbenzene (4), *m,p*-xylene (4), *o*-xylene (4), toluene (4). In addition, four detections of benzene were censored in the same samples for which ethylbenzene, *m,p*-xylene, *o*-xylene, and toluene were censored because of suspected contamination as they are all found in fuel and all the compounds tend to occur together. None of the contaminated samples of the above named compounds were used in interpretations made for this report, nor were they included in any summary tables or graphical representations of the data shown in this report. Calculations of detection frequency did not include contaminated samples as either detections or nondetections.

Although only 8 of the 23 compounds detected in blanks had detections that were censored in environmental samples, there were many low-level detections of many compounds in blanks. Because of the uncertainty of low-level detections throughout the data set, only compounds with detections above the LRL are discussed in this report. A complete set of data with all VOC detections can be obtained from the Puget Sound NAWQA web site at URL

http://wa.water.usgs.gov/ps.nawqa.html.

Three comprehensive field-matrix spikes (92 analytes) and three abbreviated field-matrix spikes (13 analytes) were collected to determine the analytical recoveries for the VOCs (App. table 4). Overall, the recoveries were biased low with a mean percent recovery of 76 for all VOC field-matrix spikes. Chloroethane, *m,p*-xylene, and 2,2-dichloropropane were the only analytes whose recoveries were below 60 percent, the suggested suitable level for analyte recovery for an earlier VOC method (Rose and Schroeder, 1995). A low bias to the recoveries could indicate that VOC concentrations in the ground water are higher than the measured concentrations and that detection frequencies of some VOCs may be underestimated.

Compounds used as surrogates for the VOC schedule were 1,2-dichloroethane-d_4, 1,4-bromofluorobenzene, and toluene-d_8. Percent recoveries for nearly all surrogate samples from the SUS and two LUS were within 86-124 percent, with medians from 96-106 percent (App. table 5). Only one sample of 1,4-bromofluorobenzene had an unusually low recovery (58 percent). These results indicate that the VOC analytical method was adequate for analysis (App. table 5).

Radon

Two sets of replicates were collected for radon and had differences of 10 and 13 percent from the associated environmental samples (App. table 3). This amount of variability seemed reasonable for a regional study.

Appendix Table 1. Summary of well construction data for wells from the study-unit survey and agricultural and urban land-use studies
[USGS, U.S. Geological Survey; ID, identification; NA, not available; --, no data]

USGS station ID	Local ID	Depth of well (feet)	Depth to top of casing (feet)[1]	Depth to bottom of casing (feet)	Depth to top of open interval (feet)	Depth to bottom of open interval (feet)
			Study-Unit Survey			
470414122513901	SU-02	72	1	67	67	72
465120122352201	SU-11	58	0	58	58	[2]--
464528122061501	SU-22	78	0	78	78	[2]--
470639122262101	SU-13	40	0	40	40	[2]--
470234122205501	SU-13A	38	0	38	38	[2]--
470422122135501	SU-14	99.5	-1	99.5	99.5	[2]--
465913122314001	SU-10	100	0	100	100	[2]--
475306122085801	SU-19	35	-1	24	24	29
475230121574201	SU-27	112	0	107	107	112
480655121511101	SU-28	186	0	182	182	186
485412122304001	SU-16	40	0	35	35	40
485932122241601	SU-17	29	0	24	24	29
474729122224801	SU-15	42	0	32	32	42
474120121553301	SU-25	75	-1	70	70	75
465927122492101	SU-01	68	0	62	62	64
470122122461601	SU-01A	65	0	60	60	65
474251122370401	SU-08	71	0	66	66	71
480541121573701	SU-18A	80	-2	75	75	80
475313121543701	SU-26	70	0	65	65	70
485930122431001	SU-07	98	2	98	98	[2]--
485703122394301	SU-07A	22.5	-1.5	17.5	17.5	22.5
481613121555001	SU-29	39	-2	39	39	[2]--
471916122064301	SU-20	60	0	60	60	[2]--
472244122031801	SU-24	38	0	38	38	[2]--
472822122494501	SU-04	63	0	58	58	63
472046122423501	SU-09	80	0	75.5	75.5	80
480638122125101	SU-18	71	0	71	71	[2]--
465532122232001	SU-12A	78	1.5	78	78	[2]--
470345122100701	SU-21	40	0	40	40	[2]--
470701122225401	SU-14A	57	0	53	53	57
			Agricultural Land-Use Study			
490011122193201	ABB4	96	-1.8	92.7	92.7	96
490023122253002	91-15	32	0	27	27	32
490020122213201	ABB2	25	-1.54	21.7	21.7	25
490031122225301	BC-B-20	20	0	12	12	20
490009122233101	ABB5	29	-1.18	25.7	25.7	29
485700122313401	AG-01	48	-1	43	43	48
485607122321401	AG-02	41	0	35	35	41
490012122240001	FT7-22	22	NA	NA	NA	NA
490101122221501	BC-A-25	25	0	16	16	24
490031122221501	BC-C-25	25	-1.2	15	15	23

Appendix Table 1. Summary of well construction data for wells from the study-unit survey and agricultural and urban land-use studies--Continued

USGS station ID	Local ID	Depth of well (feet)	Depth to top of casing (feet)	Depth to bottom of casing (feet)	Depth to top of open interval (feet)	Depth to bottom of open interval (feet)
490042122241001	ABB1	26	-1.05	22.7	22.7	26
485917122241901	AG-06	28	0	18	18	23
485751122241601	AG-04	30	0	25	25	30
485303122190901	AG-03	29	0	24	24	29
485755122253901	AG-05	28	0	18	18	23
490010122223101	AG-08	39	0	29	29	34
490009122265001	AG-09	24	0	14	14	19
490117122195901	AG-10	53	0	48	48	53
490103122240301	AG-12	37	0	27	27	32
490009122242002	AG-07	19	-1.5	11	11	14
485817122244701	AG-13	18	6	13	13	18
485749122250301	AG-15	32	0	27	27	32
			Urban Land-Use Study			
471133122335501	UR-36	97	0	92	92	97
470732122252801	UR-32	41.4	0	36.4	36.4	41.4
470135122514001	UR-06	39	0	34	34	39
470046122522301	UR-08	58	0	53	53	58
465958122481001	UR-05	48	0	43	43	48
470005122502301	UR-11	57	0	52	52	57
470045122463801	UR-02	48	0	43	43	48
470343122504501	UR-09	48	0	43	43	48
470112122493501	UR-07	29	0	24	24	29
470208122223501	UR-37	22	0	17	17	22
470135122202501	UR-21	42	0	37	37	42
470040122463601	UR-01	24	0	19	19	24
470035122444601	UR-12	51	0	46	46	51
470228122441701	UR-10	27	0	22	22	27
470306122450301	UR-14	25	0	20	20	25
470958122154301	UR-34	33	0	28	28	33
471018122143302	UR-35B	52	0	47	47	52
470330122462501	UR-15	46	0	36	36	46
470110122484201	UR-04A	67	0	62	62	67
470720122162102	UR-29B	87	0	82	82	87
470644122160801	UR-30	27	0	17	17	27
470240122214501	UR-24	47	0	37	37	42
470230122203001	UR-25	37	0	32	32	37
470328122215501	UR-23	47	0	39	39	44
470705122230501	UR-26	37	0	27	27	32
470330122181501	UR-31	76	0	71	71	76
470710122193001	UR-27	137	0	46	46	51

[1] A negative number means the top of casing is above land surface.
[2] Casing extends the full length of the well and is finished with an open end.

Appendix Table 2. Summary of nutrient, major ion, and dissolved organic carbon detections in field, equipment, and source-solution blanks
[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; ND, not detected]

Compound or element	Number of detections	Number of blanks	Median concentration (mg/L unless noted)	Range or concentration in single sample (mg/L unless noted)
FIELD AND EQUIPMENT BLANKS				
Nutrients				
Ammonia	3	7	<0.015	0.02-0.02
Ammonia and organic nitrogen	0	7	ND	ND
Nitrite plus nitrate	2	7	<0.05	0.05-0.06
Nitrite	1	7	<0.01	0.01
Orthophosphorus	3	7	<0.01	0.01-0.033
Phosphorus	1	7	<0.01	0.022
Major Ions				
Bromide	0	8	ND	ND
Calcium	1	8	<0.020	0.034
Chloride	0	8	ND	ND
Fluoride	0	8	ND	ND
Iron (µg/L)	0	8	ND	ND
Magnesium	0	8	ND	ND
Manganese (µg/L)	0	8	ND	ND
Potassium	0	8	ND	ND
Silica	3	8	0.03	0.017-0.04
Sodium	0	8	ND	ND
Sulfate	0	8	ND	ND
Other				
Dissolved organic carbon	5	8	0.15	0.1-0.4
SOURCE-SOLUTION BLANKS				
Dissolved organic carbon	4	7	0.10	0.1-0.2

Appendix Table 3. Concentrations and precision data for samples of nutrients, major ions, dissolved organic carbon, and radon from the study-unit survey and agricultural and urban land-use studies
[mg/L, milligrams per liter; µg/L, micrograms per liter; pCi/L, picocuries per liter; >, greater than; <, less than; nc, not computed]

Compound or element	Environmental concentration (mg/L unless noted)	Replicate concentration (mg/L unless noted)	Relative percent difference
	Nutrients		
Ammonia	0.02	0.02	0
	<0.015	<0.015	0
	<0.015	<0.015	0
	0.02	0.02	0
Ammonia plus organic nitrogen	<0.2	<0.2	0
	<0.2	<0.2	0
	<0.2	<0.2	0
	<0.2	<0.2	0
Nitrite	0.01	0.01	0
	<0.01	<0.01	0
	<0.01	<0.01	0
	<0.01	<0.01	0
Nitrite plus nitrate	0.90	0.95	5
	3.27	3.225	1
	3.8	3.8	0
	1	1	0
Orthophosphorus	<0.01	0.03	>100
	0.014	0.014	0
	0.03	0.03	0
	0.03	0.03	0
Phosphorus	<0.01	0.01	<100
	<0.01	<0.01	0
	0.02	0.01	67
	<0.01	0.03	>100
	Major ions		
Bromide	0.01	0.01	0
	0.03	0.03	0
	0.21	0.21	0
	0.023	0.021	9
Calcium	27	26	4
	6	6	0
	27	29	7
	12.05	12.13	1
Chloride	2.1	2.1	0
	5	5	0
	7.7	8.7	12
	3.24	3.25	0
Fluoride	<0.1	<0.1	nc
	<0.1	<0.1	nc
	<0.1	<0.1	nc
	<0.1	<0.1	nc

Appendix Table 3. Concentrations and precision data for samples of nutrients, major ions, dissolved organic carbon, and radon from the study-unit survey and agricultural and urban land-use studies--Continued

Compound or element	Environmental concentration (mg/L unless noted)	Replicate concentration (mg/L unless noted)	Relative percent difference
Iron (µg/L)	43	33	26
	<3	<3	nc
	<3	<3	nc
	<3	<3	nc
Magnesium	6.8	6.6	3
	17	17	0
	12	12	0
	5.08	5.05	1
Manganese (µg/L)	8	7	13
	<1	<1	nc
	11	12	9
	104.26	103.35	1
Potassium	0.8	0.8	0
	2.2	2.2	0
	0.9	0.9	0
	1.22	1.2	2
Silica	19	18	5
	43	43	0
	38	40	5
	27.73	27.60	1
Sodium	3.3	3.3	0
	5.2	5.2	0
	12	12	0
	10.82	10.84	0
Sulfate	3.6	3.6	0
	3.8	3.8	0
	13	13	0
	8.88	8.56	4
	Other		
Dissolved Organic Carbon	0.8	0.8	0
	0.4	0.5	22
	0.4	0.5	22
	0.2	0.2	0
Radon 222 Total (pCi/L)	220	200	10
	150	170	13

Appendix Table 4. Mean recoveries from field-matrix spikes of pesticide and volatile organic compounds

Compound	Number of samples	Mean recovery (percent)	Relative standard deviation of recoveries (percent)
		PESTICIDES	
		High-Performance Liquid Chromatography Analytical Method	
2,4,5-T	12	81	6
2,4-D	12	95	11
2,4-DB	12	90	17
3-Hydroxycarbofuran	12	120	14
4,6-Dinitro-2-methylphenol	12	68	17
Acifluorfen	12	98	13
Aldicarb	9	39	22
Bentazon	12	80	13
Bromoxynil	12	93	10
Carbaryl	12	89	10
Carbofuran	12	95	16
Chlorfamben	10	36	1
Chlorothalonil	12	42	26
Clopyralid	12	56	33
Dacthal monoacid	12	93	8
Dicamba	12	73	15
Dichlobenil	12	60	35
Dichlorprop	12	93	10
Dinoseb	12	91	12
Diuron	12	84	8
Fenuron	12	92	8
Fluometuron	12	116	28
Linuron	12	86	12
MCPA	12	80	9
MCPB	12	80	14
Methiocarb	12	79	11
Methomyl	12	88	14
Neburon	12	83	13
Norflurazon	12	89	10
Oryzalin	11	66	24
Oxamyl	12	69	8
Picloram	12	81	6
Propham	10	63	18
Propoxur	12	78	9
Triclopyr	12	82	11
		Gas Chromatography/Mass Spectrometry Analytical Method	
Acetochlor	12	99	9
Alachlor	12	107	12
Atrazine	12	102	6
Benfluralin	12	103	28
Bromacil	12	90	8
Butylate	12	96	7

Appendix Table 4. Mean recoveries from field-matrix spikes of pesticide and volatile organic compounds--Continued

Compound	Number of samples	Mean recovery (percent)	Relative standard deviation of recoveries (percent)
	PESTICIDES--Continued		
	Gas Chromatography/Mass Spectrometry Analytical Method--Continued		
Carbaryl	12	164	75
Carbofuran	12	151	47
Chlorpyrifos	12	98	13
Cyanazine	12	119	21
Dacthal	12	105	13
p,p-DDE	12	81	8
Diazinon	12	102	8
Dieldrin	12	87	7
Disulfoton	12	74	16
EPTC	12	97	10
Ethalfluralin	12	109	29
Fonofos	12	92	13
alpha-HCH	6	97	16
Lindane	12	91	12
Linuron	12	118	27
Malathion	12	107	33
Metolachlor	12	113	16
Metribuzin	12	101	15
Methyl azinphos	12	99	53
Methyl parathion	12	111	44
Molinate	12	101	10
Napropamide	12	94	7
Parathion	12	108	29
Pebulate	12	92	9
cis-Permethrin	12	43	12
Phorate	12	87	16
Prometon	12	104	11
Propachlor	12	107	12
Propanil	12	117	17
Propargite	12	102	10
Simazine	12	102	9
Tebuthiuron	12	127	30
Terbacil	12	85	20
Terbufos	12	91	14
Thiobencarb	12	103	12
Triallate	12	93	7
Trifluralin	12	112	24
	VOLATILE ORGANIC COMPOUNDS		
1,1-Dichloroethane	6	76	6
1,1-Dichloroethylene	12	76	13
1,1-Dichloropropene	6	73	8
1,1,1-Trichloroethane	12	77	9

Appendix Table 4. Mean recoveries from field-matrix spikes of pesticide and volatile organic compounds--Continued

Compound	Number of samples	Mean recovery (percent)	Relative standard deviation of recoveries (percent)
VOLATILE ORGANIC COMPOUNDS--Continued			
1,1,1,2-Tetrachloroethane	6	72	4
1,1,2-Trichloroethane	6	85	7
1,1,2,2-Tetrachloroethane	6	85	16
1,2-Dibromo-3-chloropropane	6	83	22
1,2-Dibromoethane	6	81	7
1,2-Dichlorobenzene	6	74	13
1,2-Dichloroethane	12	90	9
1,2-Dichloropropane	6	80	6
1,2,3-Trichlorobenzene	6	87	24
1,2,3-Trichloropropane	6	80	14
1,2,3-Trimethylbenzene	6	79	17
1,2,3,5-Tetramethylbenzene	6	68	4
1,2,4-Trichlorobenzene	6	69	16
1,2,4-Trimethylbenzene	6	66	28
1,3-Dichlorobenzene	6	68	12
1,3-Dichloropropane	6	87	6
cis-1,3-Dichloropropene	6	73	5
trans-1,3-Dichloropropene	6	76	5
1,3,5-Trimethylbenzene	6	70	19
1,4-Dichlorobenzene	6	69	12
2-Butanone	6	93	14
2-Chlorotoluene	6	67	9
2-Hexanone	6	94	24
2,2-Dichloropropane	6	55	6
3-Chloropropene	6	83	21
4-Chlorotoluene	6	66	11
4-Methyl-2-pentanone	6	77	20
Acetone	6	113	11
Acrolein	4	70	27
Acrylonitrile	6	89	15
Benzene	6	61	20
Bromobenzene	6	69	10
Bromochloromethane	6	76	5
Bromodichloromethane	12	85	7
Bromoform	12	90	16
Bromomethane	6	66	18
sec-Butylbenzene	6	65	11
tert-Butylbenzene	6	65	10
Carbon disulfide	6	97	34
Chlorobenzene	6	70	6
Chloroethane	6	55	18
Chloroform	6	75	5
Chloromethane	6	63	18
Dibromochloromethane	12	87	8

Appendix Table 4. Mean recoveries from field-matrix spikes of pesticide and volatile organic compounds--Continued

Compound	Number of samples	Mean recovery (percent)	Relative standard deviation of recoveries (percent)
VOLATILE ORGANIC COMPOUNDS--Continued			
Dibromomethane	6	81	7
Dichlorodifluoromethane	6	74	29
Dichloromethane	12	102	19
Diethyl ether	6	74	11
Ethyl methacrylate	6	70	13
Ethylbenzene	12	68	15
Hexachlorobutadiene	6	61	10
Hexachloroethane	6	66	8
Isopropylbenzene	6	68	10
Methyl acrylate	6	94	8
Methyl acrylonitrile	6	91	8
Methyl iodide	6	76	24
Methyl methacrylate	6	76	5
Methyl *tert*-butyl ether	6	96	4
Styrene	6	74	11
Tetrachloroethylene	12	83	11
Tetrachloromethane	12	74	10
Tetrahydrofuran	6	81	8
Toluene	12	65	58
Trichloroethylene	12	78	10
Trichlorofluoromethane	6	70	17
Vinyl bromide	6	76	16
Vinyl chloride	12	69	16
m- and p-Xylene	6	55	29
o-Xylene	6	66	21

Appendix Table 5. Percent recoveries for surrogate pesticide and volatile organic compounds in samples from the study-unit survey and agricultural and urban land-use studies

Compound	Number of samples	Percent recovery				
		Minimum[1]	First quartile	Median	Third quartile	Maximum
			Pesticides			
Diazinon-d_{10}	78	49	91	99	106	117
Terbuthylazine	78	51	105	111	117	163
alpha-HCH-d_6	78	46	89	97	105	133
BDMC	77	76	87	96	101	113
			Volatile Organic Compounds			
1,2-dichloroethane-d_4	79	87	102	106	107	122
1,4-bromofluorobenzene	79	58	89	96	100	124
Toluene-d_8	79	86	94	98	100	119

[1] Minimum values do not include samples for which recoveries were zero. These samples most likely reflect instances where the surrogate was not added, and so the recovery of the compounds was not measured.

Appendix Table 6. Summary of volatile organic compounds detected in field, equipment, and source-solution blank samples from the study-unit survey and agricultural and urban land-use studies

[µg/L, micrograms per liter; nd, not detected; e, estimated; n, number of samples]

Compound	Blanks collected with non-N_2 purged source solution			Blanks collected with N_2 purged source solution			Environmental samples	Percentage of detected concentrations in environmental samples above highest concentration in field blanks
	Source-solution blanks	Field and equipment blanks		Source-solution blanks	Field and equipment blanks			
	Detected concentrations (µg/L) n = 2	Percentage of samples with detections (number of detections) n = 10	Range of detected concentrations	Detected concentrations (µg/L) n = 2	Percentage of samples with detections (number of detections) n = 2	Range of detected concentrations	Range of detected concentrations[1]	
1,2-dichloropropane	nd	30 (3)	e0.01-e0.01	nd	nd	nd	e0.027-19.4	100
1,2,4-trimethylbenzene	0.177	70 (7)	e0.02-0.35	nd	50 (1)	e0.08	e0.0094-0.33	0
1,3,5-trimethylbenzene[2]	nd	nd	nd	nd	50 (1)	e0.017	e0.015-e0.038	75
1,4-dichlorobenzene	nd	30 (3)	e0.007-e0.01	nd	nd	nd	nd	nd
Acetone	1	20 (2)	e1-e2	nd	nd	nd	e0.4-e1.1	0
Benzene[2]	nd	10 (1)	nd	nd	50 (1)	0.181	e0.01-e0.058	0
Bromodichloromethane	nd	40 (4)	e0.007-e0.02	nd	nd	nd	e0.01-0.457	33
Carbon disulfide	0.01	40 (4)	e0.003-e0.04	nd	nd	nd	e0.002-e0.4	68
Chlorobenzene	nd	20 (2)	e0.004-e0.005	nd	nd	nd	e0.004	0
Chlorodibromomethane	0.07	80 (8)	e0.01	nd	nd	nd	e0.05	100
Chloroform	nd	10 (1)	e0.05-e0.07	nd	nd	nd	e0.005-7	12
Ethylbenzene[2]	0.02	40 (4)	e0.01-e0.02	nd	50 (1)	e0.075	e0.009-e0.01	0
o-ethyl toluene	nd	nd	nd	nd	50 (1)	e0.0087	e0.01-e0.019	100
Freon 113[2]	nd	70 (7)	e0.01-0.627	e0.014	50 (1)	0.195	nd[3]	nd[3]
Methylchloride	nd	10 (1)	e0.02	nd	nd	nd	e0.01-e0.05	31
Methylethylketone	nd	20 (2)	e0.4	e0.0	nd	nd	nd	nd
n-Propylbenzene	nd	nd	nd	nd	50 (1)	e0.015	e0.015-0.03	75
Styrene	0.007	20 (2)	e0.004-e0.007	nd	nd	nd	nd	nd
Tetrachloroethylene	nd	20 (2)	e0.004-e0.005	nd	nd	nd	e0.007-2.2	100
Tetrahydrofuran	nd	30 (3)	e0.3-e0.4	nd	nd	nd	e0.1-1.1	67
Toluene[2]	0.05	60 (6)	e0.03-0.46	0.02	100 (2)	e0.008-0.509	e0.01-0.25	0
m,p-Xylene[2]	0.03	40 (4)	e0.02-e0.04	nd	50 (1)	0.355	e0.01-e0.14	0
o-Xylene[2]	0.01	30 (3)	e0.01-e0.02	nd	50 (1)	0.0974	e0.009-e0.047	0

[1] Does not include samples that were removed from the data set because of contamination.

[2] Environmental samples of this compound were likely contaminated, based on high equipment and field blank values, and were removed from the data set.

[3] All detections of Freon 113 were contaminated.

Appendix Table 7. Concentrations of volatile organic compounds detected in field, equipment, and source-solution blank samples from the study-unit survey and agricultural and urban land-use studies

[ID, identification number; ug/L, micrograms per liter; tb, trip blank; fb, field blank; ss, source-solution blank; eb, equipment blank; <, less than; e, concentration is estimated]

Local ID	Dates	Type of blank	1,2-dichloro-propane (µg/L)	1,2,4-trimethyl-benzene (µg/L)	1,3,5-trimethyl-benzene (µg/L)	1,4-dichloro-benzene (µg/L)	Acetone (µg/L)	Benzene (µg/L)	Bromo-dichloro-methane (µg/L)	Carbon disulfide (µg/L)	Chloro-benzene (µg/L)	Chloro-dibromo-methane (µg/L)	Chloro-form (µg/L)	*o*-Ethyl toluene (µg/L)
Blanks collected with non-nitrogen-purged blank water														
SU-14	19960802	tb	<0.05	<0.05	<0.05	<0.05	e1.7	<0.05	<0.1	<0.05	<0.05	<0.1	<0.05	<0.05
SU-14	19960802	fb	<0.05	e0.03	<0.05	<0.05	<5	<0.05	<0.1	<0.05	<0.05	<0.1	e0.06	<0.05
SU-19	19960805	fb	<0.05	e0.02	<0.05	<0.05	<5	<0.05	<0.1	<0.05	<0.05	<0.1	e0.07	<0.05
SU-26	19960819	fb	<0.05	<0.05	<0.05	<0.05	<5	<0.05	e0.007	<0.05	<0.05	<0.1	e0.07	<0.05
FSU	19961118	ss	<0.05	<0.05	<0.05	<0.05	<5	<0.05	<0.1	<0.05	<0.05	<0.1	e0.07	<0.05
FSU	19961118	eb	<0.05	e0.02	<0.05	<0.05	<5	<0.05	<0.1	e0.04	<0.05	<0.1	e0.07	<0.05
UR-05	19961122	fb	e0.01	e0.03	<0.05	e0.01	<5	<0.05	e0.02	e0.009	e0.005	<0.1	e0.06	<0.05
UR-12	19961202	fb	e0.01	<0.05	<0.05	e0.008	<5	<0.05	e0.01	e0.003	<0.05	<0.1	e0.05	<0.05
UR-34	19961204	fb	e0.01	e0.02	<0.05	e0.007	e2	<0.05	e0.01	<0.05	e0.004	e0.01	e0.05	<0.05
FSU	19970131	eb	<0.05	0.18	<0.05	<0.05	<5	<0.05	<0.1	e0.02	<0.05	<0.1	e0.01	<0.05
FSU	19970210	eb	<0.05	0.35	<0.05	<0.05	e1	e0.03	<0.1	<0.05	<0.05	<0.1	<0.05	<0.05
UR-25	19970730	ss	<0.068	0.177	<0.044	<0.05	e1	<0.032	<0.048	e0.01	<0.028	<0.182	<0.052	<0.1
UR-25	19970730	fb	<0.068	<0.056	<0.044	<0.05	<4.904	<0.032	<0.048	<0.08	<0.028	<0.182	<0.052	<0.1
Blanks collected with nitrogen-purged blank water														
BC-A-75	19970902	ss	<0.068	<0.056	<0.044	<0.05	<4.904	<0.032	<0.048	<0.08	<0.028	<0.182	<0.052	<0.1
BC-A-75	19970902	fb	<0.068	<0.056	<0.044	<0.05	<4.904	<0.032	<0.048	<0.08	<0.028	<0.182	<0.052	<0.1
AG-10	19971113	ss	<0.068	<0.056	<0.044	<0.05	<4.904	<0.032	<0.048	<0.08	<0.028	<0.182	<0.052	<0.1
AG-10	19971113	fb	<0.068	e0.08	e0.017	<0.05	<4.904	0.181	<0.048	<0.08	<0.028	<0.182	<0.052	e0.0087

Appendix Table 7. Concentrations of volatile organic compounds detected in field, equipment, and source-solution blank samples from the study-unit survey and agricultural and urban land-use studies--Continued

Local ID	Dates	Type of blank	Ethyl-benzene (µg/L)	Freon 113 (µg/L)	Methyl-chloride (µg/L)	Methyl-ethyl-ketone (µg/L)	*n*-Propyl-benzene (µg/L)	Styrene (µg/L)	Tetra-chloro-ethylene (µg/L)	Tetra-hydro-furan (µg/L)	Toluene (µg/L)	*m,p*-Xylene (µg/L)	*o*-Xylene (µg/L)
Blanks collected with non-nitrogen-purged blank water													
SU-14	19960802	tb	<0.05	<0.05	<0.2	<5	<0.05	<0.05	<0.05	<5	<0.05	<0.05	<0.05
SU-14	19960802	fb	<0.05	<0.05	<0.2	<5	<0.05	<0.05	<0.05	<5	<0.05	<0.05	<0.05
SU-19	19960805	fb	<0.05	<0.05	<0.2	<5	<0.05	<0.05	<0.05	<5	e0.05	<0.05	<0.05
SU-26	19960819	fb	<0.05	<0.05	e0.02	<5	<0.05	<0.05	<0.05	<5	<0.05	<0.05	<0.05
FSU	19961118	ss	e0.02	<0.05	<0.2	<5	<0.05	e0.007	<0.05	<5	e0.05	e0.03	0.01
FSU	19961118	eb	e0.02	e0.04	<0.2	<5	<0.05	e0.007	<0.05	<5	0.46	e0.04	0.02
UR-05	19961122	fb	e0.01	e0.01	<0.2	e0.4	<0.05	e0.004	<0.05	e0.3	0.22	e0.03	0.01
UR-12	19961202	fb	e0.01	e0.01	<0.2	<5	<0.05	<0.05	e0.004	e0.4	e0.03	e0.03	<0.05
UR-34	19961204	fb	e0.01	e0.01	<0.2	e0.4	<0.05	<0.05	e0.005	e0.3	0.2	e0.02	0.01
FSU	19970131	eb	<0.05	0.12	<0.2	<5	<0.05	<0.05	<0.05	<5	<0.04	<0.05	<0.05
FSU	19970210	eb	<0.05	e0.04	<0.2	<5	<0.05	<0.05	<0.05	<5	e0.07	<0.05	<0.05
UR-25	19970730	ss	<0.03	<0.032	<0.254	<1.65	<0.042	<0.042	<0.038	<1.148	e0.09	<0.064	<0.064
UR-25	19970730	fb	<0.03	0.627	<0.254	<1.65	<0.042	<0.042	<0.038	<1.148	<0.038	<0.064	<0.064
Blanks collected with nitrogen-purged blank water													
BC-A-75	19970902	ss	<0.03	<0.032	<0.254	<1.65	<0.042	<0.042	<0.038	<1.148	e0.02	<0.064	<0.064
BC-A-75	19970902	fb	<0.03	0.195	<0.254	<1.65	<0.042	<0.042	<0.038	<1.148	e0.008	<0.064	<0.064
AG-10	19971113	ss	<0.03	e0.014	<0.254	<1.65	<0.042	<0.042	<0.038	<1.148	<0.038	<0.064	<0.064
AG-10	19971113	fb	e0.075	<0.032	<0.254	<1.65	e0.015	<0.042	<0.038	<1.148	0.509	0.355	0.0974

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