Quality of Shallow Ground Water in Alluvial Aquifers of the Willamette Basin, Oregon, 1993–95

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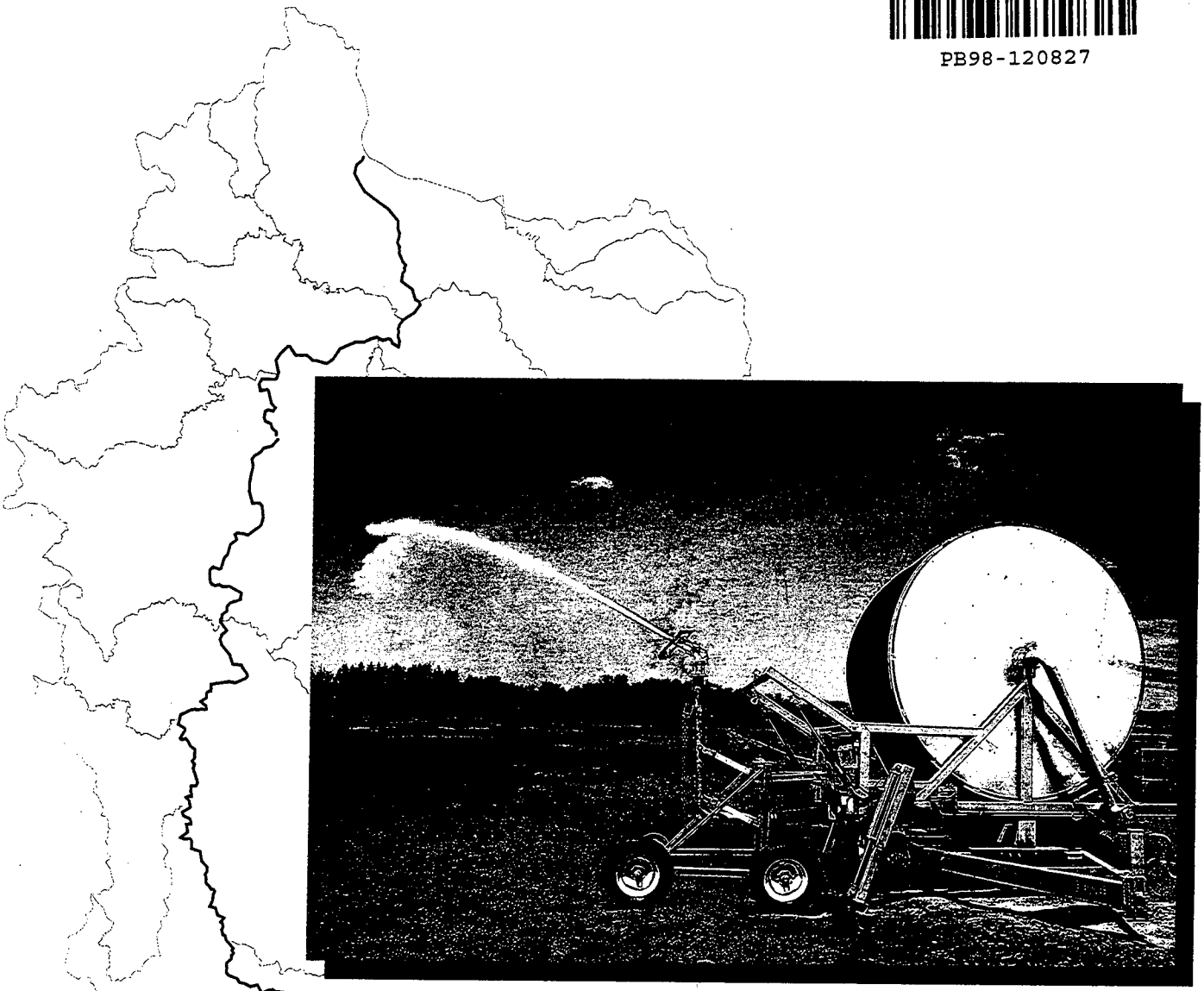

Water-Resources Investigations Report 97–4082–B

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Front cover photograph: Gun sprinkler irrigating mint near Salem, Oregon.

Back cover photographs:

Upper, Kurt Carpenter (left) and Steve Hinkle (right) adapt wellhead for sampling near Corvallis, Oregon.
Center, Ned Gates (left) records lithology of cuttings during well drilling in Portland, Oregon.
Lower, Phil Gallaway (left) and Ben Davis (right) process ground-water samples near Corvallis, Oregon.

(Photographs by Dennis A. Wentz, U.S. Geological Survey.)

Quality of Shallow Ground Water in Alluvial Aquifers of the Willamette Basin, Oregon, 1993–95

By Stephen R. Hinkle

Prepared as part of the National Water-Quality Assessment Program

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Portland, Oregon
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BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
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Information regarding the National Water-Quality Assessment (NAWQA) Program is available on the Internet via the World Wide Web. You may connect to the NAWQA Home Page at the Universal Resource Locator (URL):

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

Information regarding the Willamette NAWQA is available on the Internet by connecting to the Willamette NAWQA Home Page at:

<http://oregon.usgs.gov/projs_dir/pn366/nawqa.html>

Information regarding Oregon District Activities is available on the Internet by connecting to the Oregon District Home Page at:

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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 specific contamination problems; 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 U.S. 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:

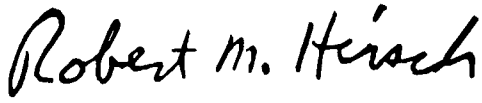
- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

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 60 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 the 60 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.



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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
	Length	
millimeter	0.03937	inch
meter	3.281	foot
kilometer	0.6214	mile
	Area	
square kilometer	247.1	acre
square kilometer	0.3861	square mile
square meter	10.76	square foot
	Volume	
liter	0.2642	gallon
	Mass	
kilogram	2.205	pound, avoirdupois
milligram	0.00003528	ounce, avoirdupois

Nanograms, micrograms, and milligrams are related as follows: 1,000,000 nanograms = 1,000 micrograms = 1 milligram

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviation	Definition
DBCP	1,2-dibromo-3-chloropropane
DO	dissolved oxygen
EDB	1,2-dibromoethane
FMS	field matrix spike
GC/EC	gas chromatography/electron capture
GC/MS	gas chromatography/mass spectrometry
GIRAS	Geographic Information Retrieval and Analysis System
HA	health advisory
HPLC/DAD	high-performance liquid chromatography/photodiode-array detection
ICP/MS	inductively coupled plasma/mass spectrometry
kg	kilogram
km	kilometer
L	liter
LHA	lifetime health advisory
LUS	Land-Use Study
m	meter
MCL	maximum contaminant level
MDL	method detection limit
mg	milligram
mm	millimeter
MPV	most probable value
MRL	minimum reporting level
N	nitrogen
NAWQA	National Water-Quality Assessment Program
ng	nanogram
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
ODEQ	Oregon Department of Environmental Quality
pCi/L	picocuries per liter
PVC	polyvinyl chloride
QC	quality control
RSDHA	risk-specific-dose health advisory
SRS	standard reference sample
SUS	Study-Unit Survey
µg	microgram
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

GLOSSARY OF SELECTED TERMS

Advection. The process by which solutes are transported by the bulk motion of flowing water.

Alluvium. Clay, silt, sand, gravel, or other particulate rock material deposited by the actions of streams and rivers. Generally unconsolidated or semiconsolidated.

Anthropogenic. Resulting from or pertaining to human activities.

Aquifer. A geologic formation, group of formations, or part of a formation containing sufficient water-saturated permeable material to yield or be capable of yielding usable quantities of water to wells and springs.

Environmental sample. A water sample collected from an aquifer or stream for the purpose of chemical, physical, or biological characterization of the sampled resource. (Compare with "quality-control sample".)

Flowpath. The pathway or course taken by particles of water and associated solutes as they move through an aquifer.

Holocene. The epoch of geologic time spanning approximately the last 10,000 years.

Inventory (a well). A standard U.S. Geological Survey procedure for obtaining information about a well prior to sampling. Consists of a field visit to determine the exact location of the well, ownership of the well, and availability and suitability of the well for project-specific measurements.

Land-Use Study. A focused investigation of water-quality conditions associated with an individual land-use setting. Land-Use Studies generally are focused on shallow ground water in regionally important land-use settings. Variability from hydrogeologic factors is reduced by restricting an individual Land-Use Study to a single aquifer or hydrogeologically related group of aquifers.

Median. The middle or central value in a distribution of data ranked in order of magnitude. The median is also known as the 50th percentile.

Nitrate reduction. Any of a number of processes by which nitrate is reduced to less oxidized forms of nitrogen, such as ammonium or nitrogen oxides. Nitrate reduction is commonly facilitated by the action of bacteria.

Nonpoint-source water pollution. Water contamination that originates from a broad region (e.g. leaching of agricultural chemicals from crop lands) and enters the water resource diffusely over a large area.

Permeability. The capacity of hydrogeologic materials to transmit fluid in response to a hydraulic gradient.

Pesticide degradation product. A chemical compound formed by transformation of a pesticide parent compound.

Point-source water pollution. Water contamination that originates from a discrete, discernible, non-diffuse source (e.g. leakage from an underground gasoline tank), and enters the water resource over a limited area.

Potentiometric surface. A map of values of static hydraulic head for an aquifer or a hydrologically related group of aquifers, contoured to facilitate interpretation of ground-water flowpaths. Equivalent to the water table elevation in an unconfined aquifer. (Static hydraulic head is the height above a standard datum of the surface of a column of water that can be supported by the static pressure at a given point in an aquifer.)

Quality Assurance. Evaluation of quality-control data to allow quantitative determination of the quality of chemical data collected during the execution of a study. Techniques used to collect, process, and analyze water samples are evaluated.

Quality-control sample. A water sample analyzed for quality-assurance purposes. (Compare with "environmental sample"; see "quality assurance".)

Recharge. The process of addition of water to an aquifer.

Redox. Pertaining to or taking part in a coupled reduction and oxidation reaction.

Solute. A substance dissolved in another substance. (In hydrologic applications, usually refers to a chemical dissolved in water.)

Sorption. Thermodynamically driven partitioning of a solute into a solid phase or onto a solid phase surface.

Study Unit. A major hydrologic system of the United States in which the National Water-Quality Assessment Program has focused or plans to focus water-quality studies. Study Units are combinations of ground- and surface-water systems. Generally, Study Units are greater than 10,000 square kilometers in area. The design of the National Water-Quality Assessment Program is based on studies in 60 Study Units. These 60 Study Units collectively represent 60 to 70 percent of national water use and represent diverse hydrologic systems.

Study-Unit Survey. Broad assessment of water-quality conditions in ground water of a Study Unit. Study-Unit Surveys generally are targeted at aquifers that represent the bulk of the used resource. Study-Unit Surveys generally are focused on the shallower portions of aquifers.

Upgradient. Of or pertaining to the place(s) from which ground water originated or traveled through prior to reaching a given point in an aquifer.

Acknowledgments

Execution of hydrochemical investigations leading to publication of this report, and production of this report itself, were greatly facilitated by invaluable contributions by numerous organizations and individuals. The logistical assistance and technical guidance of the following individuals and groups of individuals were particularly helpful: the City of Portland Bureau of Parks and Recreation provided access for well installation; Susan Hathaway-Marxer and Dave Gray were especially helpful in this regard. Greg Pettit of Oregon Department of Environmental Quality expanded upon the National Water-Quality Assessment effort by arranging to perform low-level analyses for 1,2-dibromoethane (EDB) in 45 environmental and quality-control samples. A cooperative water-quality project in the Tualatin River Basin that was jointly funded by the Unified Sewerage Agency of Washington County and the U.S. Geological Survey (USGS) provided supplemental ground-water samples for analysis of arsenic. The City of Portland Bureau of Environmental Services and Bureau of Buildings provided access to records of locations of sanitary sewers. John Hart (Oregon State University, Department of Crop and Soil Science) provided estimates of nitrogen application rates for crops and pasture. Rosemary Furfey (Planning Department, Metro, Portland Regional Government) provided large-scale, digital land-use coverages of the Portland area. Bernadine Bonn (USGS) provided summary statistics for pesticide-spike quality-control data. Mark Uhrich (USGS) created Geographic-Information-System (GIS) coverages. Dennis Wentz, Chief of the Willamette Basin National Water-Quality Assessment project, provided guidance and oversight throughout the project. Finally, this report reflects the efforts of a team of technical reviewers, illustrators, and editors. Team members included: Karen Burow, Doug Lee, Jackie Olson, Donita Parker, Stewart Rounds, Alan Welch, Dennis Wentz, and John Williams.

Quality of Shallow Ground Water in Alluvial Aquifers of the Willamette Basin, Oregon, 1993–95

By Stephen R. Hinkle

Abstract

The current (1993–95) quality of shallow ground water (generally, <25 meters below land surface) in Willamette Basin alluvium is described using results from two studies. A Study-Unit Survey, or regional assessment of shallow ground-water quality in alluvium, was done from June through August 1993. During the Study-Unit Survey, data were collected from 70 domestic wells chosen using a random-selection process and located mostly in areas of agricultural land use. An urban Land-Use Study, which was a reconnaissance of shallow urban ground-water quality from 10 monitoring wells installed in areas of residential land use, was done in July 1995.

Concentrations of nitrite plus nitrate (henceforth, nitrate, because nitrite concentrations were low) ranged from <0.05 to 26 mg N/L (milligrams nitrogen per liter) in ground water from 70 Study-Unit-Survey wells; concentrations exceeded the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) of 10 mg N/L in 9 percent of Study-Unit-Survey samples. Relationships were observed between nitrate concentrations and dissolved-oxygen concentrations, the amount of clay present within and overlying aquifers, overlying geology, and upgradient land use.

Tritium (^{3}H) data indicate that 21 percent of Study-Unit-Survey samples represented water recharged prior to 1953. Nitrogen-fertilizer application rates in the basin have increased greatly over the past several decades. Thus, some observed nitrate concentrations may reflect nitrogen loading rates that were smaller than those presently applied in the basin.

Concentrations of phosphorus ranged from <0.01 to 2.2 mg/L in 70 Study-Unit-Survey wells and exceeded 0.10 mg/L in 60 percent of the samples. Phosphorus and nitrate concentrations were inversely correlated.

From 1 to 5 pesticides and pesticide degradation products (henceforth, pesticides) were detected in ground water from each of 23 Study-Unit-Survey wells (33 percent of 69 wells sampled for pesticides) for a total of 51 pesticide detections. Thirteen different pesticides were detected; atrazine was the most frequently encountered pesticide. Although detections were widespread, concentrations were low (generally <1,000 ng/L [nanograms per liter]). (One ng/L is equal to 0.001 µg/L [micrograms per liter].) One detection (dinoseb, at 7,900 ng/L) exceeded a USEPA MCL. Relationships were observed between the occurrence of pesticides and the amount of clay present within and overlying aquifers, overlying geology, and land use.

Between 1 and 5 volatile organic compounds (VOCs) were detected at each of 7 Study-Unit-Survey sites (11 percent of 65 sites evaluated), for a total of 14 VOC detections. One detection (tetrachloroethylene, at 29 µg/L) exceeded a USEPA MCL. Other detections were at low concentrations (0.2 to 2.0 µg/L). VOC detections generally were from sites associated with urban land use.

Concentrations of arsenic ranged from <1 to 13 µg/L in 70 Study-Unit-Survey wells. Concentrations in 16 percent of samples exceeded

the USEPA Risk-Specific-Dose Health Advisory of 2 µg/L.

Radon concentrations ranged from 200 to 1,200 pCi/L (picocuries per liter) in 51 Study-Unit-Survey wells. All samples exceeded the USEPA Risk-Specific-Dose Health Advisory of 150 pCi/L.

All urban Land-Use-Study samples were well oxygenated; thus, nitrate reduction probably did not affect these samples. Urban Land-Use-Study nitrate concentrations were similar to those of the well oxygenated, agricultural subset of Study-Unit-Survey samples. Pesticides were detected in samples from three urban Land-Use-Study sites, but concentrations were low (1 to 5 ng/L). In contrast, VOCs were detected in ground water from 80 percent of urban Land-Use-Study wells; concentrations ranged up to 7.6 µg/L. Trace-element concentrations in the urban Land-Use Study samples were low. Median concentrations consistently were <10 µg/L and frequently were <1 µg/L.

INTRODUCTION

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) is a program with goals of (1) describing the status of and trends in water quality of large, representative portions of the Nation's water resources, and (2) providing an understanding of natural and anthropogenic factors affecting the quality of these resources (Hirsch et al., 1988; Gilliom et al., 1995). Ground-water studies are an integral component of the NAWQA Program. The design for ground-water studies focuses on assessments of regionally important resources within individual study units (river basins and associated aquifer systems). Emphasis is placed on the chemical quality of recently recharged water (Gilliom et al., 1995), which is the ground-water resource most likely to be affected by most anthropogenic activities.

The Willamette Basin (fig. 1), a 31,000-km^2 (square-kilometer) area in northwestern Oregon drained by the Willamette and Sandy Rivers, is one of 60 NAWQA study units located throughout the United States (Gilliom et al., 1995). An evaluation of ground-water-quality data collected between 1993 and 1995 represents one step toward addressing NAWQA goals in the Willamette Basin.

Purpose and Scope

The purposes of this report are to describe the quality of shallow ground water (generally, <25 m [meters] below land surface) in alluvial aquifers (henceforth, alluvium) of the Willamette Basin and to identify relationships between shallow ground-water quality and various natural and anthropogenic factors. Several natural and anthropogenic factors (soil characteristics, cumulative thickness of clay above open interval of well, surficial geology, and land use) were evaluated because of the potential for these factors to either control or be related to contaminant occurrence and spatial distribution. The Willamette Basin study unit did not attempt to characterize water quality in bedrock or in alluvium deeper than 25 m below land surface.

Spatial distributions of nitrite plus nitrate, phosphorus, pesticides and pesticide degradation products (henceforth referred to as pesticides), volatile organic compounds (VOCs), trace elements (primarily arsenic, a trace element of local concern), and radon were evaluated for 1993–95. Ancillary chemical data—nitrite, chloride, tritium (^{3}H), and dissolved-oxygen (DO) concentrations—also are presented. Nitrite plus nitrate and many pesticides, VOCs, and trace elements in drinking water are regulated by the U.S. Environmental Protection Agency (USEPA) (U.S. Environmental Protection Agency, 1996). Radon, although not currently regulated by the USEPA, is of concern because of its classification as a human carcinogen (U.S. Environmental Protection Agency, 1996). Thus, these analytes are of interest in defining water quality at least partly because of their potential impact on drinking-water quality. These analytes also may degrade surface-water quality upon discharge to surface-water bodies. Phosphorus, although not regulated by the USEPA, also is of interest because it has the potential to degrade surface-water quality. Other water-quality data (filtered organic carbon, uranium, and additional nutrients, inorganic ions, and field parameters) were collected, but presentation of these data is beyond the scope of this report.

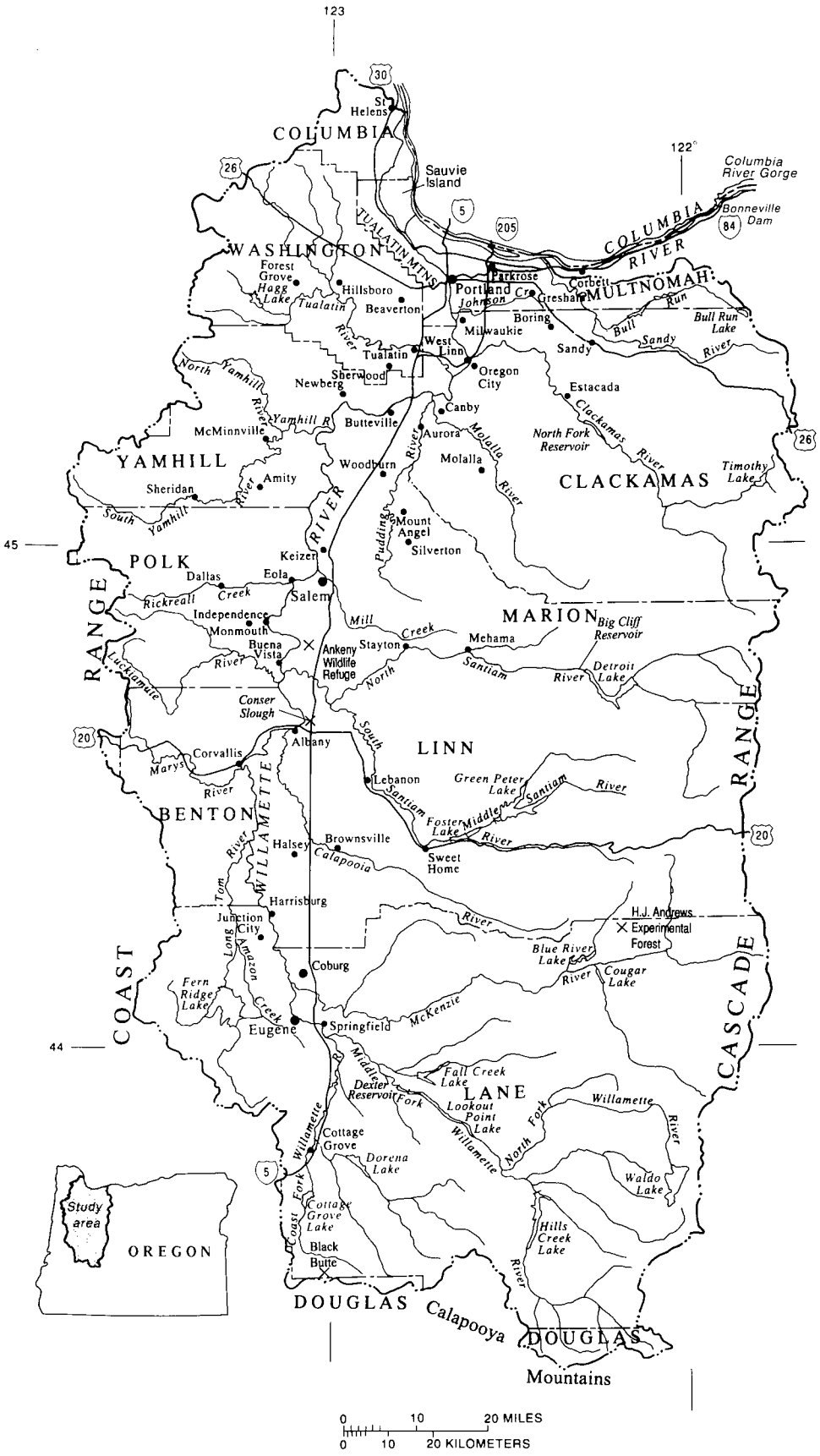

Figure 1. Location of the Willamette Basin, Oregon.

Environmental Setting

Hydrogeology

The crests of two north-south trending mountain ranges, the Coast and the Cascade Ranges, respectively define the western and eastern edges of the Willamette Basin (fig. 1). The Willamette Valley, an elongated, structural and erosional lowland, lies between these mountain ranges. The Coast and Cascade Ranges are composed of volcanic and sedimentary rocks. The Willamette Valley is filled with Tertiary and Quaternary clastic sediments of primarily alluvial origin (fig. 2). The alluvium is a heterogeneous mixture of unconsolidated and semiconsolidated clay, silt, sand, and gravel. Holocene alluvium has been deposited near rivers and streams, generally to depths of <20 m. (Gannett and Caldwell, in press). In contrast, deposits of older alluvium reach depths of up to about 500 m (Gannett and Caldwell, in press). In the Willamette Basin, permeability of Holocene alluvium generally is greater than that of the older alluvium (Piper, 1942), so faster movement of water might be expected in the Holocene alluvium. The geologic framework of the basin is described by Gannett and Caldwell (in press). Regional hydrogeology of the basin is described by Woodward et al (in press).

Of particular interest in this study is the Willamette Silt unit. The Willamette Silt is a regionally confining or semiconfining unit (Gannett and Caldwell, in press). As its name implies, this unit is composed primarily of silt, but it also contains a substantial component (on the order of 30 percent) of clay-sized particles (Glenn, 1965). The Willamette Silt is absent in the Portland Basin, but outside of the Portland Basin, the Willamette Silt generally occurs as the uppermost geologic unit within the older alluvium. Thus, ground-water recharge in much of the alluvium in the Willamette Basin passes through the Willamette Silt, and this accounts for the importance of the unit in this study. The Willamette Silt is thickest in parts of the northern Willamette Basin and thins to the south; its thickness generally decreases from a maximum of 40 m in parts of the northern basin to zero near Eugene (Gannett and Caldwell, in press).

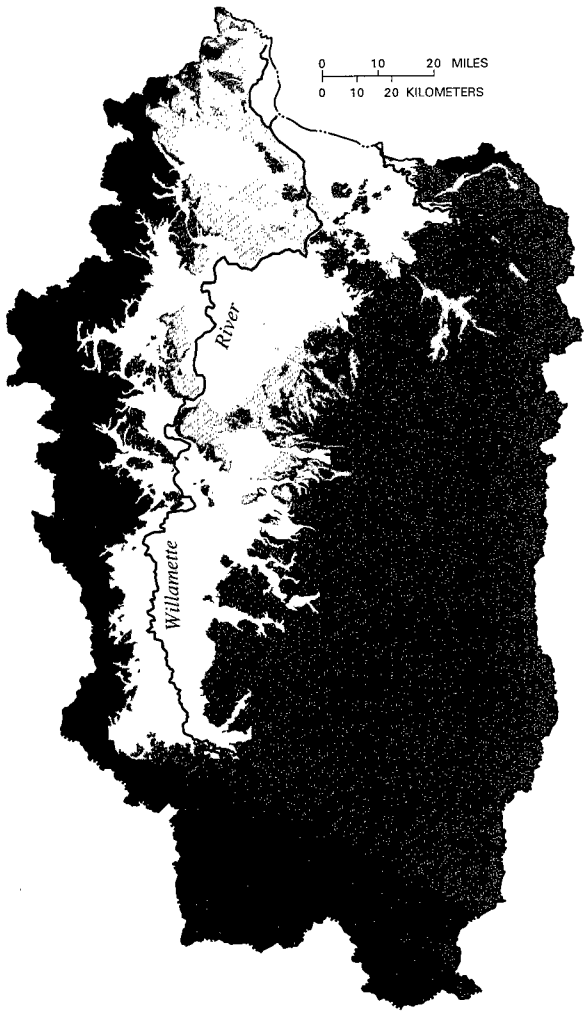

Figure 2. Generalized surficial geology of the Willamette Basin, Oregon. (Modified from Gannett and Caldwell [in press] and Walker and MacLeod [1991.])

Land Use and Population

GIRAS (Geographic Information Retrieval and Analysis System) land-use data from the 1970s (Fegeas et al., 1983; Mitchell et al., 1977), refined with 1990 population data (Hitt, 1994), were used to define the general distribution of land use in the Willamette Basin. The Willamette Basin is characterized by forested, agricultural, and urban land uses. Much (about 70 percent) of the basin is covered by forests, primarily second-

growth coniferous forests that, for the most part, coincide with bedrock areas (fig. 2). Agricultural land covers about 22 percent of the basin, primarily in the Willamette Valley. Agricultural land use in the basin is characterized by a diversity of crops (field crops, such as grains, hay, mint, and hops; seed crops such as grass and vegetable seeds; and vegetable, fruit, nut and nursery crops) and pasture. Many crops are irrigated. Estimated total acreages of major crops, plus pasture and rangeland, are given in table 1. Urban land represents about 6 percent of the total basin area; Portland is the largest city.

Although much of the basin is covered by forests, most of the areas underlain by alluvium are used for agricultural and urban purposes. Of the portion of the basin underlain by alluvium, 68 percent is agricultural, 18 percent is urban, 10 percent is forested, and 4 percent consists of water, wetlands, and barren land.

On a gross sales basis, 54 percent of Oregon's 1993 harvested crops were grown in the Willamette Basin. (This estimate was compiled using county-level data from Oregon Agricultural Statistics Service [1994].) In addition, 69 percent (1,960,000) of the State's population resided in the basin in 1990 (Broad and Collins, 1996). Thus, there is potential for substantial impacts on water resources resulting from agricultural practices and population pressures in the Willamette Basin.

STUDY DESIGN AND METHODS

The ground-water study design was composed of two components—a regional assessment of ground-water quality (Study-Unit Survey, or

Table 1. Estimated total acreages, estimated nitrogen application rates, and 3 most heavily used pesticides for the 12 highest acreage Willamette Basin crops and pasture and rangeland

[Estimated total acreage for crops from Anderson et al. (1996), as calculated from data of Rinehold and Witt (1989); 1987 data. Estimated total acreage for pasture and rangeland calculated from data of U.S. Bureau of the Census (1989) (estimated acreage for pasture and rangeland not given in Rinehold and Witt (1989)); 1987 data. Estimated nitrogen application rate from J. Hart, Oregon State University, Department of Crop and Soil Science, written commun., 1995; estimates for 1995 growing season. --, crop or cover not typically grown under conditions indicated; application rate estimates based on an assumption of typical precipitation amounts and patterns; estimated typical range given in appropriate column; where available, estimated typical range followed by estimated average in brackets. Three most heavily used pesticides (based on mass of active ingredient used per year) calculated from data of Rinehold and Witt (1989); 1987 data; listed in order of use, beginning with most heavily used compound; compounds analyzed in this study in bold type; (NA), data not available]

Crop or cover	Estimated total acreage	Estimated nitrogen application rate (pounds N per acre per year) for crop or cover that is:		Three most heavily used pesticides
		Irrigated	Nonirrigated	
Grass seed	290,000	--	120–250 [150–160]	Maneb, **diuron, atrazine**
Wheat	170,000	--	60–180 [120]	**Diuron**, diclofop-methyl, **MCPA**
Other hay	150,000	100–350 [150]	50–150 [75]	(NA)
Oats	62,000	--	0–80 [50–60]	**Diuron, MCPA**, carboxin
Clover/vetch seed	50,000	--	0–30	**Diuron**, methoxychlor, metaldehyde
Sweet corn	35,000	160–220 [200]	--	**Atrazine, alachlor, metolachlor**
Alfalfa hay	26,000	0	0	**Diuron, pronamide, EPTC**
Filberts	25,000	--	0–180 [140–150]	Copper, **2,4-D, carbaryl**
Snap beans	21,000	60–150 [100]	--	**EPTC, dinoseb**, vinclozolin
Mint	17,000	200–400 [350]	--	**Fonofos, terbacil, chlorpyrifos**
Silage corn	17,000	100–400 [200]	--	**Atrazine, alachlor, fonofos**
Christmas trees	16,000	--	[a]0–180	**Atrazine, chlorothalonil**, hexazinone
Pasture and rangeland	180,000	50–200 [75]	0–60 [50]	**2,4-D, dicamba, [b]glyphosate**

[a]Nitrogen usually applied in last 2 years of a 7-year growth cycle.
[b]Analyses performed only for urban Land-Use-Study samples.

SUS), and a reconnaissance study of ground-water quality associated with urban land use (urban Land-Use Study, or urban LUS). (NAWQA protocols for conducting SUSs and LUSs are described in detail by Gilliom et al., 1995). An overview of the occurrence and spatial distribution of water-quality constituents in samples collected in the SUS is presented in a section "Regional Occurrence and Distribution of Ground-Water-Quality Characteristics." In a subsequent section "Relationships of Regional Ground-Water Quality to Soils, Hydrogeologic Factors, and Land Use," SUS results are evaluated relative to explanatory natural and anthropogenic variables, including land use. Land use associated with SUS wells is primarily agricultural. Evaluation of SUS data from a land-use perspective allows land-use/water-quality relationships observed in the Willamette Basin SUS to contribute to the overall LUS effort within the NAWQA Program. In another section "Urban Land-Use Study," results from the urban LUS are presented. From a land-use/water-quality perspective, the urban LUS data complement the primarily agricultural SUS data, and represent another component of the NAWQA Program LUS effort.

Study-Unit Survey Design

The SUS is one of many large-scale ground-water-quality investigations that have been completed in the Willamette Basin to date. Numerous local, State, and Federal agencies conduct ground-water-quality monitoring in the basin, and extensive, targeted ground-water sampling has been done by the Oregon Department of Environmental Quality (ODEQ) (e.g. Fortuna et al., 1988). These efforts have provided valuable information about ground-water quality in many areas of the Willamette Basin, but three limitations of data generated from these studies restrict the usefulness of these data in assessments of the regional resource:

(1) Data sets often lack well-construction data. Absence of well-construction data limits interpretation of water-quality data in the context of environmental variables.

(2) Location of sampling sites has typically been biased. For example, Oregon Department of Human Resources, Health Division sampling focuses on public-water-supply wells. Locations of such wells often are biased away from areas of known or perceived contamination, and public-water-supply wells tend to be abandoned if extensive contamination is detected. In contrast, ODEQ often targets areas known or perceived to have high concentrations of contaminants. Locational bias limits applicability to regional assessments of ground-water quality.

(3) Samples often are collected at the tap, rather than at the well head. The chemistry of water at a tap often is altered by passage through holding tanks, filters, chlorinators, and (or) water softeners. For example, VOCs may degas from water into holding tank headspace, and organic contaminants sorb to carbon in carbon filters. Tap water is the water being consumed by humans—thus, the interest by regulatory agencies. However, some resource assessments, such as this one by the NAWQA Program, are designed to characterize the quality of the resource, rather than the product at the tap.

Limitations regarding the suitability of existing ground-water-quality data for addressing questions about regional ground-water quality in the Willamette Basin provided justification for a SUS, which constitutes one step towards answering questions about regional ground-water quality. The SUS is not designed to be a comprehensive study. Regional-scale assessments are inherently broad in scope, with an accompanying loss of local resolution.

The SUS was done between June and August, 1993. Shallow ground water (within 25 m of land surface) in alluvium was targeted for sampling and is referred to as the targeted resource. Alluvium was chosen because water-supply data from Broad and Nebert (1990) and Gonthier (1985) indicate that more than 80 percent of ground water used in the Willamette Basin is pumped from alluvium. Shallow ground water is more likely to show effects of anthropogenic contamination from surficial activities than is deep ground water. Thus, evaluation of shallow ground water may provide resource managers and regulators with an increased understanding of the impacts of anthropogenic activities on ground-water quality. Assessments of deep ground water in alluvium and of ground water in bedrock were beyond the scope of this study. However, a regional evaluation

of deep ground water in the basin also is needed because most public-supply wells tap deeper resources than the resource evaluated in this study. Characterization of water quality in bedrock aquifers also is needed, as areas where bedrock is at or near land surface are increasingly being developed.

SUS wells generally were open (screened or perforated) at least several meters below the water table. Thus, although SUS results generally reflect the quality of shallow ground water, they may not reflect the quality of water at the water table. Water at the water table, which may be most susceptible to surface-related anthropogenic activities, is utilized for domestic purposes by some owners of dug wells.

Water from 70 domestic wells was sampled during the SUS. Wells were chosen using a grid-based, random-selection process, as described in the section "Study-Unit Survey Well Selection". However, the population of domestic wells from which SUS wells were chosen was not evenly distributed, so although locational bias of SUS wells was minimized, it was not entirely avoided. All wells were <25 m deep. The median well depth was 18 m, the median depth of penetration of wells below the water table was 12 m, and the median depth of penetration of the top of the open interval below the water table was 9.0 m. Because most land associated with alluvium in the Willamette Basin was used for agriculture, SUS results are more representative of ground water under agricultural land than under urban or forested land.

Study-Unit Survey Well Selection

SUS wells were selected following NAWQA well-selection protocols (Lapham et al., 1995). A grid-based, random-selection process was used. The Willamette Basin was divided into square cells based on the rectangular system for subdivision of land by township and range. Each township-and-range cell is 93 km^2 in area, and is composed of 36 sections. Sections are 2.6 km^2 in area. Cells with alluvium present over at least one-half of their area were considered. (Sauvie Island [fig. 1], although technically part of the Willamette Basin, was excluded from the selection process because of its physical association with the Columbia River.) Seventy-six cells met the primary criteria.

In each cell, one section was chosen at random. If the section contained no alluvium, a new section was selected at random. This process was repeated until a section at least partially underlain by alluvium was chosen. Next, the shallowest alluvial well within the section meeting the following additional criteria was inventoried:

(1) a well-driller's report existed in USGS files (USGS files contain well-driller's reports for most wells drilled in the basin since 1955; these reports provide well-construction data),
(2) the well was <25 m deep (to focus generally on recently recharged water [Gilliom et al., 1995]),
(3) the well had not previously been inventoried (by 1993, fewer than 5 percent of existing wells in the basin had been inventoried; some inventoried wells may have been inventoried because of known or perceived water-quality problems, possibly introducing bias),
(4) the well was used for domestic purposes (in general, smaller volumes of water are pumped from domestic wells than from most other types of wells; thus, water from domestic wells is more likely to represent local ground water than is water from most other types of wells),
(5) the pump was a submersible or water-lubricated, vertical turbine pump (the negative pressure associated with other types of pumps may cause loss of volatile constituents during pumping, particularly VOCs, radon, and DO),
(6) the casing and plumbing were iron (glues used in polyvinyl chloride [PVC] plumbing may contribute VOCs to water passing through such plumbing), and
(7) the well plumbing allowed collection of samples before exposure to holding tanks, filters, chlorinators, or water softeners, which may alter water chemistry. If no wells within the chosen section met these additional criteria, a new section was chosen, and the selection process repeated. Suitable wells for sampling were found in 70 of the 76 cells.

Several deviations from the above criteria were allowed. First, many wells in the Portland Basin had been previously inventoried as part of a physical hydrogeology study. These wells were

allowed in the well-selection process for the SUS. Because the wells had not been inventoried for a water-quality study, no bias was introduced by using these wells.

One well, originally installed as a domestic well, was used for rinsing carrots at a small processing plant at the time of the SUS well inventory. No shallow domestic wells were available in this grid cell, so this well was used, even though its status as a domestic well had changed.

Submersible pumps that were present in two wells when inventoried had been replaced with jet pumps prior to sampling, and three wells presented unexpected access problems that necessitated sampling after passage through holding tanks. Samples collected from these five wells may have been altered by passage through the jet pumps or holding tanks. Thus, VOC and radon samples were not collected from these five wells, and DO concentrations measured in these wells were considered semiquantitative.

Finally, seven wells were sampled after water passed through non-iron (usually PVC) plumbing. The use of non-iron plumbing was made necessary by the fact that iron fittings at the well head were corroded to such a degree that they could not be removed to allow access. Thus, these samples were collected farther along in the plumbing system. Adhesives and primer used to glue PVC plumbing may contribute VOCs to water samples, but no VOCs were detected in water from the seven wells that were sampled after water passed through non-iron plumbing.

Urban Land-Use Study Design

An urban LUS was done in the Willamette Basin to provide ground-water data associated with this regionally important land-use setting, and to provide data that could be compared and contrasted with the predominantly agricultural SUS data. The urban LUS was done during July 1995. Ten shallow monitoring wells were installed in alluvium within Portland city limits for the urban LUS (fig. 3). Wells were installed because most existing shallow urban wells in the Portland metropolitan area tend to be located in fringe urban areas; water from such wells may reflect nonurban land-use effects. Although 20 or more wells are generally recommended for evaluating impacts of a given land use on ground-water quality in NAWQA studies (Gilliom, 1995), installation costs limited the urban LUS to 10 wells. Methods used to drill wells are described in the section "Urban Land-Use Study Well Installation."

Urban LUS wells were installed in areas of residential land use. Residential land use is the most extensive subgroup of urban land use in the Willamette Basin, representing about 80 percent of urban land use. Urban LUS sites were located in areas dominated by single-family homes on lots measuring about 400 to 500 square meters. Most upgradient homes were serviced by sanitary sewers (see section "Determination of Physical Attributes"). Long-established (on the order of several decades old) urban areas were chosen to minimize the potential for collecting water-quality data representing prior land use.

In the Willamette Basin, minor amounts of commercial land use commonly are interspersed within areas of primarily residential land use. Commercial land use in areas of primarily residential land use usually consists of narrow, discontinuous strips of service-oriented businesses such as restaurants, gasoline stations, and stores. On an area basis, such interspersed commercial land use in areas of primarily residential land use typically represents <10 percent of the land use, and for the most part, such mixed residential and commercial land uses are classified as residential land in the GIRAS land-use coverage for the Willamette Basin. However, a given area covered with commercial land use may have a different impact on underlying ground-water quality than an equivalent area covered with residential land use. Willamette Basin urban LUS water-quality data probably reflect some commercial land-use effects, and may not necessarily be representative of water quality associated with land use that is solely residential.

Access for well installation in urban areas was limited by existing development. Thus, no attempt was made to establish a network of wells distributed in a statistically random fashion. Also, areas with thick unsaturated zones were avoided to reduce drilling costs. However, sites were chosen to yield a breadth of coverage within the targeted setting (fig. 3), and the type and mixture of land use extending at least 1 km (kilometer) upgradient from each of these wells was typical of the tar-

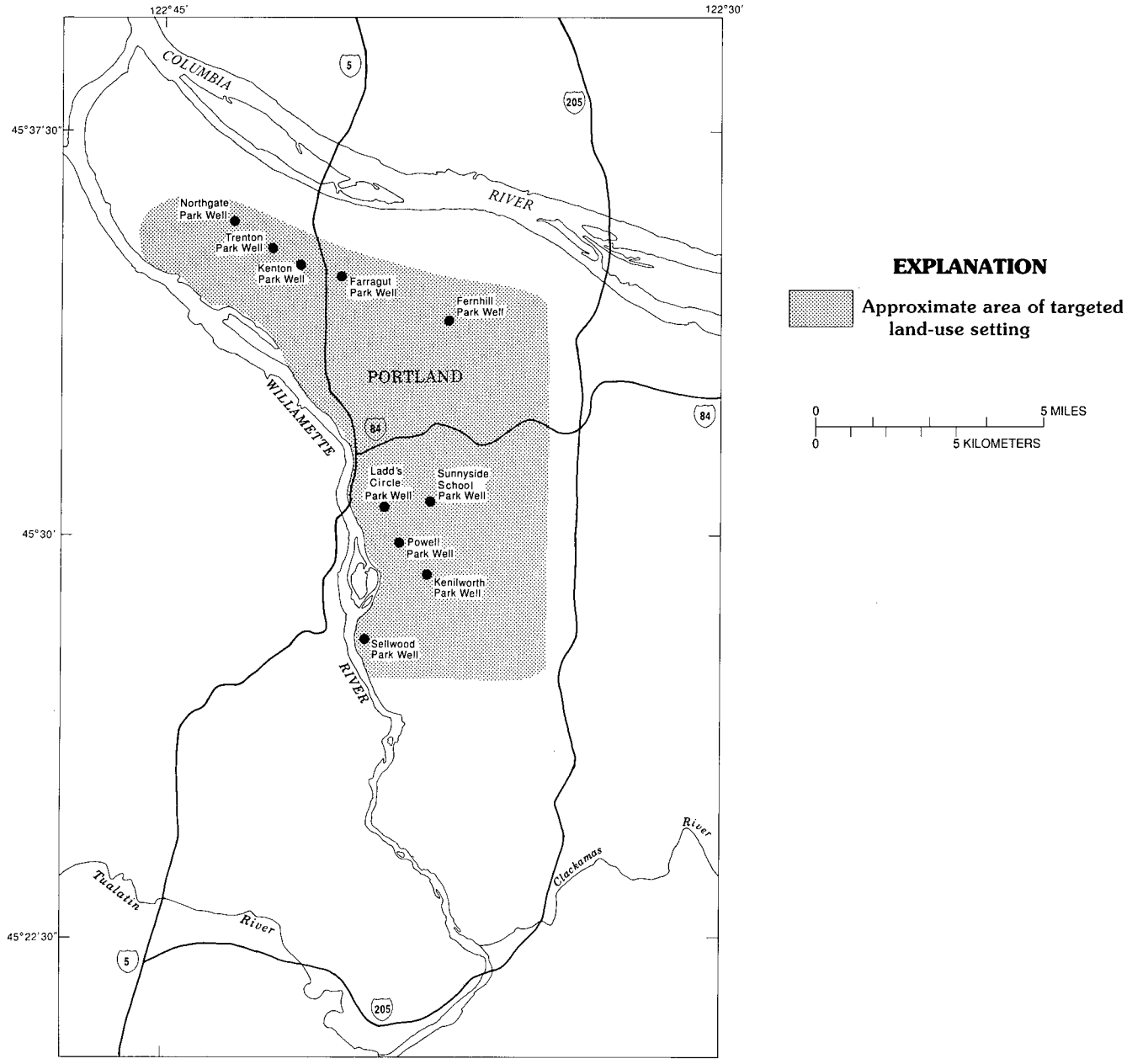

Figure 3. Locations of urban Land-Use-Study wells, Portland metropolitan area, Oregon.

geted land use in the Willamette Basin. Wells were screened below, but close to, the water table. The median well depth was 34 m, the median depth of penetration of wells below the water table was 8.5 m, and the median depth of penetration of the top of the screens below the water table was 4.6 m. The median depth of the urban LUS wells (34 m) was greater than that of the SUS wells (18 m), reflecting a generally lower water table in alluvium underlying the targeted urban areas relative to alluvium in the basin as a whole. However, the median penetration of the top of the open interval of urban LUS wells below the water table (4.6 m) was less than that of SUS wells (9.0 m).

Urban Land-Use Study Well Installation

Urban LUS wells were installed along the upgradient (relative to regional ground-water flow) edges of parks managed by the City of Portland. One well was installed in each of 10 parks. Upgradient edges were identified using potentiometric-surface maps of the Portland Basin (McFarland

and Morgan, in press). Wells were located along the upgradient edges of parks to eliminate, or at least to minimize, city park land-use effects on ground-water quality.

NAWQA protocols for well installation were followed (Lapham et al., 1995). One well was drilled using mud-rotary techniques. The remaining nine were drilled using air-rotary drilling with simultaneous advancement of casing. Wells were constructed of 0.10-m inside-diameter, steam-cleaned PVC casing. Screens were 1.5 m in length, and screen slots were 0.25 millimeters (mm) in width. Wells were developed with submersible pumps. The minimum and average volumes pumped during development were 3,000 and 13,000 liters, respectively.

Sample Collection

In general, standard NAWQA sample collection and processing protocols were followed (Koterba et al., 1995). These protocols were designed to ensure that data collected as part of the NAWQA are of high quality, and are collected in a manner consistent with other NAWQA study units.

Inorganic constituents (except radon and tritium, which were collected as unfiltered samples) were filtered as described below. Samples for pesticides were filtered through 0.7-µm nominal-pore-size, 142-mm-diameter glass-fiber plate filters. VOC samples were unfiltered.

One deviation from NAWQA protocols occurred because protocols were not finalized until 1995, 2 years after NAWQA ground-water sampling began in the Willamette Basin. Filtered samples for inorganic constituents collected in the SUS were passed through plate filters, instead of through pleated capsule filters as used in the urban LUS. Except for arsenic samples, filtered samples for inorganic constituents in the SUS were passed through 0.45-µm nominal-pore-size, 142-mm-diameter filters. Arsenic samples in the SUS were filtered through 0.10-µm nominal-pore-size, 47-mm-diameter filters.

One SUS tritium sample, broken in the laboratory, was replaced with a sample collected three months later, in November, 1993. Otherwise, for any given site, all samples were collected on the same day.

Prior to shipment, pesticides (except glyphosate, which was analyzed by direct injection of the filtered, aqueous sample) were extracted from filtered samples onto solid-phase sorbents, as described by Zaugg et al. (1995), Lindley et al. (1996), and Werner et al. (1996). Extraction usually occurred within 1 day, and always within 4 days, of sample collection.

Analytical Methods

Analysis of tritium was performed by the USGS National Research Program Tritium Laboratory in Reston, Virginia. All other USGS laboratory analyses presented in this report were performed at the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado.

Data for pesticides analyzed by gas chromatography with detection by mass spectrometry (GC/MS) were reported by the NWQL relative to method detection limits (MDLs). The MDL is defined as the minimum concentration of an analyte that can be identified and measured and that can be reported as being greater than zero with 99-percent confidence (Wershaw et al., 1987). Other NWQL analytical data presented in this report generally were reported by the NWQL relative to minimum reporting levels (MRLs). The MRL is defined as the minimum concentration of an analyte that can be reliably reported using a given analytical method (Timme, 1995). Because MRLs are not statistically determined, MRLs generally are higher than MDLs. MRLs often are used to report analytical data because MDLs frequently have not been determined (Timme, 1995).

DO was measured electrometrically in flow-through chambers in the field. Probes were calibrated daily in air and were periodically checked against anoxic solutions (deionized water with sodium sulfite added to chemically reduce oxygen).

Tritium was measured by liquid scintillation with electrolytic enrichment. Measured tritium concentrations were adjusted for radioactive decay occurring between collection and analysis of samples.

Samples were analyzed for nitrite plus nitrate by cadmium reduction. Nitrite was measured colorimetrically. Nitrite concentrations were generally $\leq$0.02 mg N/L (milligrams nitrogen per liter).

Nitrite concentrations exceeded 0.02 mg N/L in only two samples; in both cases, nitrite concentrations were less than 1 percent of nitrate concentrations. Thus, determinations of nitrite plus nitrate in this report essentially represent nitrate, and nitrite plus nitrate henceforth will be referred to as nitrate.

Phosphorus and chloride were measured colorimetrically. Analysis of arsenic and selenium was done by atomic absorption. Analysis of other trace elements (aluminum, antimony, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, silver, uranium, and zinc) was by ICP/MS (inductively coupled plasma/mass spectrometry).

Samples were analyzed for a suite of 86 pesticides by GC/MS (Zaugg et al., 1995, and Lindley et al., 1996; table 2, and high-performance liquid chromatography with photodiode-array detection (HPLC/DAD) (Werner et al., 1996; table 3). Of the 86 analytes, 45 were analyzed by GC/MS only, 38 by HPLC/DAD only, and 3 (carbaryl, carbofuran, and linuron) by both GC/MS and HPLC/DAD. Of the 48 GC/MS analytes, 47 were analyzed for any given time period. Poor dimethoate recovery (discussed in the section "Quality Assurance") lead to removal of dimethoate from the GC/MS schedule in 1994 (Zaugg et al., 1995). Acetochlor was added to the GC/MS schedule at about the same time. Thus, SUS samples were analyzed for dimethoate, but not for acetochlor; urban LUS samples were analyzed for acetochlor, but not for dimethoate. Concentrations of pesticides are presented in this report in units of ng/L (nanograms per liter); 1 ng/L is equal to 0.001 µg/L (micrograms per liter).

Glyphosate was analyzed by high-performance liquid chromatography with detection by fluorescence. The method used was an adaptation of the USEPA method for glyphosate (USEPA method 547; U.S. Environmental Protection Agency, 1990). The MRL was 5,000 ng/L.

In some cases, concentrations of pesticides are reported as estimates. The estimated concentrations are associated with greater uncertainty than are unqualified data. However, a detection with an estimated concentration is associated only with increased uncertainty of analyte concentration, and is not associated with any increased uncertainty of analyte identification. An analyte concentration may be estimated for one of four reasons: (1) quality-control (QC) data indicated poor (low and (or) variable) analyte recovery, (2) quantitative analysis was compromised by analytical interference, (3) analyte concentration was greater than the highest concentration calibration standard, or (4) the analyte was identified at a concentration below the MDL (applies to GC/MS analytes only). In order to be reported at a concentration below the MDL, the analyte must have met all identification criteria, as defined by Zaugg et al. (1995) and Lindley et al., 1996.

A suite of 60 target VOCs (table 4) was analyzed by GC/MS (Rose and Schroeder, 1995). In addition to analyzing for target VOCs, analyses also were done for nontarget VOCs. Nontarget VOCs are compounds that are not listed in table 4 that may be detected by mass spectrometry during routine analysis. Identification of nontarget VOCs can be made by comparing mass spectra of unknown compounds to reference mass spectra, as described by Rose and Schroeder (1995). The MRL for nontarget VOCs was 0.5 µg/L.

Of the 60 target compounds, MRLs for 59 were 0.2 µg/L. The MRL for one compound, 1,2-dibromo-3-chloropropane (DBCP), was 1.0 µg/L. Additional, low-level analysis for DBCP and 1,2-dibromoethane (EDB) by gas chromatography with detection by electron capture (GC/EC) was performed on 26 environmental samples. A description of the method, an adaptation of USEPA method 504 (U.S. Environmental Protection Agency, 1988), is given by Fishman (1993). MRLs with this method were 0.03 µg/L for DBCP, and 0.04 µg/L for EDB. Also, low-level analysis (MRL, 0.02 µg/L) for EDB by GC/EC was performed by ODEQ on 39 environmental samples using USEPA method 504 (U.S. Environmental Protection Agency, 1988). In all, 65 environmental samples were analyzed for EDB by low-level techniques (MRLs, 0.02 to 0.04 µg/L).

Radon was measured by liquid-scintillation counting. In most (49 of 51) cases, reported concentrations represent the mean concentrations of duplicate samples. Radon concentrations, originally done using wide-window (channels 60–1000) techniques, were recalculated from the original, raw data using narrow-window (channels 700–850) techniques (A. Mullin, USGS, written commun., 1996). Measured radon concentrations were

Table 2. Method detection limits and spike recoveries for pesticides analyzed by gas chromatography/mass spectrometry

[USEPA, U.S. Environmental Protection Agency; STORET, STOage and RETrieval system; MDL, method detection limit; ng/L, nanograms per liter; --, not applicable; e, estimated; spike data from environmental samples spiked at 100 ng/L; spike recoveries reported as percentages of expected values to the same number of significant figures as the analytical data]

Pesticide or pesticide degradation product	USEPA STORET number	MDL (ng/L)	Spike recovery (percent) (n = 7, except as noted)	
			Median	Range
Acetochlor	49260	2	[a]120	--
Alachlor	46342	2	94	27–100
Atrazine	39632	1	93	80–100
Azinphos-methyl	82686	1	e62	e34–e 90
Benfluralin	82673	2	64	53–100
Butylate	04028	2	94	89–100
Carbaryl	82680	3	e110	e76–e130
Carbofuran	82674	3	e100	e58–e110
Chlorpyrifos	38933	4	92	85–130
Cyanazine	04041	4	53	37–82
Dacthal (DCPA)	82682	2	150	83–160
p,p'-DDE	34653	6	92	72–100
Desethylatrazine	04040	2	e26	e21–e41
Diazinon	39572	2	81	65–92
Dieldrin	39381	1	100	82–120
2,6-Diethylaniline	82660	3	94	85–100
Dimethoate	82662	4	[b]<4	[b]<4–e32
Disulfoton	82677	17	69	56–74
EPTC	82668	2	92	86–110
Ethalfluralin	82663	4	87	55–100
Ethoprop	82672	3	77	62–84
Fonofos	04095	3	76	72–100
alpha-HCH	34253	2	92	69–100
gamma-HCH (Lindane)	39341	4	89	74–100
Linuron	82666	2	34	18–e270
Malathion	39532	5	64	54–77
Methyl Parathion	82667	6	82	53–93
Metolachlor	39415	2	95	70–100
Metribuzin	82630	4	52	42–66
Molinate	82671	4	94	88–100
Napropamide	82684	3	100	93–110
Parathion	39542	4	100	84–110
Pebulate	82669	4	92	86–100
Pendimethalin	82683	4	75	59–82
cis-Permethrin	82687	5	93	84–100
Phorate	82664	2	57	38–67
Prometon	04037	18	57	21–83
Pronamide	82676	3	80	69–93
Propachlor	04024	7	94	86–110
Propanil	82679	4	93	82–100
Propargite	82685	13	79	27–100
Simazine	04035	5	78	74–85
Tebuthiuron	82670	10	49	28–120
Terbacil	82665	7	e35	<7–e71
Terbufos	82675	13	61	46–83
Thiobencarb	82681	2	110	85–130
Triallate	82678	1	100	73–110
Trifluralin	82661	2	69	54–80

[a]n = 1.
[b]n = 6.

Table 3. Minimum reporting levels and spike recoveries for pesticides analyzed by high-performance liquid chromatography/photodiode-array detection

[USEPA, U.S. Environmental Protection Agency; STORET, STOage and RETrieval system; MRL, minimum reporting level; ng/L, nanograms per liter; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; --, not in field matrix spike solution, or analytical interference prevented quantification of analyte concentration; e, estimated; USGS NWQL control-spike data provided by M. R. Burkhardt (USGS, written commun., 1995) from laboratory spikes spiked at approximately 1,000 ng/L of pesticide-free blank water; ground-water spike data from environmental sample spiked at approximately 1,000 ng/L; surface-water spike data from F.A. Rinella and M.L Janet (USGS, unpub. data, 1996), from environmental samples spiked at approximately 250 ng/L to approximately 1,000 ng/L; spike recoveries reported as percentages of expected values to the same number of significant figures as the analytical data]

Pesticide or pesticide degradation product	USEPA STORET number	MRL (ng/L)	Spike recovery (percent)				
			USGS NWQL control spikes (n = 204–350)		Ground-water spike (n = 1)	Surface-water spikes (n = 7–13)	
			Mean	Standard deviation	Value	Median	Range
Acifluorfen	49315	50	83	24	92	--	--
Aldicarb	49312	50	61	31	52	10	<5–36
Aldicarb Sulfone	49313	50	53	22	40	21	<5–41
Aldicarb Sulfoxide	49314	50	100	35	90	81	<5–e110
Bentazon	38711	50	75	24	81	54	<5–140
Bromacil	04029	50	82	23	90	75	<5–98
Bromoxynil	49311	50	74	22	85	58	<5–130
Carbaryl	49310	50	61	26	87	33	5–70
Carbofuran	49309	50	80	27	90	e65	<5–160
3-Hydroxy-Carbofuran	49308	50	64	30	78	--	--
Chloramben	49307	50	60	21	--	--	--
Chlorothalonil	49306	50	11	22	<5	--	--
Clopyralid	49305	50	60	29	79	--	--
2,4-D	39732	50	71	22	63	57	<5–96
2,4-DB	38746	50	44	25	60	37	<3–58
Dicamba	38442	50	64	23	86	33	<5–77
Dichlobenil	49303	50	34	29	e65	--	--
Dichlorprop	49302	50	73	21	75	e66	<5–140
Dinoseb	49301	50	69	19	92	56	<4–120
Diuron	49300	50	61	23	88	e31	e-8.7–e85
DNOC	49299	50	35	25	e60	e66	<5–e140
Esfenvalerate	49298	50	17	21	e25	--	--
Fenuron	49297	50	66	29	84	e80	<4–e140
Fluometuron	38811	50	78	23	110	72	<5–77
Linuron	38478	50	74	24	90	120	10–140
MCPA	38482	50	66	22	51	54	<4–77
MCPB	38487	50	39	26	53	--	--
Methiocarb	38501	50	59	29	88	34	<5–72
Methomyl	49296	50	79	26	90	63	<5–76
Monoacid-Dacthal	49304	50	74	20	87	--	--
1-Naphthol	49295	50	22	26	< 5	<5	<5–<20
Neburon	49294	50	69	21	95	53	<5–74
Norflurazon	49293	50	78	22	90	--	--
Oryzalin	49292	50	68	22	e27	--	--
Oxamyl	38866	50	56	28	e74	37	<5–e55
Picloram	49291	50	55	23	84	28	<5–110
Propham	49236	50	64	28	--	72	<10–e180
Propoxur	38538	50	78	26	81	e57	<5–e76
Silvex	39762	50	73	19	82	63	5–120
2,4,5-T	39742	50	77	28	74	56	<5–110
Triclopyr	49235	50	63	24	54	--	--

Table 4. Minimum reporting levels and spike recoveries for volatile organic compounds analyzed by gas chromatography/mass spectrometry

[USEPA, U.S. Environmental Protection Agency; STORET, STOage and RETrieval system; MRL, minimum reporting level; µg/L, micrograms per liter; SUS, Study-Unit Survey; LUS, Land-Use Study; --, not in field matrix spike solution; comprehensive SUS spike data from one environmental sample spiked at 5.0 µg/L (except xylene, spiked at 15 µg/L); comprehensive urban LUS spike data from one environmental sample spiked at 2.5 µg/L (except xylene, spiked at 7.5 µg/L); abbreviated SUS spike data from environmental samples spiked at 1.9 to 2.6 µg/L; spike recoveries reported as percentages of expected values to the same number of significant figures as the analytical data]

Volatile organic compound	USEPA STORET number	MRL (µg/L)	Spike recovery (percent)			
			Comprehensive SUS spike	Comprehensive urban LUS spike	Abbreviated SUS spikes (n = 6)	
					Median	Range
Benzene	34030	0.2	68	72	--	--
Bromobenzene	81555	.2	76	84	--	--
Bromochloromethane	77297	.2	78	84	--	--
Bromodichloromethane	32101	.2	68	80	75	64–77
Bromoform	32104	.2	66	76	67	42–67
Bromomethane	34413	.2	52	48	--	--
n-Butylbenzene	77342	.2	58	76	--	--
sec-Butylbenzene	77350	.2	64	76	--	--
tert-Butylbenzene	77353	.2	70	68	--	--
Carbon tetrachloride	32102	.2	66	72	88	75–95
Chlorobenzene	34301	.2	72	80	--	--
Chloroethane	34311	.2	56	56	--	--
Chloroform	32106	.2	72	72	--	--
Chloromethane	34418	.2	[a]48	44	--	--
2-Chlorotoluene	77275	.2	70	68	--	--
4-Chlorotoluene	77277	.2	70	80	--	--
Dibromochloromethane	32105	.2	74	80	75	59–77
1,2-Dibromo-3-chloropropane (DBCP)	82625	1.0	90	76	--	--
1,2-Dibromoethane (EDB)	77651	.2	82	84	--	--
Dibromomethane	30217	.2	82	88	--	--
1,2-Dichlorobenzene	34536	.2	74	88	--	--
1,3-Dichlorobenzene	34566	.2	70	84	--	--
1,4-Dichlorobenzene	34571	.2	68	84	74	71–81
Dichlorodifluoromethane	34668	.2	54	28	--	--
1,1-Dichloroethane	34496	.2	68	72	--	--
1,2-Dichloroethane	32103	.2	76	84	82	82–86
1,1-Dichloroethylene	34501	.2	58	60	95	84–100
cis-1,2-Dichloroethylene	77093	.2	70	76	--	--
trans-1,2-Dichloroethylene	34546	.2	64	64	--	--
1,2-Dichloropropane	34541	.2	74	80	--	--
1,3-Dichloropropane	77173	.2	82	80	--	--
2,2-Dichloropropane	77170	.2	24	52	--	--
1,1-Dichloropropene	77168	.2	64	68	--	--
cis-1,3-Dichloropropene	34704	.2	56	76	--	--

Table 4. Minimum reporting levels and spike recoveries for volatile organic compounds analyzed by gas chromatography/mass spectrometry—Continued

Volatile organic compound	USEPA STORET number	MRL (µg/L)	Spike recovery (percent)			
			Comprehensive SUS spike	Comprehensive urban LUS spike	Abbreviated SUS spikes (n = 6)	
					Median	Range
trans-1,3-Dichloropropene	34699	0.2	66	76	--	--
Ethylbenzene	34371	.2	74	76	69	65–81
Hexachlorobutadiene	39702	.2	66	80	--	--
Isopropylbenzene	77223	.2	66	76	--	--
p-Isopropyltoluene	77356	.2	68	80	--	--
Methyl tert-butyl ether (MTBE)	78032	.2	92	80	92	92–100
Methylene chloride	34423	.2	70	76	--	--
Naphthalene	34696	.2	90	96	--	--
n-Propylbenzene	77224	.2	64	76	--	--
Styrene	77128	.2	74	76	--	--
1,1,1,2-Tetrachloroethane	77562	.2	80	80	--	--
1,1,2,2-Tetrachloroethane	34516	.2	84	84	--	--
Tetrachloroethylene	34475	.2	20	52	65	58–73
Toluene	34010	.2	70	72	--	--
1,2,3-Trichlorobenzene	77613	.2	82	92	--	--
1,2,4-Trichlorobenzene	34551	.2	74	92	--	--
1,1,1-Trichloroethane	34506	.2	68	68	92	90–100
1,1,2-Trichloroethane	34511	.2	84	84	--	--
Trichloroethylene	39180	.2	66	72	84	76–90
Trichlorofluoromethane	34488	.2	48	32	--	--
1,2,3-Trichloropropane	77443	.2	94	96	--	--
Trichlorotrifluoroethane	77652	.2	56	64	--	--
1,2,4-Trimethylbenzene	77222	.2	70	80	--	--
1,3,5-Trimethylbenzene	77226	.2	70	76	--	--
Vinyl chloride	39175	.2	50	48	91	87–96
Xylene	81551	.2	73	76	--	--

[a]Chloromethane recovery may reflect a small contribution of chloromethane from HCl preservative.

adjusted for radioactive decay occurring between sample collection and analysis.

NWQL data discussed in this report were retrieved from the USGS National Water Information System (NWIS) water-quality database (Maddy et al., 1990) on January 23, 1996. Updates to the NWIS database are expected as MDLs are recalculated, but the changes are expected to be minor, and the resulting changes are not expected to affect the overall conclusions of this report.

Quality Assurance

QC data were collected to allow evaluation of the quality of chemical data collected in the Willamette Basin study unit. QC data allow evaluation of techniques used to collect, process, and analyze water samples. Most of the QC data presented in this section were collected as part of project-level (as opposed to laboratory-level) quality-assurance efforts. The NWQL internal quality-assurance program is described by Pritt and Raese (1995). Unless otherwise noted, QC

data reported as a percentage of an expected value were calculated by project personnel and are reported to the same number of significant figures as are the original data.

Field blanks were collected to allow evaluation of the extent of any sample contamination that may have occurred as a result of sample collection, processing, shipping, storage and analysis. Blank water of known quality was pumped through sampling lines used to collect samples. Any processing steps used for environmental samples (e.g. filtering, preservation, extraction) also were used for field blanks.

Duplicate samples were collected to allow evaluation of the combined reproducibility (precision) of sampling, processing and analysis. The second of a pair of duplicate samples was collected immediately following collection of first sample. For filtered samples, the second of a pair of duplicate samples was collected from the same filter used for the first sample.

Prepared samples with known nitrate and phosphorus concentrations were submitted to the NWQL to facilitate evaluation of analytical accuracy. Results are reported as percentages of expected concentrations.

Pesticide and VOC field matrix spikes (FMSs) were submitted to the NWQL to facilitate evaluation of analytical accuracy. FMSs are environmental samples to which known amounts of selected pesticides or VOCs are added. For pesticides, analytical accuracy is defined to include analyte extraction and elution, as well as analysis. Results are presented as recoveries (percentages of expected concentrations). FMS recoveries are calculated by subtracting environmental concentrations (if any) from measured FMS concentrations, and dividing the difference by the expected value.

Trace-element standard-reference samples (SRSs) were submitted to the NWQL to facilitate evaluation of analytical accuracy. The USGS SRS program, an interlaboratory testing program, is described by Long and Farrar (1994). Individual SRSs used in this study are described by Long and Farrar (1991, 1992, 1994) and U.S. Geological Survey (1989a, 1989b). Results are reported as percentages of SRS-program MPVs (most probable values). An MPV for an analyte is the median of the concentrations determined by the participating laboratories.

Surrogate pesticide and VOC analytes were added to environmental samples to facilitate evaluation of method performance. Surrogate analytes are compounds with physical and chemical properties that are similar to those of at least some of the compounds being analyzed for in environmental samples. Analytes used as surrogates are not expected to be naturally present in environmental samples. Method performance for surrogate analytes is expected to reflect method performance for environmental analytes that are chemically similar to surrogate analytes (Rose and Schroeder, 1995; Zaugg et al., 1995). Surrogate analytes used for pesticide samples analyzed by GC/MS were diazinon-d_{10}, alpha-HCH-d_6, and terbuthylazine. Suitable surrogate analytes for pesticide samples analyzed by HPLC/DAD were not available (Werner et al., 1996). Surrogate analytes used for VOC samples were 1-bromo-4-fluorobenzene, 1,2-dichloroethane-d_4, and toluene-d_8. GC/MS surrogate analytes were added to deliver a concentration of about 100 ng/L and were added after sample filtration and prior to sample extraction. Thus, GC/MS surrogate recoveries should reflect performance of extraction, elution, and analysis, as well as analyte degradation and (or) loss during shipping and storage. VOC surrogate analytes were added by NWQL analysts prior to sample analysis. VOC surrogate recoveries reflect analytical performance, but do not measure the extent of analyte degradation or volatilization during shipping and storage. Surrogate results are reported by the NWQL as recoveries, expressed as percentages of expected concentrations.

Concentrations of pesticides and VOCs reported by the NWQL for environmental samples were not adjusted on the basis of FMS or surrogate recoveries. FMS and surrogate data are used solely to evaluate the quality of the data.

Nitrate

Seven SUS and three urban LUS field blanks were analyzed for nitrate. Nitrate concentrations in all 10 blanks were <0.05 mg N/L, demonstrating that field and laboratory methods were non-contaminating. Three pairs of duplicate SUS samples were analyzed for nitrate. Concentrations ranged from <0.05 to 1.6 mg N/L, and individual pairs of concentrations were within 0.11 mg N/L,

demonstrating reasonable reproducibility for a regional water-quality assessment. Three nitrate standards (deionized water with KNO_3 added), ranging from 0.67 to 5.6 mg N/L, were submitted to the NWQL. Reported concentrations were 99 to 100 percent of expected concentrations, demonstrating good analytical accuracy.

Phosphorus

Seven SUS and three urban LUS field blanks were analyzed for phosphorus. Phosphorus concentrations were <0.01 mg/L in nine blanks, and was 0.02 mg/L in one blank. The observed magnitude of contamination or analytical error in the blank associated with a concentration of 0.02 mg/L was small—a concentration equal to twice the MRL. Three pairs of duplicate SUS samples were analyzed for phosphorus. Pairs of concentrations were within 0.01 mg/L when concentrations were <1 mg/L, and within 0.1 mg/L when concentrations were >1 mg/L. Reproducibility appears to have been adequate for a regional water quality assessment. Three phosphorus standards (deionized water with KH_2PO_4 and phytic acid added) were submitted to the NWQL. Reported concentrations were as follows: low-concentration (0.069 mg/L) standard, 70 percent of expected value; medium-concentration (0.12 mg/L) standard, 81 percent of expected value; high-concentration (1.2 mg/L) standard, 99 percent of expected value. Accuracy increased with increasing concentration; on a percentage basis, low-concentration standards were associated with greater analytical uncertainty than were high-concentration standards.

Pesticides

Seven SUS and three urban LUS field blanks were analyzed for pesticides listed in tables 2 and 3). Three urban LUS field blanks also were analyzed for glyphosate. No pesticides were detected in blanks, demonstrating that field and laboratory methods were non-contaminating. Three pairs of duplicate SUS samples were collected for pesticides listed in tables 2 and 3, but no pesticides were detected in any of the three pairs of samples, so reproducibility could not be evaluated.

Seven FMSs (six in conjunction with the SUS and one in conjunction with the urban LUS) were analyzed for GC/MS analytes. Results are tabulated in table 2. Analyte recovery was adequate for most analytes, but recovery was poor for several analytes (median FMS recovery <60 percent; 60 percent recovery is the suggested minimum acceptable recovery for VOCs [Rose and Schroeder, 1995], so the 60 percent criterion was applied to pesticide recovery data). Concentrations of analytes having poor recovery likely will be biased low, and analytes having poor recovery may be associated with greater incidences of false negatives than would analytes having recoveries near 100 percent. (A false negative refers to the case in which an analyte was present in a sample, and was present at a concentration above the MDL or MRL, but was reported as a non-detect.) Desethylatrazine recovery was poor (median recovery, 26 percent), but relatively consistent (range of recoveries, 21 to 41 percent). The low median and narrow range of recoveries for desethylatrazine suggest that reported desethylatrazine concentrations had a consistently low bias. Linuron recovery also was poor (median recovery, 34 percent), but was highly variable (range of recoveries, 18 to an estimated value of 270 percent). The GC/MS method appears to be unreliable and inconsistent for linuron. Other analytes exhibiting poor recoveries included cyanazine, dimethoate, metribuzin, phorate, prometon, tebuthiuron, and terbacil.

One FMS (in conjunction with the urban LUS) was analyzed for HPLC/DAD analytes. (HPLC/DAD spike mixtures for FMSs were not available in 1993, when the SUS was done.) Results are tabulated in table 3. Additional QC data (1993–95 NWQL data from laboratory spikes of pesticide-free blank water, and 1994 surface-water FMS data collected as part of the surface-water component of the Willamette NAWQA) are also included in table 3 to supplement the single ground-water FMS. NWQL control-spike data do not reflect matrix-interference problems that may affect analysis of environmental samples, and surface-water FMS data may reflect different geochemical or biological matrices than do ground-water FMS data. In spite of these limitations, the supplemental QC data allow evaluation of a larger QC data set covering a longer period of time. HPLC/DAD QC data demonstrate recoveries that often were poor and variable. Thus, both the fre-

quencies of occurrence and the concentrations of HPLC/DAD analytes probably are underestimated.

Three surrogate analytes were added to each of 69 SUS and 10 urban LUS samples analyzed by GC/MS. Diazinon-d_{10} recoveries ranged from 50 to 200 percent, with a median of 90 percent. (Most recovery data for diazinon-d_{10} were reported by the NWQL to one significant figure.) Alpha-HCH-d_6 recoveries ranged from 70 to 100 percent, with a median of 90 percent. (Most recovery data for alpha-HCH-d_6 were reported by the NWQL to one significant figure.) Recovery of terbuthylazine ranged from 45 to 130 percent, with a median of 100 percent. Fewer than 5 percent of the surrogate recoveries were outside of the range of 70 percent to 130 percent. Surrogate data indicate that GC/MS method performance was probably adequate for analytes that are similar to surrogate analytes.

Volatile Organic Compounds

Seven SUS and four urban LUS field blanks were analyzed by GC/MS for VOCs (table 4). Also, five SUS field blanks were analyzed by GC/EC for low-level DBCP (MRL 0.03 µg/L) and EDB (MRL 0.04 µg/L). Several VOCs were detected. Chloromethane was detected in two SUS blanks. Chloromethane has been shown to be a by-product of the HCl preservative added to VOC samples (J.E. Williamson and G.C. Deizer, USGS, written commun., 1996). Chloromethane was also detected in some SUS environmental samples. Although the chloromethane conceivably could have had origins unrelated to the HCl preservative, detections (all <0.5 µg/L) were at concentrations below the USEPA Lifetime Health Advisory (defined later in section "Water Quality Standards and Health Advisories") for chloromethane (U.S. Environmental Protection Agency, 1996), and a Maximum Contaminant Level (defined later in section "Water Quality Standards and Health Advisories") has not been established for chloromethane (U.S. Environmental Protection Agency, 1996). SUS chloromethane data were not further interpreted.

Methylene chloride was detected in two SUS blanks and two urban LUS blanks. The reagent-grade water used for the urban LUS blanks became contaminated with methylene chloride during shipping and (or) storage (A.J. Driscoll, USGS, written commun., 1995). Different reagent-grade water was used for the SUS blanks, and the source of methylene chloride in the SUS blanks has not been determined. However, methylene chloride was not detected in SUS or urban LUS environmental samples, so the possibility of methylene chloride contamination does not affect the results of this study. Tetrachloroethylene was detected in one SUS blank. Because the magnitude of the contamination (concentration of 0.2 µg/L) was small relative to concentrations detected in SUS environmental samples (range, 0.9 to 29 µg/L), SUS tetrachloroethylene data presented in this report are assumed to be reliable.

Three pairs of duplicate SUS samples were analyzed by GC/MS for VOCs (table 4) and were analyzed by GC/EC for low-level DBCP (MRL 0.03 µg/L) and EDB (MRL 0.04 µg/L). No VOCs were detected, so reproducibility could not be evaluated.

Two comprehensive (60 analytes) FMSs (1 in conjunction with the SUS and 1 in conjunction with the urban LUS) and 6 abbreviated (13 analytes) FMSs (in conjunction with the SUS) were analyzed for VOCs. Results are reported in table 4. Analyte recoveries have a low bias (median of 76 percent for all FMSs), but much less variability than the pesticide FMS recoveries. Thirteen percent of all the recoveries were <60 percent of expected values. The low bias in VOC FMS recoveries is attributable to use of a micropipettor for spiking samples. In a comparison of VOC recoveries from micropipettors and gas-tight syringes (seven pairs of environmental samples), recoveries from micropipettors (70 percent) were consistently lower than recoveries from gas-tight syringes (90 percent)(J.S. Zogorski, USGS, written commun., 1996). Differences were statistically significant for 57 of the 60 VOCs tested.

Three surrogate analytes were added to each of 65 SUS and 10 urban LUS VOC samples. Recoveries were 93 to 110 percent for 1-bromo-4-fluorobenzene; 78 to 110 percent for 1,2-dichloroethane-d_4, and 80 to 110 percent for toluene-d_8. Surrogate data indicate that VOC method performance was probably adequate for a regional analysis of analytes that are similar to surrogate analytes.

ODEQ analyzed two field blanks and four pairs of duplicate samples for EDB. Concentra-

tions were <0.02 µg/L in blanks and in pairs of duplicate samples.

Trace Elements

Arsenic was the only trace element analyzed in SUS samples. Thirteen SUS field blanks were analyzed for arsenic; concentrations in all 13 blanks were <1 µg/L, demonstrating that field and laboratory methods were non-contaminating. Five pairs of duplicate SUS samples were analyzed for arsenic. Pairs of duplicate concentrations were within 1 µg/L, demonstrating reasonable sampling and analytical reproducibility. Three SRSs were submitted to the NWQL for analysis of arsenic for the SUS. MPVs for arsenic in SRSs ranged from 2.3 to 23.8 µg/L. Reported concentrations ranged from 76 to 100 percent (median, 80 percent) of MPVs, demonstrating fair analytical accuracy.

Urban LUS samples were analyzed for a suite of 17 trace elements (listed in table 5). Three urban LUS field blanks were analyzed for trace elements using methods developed for analysis of low-concentration samples. This method did not include analysis of arsenic or selenium. The low-concentration method—ICP/MS—is similar to that used for analysis of environmental samples (except arsenic and selenium) but is used by the NWQL solely for analysis of field and laboratory blanks. Trace-element concentrations in blanks were less than one-half of MRLs for environmental samples, demonstrating that field and laboratory methods were non-contaminating. (MRLs are 3 µg/L for aluminum and zinc and 1 µg/L for other trace elements in environmental samples.)

Three pairs of duplicate urban LUS samples were analyzed for trace elements. Most pairs of concentrations were within 1 µg/L of each other; one pair was within 2 µg/L (aluminum, at 5 and 7 µg/L). Sampling and analytical precision were reasonable.

Three SRSs were submitted to the NWQL for the urban LUS. Results are presented in table 5. Occasional poor accuracy was observed in some instances where analyte concentrations were near MRLs (lead—<100 percent recovery for a 1.0 µg/L SRS; nickel—200 percent recovery for a 1.7 µg/L SRS; and silver—<20 percent recovery for a 4.0 µg/L SRS). A low bias was observed for selenium determinations (median recovery 70 percent; range, <60 to 80 percent). Otherwise, good laboratory accuracy was demonstrated (recoveries between 90 and 110 percent).

Table 5. Trace elements analyzed for in samples from, and trace-element standard-reference-sample recoveries associated with, urban Land-Use Study

[SRS, USGS Standard Reference Sample; MPV, most probable value; µg/L, micrograms per liter; NWQL, National Water Quality Laboratory; --, SRS MPV unknown. Analytical concentrations in SRSs are reported as percentages of MPVs to the same number of significant figures as the analytical concentrations. One MPV for each of seven trace elements, ranging in concentration from 0.12 to 0.74 µg/L, are less than the method reporting limit of 1 µg/L; these seven were reported to be less than 1 µg/L, and thus were assigned values of 100 percent of MPVs]

Trace element	Range of SRS MPVs (µg/L) (3 SRSs)	Analytical concentration reported in SRS, as a percent of MPV	
		Median	Range
Aluminum	50–171	91.2	90–100
Antimony	0.55–8.6	100	90–100
Arsenic	0.55–4.2	100	100–100
Barium	7.6–44	100	97–100
Beryllium	0.12–17.0	100	100–100
Cadmium	0.34–3.0	100	100–100
Chromium	0.68–20	91	90–100
Cobalt	0.74–20	100	90–100
Copper	2.0–20	100	100–100
Lead	1.0–11	100	<100–110
Manganese	25.2–73	99	97–100
Molybdenum	11.9–22.5	100	99–100
Nickel	1.7–21.8	110	110–200
Selenium	1.6–9.8	70	<60–80
Silver	0.37–4.0	100	<20–100
Uranium	--	--	--
Zinc	24.8–90	110	96–110

Radon

No radon QC data were collected, but 49 of the 51 environmental samples were analyzed in duplicate. Radon concentrations in all but two of the pairs of duplicate samples were within 10 percent of the medians of the pairs. The two pair of outliers differed from the medians of the pairs by

11 and 17 percent. Analytical precision appeared reasonable.

Application of Dissolved-Oxygen Data

Effects of reducing (low-DO) conditions on ground-water quality are considered in this report. Low-DO water is defined herein as water with a DO concentration <1.0 mg/L. Conversely, well-oxygenated water is defined as having a DO concentration of ≥ 1.0 mg/L. Low-DO water is chemically reduced water or a mixture of chemically reduced water with a small amount of well-oxygenated water. The 1.0 mg/L criterion, although arbitrary, appears reasonable on the basis of the distributions of redox-sensitive species (sulfate, iron, and manganese) in these samples. Five semiquantitative DO concentrations (for samples collected from jet pumps or after passage through holding tanks; see section "Study-Unit-Survey Well Selection") were considered reliable enough for use in designating status as low-DO or well-oxygenated water. The distributions of redox-sensitive species in these five samples were consistent with these designations. Also, well-purging criteria (Koterba et al., 1995) promoted rapid replacement of holding-tank water, thereby minimizing water-air interactions in the samples collected after passage through holding tanks.

Water-Quality Standards and Health Advisories

In this report, concentrations of contaminants are compared to USEPA drinking-water standards and health advisories (U.S. Environmental Protection Agency, 1996). The USEPA drinking-water Maximum Contaminant Level (MCL) is the maximum concentration of a contaminant allowed in a public water system. Two USEPA drinking-water health advisories (HAs) used in this report for comparative purposes are the Lifetime HA (LHA) and the Risk-Specific-Dose HA (RSDHA). The LHA is defined as the concentration of a contaminant in drinking water that is not expected to cause adverse noncarcinogenic effects over a lifetime of typical exposure. Typical exposure is based on an assumption that a 70-kg (kilogram) adult drinks 2 L of such water per day for 70 years. An RSDHA is defined as the concentration of a contaminant in drinking water that is expected to result in a specified increased risk of cancer. RSDHAs presented in this report are calculated by USEPA at the 1-in-10,000 cancer risk level. Consumption of water containing a contaminant at the RSDHA 1-in-10,000 risk level is expected to be associated with the following risk: a 70-kg adult drinking 2 L of such water per day for 70 years faces an increased risk of cancer of approximately 1 in 10,000. In establishing MCLs and HAs, effects of consumption of multiple contaminants are not considered.

Determination of Physical Attributes

Methods used to characterize and quantify soil characteristics, cumulative thickness of clay above open interval of well, surficial geology, and land use are defined below. Reasons for the use of these parameters follow in the sections where these data are used.

Soil Characteristics

Characteristics of soils present at SUS well locations were assumed to be representative of soils in recharge areas for those wells. Soils were identified using U.S. Department of Agriculture, Soil Conservation Service county soil surveys (Soil Conservation Service, 1972, 1974, 1975, 1982a, 1982b, 1983, 1985, 1987a, 1987b). Weighted-mean percent clay (weighted over the vertical thickness of reported soil layers) and mean percent organic matter were calculated from data reported in the soil surveys. Where data were not available in published soil surveys, data often were available from County Soil Conservation Service offices. Data for percent clay and percent organic matter were unavailable at five and three sites, respectively.

Soil characteristics in recharge areas may differ considerably from those immediately adjacent to wells. Relationships between soil characteristics and water quality may be affected by this limitation.

Cumulative Thickness of Clay above Open Interval of Well

The cumulative thickness of clay above the open interval of SUS wells was assumed to be

proportional to the cumulative thickness of clay upgradient of those wells. Estimates of the cumulative thickness of clay above open intervals of wells were calculated from well drillers' reports. Lithologies recorded as clay, silty clay, and clay silt were classified as clay. Lithologies recorded as clay and sand, sandy clay, clay and cobbles, clay and debris, and all coarser materials were excluded.

Different drillers inevitably apply different definitions of clay, and some, if not most, material recorded by well drillers as clay likely is silt-sized rather than clay-sized. From a mineralogical standpoint, clay minerals constitute only a portion of the actual clay-sized fraction. Clay minerals provide greater surface area for sorption than do clay-sized particles of non-clay minerals. In addition to these limitations, the cumulative thickness of clay above an open interval of a well probably differs considerably from the cumulative thickness of clay lying upgradient from that well. At best, the estimated cumulative thickness of clay above the open interval of a well represents a relative, rather than an absolute, measure of clay-sized particles and clay minerals present upgradient from sampling sites.

Surficial Geology

Surficial geology at SUS well locations was assumed to be characteristic of the geology upgradient from those wells. Generalized geology of the Willamette Valley (Gannett and Caldwell, in press) was used to characterize alluvium at ground surface for SUS wells. Alluvium was grouped into two informal categories: Holocene alluvium and older (Pleistocene, Pliocene, and Miocene) alluvium. The hydrogeologic characteristics of these units have been described previously in the section "Hydrogeology."

Geologic materials present at land surface are not necessarily those present at, or upgradient of, the open interval of the well. Thus, relationships between water quality and surficial geology are unlikely to exactly mirror effects of subsurface geology on ground-water quality.

Land Use

Land use considered most likely to be associated with areas of recharge for SUS wells was determined by combining information on ground-water flow directions with published land-use data. Regional potentiometric-surface maps (Woodward et al., in press) were re-created at scales matching published land-use maps (Oregon Water Resources Department, 1979, 1980, 1981). Potentiometric-surface maps were used to construct 1-km-long flowpaths terminating at wells. The choice of flowpath length appeared reasonable given the shallow nature of the wells sampled. Flowpaths were constructed orthogonal to potentiometric-surface contour lines. Where potentiometric data were missing, flowpaths were constructed in the topographically upgradient direction. Flowpaths were overlaid on the land-use maps, and land use was assigned by calculating the percentage of flowpaths intersecting mapped areas of land use. Mapped land-use categories included irrigated agriculture, nonirrigated agriculture, urban, forest, range, water, and other. Land use classified as range was minor and was grouped with nonirrigated agriculture. The assigned land use for each site was the land use representing more than 50 percent of the apportioned land use for that site. If no single land use represented more than 50 percent of the apportioned land use, the land use was considered mixed, and data from that site were not used to quantitatively evaluate water-quality/land-use relationships. Land-use designations for the 70 SUS wells were as follows: nonirrigated agriculture, 37 wells; irrigated agriculture, 16 wells; urban, 11 wells; forest, 4 wells; other/mixed, 2 wells.

The quality of relationships between land use and ground-water quality for SUS wells may be limited by differences in the age of land-use data relative to the age of ground water collected. In other words, crop types and practices often are rotated on time scales shorter than time scales of ground-water movement. Ground water sampled in 1993 was recharged at some time prior to the time of collection, thus possibly associated with different crops, agricultural practices, and (or) chemical application rates. Land use determined from land-use surveys may or may not be representative of land use present when the ground water was recharged. For example, as grass seed prices have increased in recent years, farmers have converted some land from irrigated crops to grass seed—

generally a nonirrigated crop (Broad and Collins, 1996).

In contrast to SUS land-use determinations, the character of land use upgradient from urban LUS wells was identified prior to well installation, as previously explained in the introductory portion of the section "Study Design and Methods." However, subsequent interest in identification of unsewered areas upgradient from urban LUS wells arose. A description of the method used to identify unsewered areas follows: Information on groundwater flow directions and on houses served by septic systems were combined. Potentiometric-surface maps of the Portland Basin (McFarland and Morgan, in press) were used to construct flowpaths. Flowpaths were extended 0.4 km upgradient from urban LUS wells. The shallow penetration of urban LUS wells below the water table was reflected in the choice of flowpath length. Because septic systems are point sources of contaminants, difficulties arise in assigning individual septic systems (i.e. individual points) to individual flowpaths (i.e. individual lines). Thus, a swath (group) of flowpaths, rather than a single flowpath, was identified for each well. Homes that were within the bounding (outermost) flowpaths and were serviced by septic systems were enumerated using City of Portland Bureau of Environmental Services and City of Portland Bureau of Buildings records. The enumerated septic systems were considered to be associated with the wells.

Only a portion of the septic systems within flowpath swaths likely affect recharge to urban LUS wells. On the other hand, septic systems that lie more than 0.4 km upgradient from urban LUS wells also may affect recharge to those wells. Thus, the numbers of septic systems considered to be associated with wells probably differ considerably from the actual numbers of septic systems that affect the wells. Estimates of numbers of septic systems associated with wells should be considered relative, not absolute, estimates.

Several estimates of basin-scale parameters related to Willamette Basin land use were calculated using county-level data. These parameters were total nitrogen-fertilizer application rates (Alexander and Smith, 1990), total pesticide use (Rinehold and Witt, 1989; 1992), crop-specific pesticide use (Rinehold and Witt, 1989; 1992), total acreage of crops (Anderson et al., 1996, as calculated from data of Rinehold and Witt, 1989), and total acreage of pasture and rangeland (U.S. Bureau of the Census, 1989). Data used in the analysis were from Benton, Clackamas, Lane, Linn, Marion, Multnomah, Polk, Washington, and Yamhill Counties.

Statistical Methods

Many environmental data are not normally distributed and commonly contain censored values (unquantified data reported only as being less than some value, such as an MDL or MRL). Nonparametric statistics do not rest on an assumption that data are normally distributed, and are resistant to effects of outliers (Helsel and Hirsch, 1992). Nonparametric statistical tests were used for data analysis in this report.

The Spearman test was used to determine the degree of correlation between variables. The Spearman test (correlation coefficient, rho) is a regression analysis applied to rank-transformed data. The rank-sum (alternatively, Wilcoxon rank-sum or Mann-Whitney) test was used to evaluate differences between medians of two independent groups. Conceptually, the rank-sum test is similar to a t-test performed on rank-transformed data. Two-tailed tests were done; thus, the rank-sum test was used to determine if the medians of two groups were statistically different. The test is applied to data with values measured along a continuum (e.g. concentration). Contingency tables were used to perform Chi-square tests to evaluate differences between two independent groups of discrete (categorical) data. The test is similar to the rank-sum test, but the response variable is discrete (e.g. presence/absence) rather than continuous. Spearman and rank-sum tests were calculated using SAS/STAT® software (SAS Institute, 1989). Contingency tables were calculated by hand, using the procedure outlined by Helsel and Hirsch (1992). In this report, a significance level of 95 percent confidence was used, and the word "significant" is used exclusively in a statistical sense.

REGIONAL OCCURRENCE AND DISTRIBUTION OF GROUND-WATER-QUALITY CHARACTERISTICS

SUS results are presented in this section. The SUS was designed to characterize the quality of shallow ground water in alluvium in the Wil-

lamette Basin. Land overlying alluvial aquifers in the basin is primarily used for agriculture. Hence, some of these water-quality data may reflect effects of agriculture in addition to effects of geology and geochemistry. Ground-water quality associated with agricultural land use is qualitatively compared with ground-water quality associated with urban land use later in the section "Urban Land-Use Study."

Nitrate

Samples from 70 SUS wells were analyzed for nitrate (fig. 4; for plotting purposes in this and subsequent figures, nitrate concentrations below the MRL of 0.05 mg N/L were arbitrarily assigned values equal to the MRL). Concentrations ranged from <0.05 to 26 mg N/L, with a median of 0.40 mg N/L. Concentrations in six (9 percent) of the

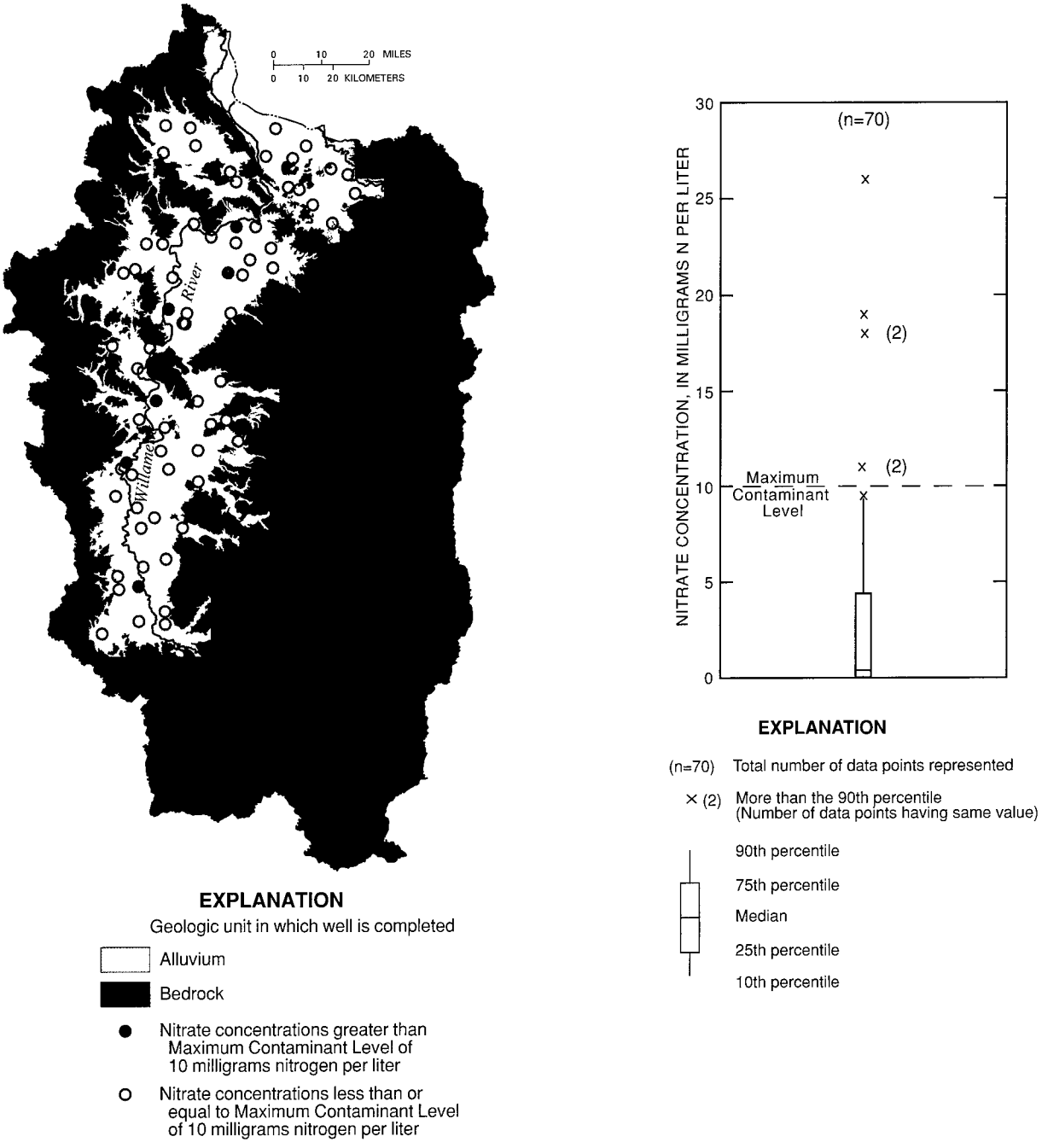

Figure 4. Nitrate concentrations in ground water from Study-Unit-Survey wells.

samples exceeded the MCL of 10 mg N/L. (The USEPA has not established an HA for nitrate in drinking water.) Five of the six occurrences of concentrations exceeding the MCL were from wells near (within 3.5 km of) the Willamette River (discussed further in section "Relationship of Regional Ground-Water Quality to Soils, Hydrogeologic Factors, and Land Use").

Ground-water age and quality often are related. Tritium was used as a tracer of young water in this study. High tritium concentrations in natural waters represent anthropogenic contributions from above-ground testing of hydrogen bombs. Bomb tritium first entered the global water cycle in detectable concentrations in 1953. The term "modern" is applied to water containing bomb tritium, and thus implies that at least part of the water was recharged no earlier than 1953 (Drever, 1988, p. 379). Prebomb tritium (from cosmic-ray production) in precipitation is estimated to have been approximately 10 tritium units (Bowen, 1988, p. 265; Drever, 1988, p. 379). With a half-life of 12.43 years (International Atomic Energy Agency, 1981, p. XIII), ground-water samples collected in 1993 should have had tritium concentrations of approximately 1.0 tritium unit if they had been recharged entirely in 1952. More recent recharge would yield a greater tritium concentration, whereas recharge further in the past, because of radioactive decay, would yield <1.0 tritium unit.

All 70 SUS wells were sampled for tritium. Fifteen (21 percent) yielded old (prebomb) water. Thus, water near (within 25 m of) land surface in the Willamette Basin is not necessarily modern.

One manner in which ground-water age and quality are related is a consequence of changes in nitrogen-fertilizer application rates over time. Estimated nitrogen-fertilizer application rates in the basin for the period 1945 to 1985 are presented on figure 5. The trend of greater nitrogen application rates with increasing time parallels national trends (Alexander and Smith, 1990), and reflects a push towards increased farm yields over that time period. Thus, ground water recharged further in the past may have been associated with smaller nitrogen input rates than water recharged more recently.

Twenty-one percent of SUS samples represent water recharged at least four decades prior

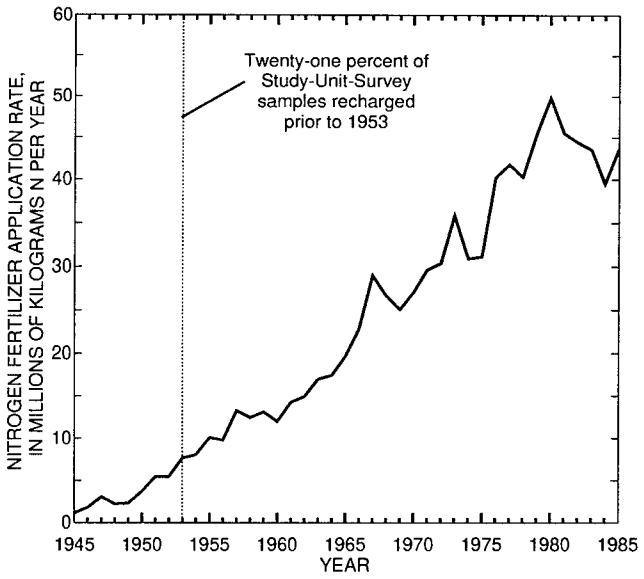

Figure 5. Nitrogen fertilizer application rates for the Willamette Basin, Oregon, from 1945 through 1985. (Data from Alexander and Smith [1990].)

to sampling, despite the fact that these were shallow wells. Presumably, many, if not most, of the remaining 79 percent of the samples represent water recharged on the order of years to decades in the past. Such a delay between the time water is recharged and the time ground water is pumped from wells indicates that there may be a similar lag between the time contaminants are released on land surface and the time they may be detected in ground-water samples. Many contaminants are reactive, but others are relatively conservative (nonreactive). Nitrate behavior in ground water is nearly conservative under oxidizing conditions. Three (20 percent) of the 15 old (prebomb) SUS samples were well oxygenated. Thus, extensive nitrate loss by way of nitrate reduction is unlikely to be occurring in all old ground water sampled. The implication is that as more recently recharged water, possibly associated with greater concentrations of nitrate, moves down flowpaths toward wells, nitrate concentrations may increase in some wells.

Nitrate reduction is the most important nitrate sink in most regional ground-water systems (Hallberg and Keeney, 1993, p. 313). Nitrate reduction generally occurs in low-DO environments. Forty-one percent of SUS samples were low-DO water. A weak (Spearman rho = 0.65) but statistically significant correlation between DO

and nitrate concentrations (fig. 6) suggests that nitrate reduction in ground water may be an important process in parts of the shallow alluvium in the basin. (Five semiquantitative DO concentrations were excluded from this analysis; see section "Study-Unit-Survey Well Selection".)

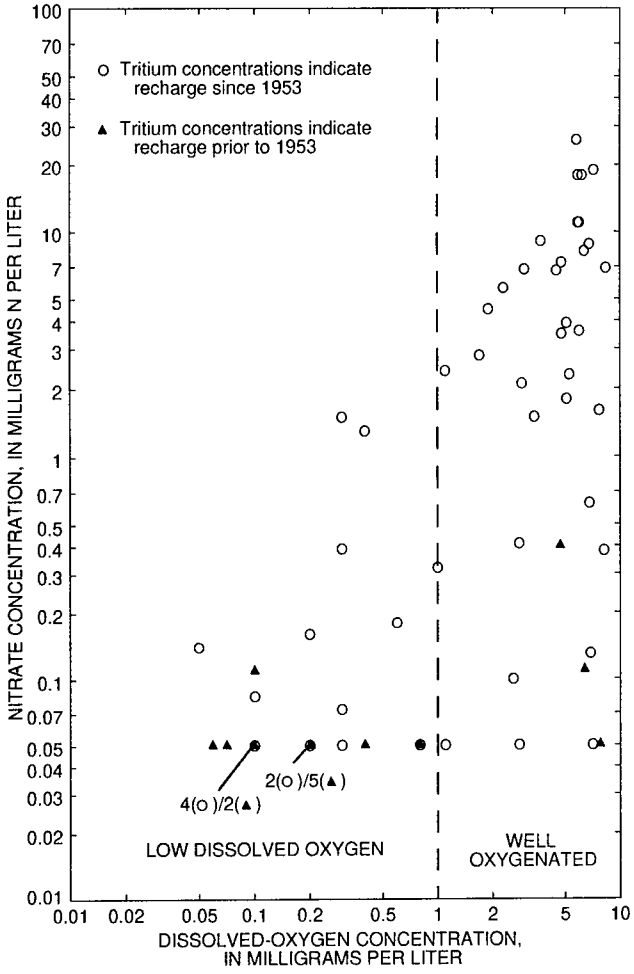

Figure 6. Relationship between nitrate and dissolved-oxygen concentrations in ground water from Study-Unit-Survey wells (dissolved-oxygen concentrations less than 0.1 milligrams per liter are associated with greater uncertainty than concentrations greater than 0.1 milligrams per liter).

A weak (Spearman rho = 0.57) but statistically significant correlation also was observed between nitrate and chloride concentrations in well-oxygenated ground water (fig. 7). Nitrate and chloride have several common sources. Both are used in agriculture (nitrate from nitrogen-based fertilizers, chloride from application of potassium chloride). Also, nitrate and chloride can be contributed to ground water from animal waste and from septic systems.

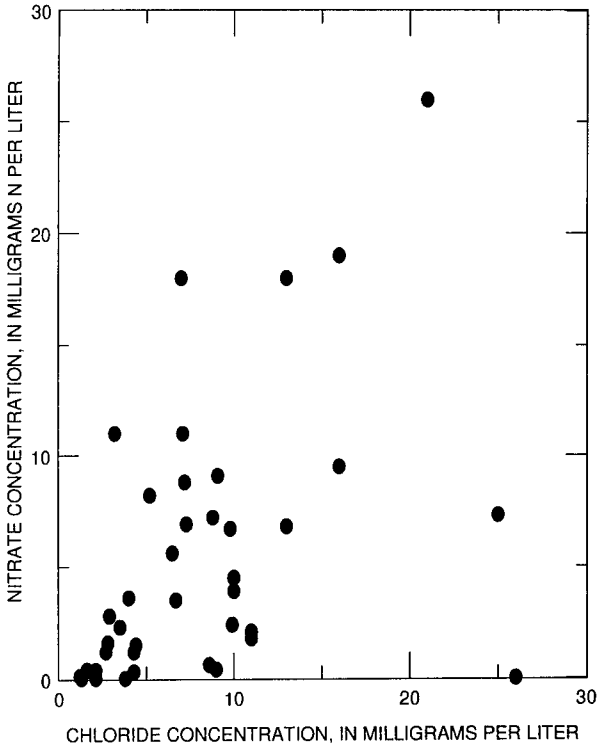

Figure 7. Relationship between nitrate and chloride concentrations in ground water from Study-Unit-Survey wells. (Dissolved-oxygen concentrations greater than or equal to 1.0 milligrams per liter.)

The correlation between nitrate and chloride concentrations, although statistically significant, is not strong. In particular, several samples contained high chloride concentrations but low nitrate concentrations (that is, they plot close to the abscissa, or x-axis; fig. 7), yet none contained low chloride concentrations and high nitrate concentrations (that is, none plot close to the ordinate, or y-axis; fig. 7). Two factors may have contributed to these relationships. First, unlike chloride, nitrate is not a conservative solute. Second, contributions of chloride from chloride-rich, nitrate-poor saline water may have been present in some samples. Deep-seated saline water is widespread in marine sedimentary rocks in the basin. Chloride concentrations exceeding 10,000 mg/L have been measured in this saline water, and ratios of chloride to nitrate (mass of chloride to mass of nitrogen from nitrate) typically are >1,000 (see, for example, U.S. Geological Survey, 1969, and Frank and Collins, 1978). This saline water appears to migrate upward along fault zones, and in some instances, into overlying alluvium, resulting in high chloride concentrations (Woodward et al., in press).

Phosphorus

Samples from 70 SUS wells were analyzed for phosphorus (fig. 8; for plotting purposes in this figure and figure 9, the one phosphorus concentration below the MRL of 0.01 mg/L was assigned a value equal to the MRL). Concentrations ranged from <0.01 to 2.2 mg/L. The USEPA has not established drinking-water standards or health advisories for phosphorus. However, to prevent excessive growth of aquatic plants in streams, the USEPA recommends that concentrations of phosphorus in stream water not exceed 0.10 mg/L (U.S. Environmental Protection Agency, 1986). Because most ground water eventually discharges to surface-water bodies, the 0.10 mg/L guideline for surface

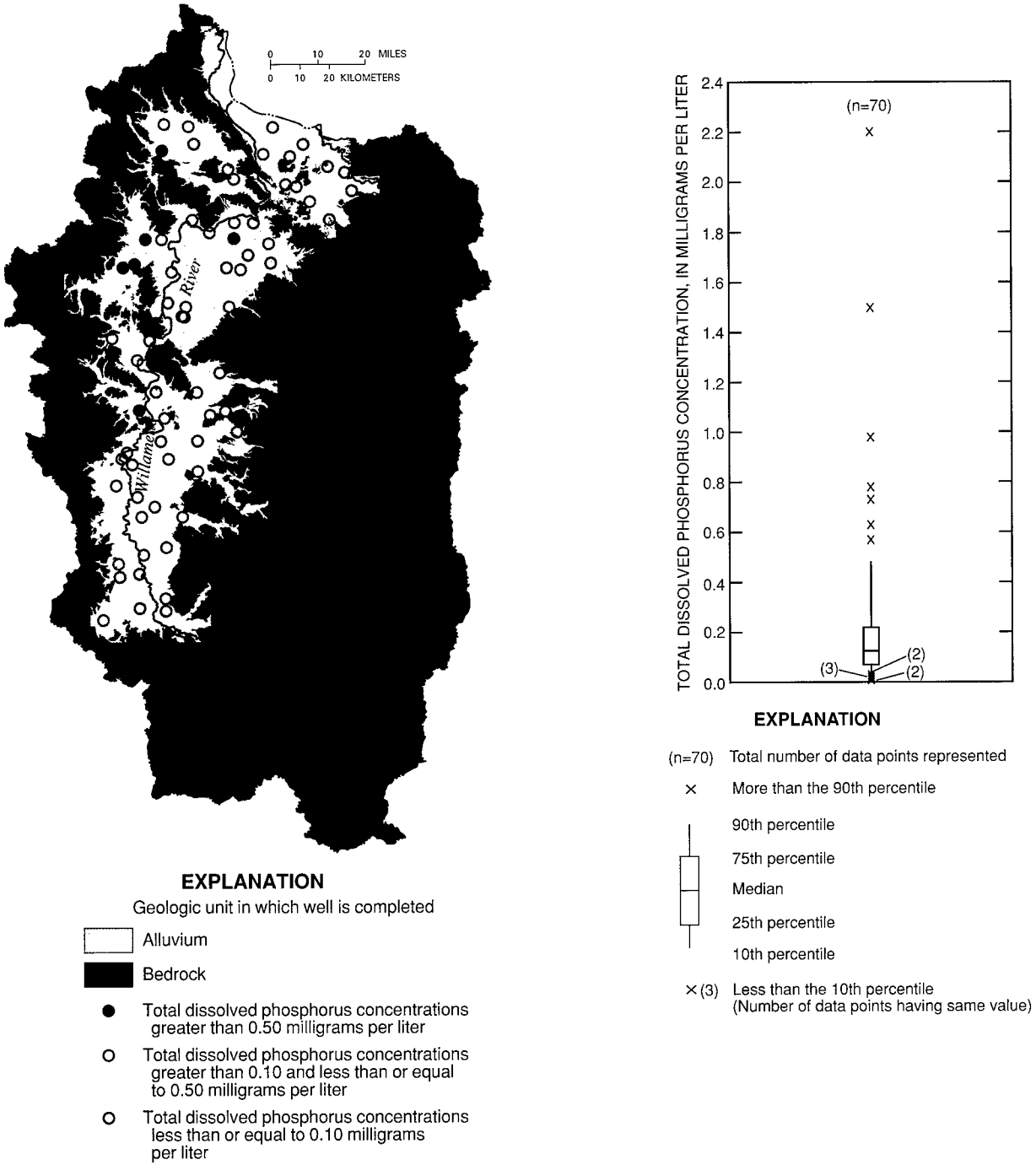

Figure 8. Total dissolved phosphorus concentrations in ground water from Study-Unit-Survey wells.

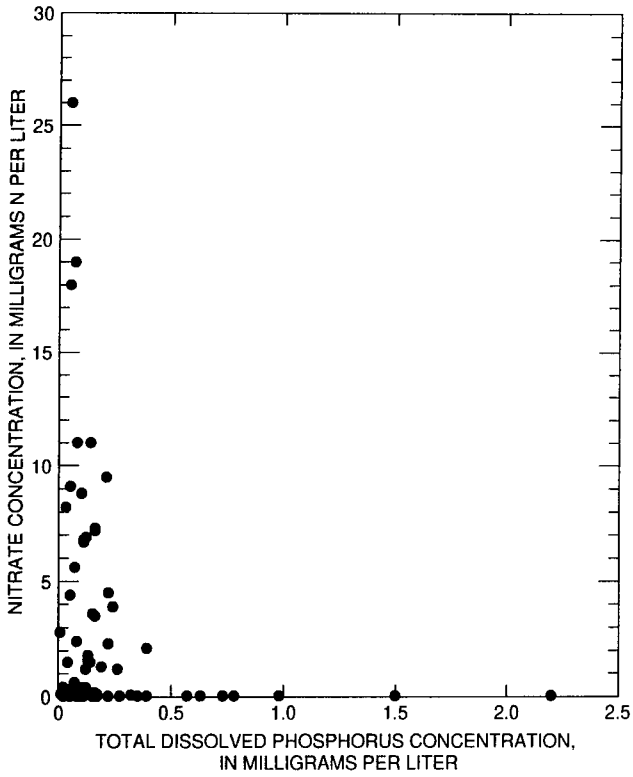

Figure 9. Relationship between nitrate and total dissolved phosphorus concentrations in ground water from Study-Unit-Survey wells.

water provides a useful standard of comparison for ground-water samples. Phosphorus concentrations exceeded 0.10 mg/L at 42 (60 percent of) SUS sites.

High concentrations of phosphorus (exceeding 0.10 mg/L) have been widely observed in detailed studies of ground water in the Tualatin River Basin (a tributary basin to the Willamette River; fig. 1), and large loads of phosphorus appear to enter surface water from seepage of ground water in the Tualatin River Basin (Rounds et al., 1994). However, little is known about phosphorus concentrations in ground water elsewhere in the Willamette Basin. Data presented on figure 8 suggest that high concentrations of phosphorus in ground water may not be uncommon in parts of the Willamette Basin outside the Tualatin River Basin, particularly in other Coast Range subbasins. Six of the seven concentrations >0.5 mg/L were in Coast Range subbasins. It is possible that ground-water seepage could represent a considerable portion of phosphorus loads to more Willamette Basin rivers than just the Tualatin River.

The median phosphorus concentration (0.17 mg/L) for low-DO samples was significantly greater than the median phosphorus concentration (0.10 mg/L) for well-oxygenated samples. The association of higher phosphorus concentrations with low-DO water contrasts with the pattern exhibited by the nitrate data. In the previous section, nitrate and DO were shown to be weakly correlated. These differences may be explained by the tendency of phosphorus to be more mobile under reducing conditions than oxidizing conditions (Patrick and Khalid, 1974), and the tendency of nitrate to undergo reduction after DO is consumed (Stumm and Morgan, 1981, p. 460 and 565).

Nitrate and phosphorus concentrations in SUS samples had a weak (Spearman rho = -0.34), but statistically significant, inverse correlation (fig. 9). Although both nitrogen and phosphorus are applied as fertilizer, nitrogen in the form of nitrate generally is much more mobile in oxidizing environments (such as the unsaturated zone and near-water-table zone) than is phosphorus (Freeze and Cherry, 1979, p. 442). This is a result of the tendency of phosphate (the common form of phosphorus in ground water) to sorb to mineral surfaces. The occurrence of nitrate in SUS samples likely reflects, in part, contributions from fertilizers. In contrast, the occurrence of phosphorus in SUS samples likely reflects geologic controls on source, and geochemical (e.g. redox) controls on transport, of phosphorus. Contributions of phosphorus from fertilizer to ground water probably are limited by sorption processes.

Pesticides

Samples from 69 SUS wells were analyzed for pesticides (analytes listed in tables 2 and 3, except acetochlor). Between 1 and 5 pesticides were detected at each of 23 sites (33 percent of sites sampled), for a total of 51 pesticide detections (fig. 10 and table 6). Thirteen different pesticides were detected. Sites at which pesticides were found were widely distributed, although pesticides were detected at a greater percentage of sites in the southern Willamette Basin (south of Salem) than in the northern Willamette Basin (discussed further in section "Relationship of Regional Ground-Water Quality to Soils, Hydrogeologic Factors, and Land Use"). Although sampling

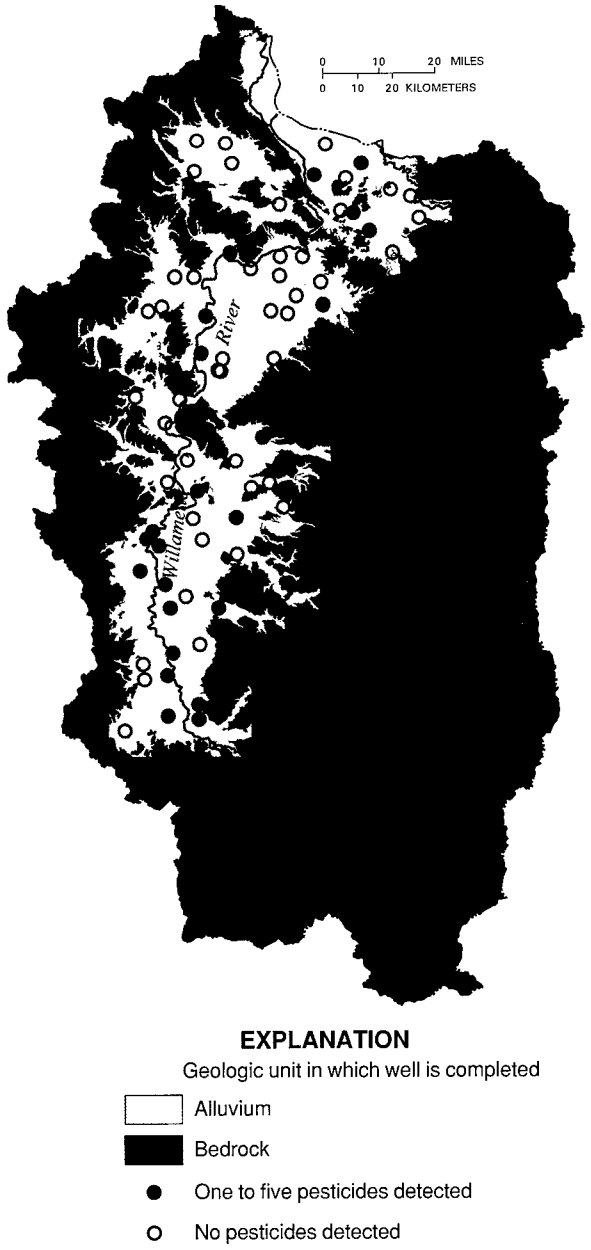

Figure 10. Detections of pesticides in ground water from Study-Unit-Survey wells.

indicated that the occurrence of pesticides is widespread in shallow ground water, most detections were at low concentrations (mostly <1,000 ng/L). It is likely, however, that detection frequencies and concentrations reported for HPLC/DAD analytes are biased low because of poor HPLC/DAD-analyte recovery (see section "Quality Assurance").

Dinoseb was present in one sample at an estimated concentration of 7,900 ng/L (table 6). Both the MCL and LHA for dinoseb are 7,000 ng/L. No other detections exceeded established MCLs, LHAs, or RSDHAs, although MCLs have been established for only 3 of the 13 analytes detected. European Union drinking-water guidelines, although not created by or for the United States, provide an alternative standard for comparison. European Union drinking-water guidelines have been established for all pesticides. European Union drinking-water guidelines for pesticides generally are more restrictive than United States standards, and are set at a blanket 100 ng/L for any individual pesticide (Rose, 1995). The large difference between United States and European Union standards may reflect, in part, uncertainty inherent in toxicology. Seven pesticide detections at six sites exceeded the European Union drinking-water guideline for pesticides of 100 ng/L.

Atrazine was the most commonly detected pesticide (detected at 20 sites). Desethylatrazine, an atrazine degradation product, was the second most frequently detected pesticide (detected at 11 sites). Analyses for other atrazine degradation products, such as desisopropylatrazine and hydroxyatrazine, were not performed. Detections of desethylatrazine were usually associated with detections of atrazine, but desethylatrazine was detected at one site at which atrazine was not detected. Thus, atrazine and (or) desethylatrazine were detected at 21 of the 23 sites at which pesticides were detected.

Atrazine has been one of the most heavily used pesticides in the Willamette Basin. In 1987, usage of atrazine (186,000 kg/year) was second only to diuron (251,000 kg/year) in the Willamette Basin (Anderson et al., 1996). The more frequent detection of atrazine (20 sites) than of diuron (2 sites), in spite of similar environmental persistence (Nash, 1988, p. 137, 159) can be explained by two factors: (1) the MDL for atrazine (1 ng/L) is much lower than the MRL for diuron (50 ng/L) (for example, atrazine data reselected at an artificial MRL of 50 ng/L results in only 5 detections), and (2) analyte recovery for diuron was considerably lower than that for atrazine (see section "Quality Assurance"), potentially yielding more false negatives than for atrazine.

Analysis of data from sites at which atrazine was detected indicates that nitrate and atrazine concentrations were not significantly correlated. However, the median nitrate concentration in sam-

Table 6. Detections of pesticides in ground water from Study-Unit-Survey wells

[ng/L, nanograms per liter; USEPA, U.S. Environmental Protection Agency; MCL, drinking-water maximum contaminant level; LHA, drinking-water lifetime health advisory; RSDHA, drinking-water risk-specific-dose health advisory (10^{-4} risk level); --, none; e, estimated. Water-quality criteria from U.S. Environmental Protection Agency (1996)]

Pesticide	Number of detections (69 samples)	Range of concentrations detected (ng/L)	USEPA MCL (ng/L)	USEPA LHA (ng/L)	USEPA RSDHA (ng/L)
Atrazine	20	3–890	3,000	[a]3,000	--
Bromacil	1	170	[b]	90,000	--
Dacthal (DCPA)	2	2	[b]	--	--
p,p'-DDE	1	e1	--	--	--
Desethylatrazine	11	e4–e180	--	--	--
Dieldrin	1	30	--	--	200
Dinoseb	1	e7,900	7,000	7,000	--
Diuron	2	60–340	--	10,000	--
Metolachlor	3	5–15	[b]	70,000	--
Propachlor	1	e4	--	90,000	--
Propanil	3	e3–15	--	--	--
Simazine	4	12–44	4,000	4,000	--
Terbacil	1	e15	--	90,000	--

[a]Under review.

[b]Listed for eventual regulation.

ples from sites at which pesticides were detected was significantly greater than the median nitrate concentration in samples from sites at which pesticides were not detected (fig. 11), perhaps reflecting common sources of nitrate and pesticides from applications in farming and landscaping.

Volatile Organic Compounds

Water samples from 65 SUS wells were sampled for a suite of 59 VOCs. Table 4 lists 60 targeted VOCs; however, chloromethane contamination in samples (see section "Quality Assurance") lead to removal of this analyte from consideration in the SUS. Analysis for nontarget compounds in 65 samples, low-level (MRLs between 0.02 and 0.04 µg/L) analysis of EDB in 65 samples, and low-level (MRL 0.03 µg/L) analysis of DBCP in 26 samples also were performed.

From 1 to 5 target VOCs were detected at each of 7 sites (11 percent of 65 sites evaluated), for a total of 14 VOC detections (fig. 12 and table 7). No nontarget compounds were identified. The occurrence of VOCs in ground water appeared to be partly explained by the presence of urban land use (discussed later, in section "Relationship of regional ground-water quality to soils, hydrogeologic factors, and land use").

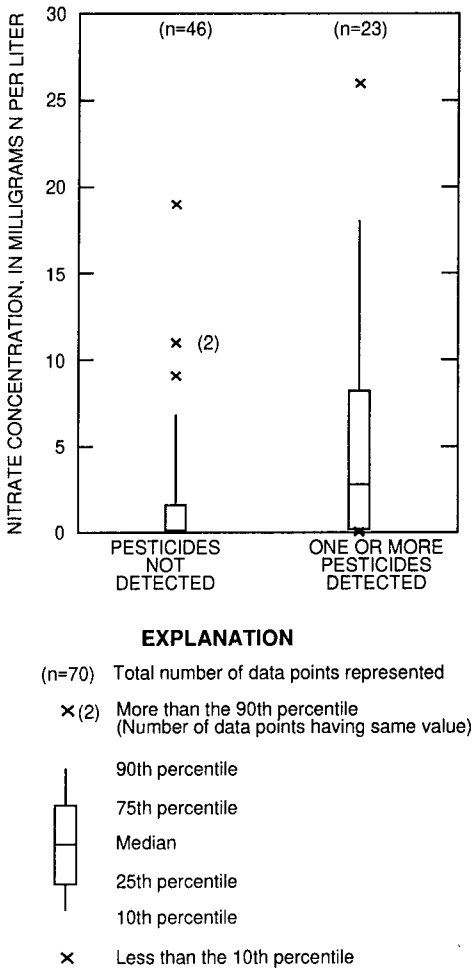

Figure 11. Nitrate concentrations in ground water from Study-Unit-Survey wells, as a function of presence or absence of detectable concentrations of pesticides.

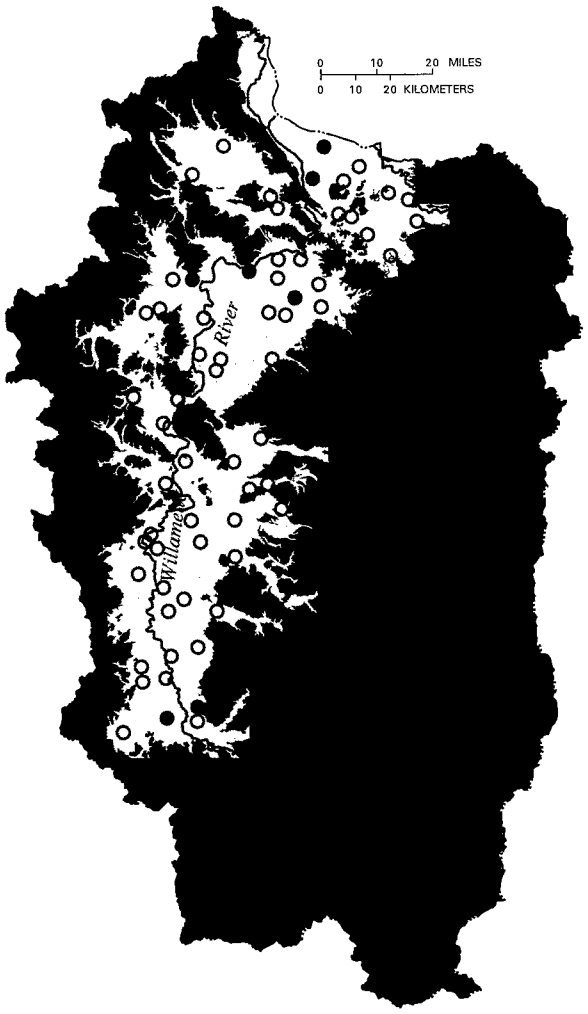

Figure 12. Detections of volatile organic compounds in ground water from Study-Unit-Survey wells.

No samples contained VOCs at concentrations exceeding LHAs or RSDHAs. One VOC was present at a concentration exceeding the established MCL: tetrachloroethylene was present in one sample at a concentration of 29 µg/L. The MCL for tetrachloroethylene is 5 µg/L. A large accumulation of household garbage at the well head of this rural site was observed during sampling. It is possible that the garbage represents a local point source of tetrachloroethylene to this well. The remaining 13 detections were at low concentrations (0.2–2.0 µg/L).

Table 7. Detections of volatile organic compounds in ground water from Study-Unit-Survey wells

[µg/L, micrograms per liter; USEPA, U.S. Environmental Protection Agency; MCL, drinking-water maximum contaminant level; LHA, drinking-water lifetime health advisory; RSDHA, drinking-water risk-specific-dose health advisory (10^{-4} risk level); --, none. Water-quality criteria from U.S. Environmental Protection Agency (1996)]

Volatile organic compound	Number of detections (65 samples)	Range of concentrations detected (µg/L)	USEPA MCL (µg/L)	USEPA LHA (µg/L)	USEPA RSDHA (µg/L)
					600
Chloroform	4	0.3–0.7	([a])	--	
1,1-Dichloro-ethylene	1	0.2	7	7	--
Tetrachloro-ethylene	3	0.9–29	5	--	70
1,1,1-Trichloro ethane	4	0.2–2.0	200	200	--
Trichloro-ethylene	1	0.8	5	--	300
Trichloro--fluoromethane	1	0.2	--	--	--

[a]An MCL specific to chloroform has not been established. Chloroform, which is a trihalomethane, is regulated with other trihalomethanes as a group. The MCL for total trihalomethanes is set at 100 µg/L.

Arsenic

Samples from 70 SUS wells were analyzed for arsenic (fig. 13); for plotting purposes in this figure and in figure 14, arsenic concentrations below the MRL of 1 µg/L were plotted at the MRL). Concentrations ranged from <1 to 13 µg/L. The MCL for arsenic is 50 µg/L (this MCL is currently under review; U.S. Environmental Protection Agency, 1996), and the RSDHA is 2 µg/L. Concentrations in 11 (16 percent) of the samples exceeded the RSDHA, but none exceeded the MCL.

The median arsenic concentration (2 µg/L) in low-DO samples was significantly greater than the median arsenic concentration (<1 µg/L) in well-oxygenated samples. This difference may be explained by two interrelated phenomena: (1) arsenic is more mobile under reducing (low-DO) conditions than under oxidizing conditions (Masscheleyn et al., 1991), and (2) phosphate (the common form of phosphorus in ground water) and arsenate (one of two common forms of arsenic in ground water) compete

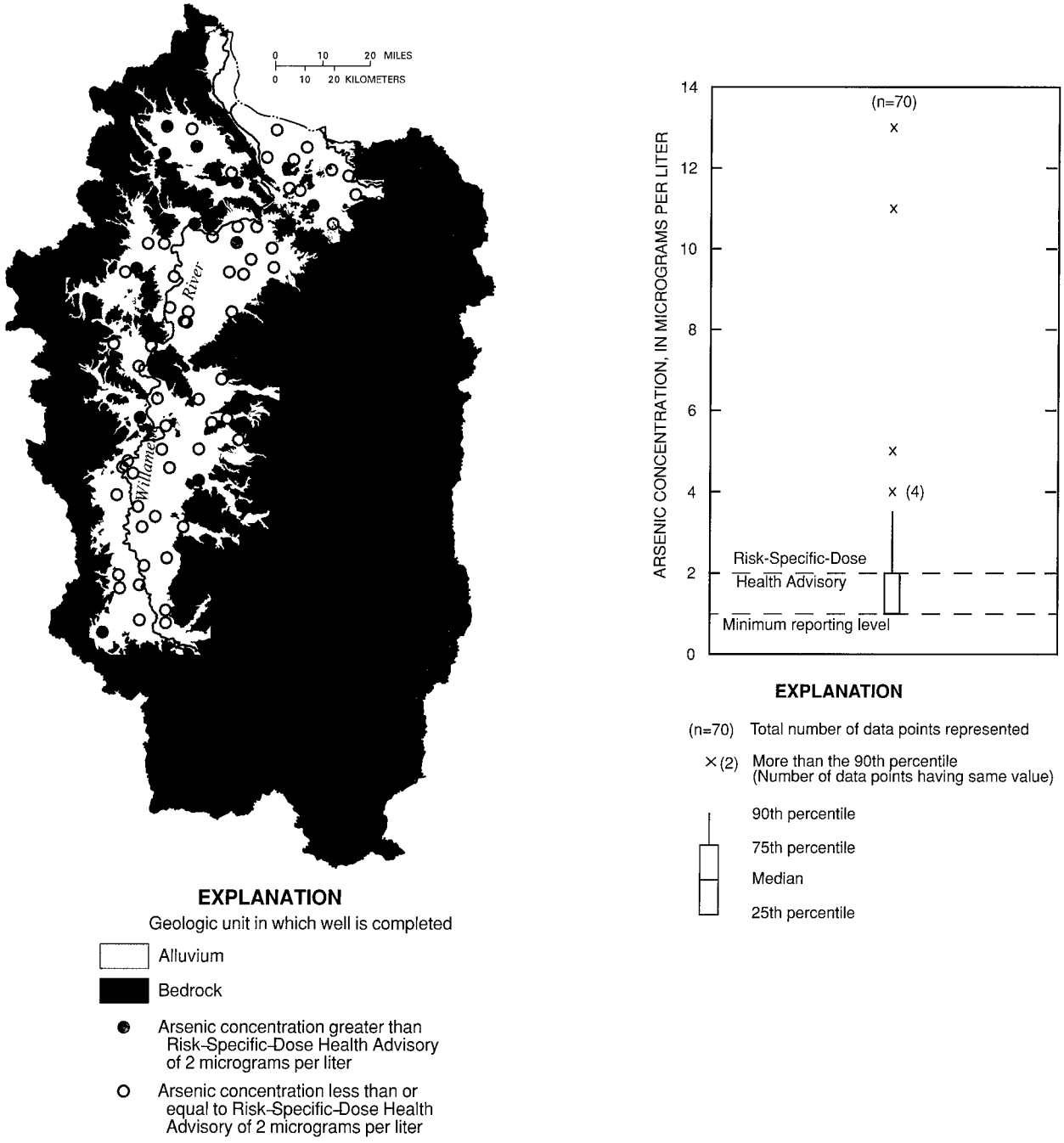

Figure 13. Arsenic concentrations in ground water from Study-Unit-Survey wells.

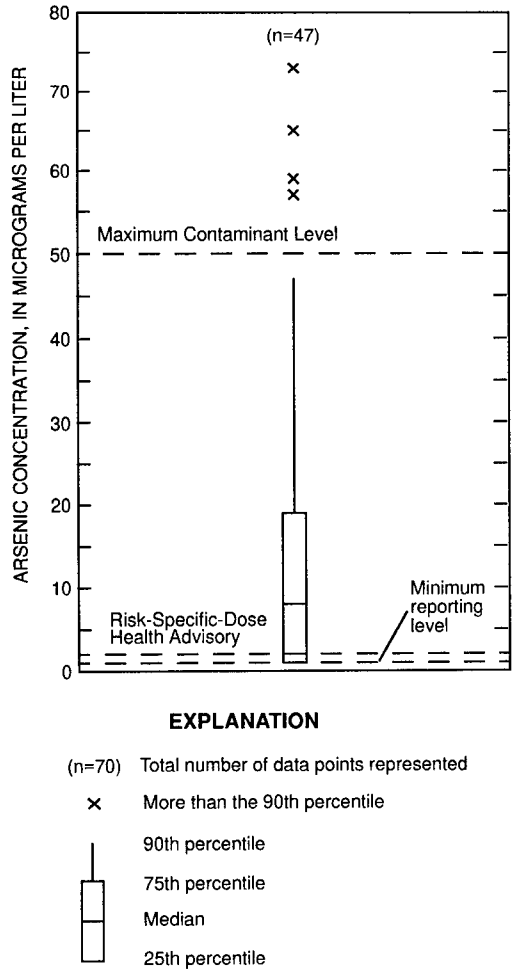

Figure 14. Arsenic concentrations in ground water from Tualatin River Basin, Oregon, wells.

centrations frequently exceed the RSDHA, and the observation that phosphorus concentrations frequently are high in the Tualatin Basin (see "Phosphorus" section), provided inspiration for further study. Thus, the Willamette NAWQA analyzed arsenic in samples collected as part of a separate USGS ground-water study of the Tualatin River Basin. The wells do not have the grid-based random-distribution characteristic of NAWQA SUS wells, but they do provide a large number of samples with which to more closely examine arsenic occurrence in the Tualatin River Basin, and allow evaluation of a larger part of the ground-water resource in the Tualatin River Basin.

Wells used for collecting water samples for arsenic as part of the Tualatin River Basin ground-water study consisted of 26 domestic wells distributed throughout alluvium in the Tualatin River Basin, and 15 drivepoints installed near, and in the bed of, the Tualatin River. The median depth of the 26 domestic wells was 32 m. The median depth of the 15 drivepoints was 2.7 m.

Samples were collected using protocols similar to NAWQA protocols. Water samples from domestic wells were filtered through 0.10-µm nominal-pore-size 47-mm-diameter plate filters; samples from drivepoints were filtered through 0.45-µm nominal-pore-size 142-mm-diameter plate filters. Five field blanks were collected; no arsenic was detected in these blanks.

Arsenic concentrations from the combined set of 47 Tualatin River Basin samples ranged from <1 to 73 µg/L (fig.14). Four of the 47 samples (9 percent) exceeded the MCL of 50 µg/L, and 31 of the 47 samples (66 percent) exceeded the RSDHA of 2 µg/L. The median arsenic concentration (11 µg/L) in low-DO samples was significantly greater than the median arsenic concentration (<1 µg/L)in well-oxygenated samples. As in the Willamette Basin SUS wells, higher arsenic concentrations were associated with low-DO samples than with well-oxygenated samples.

Although arsenic concentrations frequently exceeded the RSDHA and occasionally exceeded the MCL, the concentrations measured were low relative to some of the levels historically measured in bedrock areas in the basin. For example, arsenic concentrations of up to 1,700 µg/L have been measured in bedrock areas in the southern part of the basin (Goldblatt et al., 1963).

Radon

Water samples from 51 SUS wells were sampled for radon (fig. 15), a naturally occurring radioactive substance. Concentrations ranged from 200 to 1,200 picocuries per liter (pCi/L). All 51 samples exceeded the RSDHA of 150 pCi/L. Although high relative to the RSDHA, these concentrations are typical of radon concentrations in ground water in the U.S. (Wanty and Nordstrom, 1993, p. 432).

RELATIONSHIP OF REGIONAL GROUND-WATER QUALITY TO SOILS, HYDROGEOLOGIC FACTORS, AND LAND USE

SUS water-quality data were evaluated relative to several natural and anthropogenic factors—

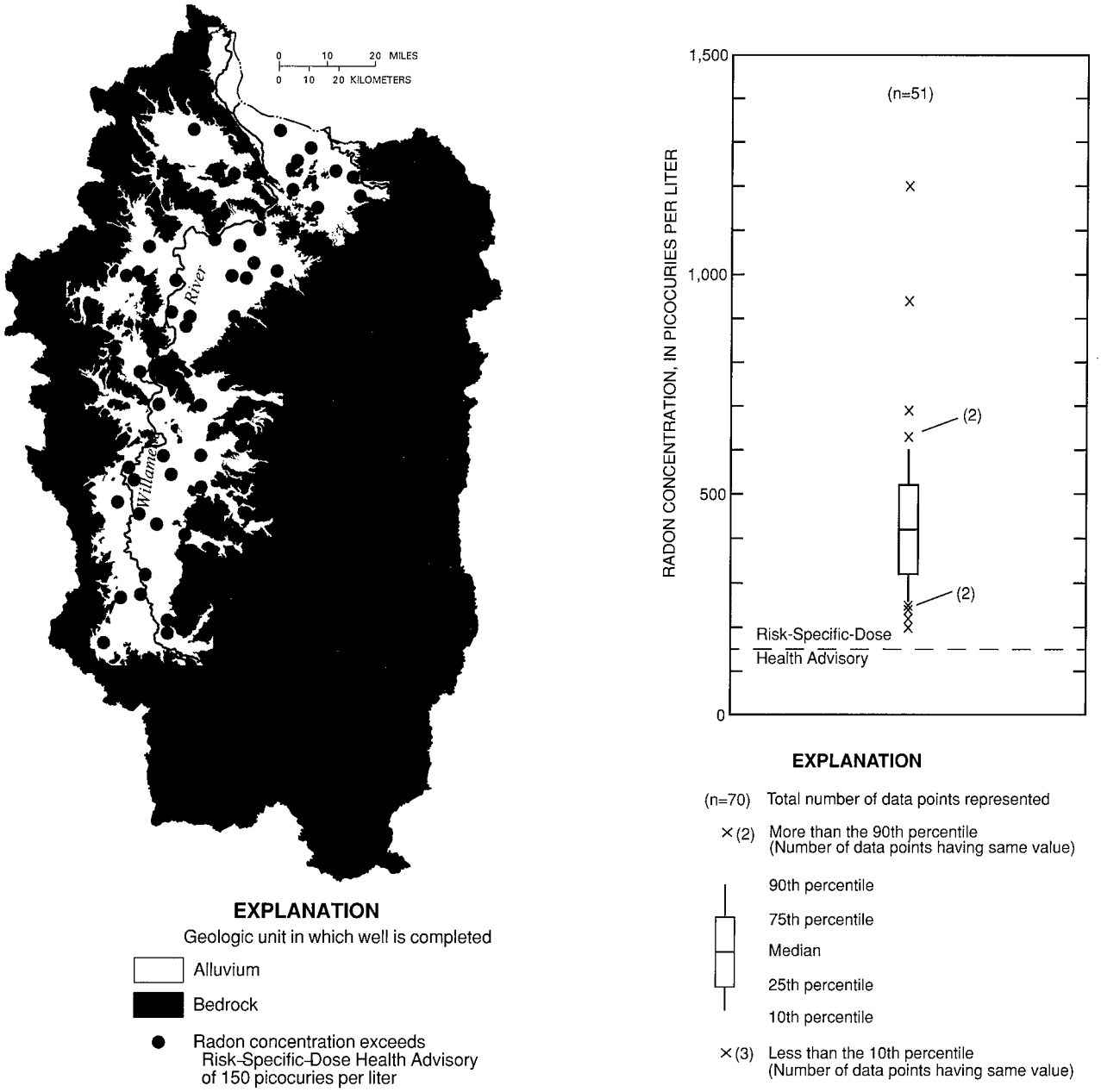

Figure 15. Locations of Study-Unit-Survey wells sampled for radon. (All samples exceeded the Risk-Specific-Dose Health Advisory of 150 picocuries per liter.)

characteristics of surficial soils, hydrogeologic variables, and land use—that may help to explain patterns of occurrence and spatial distribution of water-quality characteristics. Soils generally are the first geologic materials encountered by percolating water. Organic matter and clay minerals in soils can control sorption of synthetic organic compounds such as pesticides and VOCs. Also, coarse-textured soils (typically characterized by relatively low clay content) generally facilitate higher rates of solute leaching than do fine-textured soils (typically characterized by relatively high clay content). Slower solute-leaching rates associated with fine-textured soils provide increased time for kinetically limited near-surface solute-removal processes, such as plant uptake of nutrients, and volatilization and photodegradation of synthetic organic compounds.

Hydrogeologic conditions below the soil zone also may exert controls over the occurrence and distribution of water-quality characteristics. Texture of geologic materials, and amount of clay,

both can be important variables. Ground water generally moves more slowly through fine-grained geologic materials than through coarse-grained geologic materials. Thus, ground water at a given depth in a fine-grained aquifer may be older than ground water at a similar depth in a coarse-grained aquifer, and older water may be associated with different chemical loading rates than newer water. Overall textures of geologic materials vary among different geologic units, so selected water-quality characteristics were evaluated relative to geologic units present at land surface at SUS well locations. Selected water-quality characteristics also were evaluated relative to the cumulative thickness of clay above open interval of well (henceforth, "cumulative thickness of clay"). Ground water generally moves slowly through clay, and also, as in the case for soils, clay minerals in geologic strata may sorb synthetic organic compounds.

LUSs are an integral component of NAWQA ground-water studies (Gilliom et al., 1995). LUSs are designed to allow evaluation of the quality of shallow ground water lying under different types of land use, with the goal of fostering understanding of relationships between chemical loading (as related to land use) and ground-water quality. Most Willamette Basin SUS sites can be assigned to subcategories of agricultural land use, such as irrigated agriculture or nonirrigated agriculture. Thus, SUS data are evaluated relative to land use—primarily agricultural land use. This analysis complements results of other NAWQA LUSs.

Nitrate

In some of the following analysis, nitrate concentrations in ground water are divided into low nitrate (≤3.0 mg N/L) and high nitrate (>3.0 mg N/L) groups. Nitrate concentrations >3.0 mg N/L generally indicate anthropogenic contributions of nitrate (Madison and Brunett, 1985). Dividing the data into two groups facilitated comparison of nitrate data with various natural and anthropogenic factors.

Soils

Clay content of overlying soils was compared for high and low nitrate concentrations. Differences in median soil clay content were small between groups, and were not statistically significant. Similar results were obtained when low-DO data were removed from the data set.

Cumulative Thickness of Clay Above Open Interval of Well

Water that underlies a large cumulative thickness of clay may represent water recharged further in the past than water at similar depths that does not underlie a large cumulative thickness of clay. Water recharged further in the past may be associated with smaller nitrogen application rates (fig. 5). Alternatively, nitrate in older water may have had a greater opportunity to be reduced.

The cumulative thickness of clay for low- and high-nitrate samples is shown on figure 16. Greater cumulative thickness of clay was associated with lower nitrate concentrations than with higher nitrate concentrations; this may be explained by the low permeability of clay relative to coarser-grained materials. The differences of the medians, however, are not statistically significant (the significance level was 89 percent for the group of all data, and 61 percent for the well-oxygenated data).

Similarly, the median cumulative thickness of clay for the 6 SUS samples in which nitrate exceeded the MCL of 10 mg N/L (1.6 m) is less than that for the other 64 samples (6.2 m). Again, effects of clay on ground-water age could explain these differences.

Surficial Geology

Relationships between nitrate concentrations and surficial geology (Holocene alluvium and older alluvium) at sampling sites were evaluated. Permeability of Holocene alluvium in the Willamette Basin generally is greater than that of the older alluvium, so faster advection of nitrate might be expected in the Holocene alluvium. Relationships between nitrate concentrations and surficial geology are shown on figure 17. Median nitrate concentrations in samples associated with Holocene alluvium are not statistically different from median nitrate concentrations associated with older alluvium.

The median nitrate concentration (8.2 mg N/L) in well-oxygenated water associated with Holocene alluvium is considerably different from

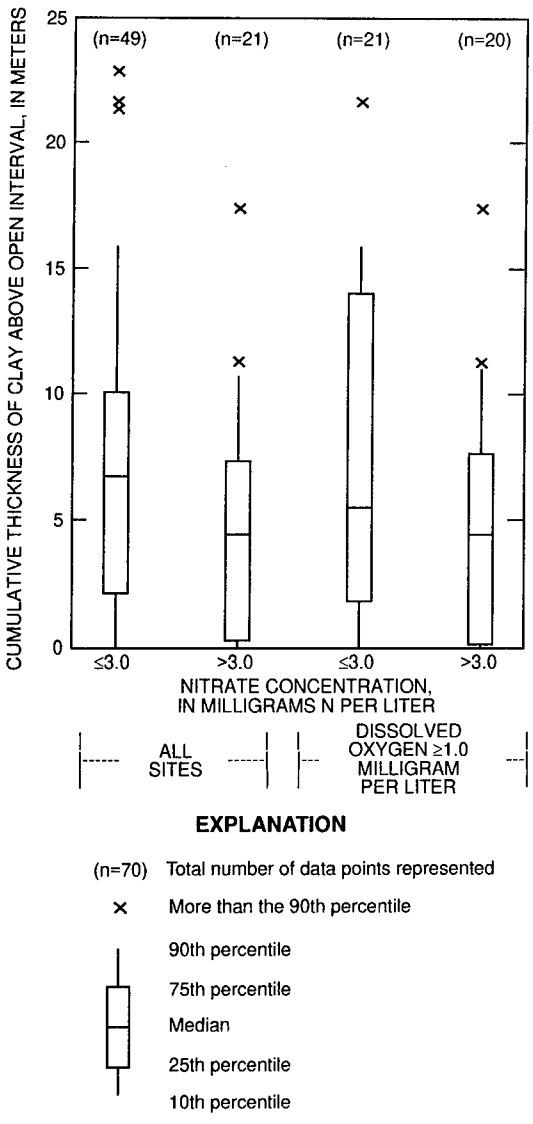

Figure 16. Cumulative thickness of clay above open interval of Study-Unit-Survey wells, as a function of nitrate and dissolved-oxygen concentrations.

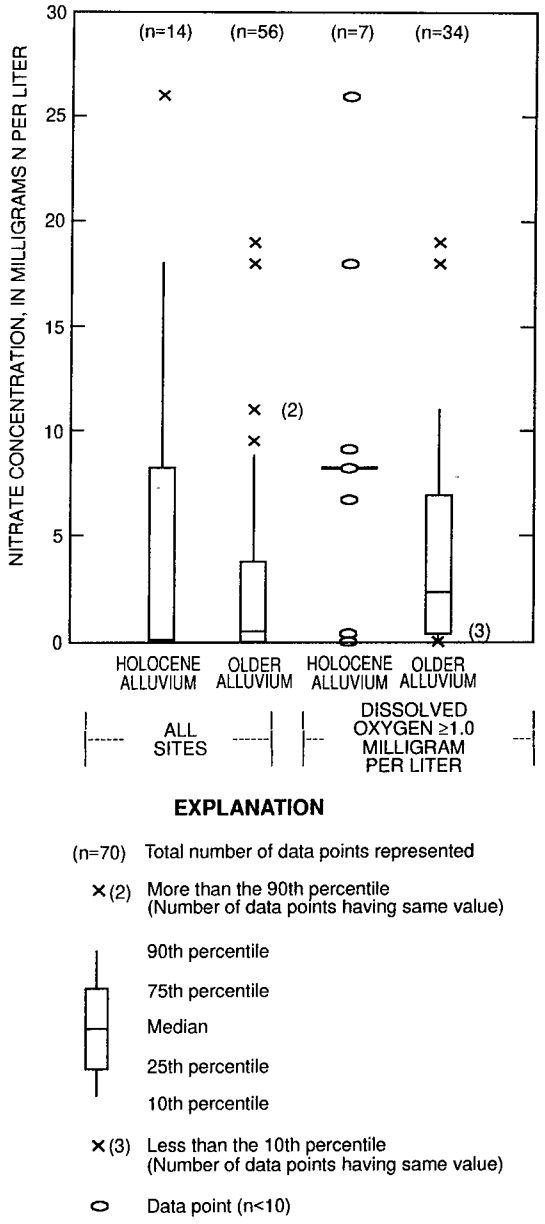

Figure 17. Nitrate concentrations in ground water from Study-Unit-Survey wells, as a function of surficial geology and dissolved-oxygen concentrations.

the median nitrate concentration (2.4 mg N/L) in well-oxygenated water associated with older alluvium. This difference is logical, given the permeability differences discussed above. This absence of a statistically significant difference at the 95-percent confidence level (the significance level was 83 percent for the well-oxygenated data) may reflect, in part, the small number (7) of well-oxygenated samples associated with Holocene alluvium.

Land Use

Nitrate may enter ground water from a number of point and nonpoint sources, including fertilizer, manure, septic systems, natural soil nitrogen, atmospheric deposition, land disposal of municipal waste, and fixation of atmospheric nitrogen. Agricultural activities typically represent the largest anthropogenic nonpoint source of nitrate to ground water (Madison and Brunett, 1985). Agricultural activities include application of fertilizer and manure, as well as farming practices such as crop-fallow rotation and irrigation. Effects of irrigated agriculture on ground-water nitrate concentrations can occur in response to generally greater nitrogen

application rates on irrigated crops and pasture relative to nonirrigated crops and pasture, and the leaching action of irrigation water (Hallberg and Keeney, 1993, p. 306). Nitrogen application rates in the basin vary but, overall, are greater for irrigated crops and pasture than for nonirrigated crops and pasture (table 1). Thus, ground water underlying areas dominated by irrigated agriculture may receive greater inputs of nitrogen than ground water underlying areas dominated by nonirrigated agriculture.

Distributions of nitrate concentrations in ground water downgradient from areas dominated by irrigated- and nonirrigated-agricultural land are shown on figure 18. The median nitrate concentration in samples associated with irrigated agriculture is greater than the median nitrate concentration in samples associated with nonirrigated agriculture, although the difference is not statistically significant. Removing the low-DO samples to minimize possible effects of nitrate reduction shifts the distributions higher on the concentration scale. The median nitrate concentration associated with irrigated agriculture remains greater than median nitrate concentration associated with nonirrigated agriculture, and the difference is statistically significant in this case.

Because older ground water may be associated with smaller nitrogen loading rates from fertilizers (fig. 5), the differences in nitrate concentrations associated with irrigated and nonirrigated agricultural land use could be affected by differences in ground-water age. For example, if ground water associated with nonirrigated agriculture was generally older than ground water associated with irrigated agriculture, differences in ground-water age could result in nitrate concentrations in wells associated with nonirrigated agriculture being lower than nitrate concentrations in wells associated with irrigated agriculture. The relationship between sites with low tritium ground water (concentrations ≤1.0 tritium unit) and land use are shown on figure 19. The percentage of sites with low tritium ground water is similar for nonirrigated and irrigated agriculture, both in the analysis of all data and in the analysis of well-oxygenated data. Tritium data only allow identification of the presence or absence of post-1953 water; they do not provide an absolute measure of ground-water age. These data are insufficient to

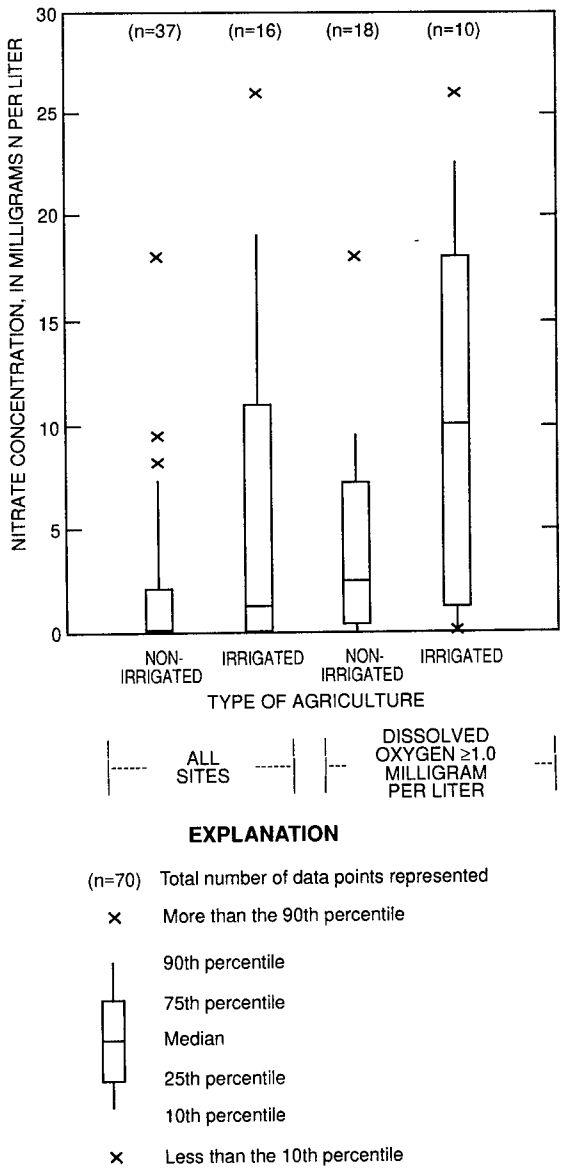

Figure 18. Nitrate concentrations in ground water from Study-Unit-Survey wells, as a function of land use and dissolved-oxygen concentrations.

conclude that the distribution of ground-water ages for the two land-use groups are similar. These data do, however, suggest that differences in nitrate concentrations measured in water associated with irrigated and nonirrigated agricultural land use were not caused by large differences in ground-water age.

The observed relationship between nitrate concentrations and land use may help explain the distribution of sites at which concentrations of nitrate exceeded 10 mg/L (fig. 4). Only two of the six sites at which concentrations of nitrate exceeded 10 mg/L were associated with Holocene

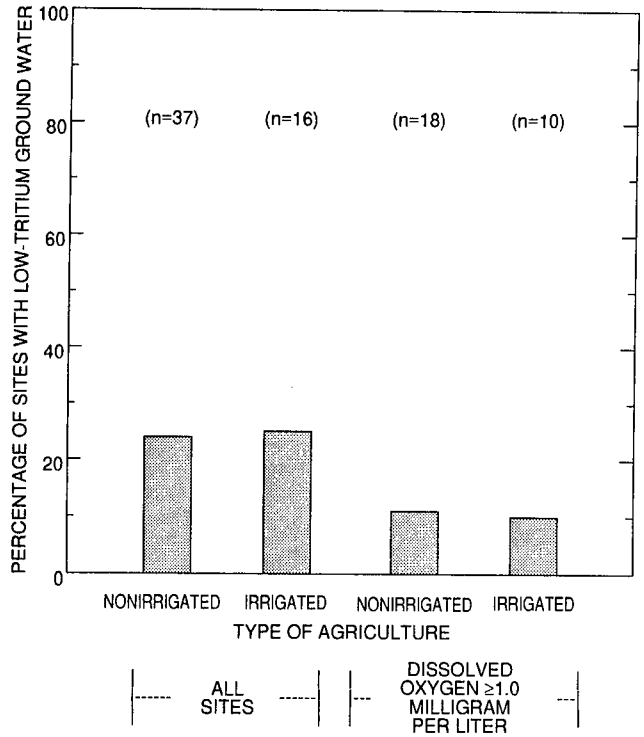

Figure 19. Percentage of agricultural Study-Unit-Survey wells with low tritium concentrations, as a function of land use and dissolved-oxygen concentrations.

alluvium, but five of the six sites were associated with irrigated agriculture. Much of the irrigated agriculture in the basin occurs near the Willamette River. Thus, the proximity to the Willamette River of sites at which concentrations of nitrate exceeded 10 mg/L (fig. 4) may reflect an association between nitrate in ground water and nitrogen inputs from overlying land use.

Pesticides

Soils

Relationships between the presence or absence of detectable concentrations of pesticides and clay or organic-matter content of overlying soils were evaluated. In comparing samples that did not contain detectable concentrations of pesticides with samples that did contain detectable concentrations of pesticides, differences in median soil clay content were small, and were not statistically significant. Similarly, differences in median soil organic-matter content were small, and were not statistically significant.

Cumulative Thickness of Clay Above Open Interval of Well

The presence or absence of detectable concentrations of pesticides in samples was compared to estimates of the cumulative thickness of clay associated with wells (fig. 20). The median cumulative thickness of clay (7.6 m) associated with samples without detectable concentrations of pesticides was significantly greater than the median cumulative thickness of clay (2.1 m) associated with samples with detectable concentrations of pesticides. The difference may be explained by two important controls exerted by clay on pesticide transport. First, ground water moves slowly through layers of clay-sized particles. Thus, advection of contaminants is slower through

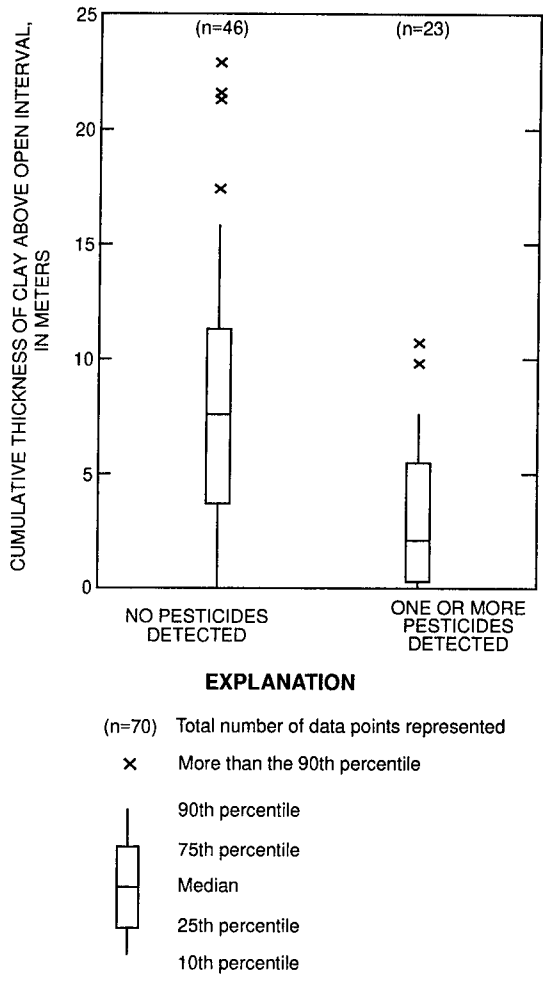

Figure 20. Cumulative thickness of clay above open interval of Study-Unit-Survey wells, as a function of presence or absence of detectable concentrations of pesticides.

layers of clay-sized particles than through layers of coarser materials, allowing more time for degradation (generally a kinetically limited process). Second, pesticides may sorb to the surfaces of clay minerals. Sorption of many pesticides is controlled predominantly by sorption to organic carbon (Grundl and Small, 1993); however, sorption of many other pesticides often is dominated by sorption to clay-mineral surfaces (Grundl and Small, 1993; Hance, 1988, p. 7).

The smaller frequency of detection of pesticides for northern basin wells (one or more pesticides in 22 percent of wells north of Salem) compared with southern basin wells (45 percent) (fig. 10) may be related to the distribution of clay in the basin. Northern basin wells were associated with greater cumulative thicknesses of clay, and fewer wells with one or more pesticides detected. For all sites sampled for pesticides, the median cumulative thickness of clay was 6.1 m. The median cumulative thickness of clay was exceeded at 64 percent of northern basin sites, but at only 33 percent of southern basin sites. The occurrence of greater cumulative thicknesses of clay in alluvium in the northern part of the basin relative to the southern part of the basin may be explained, in part, by the distribution of the Willamette Silt. As discussed in the "Hydrogeology" section, the Willamette Silt, a clay-rich unit generally occurring as the uppermost geologic unit within the older alluvium, is thickest in parts of the northern Willamette Basun and thins to the south.

Surficial Geology

The presence or absence of detectable concentrations of pesticides in ground-water samples was compared with surficial geology. Pesticides were detected in 29 percent of samples associated with older alluvium and in 50 percent of samples associated with Holocene alluvium. The greater frequency of detections at sites associated with Holocene alluvium is logical—the greater permeability of Holocene alluvium could allow faster movement of pesticides to wells. A contingency table was used to statistically evaluate these differences. The presence or absence of detectable concentrations of pesticides was not significantly different among the two geologic groups. It is possible that the lack of a statistically significant difference reflects the small number of samples (14) associated with Holocene alluvium.

Land Use

The presence or absence of detectable concentrations of pesticides in samples was evaluated relative to land use (irrigated agriculture or nonirrigated agriculture). Detection frequencies were similar among the two land-use categories—35 and 31 percent for nonirrigated and irrigated agriculture, respectively. A contingency table was used to statistically test these differences. The presence or absence of detectable concentrations of pesticides was not significantly different among the two land-use groups.

As previously discussed, atrazine and (or) desethylatrazine (an atrazine degradation product) were detected at 21 of the 23 sites where pesticides were detected. Atrazine use in the Willamette Basin in 1987 was associated predominantly with grass seed (54 percent) and corn (30 percent) (calculated from data of Rinehold and Witt, 1989; 1992). Non-agricultural use (right-of-ways, forests, etc.) accounted for <10 percent of estimated basinwide atrazine use in 1987 (calculated from data of Rinehold and Witt, 1989; 1992). Because large amounts of atrazine historically have been applied to grass seed and corn in the Willamette Basin, the relationship between the presence of detectable concentrations of atrazine and (or) desethylatrazine in ground water and the presence of corn and grass seed crops on overlying land was investigated.

The percentage of land that was planted in corn and grass seed within 0.4 km of SUS wells was determined by direct observation in summer 1995. Characterizing land use within a 0.4-km-radius circle of a well is standard NAWQA methodology for evaluating land use associated with wells (Koterba et al., 1995). Unlike the previously defined and used method that integrated ground-water flowpaths and published land-use maps (see section "Determination of Physical Attributes"), the present method (defined here as the "radial method") does not consider ground-water flowpaths. Thus, the radial method may be less reliable than the method integrating ground-water flowpaths and published land-use maps.

The presence or absence of detectable concentrations of atrazine and (or) desethylatrazine in samples was compared with the percentage of land within 0.4 km of wells planted with corn and grass seed (fig. 21). Sites at which atrazine and (or) desethylatrazine were detected had a greater median percentage of land planted in corn and grass seed (25 percent) than sites at which these compounds were not detected (9 percent), but the differences were not statistically significant. The absence of a statistically significant relationship may have been influenced by differences in ground-water age among samples. The two sites associated with the greatest percentages of corn and grass seed (93 and 92 percent; fig. 21) did not contain detectable concentrations of atrazine or desethylatrazine. Samples from these two sites appear, on the basis of tritium data, to have been recharged prior to 1953. Such old water would not be expected to contain atrazine or desethylatrazine because atrazine was first patented in 1960 (Budavari, 1989).

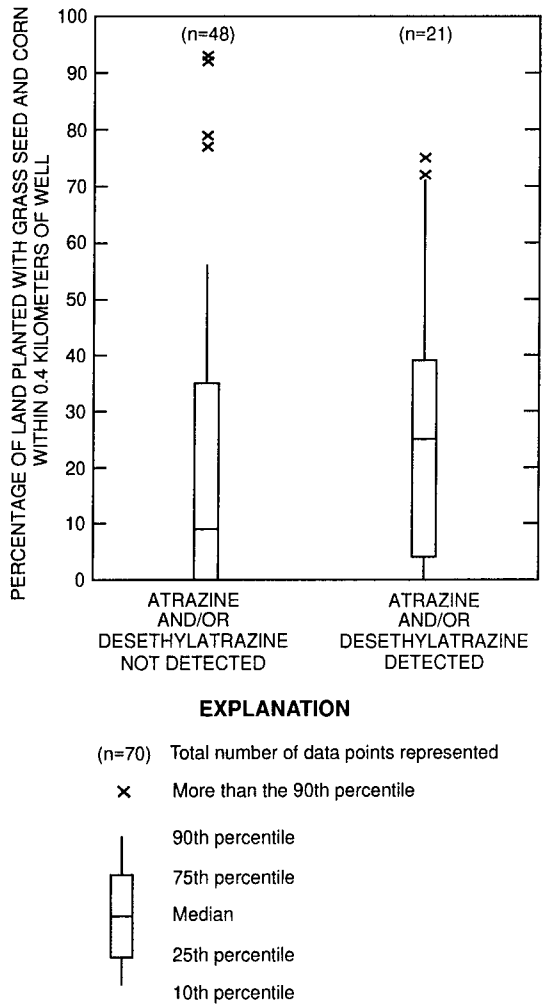

Figure 21. Percentage of land planted with grass seed and corn within 0.4 kilometers of Study-Unit-Survey wells, as a function of presence or absence of detectable concentrations of atrazine and desethylatrazine.

Fifty-four percent of 1987 atrazine use in the basin was for grass seed—the most important crop in the basin in terms of acreage (table 1). Most grass seed grown in the basin is grown in the southern basin (Anderson et al., 1996). It is possible that the more frequent occurrence of detectable concentrations of pesticides in southern basin sites, relative to northern basin sites (fig. 10), is related to extensive cropping of grass seed in the southern basin, in concert with past high atrazine use on this crop. In support of this hypothesis, detections of pesticides other than atrazine and desethylatrazine were more uniformly distributed, with detections at 5 (14 percent) of northern-basin and 6 (18 percent) of southern-basin sites.

Volatile Organic Compounds

Detections of VOCs (fig. 12 and table 7) were too few for meaningful statistical analysis of the relationship between occurrence of VOCs and environmental or anthropogenic factors, but the occurrence of VOCs was qualitatively compared with land use. Of the 14 detections (7 sites), 10 detections (3 sites) were from sites classified as predominantly (i.e. >50 percent) urban. One additional detection was from a site classified as mixed land use, of which 15 percent of the upgradient land use was urban. These data suggest an association between occurrence of VOCs and urban land use, and probably reflect the multiple sources of VOCs in urban settings.

URBAN LAND-USE STUDY

In this section, data from the 10 urban LUS wells (fig. 3) are presented, discussed, and qualitatively compared to SUS data. Land use in the vicinity of urban LUS wells is different from that associated with the predominantly agricultural SUS wells, so differences in water quality may reflect these differences in land use. However, these two groups of data are from wells of different location and construction characteristics. SUS

wells were domestic wells, with greater penetration of the water table than the LUS monitoring wells. Because of these differences, data from the urban LUS and the SUS will be compared only in general (nonstatistical) terms.

Nitrate

All 10 urban LUS samples were well oxygenated. Nitrate concentrations for samples from the 10 urban LUS wells ranged from 3.7 to 15 mg N/L (fig. 22). For comparative purposes, nitrate concentrations from well-oxygenated SUS sites classified as agricultural also are shown on figure 22. Median nitrate concentrations were similar for the two groups.

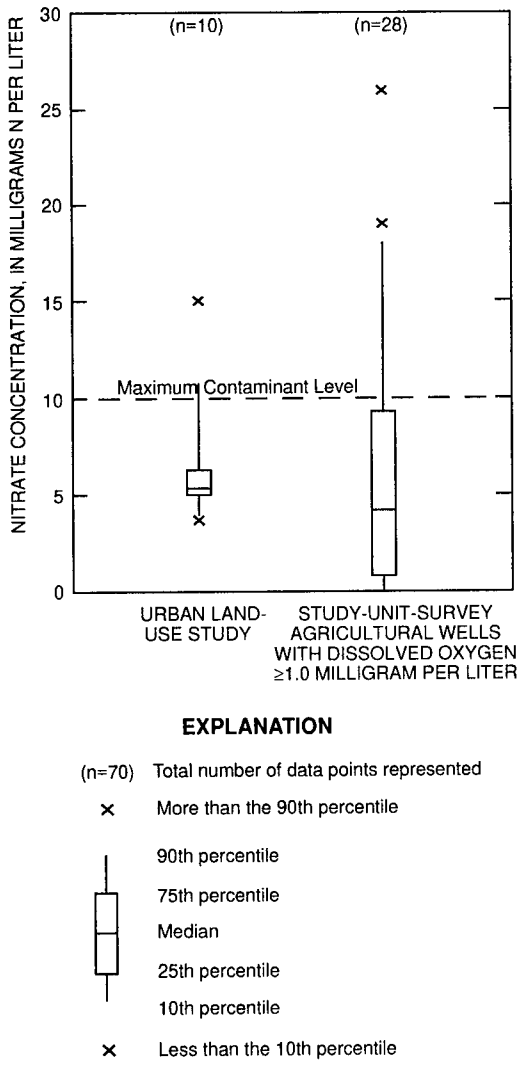

Figure 22. Nitrate concentrations in ground water from urban Land-Use-Study wells and agricultural Study-Unit-Survey wells having dissolved-oxygen concentrations greater than or equal to 1.0 milligrams per liter.

Septic systems can contribute nitrate to ground water. Nitrate from septic systems can be particularly problematic in unsewered urban areas, where septic systems associated with high population densities can result in high nitrogen loading to aquifers. Thus, nitrate concentrations in samples from urban LUS wells could be related to the number of unsewered homes associated with the wells. For the most part, local upgradient homes were serviced by sanitary sewers. However, small pockets of unsewered homes were associated with three urban LUS wells: Northgate Park (41 homes), Trenton Park (23 homes), and Fernhill Park (17 homes) (fig. 3).

Of the urban LUS wells, the Northgate Park well was associated with the greatest number of unsewered homes. The highest nitrate concentration among urban LUS samples, and the only urban LUS sample to exceed the MCL for nitrate, was collected from the Northgate Park well. Concentrations of phosphorus and chloride in this sample also were higher (by factors of 6.7 or more, and 1.7 or more, respectively) than in other urban LUS samples. Phosphorus and chloride are commonly associated with septic-system effluent (Denver, 1989). It is possible that septic-system effluent from unsewered homes is an important source of nitrate to water tapped by this well.

Pesticides

Water samples from urban LUS wells were analyzed for pesticides (glyphosate, a herbicide of high usage in urban areas in the Willamette Basin [Rinehold and Witt, 1989, 1992], and analytes listed in tables 2 and 3, except dimethoate). Trace concentrations of three pesticides—atrazine and desethylatrazine at each of two sites and triallate at one site—were detected. Estimated concentrations of these three pesticides ranged from 1 to 5 ng/L. (Concentrations of desethylatrazine are reported as estimates [see "Quality Assurance" section]. Concentrations of atrazine and triallate in urban LUS samples were greater than or equal to MDLs, but quantitative determination was compromised by analytical interference, so concentra-

tions of these two analytes also were reported as estimated concentrations.)

Of the three pesticides, only atrazine has an established MCL or LHA; none have established RSDHAs. Both the MCL and LHA for atrazine are 3,000 ng/L, about three orders of magnitude greater than the estimated concentrations found in urban LUS wells.

Concentrations of pesticides in urban LUS samples were low compared to concentrations in SUS samples (range, 1 to 7,900 ng/L). Atrazine concentrations in urban LUS samples in which atrazine was detected (2 to 3 ng/L) were about an order of magnitude less than the median atrazine concentration in SUS samples in which atrazine was detected (21 ng/L). Similarly, desethylatrazine concentrations in urban LUS samples in which desethylatrazine was detected (2 to 5 ng/L) were about an order of magnitude less than the median desethylatrazine concentration in SUS samples in which desethylatrazine was detected (46 ng/L). Urban LUS wells generally are screened closer to the water table than are SUS wells, so vertical well placement within aquifers does not appear to explain the observed differences. Most SUS sites were in agricultural areas, whereas all urban LUS sites were in urban areas. Although pesticides are widely used in urban areas (Whitmore et al., 1992), little is known regarding urban application rates in the Willamette Basin. Thus, it is possible that differences in pesticide concentrations between samples from urban LUS wells and SUS wells reflect differences in pesticide application rates.

Volatile Organic Compounds

Samples from urban LUS wells were analyzed for a suite of 60 VOCs (table 4). Analysis for nontarget compounds also was performed. From 1 to 4 target VOCs were detected in ground water from each of 8 LUS wells (80 percent of sites sampled), for a total of 19 VOC detections (table 8). Concentrations ranged from 0.2 to 7.6 µg/L. No nontarget compounds were identified. No samples contained VOCs at concentrations exceeding LHAs or RSDHAs. One VOC was detected at a concentration exceeding its established MCL: tetrachloroethylene was present in one sample at a concentration of 7.6 µg/L. The MCL for tetrachloroethylene is 5 µg/L.

The greater percentage (80 percent) of urban LUS sites with one or more VOCs detected, compared with SUS sites (11 percent), may be related to differing land uses. SUS sites were predominantly agricultural, and, thus, should have been associated with fewer sources of VOCs. Also, most VOC detections in SUS samples were associated with urban, rather than agricultural, land use.

Despite different populations of wells, most VOC detections in the SUS (86 percent) and urban LUS (95 percent) were for four compounds: chloroform, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene. These four VOCs are among the most commonly detected VOCs in regional and national ground-water assessments (Mackay and Smith, 1993). Tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene are ubiquitously used industrial and commercial solvents. Chloroform is a component of automobile exhaust (Squillace et al., 1995), and is a by-prod-

Table 8. Detections of volatile organic compounds in ground water from urban Land-Use-Study wells

[µg/L, micrograms per liter; USEPA, U.S. Environmental Protection Agency; MCL, drinking-water maximum contaminant level; LHA, drinking-water lifetime health advisory; RSDHA, drinking-water risk-specific-dose health advisory (10^{-4} risk level); --, none. Water-quality criteria from U.S. Environmental Protection Agency (1996)]

Volatile organic compound	Number of detections (10 samples)	Range of concentrations detected (µg/L)	USEPA MCL (µg/L)	USEPA LHA (µg/L)	USEPA RSDHA (µg/L)
Carbon tetrachloride	1	0.3	5	--	30
Chloroform	5	0.2–1.0	([a])	--	600
Tetrachloroethylene	6	0.3–7.6	5	--	70
1,1,1-Trichloroethane	2	0.3–0.4	200	200	--
Trichloroethylene	5	0.3–3.3	5	--	300

[a]An MCL specific to chloroform has not been established. Chloroform, which is a trihalomethane, is regulated with other trihalomethanes as a group. The MCL for total trihalomethanes is set at 100 µg/L.

uct of disinfection by chlorine (Christenson and Rea, 1993, p. 608). The presence of chloroform in samples could indicate nonpoint-source pollution from automobiles or recharge of chlorinated tap water from lawn watering in urban areas.

Trace Elements

Water samples from urban LUS wells were analyzed for a suite of 17 trace elements (table 9). Trace-element concentrations were low (median concentrations consistently <10 µg/L, and frequently <1 µg/L). No samples were observed to contain trace elements at concentrations exceeding established MCLs, LHAs, or RSDHAs. (The MRL for beryllium [1 µg/L] exceeds the RSDHA [0.8 µg/L]; it is possible, but unlikely, that the RSDHA for beryllium was exceeded.)

SUMMARY AND CONCLUSIONS

The Willamette Basin, a 31,000-square-kilometer area in northwestern Oregon drained by the Willamette and Sandy Rivers, is one of 60 study units in the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey. Selected results of ground-water investigations done in the Willamette Basin as part of the NAWQA are presented in this report. The purpose of these investigations was to characterize the current (1993–95) quality of shallow ground water (generally <25 meters below land surface) in Willamette Basin alluvium and to investigate relationships between shallow ground-water quality and various natural and anthropogenic factors.

The study design was composed of two components: a Study-Unit Survey (SUS), done from June to August 1993, and an urban Land-Use Study (LUS), done in July 1995. The SUS was a regional assessment of shallow ground-water quality in alluvium. The study consisted of 70 domestic wells chosen using a random-selection process. Most SUS wells were located in areas of agricultural land use. The urban LUS was a reconnaissance survey of the quality of shallow urban ground water. The study consisted of 10 monitoring wells installed in areas of residential land use. In both study components, protocols that facilitated collection of ground-water samples represen-

Table 9. Trace-element concentrations in ground water from urban Land-Use-Study wells

[µg/L, micrograms per liter; USEPA, U.S. Environmental Protection Agency; MCL, drinking-water maximum contaminant level; LHA, drinking-water lifetime health advisory; RSDHA, drinking-water risk-specific-dose health advisory (10^{-4} risk level); --, none. Water-quality criteria from U.S. Environmental Protection Agency (1996)]

Trace element	Range of concentrations (10 samples) (µg/L))	Median concentration (µg/L)	USEPA MCL (µg/L)	USEPA LHA (µg/L)	USEPA RSDHA (µg/L)
Aluminum	<3–11	<3	[a]	--	--
Antimony	<1	<1	6	3	--
Arsenic	<1–2	2	[b]50	--	2
Barium	4–30	8	2,000	2,000	--
Beryllium	<1	<1	4	--	.8
Cadmium	<1	<1	5	5	--
Chromium	<1–3	<1	100	100	--
Cobalt	<1–2	<1	--	--	--
Copper	<1–3	<1	1,300	--	--
Lead	<1	<1	15	--	--
Manganese	<1–58	2	[a]	--	--
Molybdenum	<1–2	<1	[a]	40	--
Nickel	<1–4	2	[c]100	100	--
Selenium	<1–<2	<1	50	--	--
Silver	<1	<1	--	100	--
Uranium	<1	<1	--	--	[b]--
Zinc	<3–5	<3	[a]	2,000	--

[a]Listed for eventual regulation.
[b]Under review.
[c]Being remanded.

tative of the resource were followed. Extensive quality-control data were collected to allow quantitative evaluation of the quality of chemical data collected from wells.

Concentrations of nitrite plus nitrate (henceforth, nitrate, because nitrite concentrations were low) ranged from <0.05 to 26 mg N/L (milligrams nitrogen per liter) in the 70 SUS wells. Nitrate concentrations exceeded the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) of 10 mg N/L in 9 percent of these samples. A statistically significant correlation between nitrate and dissolved-oxygen (DO) concentrations was observed, suggesting that nitrate reduction may be an important nitrate sink in shallow ground water in parts of the basin.

Tritium (^3H) data indicate that 21 percent of SUS samples represented water recharged prior to 1953. The remaining 79 percent of SUS samples were recharged up to 40 years prior to sampling. Nitrogen-fertilizer application rates increased by about a factor of five between 1953 and 1985. Thus, nitrate concentrations measured in SUS samples collected in 1993 probably reflect nitrogen loading rates that were smaller than the average nitrogen loading rate in 1993. As more recently recharged ground water (possibly associated with greater nitrogen loading rates) moves along ground-water flowpaths toward wells, nitrate concentrations in some of those wells may increase.

Nitrate in low-DO (<1.0 mg/L) ground water is more likely to have undergone reduction than is nitrate in well-oxygenated (≥1.0 mg/L) ground water. Thus, relationships between nitrate concentrations and environmental variables may be clearer when nitrate data are reselected to exclude low-DO data. The following statements reflect analysis of well-oxygenated samples: smaller cumulative thicknesses of clay were associated with higher nitrate concentrations. (Clay slows movement of ground water. Water underlying smaller cumulative thicknesses of clay may be younger, and thus may have received greater application rates of nitrogen fertilizer, than water underlying larger cumulative thicknesses of clay.) Higher concentrations of nitrate were observed in association with the generally more permeable Holocene alluvium than with the generally less permeable older alluvium. (Water moves more slowly through low-permeability material than through high-permeability material.) Finally, concentrations of nitrate in wells downgradient from areas of irrigated agriculture were statistically greater than those downgradient from areas of nonirrigated agriculture. (The observed relationship may reflect the generally greater rate of application of nitrogen on irrigated crops and pasture compared with nonirrigated crops and pasture, and the leaching effect of irrigation water.)

Concentrations of phosphorus ranged from <0.01 to 2.2 mg/L in the 70 SUS wells and exceeded 0.10 mg/L in 60 percent of these samples. Concentrations of phosphorus exceeding 0.10 mg/L could be of concern when ground water discharges to surface water; USEPA recommends that phosphorus concentrations in streams not exceed 0.10 mg/L to avoid excessive plant growth. Higher concentrations of phosphorus were associated with low-DO water than with well-oxygenated water, probably reflecting redox controls on phosphorus mobility.

From 1 to 5 pesticides and pesticide degradation products (henceforth, pesticides) were detected in ground water from 23 SUS wells (33 percent of 69 sites sampled for pesticides). Thirteen different pesticides were detected. Atrazine was the most frequently detected pesticide. Atrazine and (or) desethylatrazine (an atrazine degradation product) were detected at 21 of the 23 sites where pesticides were detected. Although detections were widespread, concentrations were low (generally <1,000 ng/L [nanograms per liter]). (One ng/L is equal to 0.001 µg/L [micrograms per liter].) One detection (dinoseb, at 7,900 ng/L) exceeded a USEPA MCL and Lifetime Health Advisory (LHA); no other detections exceeded USEPA MCLs, LHAs or Risk-Specific-Dose Health Advisories (RSDHAs).

Nitrate concentrations in samples from sites at which pesticides were detected were statistically greater than nitrate concentrations in samples from sites at which pesticides were not detected. This relationship may reflect common sources of nitrate and pesticides from applications in farming and landscaping.

Statistically smaller cumulative thicknesses of clay were present at wells where pesticides were detected than at wells where pesticides were not detected. Clay-sized particles slow movement of

ground water, allowing more time for pesticide degradation. Also, clay minerals sorb some pesticides. The identification of one or more pesticides in samples occurred more frequently in samples associated with Holocene alluvium than with older alluvium. The generally greater permeability of Holocene alluvium relative to that of older alluvium in the Willamette Basin probably facilitates faster movement of ground water in Holocene alluvium. Finally, greater percentages of grass seed and corn crops were associated with wells where atrazine and (or) desethylatrazine were detected than wells where atrazine and (or) desethylatrazine were not detected. Eighty-four percent of 1987 atrazine use in the basin was on grass seed and corn.

Pesticides were detected in ground water at a greater percentage of southern-basin sites than northern-basin sites. Historical atrazine use patterns in the basin and the predominance of atrazine and desethylatrazine among pesticide detections could explain this observed distribution. Grass seed, the most important Willamette Basin crop in terms of acreage, received large applications of atrazine (54 percent of basinwide atrazine use) in 1987 and is grown primarily in the southern basin. Most sites at which one or more pesticides were detected contained atrazine or desethylatrazine. Thus, the larger percentage of southern-basin sites yielding detections of pesticides may be related to past high use of atrazine on grass seed and the large number of atrazine and desethylatrazine detections among pesticide detections. Alternatively, the generally smaller cumulative thicknesses of clay above the open intervals of southern-basin wells relative to northern-basin wells could, through the control clay exerts over pesticide transport and fate, explain the distribution of wells containing detectable concentrations of pesticides. Results of this study were not sufficiently detailed to allow separation of these hypotheses.

From 1 to 5 volatile organic compounds (VOCs) were detected at each of 7 SUS sites (11 percent of 65 sites evaluated). One detection (tetrachloroethylene, at 29 µg/L) exceeded a USEPA MCL; no detections exceeded USEPA LHAs or RSDHAs. Other detections were at low concentrations (0.2 to 2.0 µg/L). VOC detections generally were from sites associated with urban land use.

Concentrations of arsenic ranged from <1 to 13 µg/L in the 70 SUS wells. Concentrations did not exceed the USEPA MCL of 50 µg/L, but concentrations in 16 percent of samples exceeded the USEPA RSDHA of 2 µg/L. Additional sampling of 41 wells in the Tualatin River Basin (a tributary basin to the Willamette River), combined with the 6 SUS wells in the Tualatin River Basin, yielded arsenic concentrations from <1 to 73 µg/L; 9 percent exceeded the USEPA MCL, and 66 percent exceeded the USEPA RSDHA. As was observed for phosphorus, higher concentrations of arsenic were associated with low-DO ground water than with well-oxygenated ground water, probably reflecting redox controls on arsenic mobility.

Concentrations of radon ranged from 200 to 1,200 picocuries per liter (pCi/L) in 51 SUS wells. All samples exceeded the USEPA RSDHA of 150 pCi/L. These radon concentrations, although high relative to the USEPA RSDHA, are not unusual for ground water in the United States.

Whereas SUS data are primarily associated with agricultural land use, urban LUS data, by design, are associated with urban land use; thus, the data are complementary. However, wells sampled in the SUS and the urban LUS are of different construction and tap different components of the resource. Thus, water-quality data obtained from SUS and urban LUS wells are not quantitatively comparable.

Ten urban LUS samples were collected; all were well oxygenated. Urban LUS nitrate concentrations ranged from 3.7 to 15 mg N/L and were similar to nitrate concentrations in the well-oxygenated, agricultural SUS samples. Nitrate in water from one urban LUS well exceeded the USEPA MCL; unsewered homes associated with this well may have contributed nitrate to water pumped from this well.

Trace concentrations of one to two pesticides were detected in ground water from each of three urban LUS wells. Three different pesticides were detected. No detections exceeded USEPA MCLs, LHAs, or RSDHAs. The percentage of urban LUS sites at which pesticides were detected (30 percent) was similar to that in the SUS (33 percent). However, concentrations of pesticides in urban LUS samples generally were smaller than in SUS samples. Atrazine concentrations in urban LUS samples in which atrazine was detected (2 to

3 ng/L) were about an order of magnitude less than the median atrazine concentration in SUS samples in which atrazine was detected (21 ng/L). Similarly, desethylatrazine concentrations in urban LUS samples in which desethylatrazine was detected (2 to 5 ng/L) were about an order of magnitude less than the median desethylatrazine concentration in SUS samples in which desethylatrazine was detected (46 ng/L). The generally lower concentrations in urban LUS samples compared with SUS samples may reflect differences in pesticide application rates on urban verses agricultural land.

From one to four VOCs were detected in ground water from each of eight urban LUS wells. Concentrations ranged from 0.2 to 7.6 µg/L. One detection (tetrachloroethylene, 7.6 µg/L) exceeded a USEPA MCL; no detections exceeded USEPA LHAs or RSDHAs. The percentage of urban LUS sites at which one or more VOCs was detected (80 percent) was larger than that in the SUS (11 percent of sites evaluated). These differences probably reflect the small number of urban wells in the SUS.

Trace-element concentrations in ground water from LUS wells were low. Median concentrations consistently were <10 µg/L, and frequently were <1 µg/L. No samples were observed to contain trace elements at concentrations exceeding established USEPA MCLs, LHAs, or RSDHAs.

Although NAWQA ground-water studies have furthered the understanding of ground-water quality in the Willamette Basin, the current understanding of regional ground-water quality still is limited. In particular, bedrock aquifers in the basin historically have received little attention. Also, existing data from alluvial aquifers are inadequate to ascertain in detail the spatial extent of ground-water contamination, or to clearly identify the relative importance of different processes controlling contaminant transport and fate.

The importance of the effect of land use on contaminant occurrence and spatial distribution in ground water was supported by this work. Ground-water-vulnerability assessments and ground-water-quality studies should benefit from analysis of land-use patterns. The importance of analysis of natural factors long known or thought to control contaminant occurrence and distribution also was supported by this work. Results presented in this report suggest that quantitative analysis of relationships between thicknesses of clay above well open intervals and ground-water quality, and between texture of geologic materials and ground-water quality, may be particularly valuable in ground-water-vulnerability assessments and ground-water-quality studies. Although ground-water-flow approximations were not incorporated in the analysis of the effects of thicknesses of clay and of geologic materials on ground-water quality in this study, such efforts might improve results in future studies. Finally, evaluation of ground-water age and redox conditions, both successfully used in this report to facilitate understanding of ground-water quality, also may deserve consideration in future studies.

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